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Dissertation

19

Electrocoagulation in the treatment of industrial waters and wastewaters

Mikko Vepsäläinen

VTT SCIENCE 19

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Mikko Vepsäläinen

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Electrocoagulation in the treatment of industrial waters and wastewaters

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Abstract

Chemical coagulation is commonly used in raw water and wastewater treatment plants for the destabilisation of pollutants so that they can be removed in the subsequent separation processes. The most commonly used coagulation chemicals are aluminium and iron metal salts. Electrocoagulation technology has also been proposed for the treatment of raw waters and wastewaters. With this technology, metal cations are produced on the electrodes via electrolysis and these cations form various hydroxides in the water depending on the water pH. In addition to this main reaction, several side reactions, such as hydrogen bubble formation and the reduction of metals on cathodes, also take place in the cell. In this research, the applications of electrocoagulation were investigated in raw water treatment and wastewater applications.

The surface water used in this research contained high concentrations of natural organic matter (NOM). The effect of the main parameters – current density, initial pH, electric charge per volume, temperature and electrolysis cell construction – on NOM removal were investigated. In the wastewater treatment studies, the removal of malodorous sulphides and toxic compounds from the wastewaters and debarking effluents were studied. Also, the main parameters of the treatment, such as initial pH and current density, were investigated. Aluminium electrodes were selected for the raw water treatment, whereas wastewaters and debarking effluent were treated with iron electrodes.

According to results of this study, aluminium is more suitable electrode material for electrocoagulation applications because it produces Al(III) species. Metal ions and hydroxides produced by iron electrodes are less effective in the destabilisation of pollutants because iron electrodes produce more soluble and less charged Fe(II) species. However, Fe(II) can be effective in some special applications, such as sulphide removal. The resulting metal concentration is the main parameter affecting destabilisation of pollutants. Current density, treatment time, temperature and electrolysis cell construction affect the dissolution of electrodes and hence also the removal of pollutants. However, it seems that these parameters have minimal significance in the destabilization of the pollutants besides this effect (in the studied range of parameters). Initial pH and final pH have an effect on the dissolution of electrodes, but they also define what aluminium or iron species are formed in the solution and have an effect on the ζ-potential of all charged species in the solution. According to the results of this study, destabilisation mechanisms of pollutants by electrocoagulation and chemical coagulation are similar.

Optimum DOC removal and low residual aluminium can be obtained simultaneously with electrocoagulation, which may be a significant benefit of electrocoagulation in surface water treatment compared to chemical coagulation. Surface water treatment with electrocoagulation can produce high quality water, which could be used as potable water or fresh water for industrial applications. In wastewater treatment applications, electrocoagulation can be used to precipitate malodorous sulphides to prevent their release into air. Technology seems to be able to remove some toxic pollutants from wastewater and could be used as pretreatment prior to treatment at a biological wastewater treatment plant. However, a thorough economic and ecological comparison of chemical coagulation and electrocoagulation is recommended, because these methods seem to be similar in pollutant destabilisation mechanisms, metal consumption and removal efficiency in most applications.

Keywords Electrocoagulation, water treatment, wastewater treatment

Preface

This study was carried out between 2006 and 2011 at the Laboratory of Green Chemistry, Mikkeli, Finland with financial support from the European Union, the City of Mikkeli, Savcor Forest Oy and UPM-Kymmene Oyj.

I am highly grateful to my supervisor Professor Mika Sillanpää for giving me the opportunity to conduct these studies at the Laboratory of Green Chemistry and for his guidance and support. I am also very grateful to Martti Pulliainen for his guidance, encouragement and support throughout the whole process. I would like to thank my amazing colleagues at the Laboratory of Green Chemistry, my former employer Savcor Forest Oy and my current employer VTT Materials and Building for their help, support and great company. I am naturally very thankful to my co-authors for their contribution and support.

I am grateful for my friends and family for their support, encouragement and love. Somehow they always thought I would finish this work, even when I was ready to give up. Last but not least, I would like to express my deepest gratitude to my partner, for the love, support, humour, sensibility, care and all other great things you brought into my life.

Academic dissertation

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List of publications

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II M. Vepsäläinen, M. Pulliainen, M. Sillanpää, Effect of electrochemical cell structure on natural organic matter (NOM) removal from surface water through electrocoagulation (EC), Sep. Purif. Technol. 99 (2012) 20–27.

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IV M. Vepsäläinen, J. Selin, P. Rantala, M. Pulliainen, H. Särkkä, K. Kuhmonen, A. Bhatnagar, M. Sillanpää, Precipitation of dissolved sulphide in pulp and paper mill wastewater by electrocoagulation, Environ. Technol. 32 (2011) 1393–1400.

V M. Vepsäläinen, H. Kivisaari, M. Pulliainen, A. Oikari, M. Sillanpää, Removal of toxic pollutants from pulp mill effluents by electrocoagulation, Sep. Purif. Technol. 81 (2011) 141–150.

Author's contributions to the publications

I–III	The author carried out all experiments, analysed the data, and prepared the first draft of the manuscript.
IV–V	The author planned and supervised the experiments and conducted part of the experiments. The author analysed the most of the data and prepared the first draft of the manuscript.

Contents

Appendices

Publications I–V

Abbreviations

AC	Alternating current
ANOVA	Analysis of variance
BOD	Biological oxygen demand
CCF	Central composite face
COD	Chemical oxygen demand
DAF	Dissolved air flotation
DC	Direct current
DHAA	Dehydroabietic acid
DLVO	Derjaguin-Landau-Verwey-Overbeek (theory)
DOC	Dissolved organic carbon
DOE	Design of experiments
EC	Electrocoagulation
EC_{50}	Half maximal effective concentration
EDL	Electrical double layer
EF	Electroflotation
FTIR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatograph - mass spectrometry
HMM	High molecular mass
HPAC	Highly efficient composite polyaluminium chloride
ICP-OES	Inductively coupled plasma optical atomic emission spectrometry
IPA	Isopimaric acid
MLR	Multiple linear regression
NOM	Natural organic matter
NTU	Nephelometric turbidity unit

OHP	Outer Helmholtz plane
ORP	Oxidation-reduction potential
PACl	Polymeric aluminium chloride
PAF-SiC	Polyaluminium ferric silicate chloride
PASiC	Polyaluminium silicate chloride
PDADMAC	Polydiallyl dimethyl ammonium chloride
PFC	Polyferric chloride
PFS	Polyferric sulphate
PFSiS	Polyferric silicate sulphate
PICl	Polymeric iron chloride
PLS	Partial least squares
PSF	Polysilicate ferric
PtCo	Platinum-cobalt scale
PXRD	Powder X-ray diffraction
RSM	Response surface model
SCE	Saturated calomel electrode
SEM-EDS	Scanning electron microscope with energy dispersive spectroscopy
SRB	Sulphate reducing bacteria
SUVA	Specific ultraviolet absorbance
SVI	Sludge volume index
TOC	Total organic carbon
TSS	Total suspended solids
USD	United Stated dollar
UV/VIS	Ultraviolet-visible spectroscopy
XPS	X-ray photoelectron spectroscopy

1. Introduction

There is a growth in demand for new water treatment technologies as the world's population increases and fresh water sources are polluted. Waterborne diseases are still common in developing countries due to the lack of funding or appropriate know-how for water purification. Industry also uses these limited water sources and has to acquiesce to lower quality raw water as a higher proportion of fresh water is required for human consumption. Wastewater treatment technologies used in both municipal and industrial applications have to be further developed in order to reduce the pollution of receiving water bodies.

Chemical coagulation and flocculation are commonly used as a part of the water purification systems for the removal of pollutants from raw waters and wastewaters. Their main function is to enhance particle separation in the subsequent processes, such as filtration, sedimentation or flotation. In order to understand destabilisation of particles by coagulants and flocculants, it is crucial to understand the mechanisms which stabilise particles in aqueous solutions. Chemical coagulation and flocculation are used in both industrial and municipal raw water and wastewater treatment systems. They can enhance the removal of several types of pollutants from the water streams. Typical examples of pollutants to be removed are nutrients, toxic heavy metals and natural organic matter (NOM). The most commonly used coagulants are aluminium or iron salts, such as sulphates and chlorides. These metal salts form various hydrolysis products in the water depending on water chemistry, such as pH and the concentration of anions. Metal cations and hydroxides destabilise colloid pollutants in water by reducing repulsion forces between the colloids and by entrapping particles in the sludge.

Electrocoagulation (EC) has been suggested as an advanced alternative to chemical coagulation in pollutant removal from raw waters and wastewaters. In this technology, metal cations are released into water through dissolving metal electrodes. Simultaneously, beneficial side reactions can remove flocculated material from the water. However, there are also adverse side reactions, such as deposition of salts on the electrode surface, which may cause deterioration of removal efficiency after long operation. As in the case of chemical coagulation with metal salts, aluminium or iron cations and hydroxides are the active compounds in EC. Chemical coagulation and EC have fundamentally similar destabilisation mechanisms and it is therefore important to go through the theory of colloid destabilisation with metal salt coagulants, because chemical coagulation has been studied more extensively than EC.

1.1 Basic concepts and theory of coagulation and flocculation with hydrolysing metal salts

Pollutants in raw waters and wastewaters are typically colloidal particles, which are not easily removed with typical filtration sedimentation or flotation due to their stability in water. These particles have special properties due to their small size and large total surface area. The properties of the interface of colloidal particles and the stabilisation of colloidal particles by hydrolysing metal salts are discussed in the first section of this work.

1.1.1 Interface of colloidal particles

Colloid is a microscopic particle, typically having at least one dimension in the range of 1 nm to 10 µm, which is dispersed throughout the other substance [1]. This medium where particles are dispersed can be gas, liquid or solid. The combined surface area of colloids in dispersions is large due to their small size and therefore surface properties play an important role in their characteristics. Natural waters and typical wastewaters are heterodispersions, having a wide variety of particles with different particles sizes [2].

Stability and destabilisation of colloids in solutions is the result of their surface charge. Surface immersed into a solution can attain a charge by ionisation of surface groups, by ion adsorption, by dissolution of ionic solids or by isomorphous substitution [1]. Many surfaces contain ionisable functional groups, such as –OH, –COOH or $–NH_2$. Surface charge therefore depends on the ionisation of these functional groups and consequently on the pH of the solution [3]. Isomorphous substitution occurs when lattice imperfection occurs at the crystal due to the replacement of some atom in the crystal by another ion that has a different amount of electrons, which results in a charged surface. This occurs for example in clay particles. Adsorption of ions has an impact on surface charge of the particles. Dissolution of ionic solids can cause a charge on the surface if the dissolution of anions and cations from the solid is unequal.

When a charge forms on the surface it also affects the ions in the surrounding solution. The ions of opposite charge are attracted towards the surface, whereas the ions of the same charge are repelled from the surface. This separation of charges on the particle surface results in the formation of electrical double layer (EDL) presented in Fig. 1 [1–4].

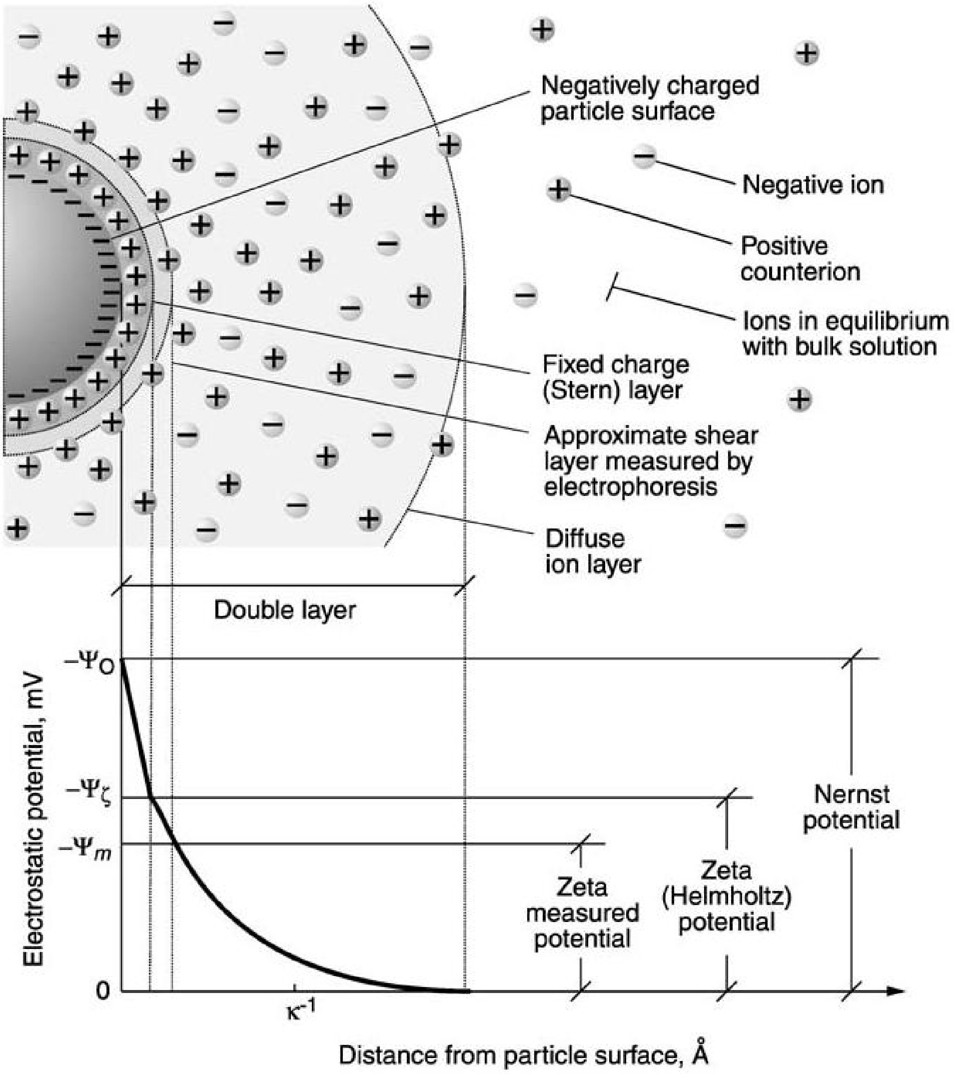


Figure 1. Conceptual representation of the electrical double layer (reprinted from [2] with permission from John Wiley & Sons).

The interface of a charged surface has been explained by the models of Helmholtz, Gouy and Chapman [4]. Stern later combined these models and further developed the model of the electrical double layer. In this model there is an inner region (Stern layer or Helmholtz layer) and an outer diffusion region (Gouy-Chapman layer). In inner layer ions are tightly bound to the surface whereas in the outer layer they move about under the influence of diffusion. According to Gouy-Chapman model, the potential distribution in a flat double layer can be described by Eq. 1:

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\varepsilon} \tag{1}$$

where ψ is the potential at a point in the diffuse layer versus infinity at the bulk solution, ρ is the charge density at the same point and ε is permittivity. In Eq. 1 the charge density at the potential ψ is described by Eq. 2. The number of positive and negative ions in the diffuse layer is distributed according to the Maxwell-Boltzmann distribution (Eq. 3 for cations and Eq. 4 for anions):

$$\rho = ze(n_+ - n_-) \tag{2}$$

$$n_+ = n_0 * \exp\left(\frac{ze\psi}{kT}\right) \tag{3}$$

$$n_- = n_0 * \exp\left(-\frac{ze\psi}{kT}\right) \tag{4}$$

where n_+ and n_- are the respective numbers of positive and negative ions per unit volume at the point where potential is ψ. n_0 is the concentration of ions at the infinity (bulk solution). z is the valency of the ions, e is the charge of electron, k is Boltzmann's constant and T is temperature. The potential of the particle surface versus bulk solution is called Nernst potential (ψ_0). Between the inner layer and the outer layer is the Outer Helmholtz plane (OHP), which has potential, ψ_ζ,versus bulk solution. However, this potential cannot be directly measured and therefore a common parameter, which depicts the surface charge of the colloid, is ζ-potential (ψ_m), which is the electrical potential between the plane of shear and the bulk solution. The diffuse part of the double layer is analogous to the plate condenser. Even though in reality the double layer extends to infinity, the Debye-Hückel length, K^{-1}, is used to describe the thickness of the double layer.

1.1.2 Stability of colloids in aqueous solutions

Colloids are said to be stable in aqueous solutions when their aggregation or sedimentation is so slow that they make virtually stable dispersions. This is important when considering raw water or wastewater treatments because these particles cannot be removed by sedimentation in a reasonable period of time.

Stability (or destability) of colloids in water is a balance between the repulsive electrostatic force and attractive, London-van der Waals force. The theory of Derjaguin-Landau-Verwey-Overbeek (DLVO) estimates these energies of attraction and repulsion [5, 6]. The London-van der Waals forces of attraction, caused by the permanent or induced dipoles, are important at very short distances. The repulsion force is caused by the overlapping of the electrical double layers, which leads to higher counterion concentration and hence to repulsion between the particles. The repulsion force is an exponential function of the distance between the particles with a range of the order of the thickness of the electrical double layer, whereas the attraction force decreases as an inverse power of the distance between the particles.

There are two minimums in the summation of attraction and repulsion forces between the particles having similar charges. The primary minimum, at a close distance between the particles, is where particles reside after coagulation. There is also a secondary minimum at longer distance and this is the energy minimum of flocculation. Potential energy at the primary minimum is significantly smaller than at the secondary minimum and hence the particles at the primary minimum are more tightly attached. Between the primary and secondary potential energy minimums, an energy barrier exists which the particles have to overcome with their kinetic energy before coagulation can take place. Detailed calculations of attraction and repulsion forces have been discussed in the articles of Overbeek [7] and Verwey and Overbeek [6].

Ionic strength affects the thickness of double layer. The double layer compresses when ionic strength increases according to Eq. 5. In addition to ionic strength, the valence of the ions also affects the thickness of the EDL. Multivalent counterions are concentrated in the double layer more than monovalent ions according to Eq. 3 and 4. According to the Schulze-Hardy rule, the optimum concentration for coagulation for tri-, di- and monovalent cations is 800:12:1. However, the required ion concentration of multivalent ions is often less than the Schultze-Hardy rule predicts [2].

$$\frac{1}{K} = 10^{10}\left[\frac{2000e^2 N_A I}{\varepsilon\varepsilon_0 kT}\right]^{-1/2} \tag{5}$$

where 1/K is Debye length, N_A is Avogadro's number, I is ionic strength and ε_0 is permittivity in vacuum.

1.1.3 Destabilisation mechanisms of colloids

As discussed in Section 1.1.2, colloids can be stable in water due to electrostatic repulsions between the particles. In coagulation and flocculation technologies, particles are destabilised with the addition of inorganic or organic chemicals which have an effect on the properties of EDL. Coagulants are chemicals which reduce the repulsive energy between the particles (energy barrier). Therefore particles can more easily agglomerate at the primary minimum of potential energy. Flocculation occurs when these agglomerated particles attach to each other with a weak bond (the secondary minimum of potential energy). Flocculation aids improve floc properties, such as settleability and filterability.

Mechanisms which can destabilise colloidal particles in water are [2, 3]:

- **Compression of electrical double layer.** The increase of the concentration of ions in bulk solution compresses EDL and particles come together more easily as the length of EDL decreases. Optimum destabilisation is achieved when ζ-potential is close to 0 mV. Excess salt concentration does not lead to restabilisation of the particles. This mechanism is not employed in water treatment because very high salt concentrations are required for destabilisation.

- **Adsorption destabilisation.** This occurs when oppositely charged ions or polymers are adsorbed on the surfaces of particles. They reduce surface charge and thus repulsive force between the particles. Destabilisation occurs typically at ζ-potential values close to 0 mV. Too high a coagulant dose can lead to the restabilisation of the particles because the charge is reversed.
- **Inter-particle bridging.** Polymerised metal coagulants or organic chemicals can form bridges between the particles. Polymer can adsorb on the particle surface by several mechanisms, such as charge-charge interactions, dipole interactions, hydrogen bonding or van der Waals interaction. When one polymer chain adsorbs on multiple particles, bridging occurs and molecular weight increases. Bridging is a typical mechanism with long-chained, high molecular weight organic polymers. The ζ-potential of the particles which are destabilised by bridging mechanism is not typically close to zero. Restabilisation can occur when the surface is completely covered by the polymer.
- **Precipitation and enmeshment mechanism.** This destabilisation mechanism is typical with the high concentrations of metal salts in near neutral pH. In this pH, metal salts, such as alum or ferric sulphate, form insoluble hydrolysis products and polymerise. Colloidal particles can then be enmeshed into these sweep flocs. The required dosage of coagulant is virtually independent of the type and concentration of colloids in the solution.

Adsorption destabilisation and inter-particle bridging mechanisms are susceptible to restabilisation when excess coagulant is added. In the bridging mechanism, restabilisation occurs when the adsorption sites of the particles are occupied and no further bridging can occur. In the overcharging phenomenon the inner part of the EDL carries more countercharge than exists on the surface of the particle [8, 9]. In this case, potentials ψ_ζ and ψ_m are reversed from negative values to positive ones in typical colloids existing in raw water and wastewaters. However, double layer compression and precipitation mechanisms can again destabilise particles when even higher coagulant concentrations are used.

In typical coagulation processes of raw water and wastewater treatment plants there are several mixing stages. At the point of coagulation, fast mixing is required to properly disperse chemicals into the water stream and promote particle collisions. After this short fast mixing stage, water goes into slow mixing stage (flocculation) where induced velocity gradients provide particles opportunities for contact and further particle size growth. However, if the water velocity in the flocculation is too high it may cause floc breakdown. There are several types of mixers for fast and slow mixing stages and required conditions depend, e.g., pollutants to be removed and primary mechanism of destabilisation. Detailed description can found in [2, 3].

1.1.4 Commonly used metal salt coagulants

Aluminium and iron metal salts are used in raw water and wastewater treatment. Both metals can form multivalent ions, Al^{3+}, Fe^{2+} and Fe^{3+}, and various hydrolysis products [10]. Fe(II) is poor coagulant itself and is typically oxidised to Fe(III) form during the coagulation process to obtain higher efficiency. The most commonly used metals salts are simple aluminium and iron sulphates and chlorides. Metal cations go through a series of hydrolytic reactions depending on the pH of the solution and mononuclear (Fig. 2 and Eq. 6) and polynuclear hydroxides form in the solution. Neutral amorphous metal hydroxides, $Al(OH)_3$ and $Fe(OH)_3$, are poorly soluble species. Distribution of mononuclear species of metals can be presented as solubility diagrams.

$$\mathrm{Me}^{3+}(aq) + n\mathrm{H_2O} \leftrightarrow \mathrm{Me(OH)}_n^{3-n} + n\mathrm{H}^+(aq) \tag{6}$$

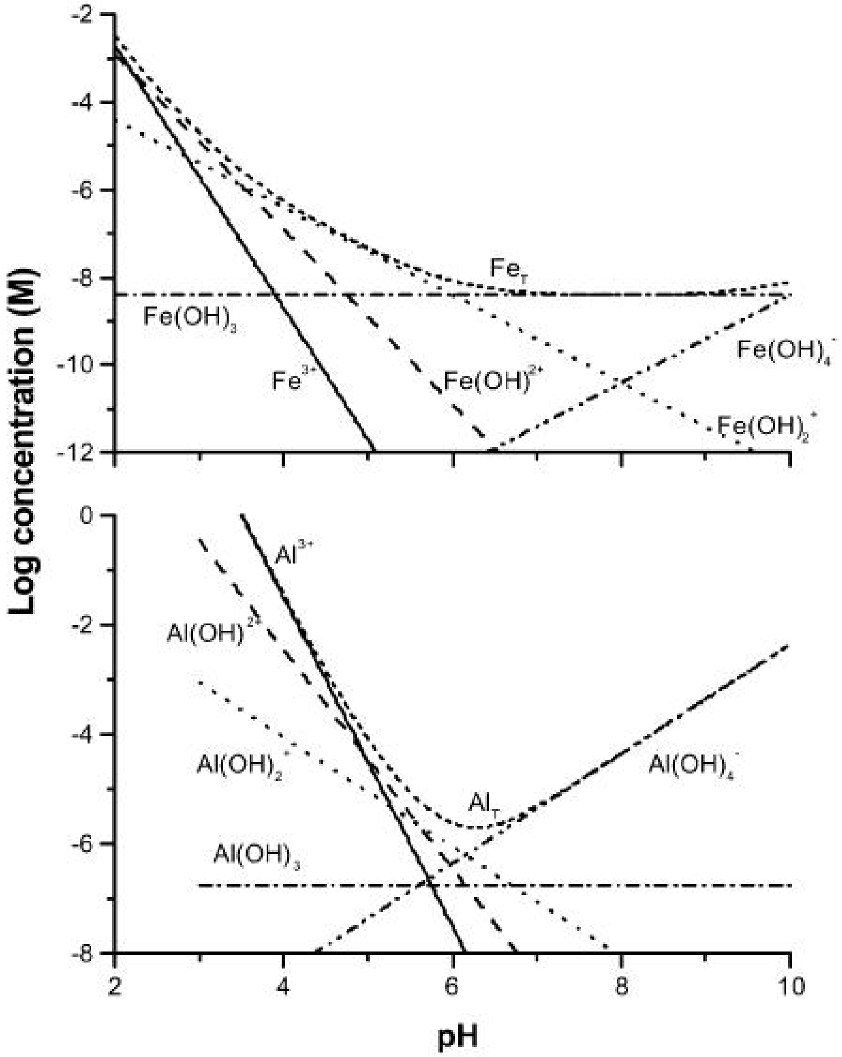


Figure 2. Concentrations of soluble monomeric hydrolysis products of Fe(III) and Al(III) in equilibrium with the amorphous hydroxides at zero ionic strength and 25 °C (reprinted from [10] with permission from Elsevier).

Polynuclear species, e.g., Al_{13} $[AlO_4Al_{12}(OH)^{7+}{}_{24}]$ are effective in destabilisation of colloids due to their large size and high positive charge [10, 11]. In prehydrolysed metal coagulants, such as polyaluminium chloride (PACl) and polyferric chloride (PICl), these polymerised species are preformed by partially neutralising metal salt solution to different basicity ratios. These coagulants have less temperature or pH dependence and their alkalinity consumption is lower. Recently new types of coagulants have been developed where prehydrolysed aluminium or iron coagulants are supplemented with silicates or organic polymers [12]. Commonly used and recently studied metal and composite coagulants are presented in Table 1. A more detailed description of these coagulants can be found in our review article [12].

Table 1. Overview of the metal salt and composite coagulants used in recent research studies [12].

Coagulant	Features	Positive	Negative	Ref.
Alum, Aluminium chloride	Trivalent aluminium ions are released into a solution from the respective salt. They are hydrolysed and form soluble complexes possessing high positive charges. Coagulation efficiency depends on, e.g., coagulant dose, mixing, pH, temperature, particle and NOM properties. During coagulation, the most effective range of pH is suggested to be 5.0–6.5.	Stable, easily handled, readily soluble. Better turbidity removal than with ferric salts in many cases. Can be more effective than ferric in low doses. Higher colour removal efficiency.	Relatively high coagulant residuals in the finished water in some cases. Possible link with Alzheimer's disease. Ferric salts have been noted to be better at removing NOM than aluminium salts in many investigations. High alkalinity consumption. Sulphate and/or chloride in finished water increases corrosivity.	[11, 13–26]
Ferric chloride, Ferric sulphate	Ferric salts hydrolyse similarly as aluminium salts when added to water and form different hydrolysis products. Effectiveness of coagulation depends on the same factors as during alum salt coagulation. The most effective range of pH is suggested to be pH 4.5–6.0.	Ferric salts have been noted to be better at removing NOM than aluminium salts in many investigations. Especially, the removal of middle size NOM fractions is noted to be more efficient. Not as sensitive to temperature changes as alum.	Ferric-based coagulant acid strength and associated optimised flocculation pH ranges can produce purified water with less buffering capacity and require greater chemical addition for stabilisation and corrosion control. High alkalinity consumption. Sulphate and/or chloride in finished water increases corrosivity.	[15, 16, 20, 25, 27–29]
PACl	Made by partially neutralised (prehydrolysed) aluminium chloride. Enhanced amounts of high-charged, moderate-molar-mass hydrolysis species, e.g., Al_{13}.	Less temperature and pH dependent than alum salts. Lower alkalinity consumption. Better NOM removal capacity than alum in many cases. Lower dose requirement and less sludge produced. Lower residual aluminium in treated water.	The effectiveness of coagulant is significantly affected by coagulant hydrolysis species speciation. Preformed Al species are stable and cannot be further hydrolysed during coagulation. Might not be so efficient at removing HMM and highly hydrophobic NOM.	[11, 26, 30–33]

PICl, PFC	Made by partially neutralised (prehydrolysed) ferric chloride. Enhanced amounts of high-charged, moderate-molar-mass hydrolysis species.	Wider pH range, lower sensitivity to temperature, reduced amounts of coagulants, lower residual iron concentration. Less corrosive than ferric chloride.	More at development stage. Not so widely used.	[34, 35]
PFS	Made by partially neutralised (prehydrolysed) ferric sulphate. Enhanced amounts of high-charged, moderate-molar-mass hydrolysis species.	Wider pH range, lower sensitivity to temperature, reduced amounts of coagulants, lower residual iron concentration. Less corrosive than ferric chloride.	Hydrolysis conditions have major impact on speciation of hydrolysis/polymeric species. More at development stage. Not so widely used.	[36, 37]
PASiC, PAF-SiC, PFSiS, PSF	Combination of aluminium and/or ferric-based polymeric flocculants with polysilicate.	Enhancement of bridging ability of coagulant. Flocs formed are relatively large. More resistant to pH variations. Wider pH range.	Although flocs are large, they are non-settleable, thus creating high turbidity values with overly low dosages. More at development stage (especially ferric-based coagulants).	[31, 38–45]
HPAC	Composition of organic polymer (PDADMAC) and inorganic polymeric coagulant (PACl) with additives such as active silicates.	Effective in waters with high alkalinity or pH. Wider working pH range.	Flocs formed can be small or incompact, thus not favourable to sedimentation, although flotation is much more efficient.	[26, 38, 46, 47]
PFC-PDADMAC	Composition of organic polymer (PDADMAC) and inorganic polymeric coagulant (PFC). High content of Fe_b hydrolysis species.	Stronger charge neutralisation and hence efficient DOC, SUVA and turbidity removal capacity.	More at development stage. Not so widely used.	[35, 48–51]

In addition to pH, competing anions also have an influence on the composition of metal hydroxides. The effect of anion depends on its electronegativity and tendency to react with metal ion or the positively charged sites of metal hydroxide precipitates [3]. Sulphate ions are weakly basic and strongly coordinated with metal ions. They broaden the pH zone of destabilisation to acidic side. Phosphates shift the optimum pH of destabilisation to the acidic side. Chlorides and nitrates have only a slight effect in high concentrations.

1.1.5 Applications of metal salt coagulants in industrial raw water and wastewater treatment

Metal salt coagulants are used in industrial raw water treatment processes and wastewater treatment plants to remove various pollutants. Typical contaminants in surface waters that can be removed by coagulation are for example NOM, mineral substances and microorganisms. The variety of pollutants found in industrial wastewaters is enormous and only some examples of applications could be given in this study.

NOM is one of the most important pollutants found in surface waters. Basically, NOM is a complex mixture of different organic materials, such as bacteria, viruses, humic acids, fulvic acids, polysaccharides and proteins. NOM can be divided into hydrophilic and hydrophobic fractions [52, 53]. The hydrophilic fraction of NOM is composed mostly of aliphatic carbon and nitrogenous compounds, such as carboxylic acids, carbohydrates and proteins, whereas the hydrophobic NOM primarily consists of humic (Fig. 3) and fulvic acids [54]. Humic substances are highly heterodisperse macromolecules with high molecular weights.

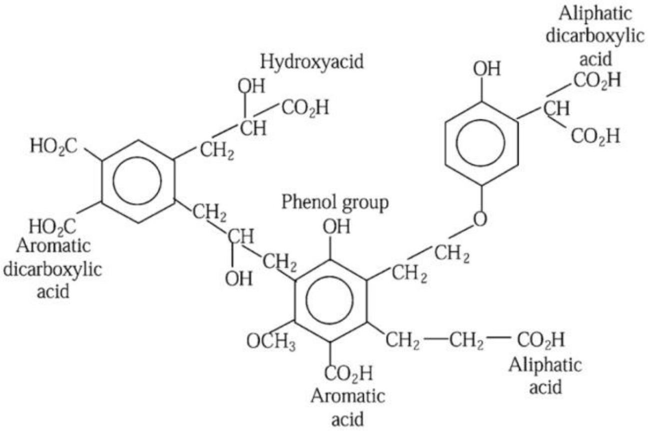


Figure 3. Hypothetical molecular structure of humic acid (reprinted from [10] with permission from Elsevier).

High molecular weight hydrophobic NOM fractions are more easily destabilised than low molecular weight hydrophilic fractions [3, 52, 53, 55]. Hydrophilic fractions can be partially removed when sufficiently high coagulant concentrations are used at low pH. In these conditions, metal ions form complexes with ionogenic groups of the hydrophilic colloid and electroneutral precipitate forms. Hydrophobic NOM contains more aromatic compounds than hydrophilic fractions and has a higher level of charge due to ionisable groups, such as carboxylic and phenolic groups. Humic substances can also be classified as humus coal, fulvic acids, hymatomelanic acids and humic acids. Humus coal is an insoluble fraction, whereas others are soluble in neutral water. Molecular weights of the soluble fractions of humic substances in order of decreasing molecular weight are humic acid > hymatomelanic acid > fulvic acids. Humic acid fraction is more hydrophobic than fulvic acid fraction and is therefore more easily destabilised by coagulation.

Industrial wastewaters often contain colloidal suspensions which can be destabilised by the addition of chemical coagulants [56]. Coagulant technologies can be used before biological wastewater treatment to remove toxic substances from the wastewater stream that could affect the survival of microbes at biological wastewater treatment plants [57]. Coagulant chemicals can be added into primary clarifiers to reduce the load on biological processes. With coagulation technology it is common to achieve high removals of pollutants; 95% total suspended solids (TSS), 65% chemical oxygen demand (COD) and 50% biological oxygen demand (BOD). Chemical coagulation can also be used after the biological wastewater treatment plant to remove residual phosphorus from the water stream. Phosphorus causes eutrophication in the receiving wastewaters and therefore, discharges of wastewater treatment plants have to be minimised. Chemical precipitation can be used to remove orthophosphates and particulate phosphorus species [3]. The stoichiometric of $Al_{added}:P_{removed}$ has been reported to vary from 1.4 to 4.3. The stoichiometric relationship is valid at high phosphorus concentrations and higher doses are required when concentration decreases. Typically optimum phosphorus removal occurs within the pH range of 5.5 to 6.0.

Iron (II) and iron (III) salts are also used in wastewater treatment plants or long pipeline systems to precipitate dissolved sulphides present in the wastewater. Hydrogen sulphide (H_2S) has a low odour threshold and besides common odour problems, hydrogen sulphide also has adverse effects on human health and causes corrosion of the sewers and other equipment [58–62]. Precipitation of dissolved sulphides is normally performed using iron salts, such as ferric chloride or ferrous sulphate [63–65]. Iron salts can be added prior to sulphide formation or into wastewater already containing sulphides. A higher concentration of iron salt is required if dosing is conducted before sulphide formation, because iron hydroxides and carbonates are formed, and iron cations only partially react with dissolved sulphide ions. Sulphides form black ferrous sulphide (FeS) according to Eq. 7 in the presence of Fe(II). Fe(III) can remove sulphides by chemically oxidising them to elemental sulphur (Eq. 8), while the Fe(II) formed during the reaction can subsequently produce FeS (Eq. 7). According to Firer et al. [64], the stoichiometry of the reaction with Fe(II) is approximately 1.3 mole of Fe^{2+} per 1 mole of S^{2-} removed, and with Fe(III) 0.9 mole is required per 1 mole of S^{2-} removed.

$$Fe^{2+}(aq) + HS^{-}(aq) \rightarrow FeS(s) + H^{+} \quad (7)$$

$$2Fe^{3+}(aq) + HS^{-}(aq) \rightarrow 2Fe^{2+}(aq) + S^{0}(s) + H^{+} \quad (8)$$

Common issues that arise when iron chemicals are used include the corrosion of equipment and a localised decrease in pH at the feeding point, which can release hydrogen sulphide into the sewer atmosphere. Due to the corrosive nature of the chemicals, special materials, such as titanium, are used in the tanks and piping, increasing capital costs of the equipment [66].

1.2 Theory of electrocoagulation

EC has a long history: the first plant was built in London in 1889 for the treatment of sewage [67, 68]. Despite some promising results, the success of this technology has been limited. However, there has been renewed scientific, economic and environmental interest in this technology in recent years due to demand of alternative water treatment technologies. EC understandably has several similarities with the chemical coagulation but also significant differences, such as side reactions, which are discussed in this section.

In the EC system there are multiple electrochemical reactions occurring simultaneously at the anodes and cathodes. These mechanisms can be divided into the main mechanisms that cause destabilisation of pollutants, and side reactions, such as hydrogen formation. The most important reactions are summarised in Fig. 4.

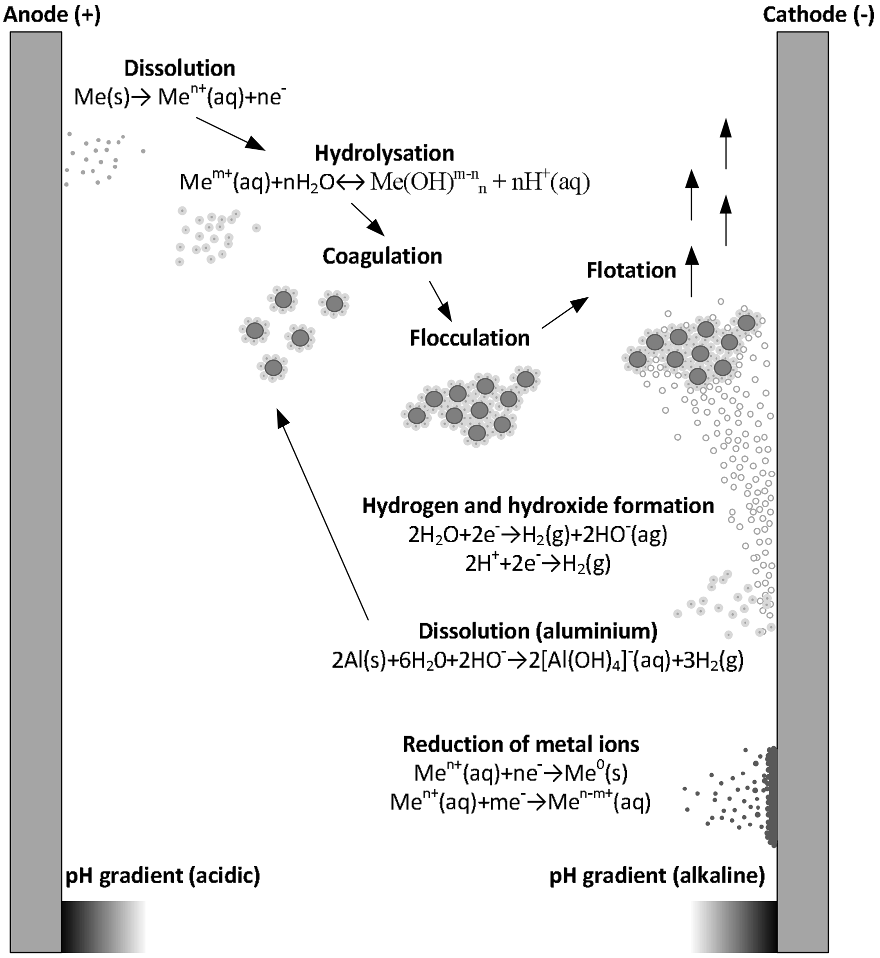


Figure 4. Schematic representation of typical reactions during the EC treatment.

1.2.1 Main reactions

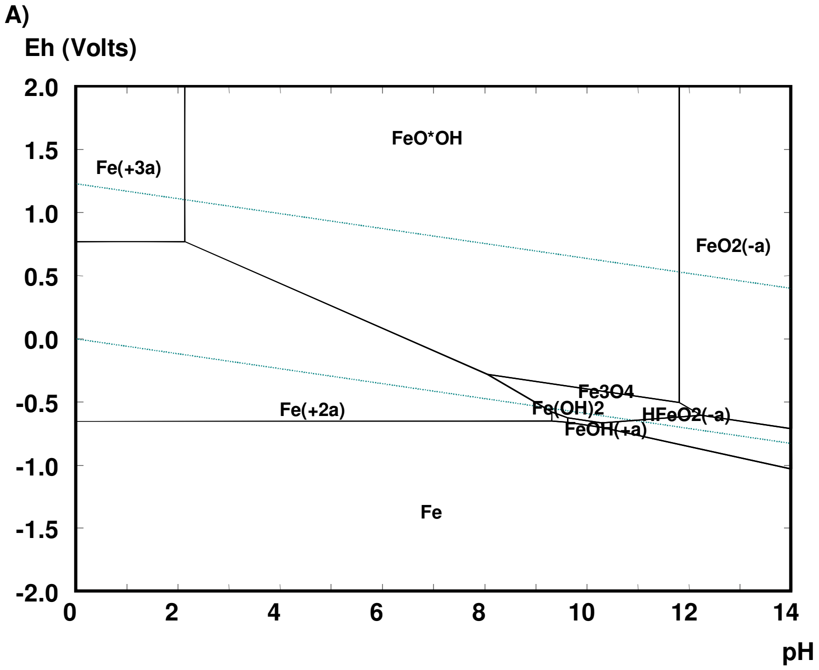
Electrodes which produce coagulants into water are made from either iron or aluminium. In addition, there can be inert electrodes, typically cathodes, which are sometimes used as counter-electrodes in the system. Iron and aluminium cations dissolve from the anodes according to Eqs. 9 and 10.

$$\mathrm{Fe}(s) \rightarrow \mathrm{Fe}^{n+}(aq) + n\mathrm{e}^{-} \tag{9}$$

$$\mathrm{Al}(s) \rightarrow \mathrm{Al}^{3+}(aq) + 3\mathrm{e}^{-} \tag{10}$$

In typical aqueous environments and conditions of the EC process, iron can dissolve in divalent Fe(II) and trivalent Fe(III) forms, whereas aluminium dissolves only in trivalent form Al(III). Fe(II) can further oxidise to Fe(III) (Eq. 11) if oxidation-reduction potential (ORP) and pH conditions are suitable. Oxygen has to present and pH has to be neutral or alkaline to achieve a reasonable reaction rate [69]. Thermodynamically stable forms of iron and aluminium in different ORP and pH conditions can be estimated using E-pH diagrams (Fig. 5).

$$4\mathrm{Fe}^{2+}(aq) + 10\mathrm{H_2O} + \mathrm{O_2}(aq) \rightarrow 4\mathrm{Fe(OH)_3}(s) + 8\mathrm{H}^{+} \qquad (11)$$



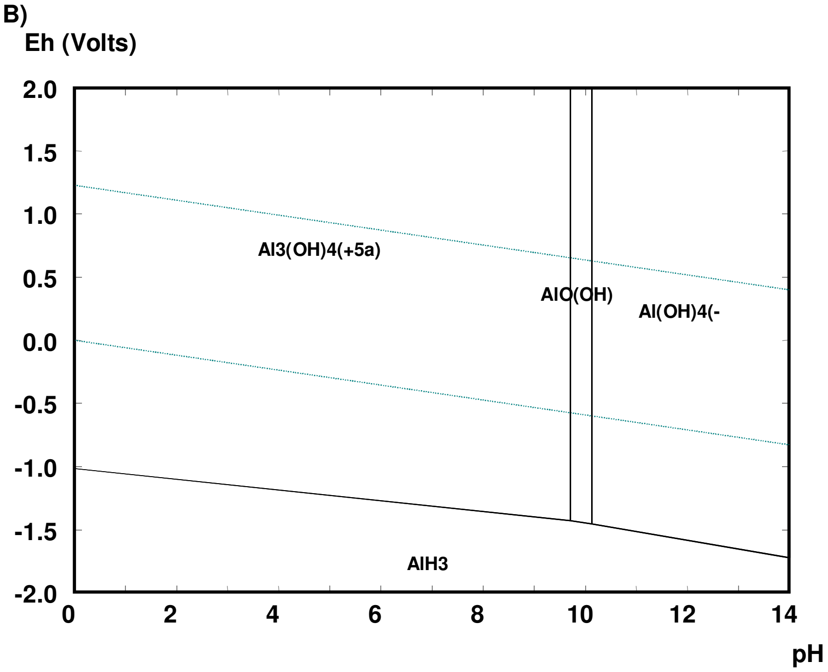


Figure 5. E-pH diagrams of a) iron and b) aluminium at 25 °C, 1 bar and 10–6 M.

Moreno et al. [67] studied the electrochemical reactions of iron electrodes in EC system. According to their results and the thermodynamical data they presented, the potential of the iron anode in an EC system is in the region where Fe(III) iron is produced. However, some authors suggest that the potential of the cathode is in the region where Fe(III) is reduced to Fe(II) form and therefore, both forms exists in the EC system [70, 71]. Iron is produced on the anodes mainly in Fe(II) form [72]. In low pH the chemical dissolution of iron can be significant and total iron concentration can be higher than would be theoretically expected. Sasson et al. also studied oxidation of produced Fe(II). According to their results, no significant oxidation occurred at pH 5, oxidation rate was moderate at pH 6 and very rapid oxidation occurred at pH 7–9.

The amount of metal cations dissolved during the reactions at the anode can be calculated according to Faraday's law (Eq. 12).

$$m = \frac{ItM_w}{zF} \quad (12)$$

where I is the current, t is the operation time (s), M_w is molecular weight of the substance (g/mol), F is Faraday's constant (96485 C/mol), z is the number of electrons involved in the reaction (2 for Fe^{2+} and 3 for Fe^{3+} and Al^{3+}) and m is the quantity of metal dissolved (g). Several studies have reported current yields higher than 100% for the dissolving of aluminium electrodes [73]. It seems that aluminium also dissolves from the cathodes. This occurs when pH on the surface of the cathode decreases due to the formation of HO^- (Eq. 13) or by the consumption of hydronium ions/protons (Eq. 14).

$$2H_2O + 2e^- \rightarrow H_2(g) + 2HO^-(aq) \tag{13}$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \tag{14}$$

At high pH, aluminium dissolves as aluminate (Eq. 15).

$$2Al(s) + 6H_2O + 2HO^-(aq) \rightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g) \tag{15}$$

Picard et al. [73] studied cathodic dissolution during the EC process. They compared hydrogen evolution from the stainless steel cathodes and aluminium cathodes. Hydrogen produced at the stainless steel cathodes followed Faraday's law. In tests with the aluminium cathodes, hydrogen production was higher due to the chemical dissolution of aluminium according to Eq. 15. Hydrogen formation and aluminium dissolved from the cathodes increased exponentially with the current intensities.

When aluminium ion, aluminate or iron ions are produced on the electrodes they experience hydrolysis or dehydrolysis reactions in the solution. Green rust is formed when iron electrodes are used [67]. Green rust contains both Fe(II) and Fe(III) hydroxides and anions, such as Cl^-, CO_3^{2-} and SO_4^{2-}. Other metal cations, such as Cu(II) and Ni(II), can also substitute Fe(II) in green rust if they exist in the solution [74, 75]. In an EC system, green rust and hydrogen are formed according to Eq. 16.

$$6Fe(s) + (12 + x)H_2O \rightarrow ½(12 - x)H_2(g) + xFe(OH)_3 \cdot (6 - x)Fe(OH)_2(s) \tag{16}$$

Mononuclear hydrolysis products of Fe(III) and Al(III) were presented in Fig. 2 as a function of pH. It is probable that similar polynuclear species are formed in EC and chemical coagulation. However, this has not been verified by experimental studies.

1.2.2 Side reactions

In addition to dissolving of aluminium and iron production, other electrochemical reactions can also take place in the EC system. They are:

- hydrogen formation at the cathodes due to Eqs. 13–15
- increase of pH due to the formation of hydroxyl ions or the consumption of hydronium ions/protons (Eqs. 13 and 14)
- reduction of metal ions on the cathodes.

Some articles have also speculated that oxygen is also produced on the anodes [76, 77]. However, it seems that this does not take place in typical conditions (electrochemical potential) of EC systems as dissolution of anodes follows Faraday's law [72, 78]. However, at alkaline pH, dissolution of iron anodes is lower than calculated according to Faraday's law, which indicates that other electrochemical reactions are taking place in these conditions.

There is technology called electroflotation (EF), which can be used to produce bubbles that can effectively separate particles from the solution [79–81]. In electroflotation technology, oxygen bubbles are produced on the anodes and hydrogen bubbles on the cathodes, whereas in EC technology only hydrogen bubbles are produced on the cathodes. The efficiency of the flotation in EC and EF technologies depends on the size of the bubbles. Smaller bubbles can provide a larger surface area for particle attachment. EF produces smaller diameter bubbles than commonly used dissolved air flotation (DAF) technology. The mean diameter of the hydrogen and oxygen bubbles generated in EF range from 17 to 50 µm, whereas in DAF the typical mean diameter of the bubbles range from 48 to 60 µm [80]. Usually, the diameters of the electrolytically generated bubbles obey log-normal distribution.

Electrode material, current density and pH affect bubble size. The smallest hydrogen bubbles are produced at neutral or acidic pH [80]. Stainless steel plates have been found to produce the smallest bubbles. There has been some controversy in the reported effects of current density on the bubble size. Sarkar et al. [82] studied the effect of current density and electrode on bubble size produced on the cathodes. They discovered that a significant proportion of hydrogen produced on the cathodes can be dissolved in the solution. According to their results, bubble size diameter is a function of hydrogen production rate, bubble nucleation rate and dissolved gas concentration field.

In contrast to chemical coagulation, EC treatment increases the pH of the solution when it is in an acidic, neutral or slightly alkaline region and decreases when it is highly alkaline. This change of pH during the EC treatment affects the speciation of aluminium and iron hydroxides. At highly acidic pH (pH 2) the alkalinity produced during the EC is not sufficient to increase the pH of the solution, whereas at pH 3 and higher initial pH values pH rises during the treatment [78]. This is easily understandable, as concentration of hydronium ions increases by factor 10 when pH decreases from pH 3 to pH 2. When initial pH is significantly alkaline (pH > 9), pH probably decreases due to the formation of aluminate [$Al(OH)_4^-$], which is an alkalinity consumer [83, 84]. It seems that the pH change rate and final steady-state pH depends on the concentration of anions in the solution. According to Trompette and Vergnes [85], pH increases more in sulphate solution than in chloride solution. As mentioned in Section 1.1.4 sulphates can replace hydroxyl ions in the hydroxide precipitates and therefore less hydroxyl ions are bound to hydroxides.

Because electrochemical reactions occur at the surface of the electrodes, the concentration of reaction products is highest at the electrode surface and the concentration gradient exists from the surface towards the bulk solution. Therefore, pH decreases at the vicinity of the anodes and vice versa at the cathode surface. This can lead to precipitation of inorganic salts on the electrode surface if their solubility changes as a function of pH, e.g., precipitation of calcium carbonate on the cathodes [86].

If electrochemical potential at the cathodes is in the right region, the direct electrochemical reduction of metal cations may occur at the cathode surface (Eq. 17).

$$\mathrm{Me}^{n+}(aq) + n\mathrm{e}^- \rightarrow \mathrm{Me}^0(s) \tag{17}$$

There are several studies where the removal of metals from wastewaters has been studied, as discussed later in Section 1.3.2. Results indicate that metals are mostly removed by coagulation and co-precipitation. However, the reduction of metal ions may have some effect on removal efficiency even if they are not reduced to the metallic state. Heidmann and Calmano [87] studied the removal of Zn(II), Cu(II), Ni(II), Ag(I) and Cr(VI) from aqueous solution by EC. They proposed that Zn(II), Cu(II), Ni(II) and Ag(I) were removed from the solution by hydrolysation and co-precipitation, whereas Cr(VI) was reduced first to Cr(III), after which it was precipitated as hydroxide. It is probable that dissolving of aluminium at the cathodes prevents plating of the cathode with other metals. With iron or inert cathodes, some plating could be expected at least with some metal ions, e.g., Ni(II) and Cu(II). It is possible that plating is a slow reaction in typical concentrations and removal occurs mainly by coagulation co-precipitation due to these kinetic reasons.

1.2.3 Properties of the sludge

The properties of produced sludge are important because sludge treatment and disposal are one of the major cost factors in water and wastewater treatment, especially when sludge has been produced by chemicals. The dried EC sludge produced by different combination electrodes during arsenic removal has been characterized by FTIR, PXRD, XPS, SEM-EDS and Mössbauer spectroscopy [71]. Dried sludge formed by Al-Al electrodes contained amorphous aluminium hydroxide and/or aluminium oxyhydroxide. Fe-Fe electrodes produced crystalline phases, such as magnetite, and poorly crystalline phases, such as iron oxyhydroxides and lepidocrocite. Sludge produced by combined Fe-Al electrodes contained the aforementioned products as well as mansfeldite, diaspore and iron oxide. Crystallinity of iron species decreased, possibly due to the substitution of iron by aluminium. Emamjomeh and Sivakumar studied the sludge produced during the fluoride removal by EC using XRD [88]. Identified products were aluminium fluoride hydroxide complexes and aluminium hydroxide. Shafael et al. [89] identified amorphous manganese and aluminium species in sludge produced by EC during Mn(II) removal.

The settleability of sludge produced by EC during paper mill [90] and textile wastewater treatment has been studied [91]. When paper mill wastewater was treated, the sludge volume index (SVI) was 0.207–0.310 L/g and 0.081–0.091 L/g for aluminium and iron electrodes, respectively. The sludge formed by iron electrodes was heavier and produced a more compact layer. The authors observed similar results with textile wastewaters. Hydrogen produced during the EC induces flotation of particles and decreases settling velocity. As discussed in Section 1.2.2, the operating parameters of EC affect the properties of hydrogen bubbles. Lai and Lin [92] treated chemical mechanic polishing wastewater by Al-Fe electrodes and studied settling properties of produced sludge. They concluded that complex models of third or fourth order described the sludge settling data.

The heat value of the sludge produced by EC has been measured using a bomb calorimeter [93]. Heat value was 5.3 MJ/kg and authors concluded that it could be used as a fuel in the furnaces and the produced ash could be blended with the cementitious mixtures. It is probable that sludge produced during the treatment of other wastewaters containing high organic matter also has a high heat value. The combination of EC and electrodewatering has been studied for the reduction of water content in sewage sludge [94]. The combination of EC and electrodewatering reduced water content of the sludge to 55%, whereas water content in sludge treated with only pressure filtration was 78%.

1.2.4 Treatment parameters

There are various parameters which have an effect on the efficiency of the EC in removing the pollutants from water. Parameters which are known to have an effect are:

- **Material of the electrodes** can be iron, aluminium and/or inert material (typically cathodes). Iron and aluminium ions and hydroxides have different chemistries and applications.
- **pH of the solution** has an effect on the speciation of metal hydroxides in the solution and also on the ζ-potential of the colloidal particles. It also affects the dissolution of aluminium cathodes.
- **Current density** is proportional to the amount of electrochemical reactions taking place on the electrode surface.
- **Treatment time** or electric charge added per volume is proportional to the amount of coagulants produced in the EC system and other reactions taking place in the system.
- **Electrode potential** defines which reactions occur on the electrode surface.
- **Concentration of the pollutants** affects the removal efficiency because coagulation does not follow zeroth-order reaction kinetics but rather pseudo second or first-order kinetics.

- **Concentration of anions**, such as sulphate or fluoride, affects the composition of hydroxides because they can replace hydroxide ions in the precipitates.
- **Temperature** affects floc formation, reaction rates and conductivity. Depending on the pollutant, increasing temperature can have a negative or a positive effect on removal efficiency.
- **Other parameters,** such as hydrodynamical conditions and inter-electrode distance, may have effect on efficiency of the treatment and electricity consumption. However, these parameters have not been widely studied or they have a negligible effect on the removal efficiency.

Electrode materials

Electrode material defines which electrochemical reactions take place in the EC system. Aluminium and iron electrodes have both been used successfully in EC systems. Aluminium dissolves in all cases as Al(III) whereas there is some controversy as to whether iron dissolves as Fe(II) or Fe(III) [67, 72]. Most results indicate that iron dissolves as Fe(II), such as [72, 95, 96], and is oxidised in bulk solution to Fe(III) if there are oxidants, such as oxygen, present in sufficient concentration and pH is alkaline (Fig. 5a, see p. 28). Fe(II) is a poor coagulant compared to Fe(III) due to higher solubility of hydroxides and lower positive charge, which explains some poor results obtained with iron electrodes, such as in the study of Bagga et al. [96]. Optimal material selection depends on the pollutants to be removed and the chemical properties of the electrolyte. In general, aluminium seems to be superior compared to iron in most cases when only the efficiency of the treatment is considered. However, it should be noted that aluminium is more expensive than iron.

Inert electrodes, such as metal oxide coated titanium, are used as cathodes in some constructions. When water has significant amounts of calcium or magnesium ions, the inert cathode material is recommended [76]. There are also some studies where combinations of aluminium and iron electrodes have been used. Linares-Hernández et al. [95] obtained high removal of colour with aluminium electrodes, while iron was more effective than aluminium in reducing COD from industrial wastewater. A combination of iron and aluminium removes both colour (71%) and COD (69%) with high efficiency. Similar results were obtained when paper mill wastewaters were treated with various aluminium and iron electrode combinations [97]. Aluminium electrodes were most effective in removing colour of the wastewater, whereas iron electrodes removed COD and phenol from the wastewater more effectively than aluminium electrodes. A combination of aluminium and iron electrodes removed colour, COD and phenol with high efficiency. Combination electrodes have been studied for arsenic removal from groundwater [71]. Iron electrodes and a combination of iron and aluminium electrodes gave the highest arsenic removal efficiencies. Similar results were obtained for copper, chromium and nickel removal from metal plating wastewater [98]. Fe-Al pair has been most effective in removing indium from water [99].

pH of the solution

One key parameters of EC treatment is the pH of the solution to be treated. It has an effect on the conductivity of the solution, dissolution of the electrodes, speciation of hydroxides and ζ-potential of colloidal particles. As discussed in Sections 1.1.3 and 1.1.4, aluminium and iron cations and hydroxides cause destabilisation of colloids. Effective coagulant species are formed in acidic, neutral and slightly alkaline pH. In highly alkaline pH $Al(OH)_4^-$ and $Fe(OH)_4^-$ ions are formed and these ions have poor coagulation performance. As can be seen in Fig. 2 (see p. 20), Fe(III) is effective in a wider pH area than Al(III) and works also in slightly alkaline pH. It is also known that competing anions have an effect on the optimum pH of the coagulation. The effect of water pH on the efficiency of pollutant removal can mostly be explained by the aforementioned mechanisms. However, as discussed in Section 1.2.3, pH increases during the EC treatment, making it a constantly changing parameter; therefore mechanistic studies of EC systems are difficult to conduct.

In pHs lower than 3, the release rate of aluminium during electrolysis with a constant charge per volume was lower than in pHs above 3 [78]. Chemical dissolution of aluminium cathodes occurs because pH increases to a level where aluminate is formed. It is probable that acidic bulk solution inhibits this reaction because produced hydroxyl ions are consumed by the acid in the solution. In acidic pH the dissolution of iron electrodes was significant even without electricity, whereas oxidation of Fe(II) to Fe(III) occurs only at pHs above 5 [72]. The dissolution rate decreases at high pH, which is understandable as the corrosion rate of iron decreases in alkaline pH in the presence of oxygen because a passive layer forms on the surface. It has been suggested that initial pH is key parameter when either chemical coagulation or EC is selected for the water treatment [100]. EC is more suitable when higher pH is desired (acidic solutions), whereas chemical coagulation is preferred when pH should decrease before discharge.

There are also some pollutants which have specific optimum pHs of treatment, such as phosphorus and metal cations. The effect of initial pH on phosphate removal from wastewater by EC with iron electrodes has been studied [101]. The highest removal efficiency was observed at the lowest tested initial pH (pH 3). Wastewater pH increased to a highly alkaline level (pH 10–12) during the long treatment, probably due to partial replacement of HO^- by PO_4^{3-}. In high pH the removal rate was poor due to the formation of $Fe(OH)_4^-$ and higher solubility of $FePO_4$. In higher pH there are more HO^- ions to compete with PO_4^{3-} and therefore less $FePO_4$ is formed. Other researchers have had similar results with iron electrodes when they studied the removal of phosphorus from secondary effluent [102]. According to Janpoor et al., phosphorus removal from laundry wastewater with aluminium electrodes was poor when initial pH was lower than 6 or higher than 8 [103].

As with aluminium and iron, other metal cations can also form hydroxides in water. Most non-ionic hydroxides have low solubility in water and can be removed by precipitation and co-precipitation with EC systems. Hanay and Hasar [104] studied removal of Cu(II), Mn(II) and Zn(II) by aluminium electrodes. Removal efficiency increased when initial pH of the wastewater increased. Similar results have been obtained for the removal of Co(II) [105], As(V) [106], Cu, Cr and Ni [98], Cu(II), Pb(II) and Cd(II) [107], Cu(II), Ni(II), Zn(II) and Mn(II) [108], In(III) [99], Mn(II) [89] and Cr(III) [109]. Hg(II) removal was not significantly affected by initial pH in the range of 3–7 [110].

Current density and treatment time

Current density is directly proportional to the rate of electrochemical reactions taking place on the electrode surface and it also has an influence on the electrode potential, which defines the reactions taking place on the electrode surface. It seems that on iron and aluminium anodes, dissolution reaction is the primary reaction, and the proportion of other reactions is insignificant at the typical current densities and electrode potentials when pH is neutral or acidic [72, 78]. At alkaline pH the dissolution rate of iron anodes can be lower than the value calculated by Faraday's law, which indicates that there can be other reactions at the anode in these conditions [72].

Coagulant produced by electrolysis can usually be calculated according to Faraday's law when current and treatment times are known (Eq. 12). Coagulant concentration produced by electrolysis on anodes is typically directly proportional to the electric charge added per volume (coulombs per litre). However, the total amount of coagulant dissolved also includes chemical dissolution of the electrodes in low pH and the dissolution of aluminium cathodes. Current density probably has some influence on the chemical dissolution of aluminium cathodes, as it affects the rate of hydroxyl ion production at the cathodes. Mouedhen et al. [78] studied aluminium dissolution from the cathodes with an electrochemical cell constructed of platinised titanium anode and aluminium cathode. They used constant charge per volume (540 C/L) and various current densities. According to their results, as the current density decreases the amount of aluminium generated increases. These results indicate that even low current density (< 1 A/dm^2) initiates the dissolving reaction on the cathodes if solution pH is not highly acidic and therefore the produced amount of aluminium on the cathodes depends more on the treatment time than the electric charge added per volume.

Concentration of anions

Concentration of anions in the solution affects the stability of passive layer of the aluminium electrodes. Sulphate anions are passivating agents and therefore reduce the production of metal cations [111]. Chloride, on the other hand, induces the breakdown of the passive layer and pitting corrosion. The effect of supporting electrolytes on the efficiency of an EC system has been studied by treating unskimmed milk samples and a cutting oil emulsion by aluminium electrodes in the presence of $NaCl$, Na_2SO_4, NH_4Cl and $(NH_4)_2SO_4$ [85]. According to results, sulphate anions increase electrical consumption and have a negative effect on EC efficiency. Ratio of $[Cl^-]/[SO_4^{2-}]$ should be 0.1 or higher to ensure breakdown of the passive film. Mouedhen et al. [78] reported that optimum concentration of Cl^- ions was 61 mg/l. In addition to the effect on the passive layer, some salts can precipitate on the cathodes if the concentration of salts in water is sufficiently high [86]. This insulating layer increases power consumption significantly [76].

As discussed in Section 1.1.4, competing anions can replace hydroxyl anions in the precipitate, which has an effect on the properties of hydroxide and therefore, also on efficiency and optimum conditions of coagulation processes. Competing anions can also have a direct influence if the pollutant is anion e.g. fluoride or phosphate. Hu et al. [112] studied fluoride removal in the presence of chloride, nitrate and sulphate anions. They obtained the best results in the absence of these anions. Sulphate ion concentration had a significant effect on the removal efficiency of the fluoride, probably because it can compete with fluoride ions from Al(III). According to Vasudevan et al. [113] fluoride and arsenate compete with phosphate ion and reduce its removal by EC.

Temperature

The effect of temperature on the removal of pollutants through EC has been studied in a few articles. The effect of solution temperature on boron removal by EC has been studied in the range of 293–333 K [114]. When temperature increased from 293 K to 333 K, the boron removal efficiency increased from 84% to 96%. The opposite effect has been reported when paper mill wastewater was treated at temperatures between 293 and 333 K [97]. Removal of colour, COD and phenol decreased by 10–20% when temperature increased from 293 K to 333 K. The effect of temperature on phosphate removal from wastewater by EC has been studied in the range of 293–333 K [113]. Removal efficiency was 29% lower at 293 K than in higher temperatures. Authors concluded that at low temperatures the dissolution of anode occurs at a lower rate. However, they did not present any results, such as concentrations of aluminium dissolved from electrodes, which would support this conclusion.

It has been suggested that when temperature is too high, there is a shrinkage of large pores of the $Al(OH)_3$ gel, which causes the formation of dense flocs that are more likely to deposit on the electrode surface [76]. Increasing temperature also enhances the solubility of aluminium. However, it seems that increasing temperature can have positive and negative effects on the removal efficiency. It is possible that the effect of temperature on removal efficiency depends on the removal mechanism of pollutants.

1.2.5 Comparison of electrocoagulation and chemical coagulation

There are only a few published studies in which chemical coagulation and EC have been compared. However, these technologies can be considered competing technologies and therefore, the comparisons of treatment efficiencies are important. As previously mentioned, reliable comparisons are difficult to conduct due to the dynamic nature of the EC process.

Change of pH during the EC and its effect on aluminium species formed has been studied [100]. The formation of monomeric and polymeric aluminium hydroxides were compared when aluminium was added as $AlCl_3$ or by EC. According to results, there are no significant differences in the speciation of aluminium obtained by these two methods. Authors concluded that both processes are similar in terms of removing the pollutants from the wastewater under the same dynamic conditions, doses of aluminium and steady-state pHs.

EC and chemical coagulation have been compared in the treatment of ultrafine quartz suspensions [115], the removal of Cr(VI) [116] and as a pretreatment before microfiltration membranes [96, 117]. Kiliç et al. [115] compared chemical coagulation and EC and the effect of initial pH and aluminium dosage on the removal efficiency of a model pollutant (ultrafine quartz particles). They used aluminium anodes and stainless steel cathodes. The optimum pH for the removal of particles was 9 for EC and 6–9 for chemical coagulation. Wider optimum coagulation pH with chemical coagulant was probably a result of higher sulphate concentration because aluminium sulphate was used as a chemical coagulant. The effect of aluminium dosage on the destabilisation of pollutants and optimum aluminium dosages were similar with both technologies. Both technologies removed turbidity equally well. Researchers suggested, based on the ζ-potential measurements, that destabilisation mechanisms are similar with both technologies.

EC was more effective (42%) than chemical coagulation (approximately 11.5%) at removing Cr(VI) from aqueous solution [116]. Some Cr(VI) was removed by deposition on the cathode. Alum and aluminium sulphate showed poor Cr(VI) removal, which was probably due to competitive adsorption of sulphate ions on the sludge matrix. Zhu et al. [117] compared EC and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes. Both technologies improved virus removal but EC outperformed chemical coagulation in removal efficiency. The researchers suggested that the enhanced removal by EC was due to electrophoretic movement of viruses on electrodes. However, the effect of electrophoresis on removal efficiency in EC has not been reliably verified by experimental studies. Somewhat opposite results were obtained when chemical coagulation and EC were compared at pretreatment for surface water microfiltration [96]. Chemical coagulation with ferric chloride was superior compared to EC with iron anode and stainless steel cathode. Iron dissolved in Fe(II) form which had higher solubility and poor coagulation performance compared to Fe(III) in ferric chloride. NOM can prevent oxidation of Fe(II) to more effective Fe(III) form [118]. Zhu et al. [117] used synthetic freshwaters which did not include NOM in their studies, which may explain better performance of EC in their research.

According to studies in which EC and chemical coagulation have been compared, it seems that these technologies have similar destabilisation mechanisms. However, a chemical coagulant is added together with anion, such as sulphate or chloride, which may have some influence on the efficiency of the process. In some cases, side reactions, such as reduction on the cathode surface, may play an important role in the destabilisation of pollutants. Iron is dissolved from the iron electrodes in Fe(II) form and hence oxidation to more effective Fe(III) form is important in order to obtain high removal efficiency. Therefore, it would be more descriptive to compare Fe(II) coagulants, such as ferrous sulphate, and EC with iron electrodes.

1.3 Practical considerations of electrocoagulation

1.3.1 Constructions of electrocoagulation systems

EC systems are typically constructed of plate electrodes and water flows through the space between the electrodes [76]. There are several methods how electrodes can be arranged in the EC system. Flow between the electrodes can follow a vertical or horizontal direction. Electrodes can be monopolar or bipolar. In the monopolar systems (Fig. 6a) all anodes are connected to each other and similarly all cathodes are also connected to each other. In the bipolar systems (Fig. 6b) the outermost electrodes are connected to a power source and current passes through the other electrodes, thus polarising them. In the bipolar systems the side of the electrode facing the anode is negatively polarised and vice versa on the other side facing the cathode.

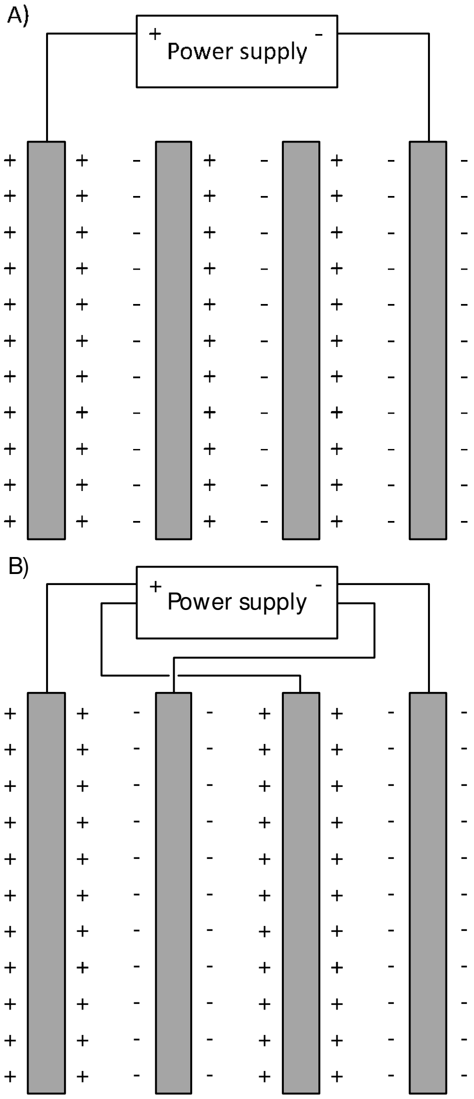


Figure 6. Connections and electrode polarity in a) bipolar and b) monopolar EC systems.

The pollutant removal efficiencies and operating costs of monopolar and bipolar configurations have been compared in several studies [119–124]. Slaughterhouse wastewaters have been treated with mild steel and aluminium electrodes arranged in bipolar or monopolar configurations [123]. The best performance was obtained using mild steel electrodes in bipolar configuration. Economic calculations were made based on the results but electrode consumption was calculated according to Faraday's law which gives false results, especially when aluminium electrodes are used. Golder et al. [119] studied Cr^{3+} removal with EC by mild steel electrodes. Current efficiency for the dissolving of the mild steel electrodes was lower when electrodes were in bipolar configuration (64.5%) than when they were in monopolar configuration (91.7%). This is probably due to the higher electrode potential of the electrodes in bipolar arrangement and competing reactions taking place on the electrodes. A complete removal of Cr^{3+} was obtained when electrodes were in the bipolar arrangement. However, treatment cost was lower with a monopolar arrangement when the treatment was continued to the discharge limit. Similar results were reported when EC was used for the removal of fluoride from drinking water [120]. The bipolar connection removed fluoride more effectively but operating costs of the treatment were higher with this configuration. Monopolar configuration has been reported to be better in the treatment of laundry wastewater [121], oily bilge water [122] and textile wastewater [124]. Results of the aforementioned studies could be summarised so that monopolar configuration has lower operating cost but in some cases higher removal of pollutants can be achieved with bipolar configuration, possibly due to additional side reactions.

Typically, direct current (DC) has been used in EC systems. However, there are a few studies in which alternating current (AC) has been tested. Vasudevan et al. [125] studied the removal of fluoride from water with DC and AC EC systems. They observed similar removal efficiencies with both technologies. However, energy consumption was slightly lower with AC technology. Eyvaz et al. [126] used alternating pulsed current in their study. Alternating pulsed current enhanced removal efficiency compared to DC current. Pollutant removal decreases over the course of time with DC systems, possibly due to passivation of electrodes, whereas in an alternating pulse current system this was not observed. Polarity reversal has also been suggested by other authors to reduce passivation of electrodes [127].

In addition to actual coagulation procedure, some sludge removal process has to follow EC. As with chemical coagulation, these can be flotation, sedimentation or filtration. Due to hydrogen bubble production, flotation is often the preferred choice. These separation technologies are discussed in detail in books such as [1, 3, 127].

1.3.2 Applications of electrocoagulation

Most of the articles published on EC concentrate on the removal of some specific pollutant or pollutants from synthetic or real solutions. The majority of these application studies can be divided into the following categories:

- **Removal of metal ions and/or hydroxides** from synthetic solutions, groundwaters or wastewaters (Table 2). Typically high or complete removal could be obtained when treatment parameters are optimised. Aluminium, iron and combination electrodes can be used in EC system.

- **Removal of organic material** from wastewaters or synthetic solutions (Table 3). High removal (> 70%) is typically obtained with optimum parameters. Aluminium, iron and combination electrodes can be used. In general, iron electrodes give higher organic matter removal, whereas higher colour removal is obtained with aluminium electrodes.
- **Purification of surface waters** from natural organic matter, inorganic pollutants or microbes (Table 4). Typically high removal of pollutants (> 90%). Aluminium electrodes are more commonly used than iron electrodes in these applications.

Tables 2–4 review relevant and recent publications in these categories. There is also a review article where most of the applications have been discussed [128]. Practically all articles report a higher removal percentage when higher current density and/or treatment times are used. Therefore, this finding was not included in Tables 2–4. This result is easily understandable as produced coagulant concentration in solution increases as a function of electric charge added as discussed in Section 1.2.4.

Table 2. Recent studies in which EC has been used to remove metal pollutants from water.

Pollutants	Matrix	Electrode material	Studied parameters	Optimum conditions and notes	References
Arsenic as As(VI) or As(III)	Synthetic solutions, groundwater	Fe, Al and combination electrodes	Initial pH, initial concentration, current density, treatment time, electrochemical cell designs	Can obtain practically total removal of As. Optimum removal with modified flow or airlift reactor and neutral to alkaline pH. Oxidation of As(III) to As(VI) can take place.	[70, 71, 106, 129–131]
Chromium as Cr(VI) or Cr(III)	Synthetic solutions, wastewaters	Al, Fe and combination electrodes	Initial pH, current density, electrolyte concentration, electrode material, conductivity, treatment time	Practically complete removal of Cr possible. Reduction of Cr(VI) to Cr(III) can take place during EC.	[70, 87, 98, 109, 116, 119, 132–136]
Cobalt as Co(II)	Synthetic solutions	Al electrodes	Current density, initial pH, conductivity, initial concentration, treatment time	Initial pH has significant effect on removal efficiency. Higher removal efficiency in neutral or alkaline initial pH.	[105]
Iron as Fe(II)	Fe(II) added into tap water	Al electrodes	Current density, initial concentration, treatment time, inter-electrode distance	Practically complete removal with long treatment time and/or high current density.	[137]
Mercury as Hg(II)	Synthetic solutions, surface water	Al and Fe electrodes	Current density, initial pH, treatment time, inter-electrode distance, electrode material	Practically complete removal of mercury. Higher efficiency of treatment with iron electrodes.	[110]
Indium as In(II)	Synthetic solutions	Al, Fe and combination electrodes	Initial concentration, supporting electrolytes, electrode material, initial concentration, applied voltage	Highest removal efficiency with Fe-Al electrodes. Kinetics of indium removal follows pseudo-second order mechanism.	[99]
Manganese as Mn(II)	Synthetic solutions	Al electrodes	Initial pH, current density, treatment time, anions, conductivity, initial concentration.	Improved removal in neutral and alkaline pH. Possible direct reduction at the cathode surface.	[89, 104]
Mixed metal wastewaters	Synthetic solutions, wastewaters	Al, Fe and combination electrodes, stainless steel	Electrode material, current density, initial pH, conductivity, treatment time, anions, flow rate, initial concentration	Generally improved removal at neutral or alkaline pH. Iron or combination electrodes may give improved results compared to aluminium. Reduction of metals can take place.	[70, 87, 98, 104, 107, 134–136, 138]

Table 3. Recent studies in which EC has been used to remove organic pollutants from wastewaters.

Pollutants	Matrix	Electrode material	Studied parameters	Optimum conditions and notes	References
Dyes, textile wastewater	Synthetic solutions, wastewaters	Al, Fe and stainless steel electrodes	Pulsed current frequency, power supply type, initial pH, current density, treatment time, electrode potential, dye auxiliary chemicals	Alternating pulsed current gives improved results compared to DC (passivation prevention). High removal efficiency (> 90%) obtained with optimal parameters. Na_2CO_3 causes adverse effects. Colour and COD abatement followed pseudo-first order kinetics.	[124, 126, 139–142] [70, 71, 106, 129–131]
Slaughterhouse wastewaters, manure	Wastewaters	Al and Fe electrodes	Treatment time, current density, initial pH, supporting electrolyte, electrode material	Over 70% removal of COD, colour and oil-grease obtained. Highest removal efficiency in acid or neutral pH. Al electrodes are more effective in removing COD and colour, whereas iron is more effective in removing oil-grease.	[143, 144]
Tannery wastewaters	Wastewaters	Al and Fe electrodes, stainless steel cathodes	Current density, initial pH, conductivity, initial concentration, treatment time, electrode configuration	Fe electrodes are more effective for the removal of COD and sulphide than compared with aluminium electrodes. Better treatment efficiency obtained when initial pH was acidic. Typically high removal of COD, BOD, TSS, sulphide, oil-grease, Cr, Fe and turbidity (80–100%) obtained. Kinetics follows pseudo first or second-order kinetics.	[145–149]
Pulp and paper wastewaters and streams	Wastewaters, waste streams	Al and Fe electrodes and combinations	Electrode material, initial pH, current density, treatment time, supporting electrolyte, stirrer speed, electrode distance, temperature	Al is more effective. Slightly acidic or neutral initial pH gives higher removals. Increasing rotation speed and electrode distance increases removal of pollutants. Increasing temperature from 20 °C to 60 °C decreases efficiency. Typically 70–100% removal of COD, BOD, polyphenols and colour. Combination electrode gives high efficiency.	[90, 97, 150–154]
Olive mill wastewaters	Wastewaters	Al and Fe electrodes	Current density, initial pH, treatment time, supporting electrolyte, supporting oxidants and coagulants	Typically over 70% removal of COD, polyphenols, turbidity, SS and colour. Significantly decreases toxicity of wastewater. Highest removal obtained when initial pH is neutral or slightly acidic. Fe can give higher removal efficiency than Al. Oxidants and other coagulants can improve removal.	[155–157]
Oily waters, petroleum refinery wastewaters	Wastewaters	Al, Fe and stainless steel electrodes	Electrode configuration, treatment time, electrode material, initial pH, initial concentration, supporting electrolyte, temperature	Typically > 90% removal of BOD_5, oil and grease, petroleum hydrocarbons, TSS, turbidity and sulphate obtained. High removal when initial pH is acidic, neutral or slightly alkaline. Fe electrodes can be more efficient than Al. Removal increases at lower temperatures.	[122, 158, 159]

Table 4. Recent studies in which EC has been used to remove pollutants from surface waters or groundwaters and nutrients from wastewaters.

Pollutants	Matrix	Electrode material	Studied parameters	Optimum conditions and notes	References
Surface water, natural organic matter	Synthetic solutions, surface waters	Al and Fe electrodes	Initial pH, current density, applied voltage, supporting electrolytes, initial concentration, treatment time, inter-electrode distance	Slightly acidic initial pH gives optimum results by preventing formation of gel layer on the electrode surface. NaCl or Na_2SO_4 are favourable supporting electrolytes. Simultaneous removal of microbes obtained.	[160–165]
Boron	Geothermal waters	Al electrodes	Initial pH, current density, temperature, treatment time	High boron removal efficiency (96%) obtained. Increasing temperature increases removal efficiency. Optimal pH is slightly alkaline (pH 8).	[114]
Fluoride	Synthetic solutions	Al electrodes	Anions, current density, initial concentration, initial pH, flow rate, residence time	Fluoride competes with other anions. Sulphate inhibits localised corrosion of the electrodes. Chloride and nitrate prevent the effect of sulphate and enhance corrosion. Neutral pH is optimum. Practically complete removal of fluoride possible.	[88, 112, 166]
Microorganisms	Synthetic solution	Al, Fe and stainless steel electrodes	Current density, treatment time, electrode material, initial pH, treatment time, salinity	Al electrodes were slightly more effective than Fe or stainless steel. Complete removal of microorganisms is possible. Efficiency of the treatment increases with increasing temperature.	[165, 167, 168]
Nitrate	Synthetic solutions	Al and Fe electrodes	Initial pH, treatment time, current density, initial concentration	Optimal removal at alkaline pH (pH 10–11). Nitrate removal follows first-order reaction kinetics. Current density did not affect removal when same dose of coagulant was added during EC. Over 90% removal can be obtained.	[169, 170]
Phosphates and phosphorus	Wastewaters, synthetic solutions	Al and Fe electrodes, stainless steel cathodes	Electrode material, treatment time, initial pH, controlled pH, current density, temperature, anions, initial concentration, inter-electrode distance, conductivity, supporting electrolyte	Practically complete removal of phosphate is possible. The adsorption process follows second-order kinetics. Competing anions affect removal efficiency. Very low temperature decreases removal efficiency. Al more efficient than Fe. High efficiency in acidic initial pH.	[101–103, 113, 171, 172]

1.3.3 Combinations of electrocoagulation and other water treatment technologies

Besides the sludge separation technologies, filtration, flotation and sedimentation, other water treatment technologies have also been combined with EC. EC has been combined with chemical coagulants [173], Fenton-oxidation [174], hydrogen peroxide [175, 176], ozone [177], photocatalysis [178–180] and biofiltration [102].

The addition of oxidants such as hydrogen peroxide or ozone increases the removal of organic material from wastewaters. Kabdaşli et al. [174] studied the removal of organic matter and heavy metals from metal plating effluents using a combined EC-Fenton process. Stainless steel electrodes were used as anodes and cathodes. The combined process increased the removal of organic matter compared to EC only. The optimal dose of hydrogen peroxide was 15–30 mM. Roa-Morales et al. [176] treated wastewater from pasta and biscuit processing with aluminium EC combined with peroxide additions. Hydrogen peroxide additions slightly increased COD removal compared to pure EC. Ozonation of effluent after EC can further decrease the concentration of organic matter in the effluent [177]. Higher removal efficiencies could be obtained when iron electrodes are used instead of aluminium because the presence of Fe(II) catalyses the decomposition of oxidants to hydroxyl radicals, which can mineralise organic pollutants. Residual organic matter after EC can be also removed with photocatalysis according to our study [180] and Boroski et al. [178, 179].

Can et al. [173] combined EC with chemical coagulants PACl and alum. The addition of chemical coagulants decreases pH, whereas EC increases it and with a combination system, the final pH can be stabilised to neutral region. EC combined with PACl gave higher COD removals than combination with alum. PACl has more prepolymerised species, which can be more efficient in pollutant removal and it also contains chlorides which increase localised corrosion of electrodes and reduce energy consumption. Yu et al. [102] combined EC with biofiltration. Combining EC to biofiltration increased the removal of COD and phosphorus from 69.1% and 9.6% to 76.6–83.7% and 70.7–93.0%, respectively.

1.3.4 Economical and ecological considerations

Operating cost calculations have been made in a few articles. Calculations typically include the cost of chemicals, electrodes and energy. It should be noted that the price of materials and energy changes over the course of time and therefore, operating costs are only rough estimates. Cost calculations do not typically include investment costs, which may be significant including, for example power supplies, electrochemical cell vessels and sludge separation systems.

The treatment cost of dye polluted wastewaters has been estimated by Eyvaz et al. [126]. The estimated operating cost was USD 1.3–3.4 per kg TOC removed depending on parameters, such as treatment time. Sridhar et al. [151] carried out an economic analysis of the operating cost of EC treatment of pulp and paper industry bleaching effluents. Operating costs varied from USD 1.52 per m^3 to 1.72 per m^3. Ölmez [133] estimated the cost of Cr(VI) removal from wastewaters. The total cost of the EC process was about two-fold compared to the conventional process because of higher electricity consumption. Meunier et al. [135] compared the cost of electrochemical and chemical precipitation with calcium hydroxide or sodium hydroxide. EC was up to five times cheaper than chemical precipitation. Emamjomeh et al. [88] estimated operating costs of fluoride removal from water. Operating cost was AUD 0.36–0.61 per m^3 when initial fluoride concentration was 5 mg/l. Kobya et al. [181] have published their operating cost calculations on the treatment of waste metal cutting fluids using EC. The operating cost was USD 0.025–0.90 per m^3 and USD 0.01–0.79 per m^3 with iron and aluminium electrodes, respectively. Espinoza-Quiñones et al. [149] made operational cost calculations for tannery wastewater treatment with EC. They estimated that a 60 min treatment (high removal of pollutants) costs USD 1.64 per m^3, which was less than with conventional coagulants. According to Bayramoglu et al. [124], the operating cost of chemical treatment of textile wastewater by chemical coagulation was 3.2 times as high as that of EC.

It can be noticed that there are few articles where the costs of chemical coagulation and EC have been compared. It might be difficult to obtain reasonable information on the price of common coagulants. Some chemical coagulants, such as aluminium sulphate and ferric chloride, are bulk chemicals and have a low price, whereas prehydrolysed metal coagulants are more expensive. The price of chemicals naturally depends on the amount that is required in the process and therefore, major consumers, such as pulp and paper mills or municipal water treatment plants, pay less for their chemicals than small users. However, iron and aluminium are typically more expensive in their metallic state than as metal salts because production of metals is energy consuming. Coagulation chemicals are produced from the minerals and are not transformed into the metallic state during this process. For example, aluminium sulphate is manufactured through the reaction of aluminium trihydrate and sulphuric acid. Aluminium trihydrate is made from bauxite mineral by purification. Also the ecological effects of EC are somewhat unknown. As mentioned earlier, production of metallic aluminium and iron consume high amounts of energy [182]. It has been estimated that aluminium production consumes 5% of the electricity generated in the USA. Typically, aluminium is recycled and this process requires significantly less energy than the production of pristine metal. The ecological effect of water purification with EC and chemical coagulants should be compared, taking energy and material consumption into account during the manufacture of metals or chemicals.

2. Objectives and structure of the work

2.1 Surface water treatment by electrocoagulation

The objective in Publications **I–III** was to study the parameters affecting NOM removal by EC. The effect of current density, treatment time, electric charge added per volume, temperature, initial pH and electrochemical cell structure on the removal efficiency of NOM were investigated. Relevant water quality parameters were measured before and after treatment to evaluate the performance of the treatment. In Publication **I**, one objective of the study was to investigate whether chemical coagulation and EC could be used in combination. Statistical design of experiments (DOE) and models were used in Publication **II–III** to interpret the effect of treatment parameters and their combinations on NOM removal and to optimise parameters of EC.

2.2 Wastewater treatment by electrocoagulation

The objective in Publications **IV** and **V** was to investigate two specific applications of EC in wastewater treatment; the removal of sulphides in Publication **IV** and the removal of toxic pollutants in Publication **V**. In both papers, the main parameters affecting removal efficiency were studied. Wastewaters and effluents used in the studies were collected from pulp and paper mills. Synthetic pollutants were also used in Publication **V** in order to study the removal of single pollutants using EC treatment. Statistical methods were used in Publication **V** to interpret the results and to optimise the treatment parameters.

3. Materials and methods

3.1 Water samples and chemicals

Surface water samples (**I–III**) were collected from a water treatment plant of a Finnish paper mill. In the mill, water passed through a mechanical sieve that removed coarse material from water but concentrations of colloidal and dissolved material were not affected. The water was typical Nordic surface water that contained high concentrations of NOM and was highly coloured but had low turbidity (Table 5). The water was neutral (pH 6.2–6.5) and it had low conductivity (2.8–3.6 mS/m).

Table 5. Initial quality of surface waters used in the studies.

	Publ. II	**Publ. III**
Turbidity (NTU)	0.34	0.51
Apparent colour (mg/L PtCo)	102	83.7
TOC (mg/L)	18.29	16.41
SUVA [L/(m mg)]	4.52	3.51
ζ-potential (mV)	-15.2	-17.1
Residual Al (mg/L)	0.315	0.257
Residual Fe (mg/L)	0.884	0.348
Residual Mn (mg/L)	0.121	

Wastewaters and effluents were also collected from pulp and paper mills (Table 6). Wastewater used in the sulphide experiments (**IV**) contained high amount of organic matter and sulphurous anions. Before the experiments, wastewater was filtered through a coarse filter and gently stirred at 40 °C to promote the growth of sulphate reducing bacteria (SRB) which converted sulphates to sulphides. Debarking effluent used in the toxicity removal tests (**V**) was highly coloured and contained high concentrations of organic matter. Debarking effluents are known to contain tannins and resin acids which are both toxic to microorganisms and also to animals, such as fish [183–189]. Debarking effluent was also filtered through a coarse filter prior to the experiments.

Table 6. Initial parameters of the wastewaters and debarking effluents used in the studies.

	Wastewater (IV)	Debarking effluent (V)
Turbidity (NTU)		216
pH	6.5-7.1	5.21
Conductivity (mS/cm)	1.4-3.0	0.86
ORP (mV vs. SCE)	-300-(-200)	
Apparent colour (mg/L PtCo)		1910.00
TOC (mg/L)		575.00
DOC (mg/L)	300-450	437.00
COD_{cr} (mg/L)	800-1500	
ζ-potential (mV)		-18.5
Sulphate (mg/L)	600	
Dissolved oxygen (mg/L)	0.5-2.0	
Dissolved sulphide (mg/L)	7.5-9.5	
Phosphorus (mg/L)	1.3-1.5	
Toxicity (EC_{50})		7.6

Synthetic resin solutions were used in the toxicity removal tests in order to analytically study the removal of resin acids and metal pollutants and their toxicity by EC (**V**). Solutions were prepared using Polish wood rosin (Hercules Corporation, USA) and copper nitrate $Cu(NO_3)_2$. The composition of Polish wood rosin is presented in Table 7. Additional tests were conducted using pure dehydroabietic acid (DHAA) and isopimaric acid (IPA) (99%, Helix Biotechnologies, Canada). Lake water was used to dilute solutions to obtain a realistic background for EC tests.

Table 7. Breakdown of resin acids content of the Polish wood rosin (Hercules Corporation, USA).

Resin acid	% (w/w)
Pimaric acid	8.0
Sandaracopimaric acid	1.7
Isopimaric acid	3.1
Palustric acid	20.7
Dehydroabietic acid	30.6
Abietic acid	22.4
Neoabietic acid	5.3
Levopimaric acid	8.2

Water pH was adjusted (**I–III, V**) to the desired level using sulphuric acid and sodium hydroxide solutions. Auxiliary electrolytes, sodium chloride (NaCl) (**I**) and sodium sulphate (Na_2SO_4) (**V**), were used in some studies to acquire reasonable conductivity. A chemical coagulant, PACl, was used in tests of combined EC and chemical coagulation (**I**). All inorganic salts and pH adjustment chemicals used in this study were of analytical grade except PACl, which was typical commercial grade used in the water treatment plant of a paper mill.

3.2 Water treatment procedure

Possible auxiliary chemicals were added into the water prior to electrochemical treatment. Electrochemical treatments were conducted in regular glass beakers. During the treatment, water was stirred with a standard magnetic stirrer. The electrochemical cell was constructed of either aluminium (**I–III**), iron (**IV, V**) or combinations of aluminium and inert electrodes (**II**). Combinations of aluminium and inert electrodes were constructed so that either anode (Cell A) or cathode (Cell C) or both electrodes (Cell T) were made of aluminium. In the Cell A and Cell C other electrodes were made of inert material which does not dissolve in these conditions. In all tests, electrodes were in a monopolar configuration. Electrode assembly was constructed of 70 mm * 120 mm (**I**) or 50 mm * 70 mm (**II–V**) plate electrodes. In total, four (**I, IV, V**) or 6 (**II, III**) electrode plates were used (half anodes and other half cathodes). The distance between the electrode plates was 5 mm (**IV**) or 10 mm (**I–III, V**). Electrochemical cells was constructed using plastic nuts and bolts to prevent short-circuiting of electrode plates. Standard laboratory power supplies were used in the experiments. Electrolysis parameters are presented in Table 8.

Table 8. Electrolysis parameters of this study.

	Cur. density (mA/cm^2)	Electric charge (C/L)	Voltage (V)
Surface water (**I-III**)	0.36-1.79	0-150	3-32
Wastewater (**IV**)	3.6-17.9	0-4500	2-11
Debarking effluent (**V**)	7.1-21.4	0-2700	8-25

In some of the studies, samples were transferred into a programmable stirrer (**I**) or an overhead stirrer (**II, III**) to promote flocculation. Sedimentation was used (**I– III, V**) to enhance removal of coagulated material from the electrochemically treated water. Filtration through filter paper (**I, III, IV**) (Whatman or VWR) or GF/C glass fibre filter (Whatman) (**II, V**) was used in most of the studies for the separation of coagulated material from the treated water. In few tests, samples were conveyed by pipette from the glass beakers from the centre of the beaker after sedimentation or flotation (**I**). Flocculation, sedimentation and filtration steps were used to simulate particle separation in full-scale water treatment plants by filtration, sedimentation or flotation. In addition, a few flotation tests were conducted using the bench-scale DAF system (**I**).

Temperature adjustment (**III**) during the tests was undertaken at 295 K using heating plate, at 285 K using water flow and at 275 K with an ice bath. According to measurements, temperature was maintained within a ±1 K range of the set temperature throughout all stages. Oxidation of sulphide was prevented during the sulphide precipitation tests (**IV**) by adding nitrogen into the sample bottle. Samples were pumped into the beakers to further ensure that mixing with air was minimised. After electrochemical treatment, the electrodes were washed with 4–10% HCl solution and distilled water.

3.3 Analytical methods

3.3.1 Chemical analysis

Water samples were stored, after filtration, in the cold, except sulphide samples which were measured right after the experiment because sulphides oxidise to sulphates when they come into contact with air. Water pH, conductivity, ORP and dissolved oxygen were measured using standard laboratory devices and sensors. The turbidity of samples was measured with Spectroquant NOVA60 (Merck) (**I**) or Model 2100P ISO turbidimeter (Hach) (**II, III, V**). Apparent colour was measured using a photometer 2100AN (**I**) or DR 2800 (Hach Lange) (**II, III, V**) according to standard EN ISO 7887:1994. Absorbance of the samples at 254 nm wavelength was measured with a Lambda 45 UV/Vis spectrophotometer (**II–III**).

The organic matter content of surface water and wastewater samples was investigated by analysing permanganate index (**I**), COD (**IV**), TOC (**II, III, V**) or DOC (**IV, V**). The permanganate index was measured as stated in standard EN ISO 8467:1995 using a 2100AN (Hach) photometer. COD was measured according to standard SFS 5504:1998. TOC was measured using a TOC analyser (Shimadzu) and DOC was measured with the same analyser after the samples were filtered through a 0.45 µm pore size membrane.

Absorbance at 254 nm wavelength was measured to study the composition of residual NOM. Specific UV absorbance (SUVA) is absorbance at 254 nm divided by DOC concentration. When long-chained humic acids are present in water, SUVA values is high [3]. When SUVA value is 4–5 L/(m mg) the water is composed of hydrophobic material which is high in aromatic structures. When SUVA is less than 3 L/(m mg) the water is composed mainly of hydrophilic material. SUVA values were measured during the temperature and cell construction tests (**II, III**).

The concentration of metals was measured from acidified samples (0.2 ml 37% HNO_3 to 10 ml sample) using iCAP 6000 series ICP-OES (Thermo Electron) (**II–V**) or photometric method (**I**). Residual metal concentrations were measured after filtration, whereas metals dissolved from the electrodes were measured from the samples which were taken during or directly after the treatment. The ζ-potential of the samples was measured using a Zetasizer Nano ZS analyser (Malvern). Resin acids were measured according to the method described by Soimasuo et al. [190] using the HP 6890 GC-MS system (Hewlett-Packard) with HP-5 capillary column. Sulphate, sulphide and phosphorus concentrations of the samples were measured using photometric methods (Lange). Dissolved sulphide and phosphorus concentrations were measured after passing the samples through a 0.45 µm pore size membranes.

3.3.2 Toxicity analysis

Bacterial toxicity was measured using a Microtox-Flash assay based on the bioluminescence of the marine bacterium *Vibrio fischeri*. Toxic substances affect the metabolism of the cells and break their structure, thus reducing bioluminence. Bacterial toxicity tests were conducted according to the BioTox^{TM} method (Aboatox, BO1243-500), standard draft ISO CD 2006b and the method developed by Lappalainen et al. [191] using a Sirius luminometer. 2% NaCl solution was used as negative control, whereas $K_2Cr_2O_7$ was used as a positive reference chemical. In addition to bacterial toxicity, toxicity of samples to algae was also measured. Analysis was carried out according to standard ISO 8692:2004. The sample size was reduced to fit 48-well microplates (Greiner bio-one GmbH). The average algal cell concentration prior to exposure to wastewaters was measured using a microscope (Olympus BX40) and cytometer (Assistant). Fluorescence after 0 hrs, 24 hrs, 48 hrs and 72 hrs exposure was measured using Fluoroscan Ascent fluorometer (Labsystems). Negative control solutions contained nutrients, whereas $K_2Cr_2O_7$ was used as the positive reference substance.

3.4 Statistical methods

Statistical design of experiments (DOE) and statistical models were used to study the effect of treatment parameters (factors) and their interaction terms on pollutant removal. Either full factorial design containing all possible variations (**II, III**) or central composite face (CCF) (**V**) design was used. The factors range and levels are presented in Tables 9–11. Full factorial design (Table 9) was conducted separately for all three electrolysis design cells when the effect of cell construction on NOM removal was studied (**II**).

Table 9. Factor range and levels used in electrolysis cell construction studies (**II**).

	Factor range and levels		
Variable	-1	0	1
X_1, Electric charge (C/L)	48	96	144
X_2, Initial pH	3	4	5

Table 10. Factor range and levels used in temperature studies (**III**).

	Factor range and levels		
Variable	-1	0	1
X_1, Electric charge (C/L)	48	96	144
X_2, Initial pH	4	5	6
X_3, Temperature (K)	275.15	285.15	295.15

Table 11. Factor range and levels used in debarking effluent studies (**V**).

	Factor range and levels		
Variable	-1	0	1
X_1, Current (A)	1	2	3
X_2, Time (s)	60	210	360
X_3, Initial pH	4	6	8

Statistical models were made of the results using MODDE software (Umetrics) with either partial least squares regression (PLS) (**II, V**) or multiple linear regression (MLR) (**III**). Both are commonly used statistical methods which are used to interpret the effect of variables (factors) to responses. In MLR and PLS the coefficients of the model are computed to minimise the sum of squares of residuals, i.e. the variance not explained by the model. MLR assumes responses to be independent, whereas in PLS the covariances of responses are taken into account. These methods are described in detail elsewhere, such as [192]. An equation describing the relationship between the response variable and predictor variables (factors) is obtained. The general form of the regression equation including single terms, square terms and interaction terms is presented in Eq. 18:

$$Y = b_0 + \underbrace{\sum_{i=1}^{k} b_i X_i}_{single\ terms} + \underbrace{\sum_{i=1}^{k} b_{ii} X_i^2}_{square\ terms} + \underbrace{\sum_{i}^{i<j} \sum_{j} b_{ij} X_i X_j}_{interaction\ terms} \tag{18}$$

where Y is the response variable, b represents the coefficients of the model, and X represents the factor variables. Both MLR and PLS models consider the effects of linear, quadratic and interaction terms on responses. The quality of regression equation can be evaluated using analysis of variance (ANOVA). R^2 is the amount of variance explained by the model, whereas Q^2 is an estimate of the predictive ability of the model. Q^2 is calculated using the results of cross-validation. Detailed descriptions of model quality terms are given elsewhere [192].

4. Results and discussion

4.1 Quality of the statistical models

Variation of TOC, DOC, final pH, aluminium added, UV_{254nm} absorbance, water colour (PtCo), toxicity and residual aluminium and iron concentrations were explained with high accuracy ($R^2 \geq 0.8$) by the model terms (**II, III, V**). R^2 was moderate (**III**) or good (**II, V**) for the ζ-potential of the samples. Moderate ζ-potential was due to pure error of the measurements according to reproducibility values. Iron concentration and toxicity of the debarking effluents had low Q^2 values, thus indicating poor results in cross-validation and therefore low predictability of these responses by the model. According to ANOVA, this was mainly related to model error. Turbidity of the samples had moderate R^2 for the model of Cell C (**II**). Cell C had low predictability ($Q^2 < 0.5$) for turbidity, apparent colour, TOC, aluminium added and residual concentrations of iron and manganese. This was due to both model error and replicate error. In general, model qualities for different cell constructions were in order of Cell C < Cell T < Cell A, which could be explained by the different dissolution mechanisms. Dissolution of aluminium in Cell A depended linearly on electric charge added per volume, whereas in Cell C and Cell T the dissolution rate of cathode changed over the course of time. As most of the water quality parameters depended on aluminium added to the solution, the linear behaviour of Cell A was more easily explained by the model. Therefore, it is also recommended that aluminium added is used as factor in possible future studies.

4.2 Dissolving of electrodes

Dissolving of aluminium and iron electrodes was studied in various conditions. Dissolving of both electrode materials followed or were higher than estimated according to Faraday's law. The effect of current density on electrode dissolution was not studied because highest removal of NOM per electric charge was obtained with lowest current densities (**I**) and therefore low current densities were selected for the further studies. The effect of current density on dissolution of aluminium has been studied by [78].

Aluminium electrodes were selected for NOM removal studies because aluminium does not significantly increase the colour of water, even when there is some residual concentration, and were therefore more suitable for surface water treatment when water should be used as industrial fresh water. Iron electrodes were selected for the wastewater treatment studies because iron is known to react with sulphides more effectively than aluminium [148] and aluminium may have some toxicity towards microorganisms [193].

4.2.1 Aluminium electrodes

Water temperature had a significant effect on the dissolving speed of the aluminium electrodes (**III**). First, the effect of temperature on the dissolving rate of aluminium electrodes was studied in preliminary tests, in which the treatment time was short (low electric charge per volume). Longer tests were made according to DOE (Fig. 7). The dissolving rate of aluminium was 0.13–0.30 mgAl/C in long tests, whereas the theoretical dissolution rate calculated according to Faraday's law is 0.093 mgAl/C. According to both tests, the dissolving rate obtained at 275.15 K was significantly lower than at 295.15 K, especially when electric charge per volume increased. The dissolving rate was close to theoretical values at the beginning of the treatment and increased over the course of time. The dissolution of anodes followed Faraday's law [78] and it is not expected that temperature has a significant effect on this electrochemical dissolution mechanism because current passing through the cell was directly proportional to the dissolution rate, and the current did not fluctuate during the test (galvanostatic test). According to the results, the chemical dissolution of aluminium cathodes was affected by temperature. At low temperatures, chemical dissolution initiated more slowly than at higher temperatures. However, the test duration was short and therefore it is not known when and where the dissolution rate stabilised and if there was any difference in the dissolution rates at different temperatures when the reaction rate had stabilised.

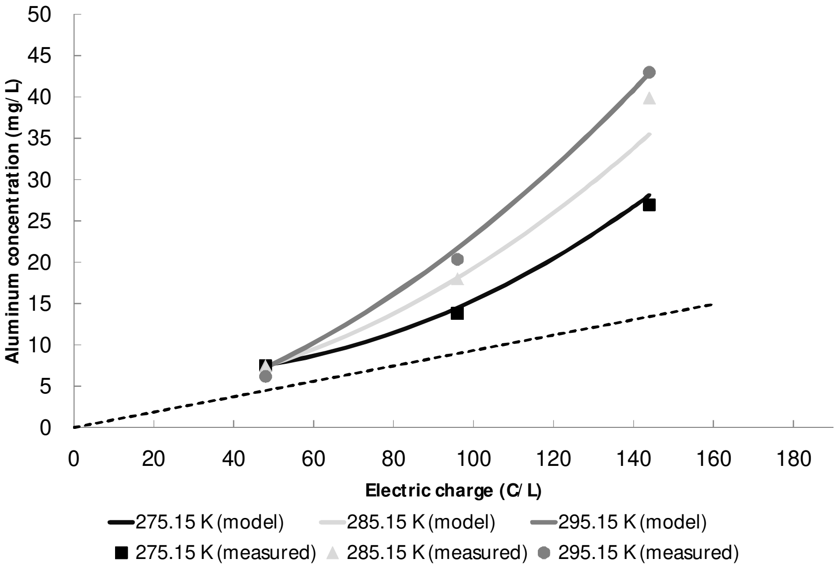


Figure 7. Dissolving of aluminium electrodes in various temperatures when initial pH was 6 (**III**). The dotted line represents the theoretical aluminium dissolution rate calculated according to Faraday's law.

Increased removal of pollutants at high temperatures has been obtained by [114] and [113], whereas Katal and Pahlavanzedah [97] and El-Naas et al. [159] reported the opposite effect in their studies. Studies of other researchers have been made at 293–333 K, whereas this study was made at the lower temperatures of 275–295 K. According to results of this study, in temperature range 275–295 K, increasing temperature increased the dissolving of cathodes but possible negative effects of increasing temperature on organic matter removal were not significant at this range, as discussed later in Section 4.4.1. At temperatures above 295 K, negative effects seems to be possible, depending on the pollutant to be removed, which might be due to the different removal mechanisms of inorganic pollutants, such as boron and phosphate, and organic matter. However, the results are not fully comparable, because coagulant concentrations have not been presented in other studies.

The effect of initial water pH on dissolving of aluminium electrodes was studied at initial pHs 3–5 (**II**) and 4–6 (**III**). When both electrodes were made of aluminium, the dissolution rate was affected by the initial pH (Fig. 8). At low electric charges per volume there was no significant difference in dissolution rates and they were close to theoretical values. However, when electric charge per volume increased, there was some difference in dissolving rates. As with temperature, initial pH also affected the dissolution rate of aluminium cathodes. At 144 C/L the dissolution rates were in the order of pH 6 > pH 4 > pH 5. This order was the same at all tested temperatures.

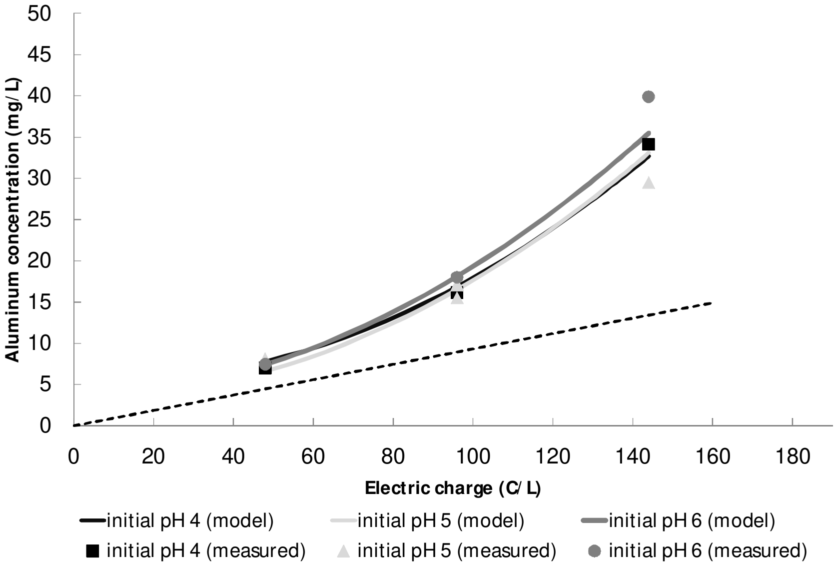


Figure 8. Dissolution of aluminium electrodes in various initial pHs at 285 K (**III**). The dotted line represents a theoretical aluminium dissolution rate calculated according to Faraday's law.

The effect of initial pH on the dissolution rates of aluminium anodes and cathodes was studied with different cell constructions (**II**). Dissolution of Cell A was close to the theoretical values calculated according to Faraday's law at the tested initial pHs. According to this, the proportion of side reactions on anode, such as the production of oxygen or chlorine, was low or negligible in the tested conditions. Mouedhen et al. [78] obtained similar results in their tests with aluminium electrodes.

The results of Cell C indicated that there was short time lag at acidic initial pH (pH 3 and pH 4) before the chemical dissolution of cathodes initiated. Mouedhen et al. [78] reported that in pHs lower than 3, the released amount of aluminium during the electrolysis with constant charge per volume was significantly lower than in pHs above 3. Acidic pH seemed to inhibit or decrease the dissolution rate of cathodes depending on the pH.

The highest aluminium concentrations per added electric charge were measured for Cell T but it should be noted that aluminium concentrations of Cell T were not the sum of concentrations measured from samples treated with Cell A and Cell C. There was some variation in dissolved aluminium concentrations in temperature tests (**III**) and cell construction tests (**II**), even when initial pH and temperature were the same in both tests (initial pH 5 and temperature 295.15 K). Variation in initial water quality in these tests, such as different amount of salts in water, might have caused this effect. It is known that chlorides and sulphates have a significant effect on the dissolution rate of electrodes during EC [85].

4.2.2 Iron electrodes

Dissolution of iron electrodes was studied in various current densities during the sulphide treatment (**IV**). According to the results, current density did not have a significant effect on the dissolution rate in the studied range (3.6–17.9 mA/cm^2) (Fig. 9). Iron dissolved at the rate of 0.27 mgFe/C, while the theoretical value for dissolution of Fe(II) is 0.29 mgFe/C. It can be concluded that iron dissolved in Fe(II) form and dissolution followed Faraday's law. This was consistent with the results of other researchers [72, 95, 96]. This result was significant because it is known that Fe(II) is a poor coagulant and should be oxidised to Fe(III) form before it can be used to remove organic matter [3]. However, Fe(II) can form precipitates with sulphides according to Eq. 7. The proportion of other electrochemical reactions on anodes was low in the tested conditions. Water pH does not have significant effect on the dissolution of iron electrodes in near neutral pHs [72].

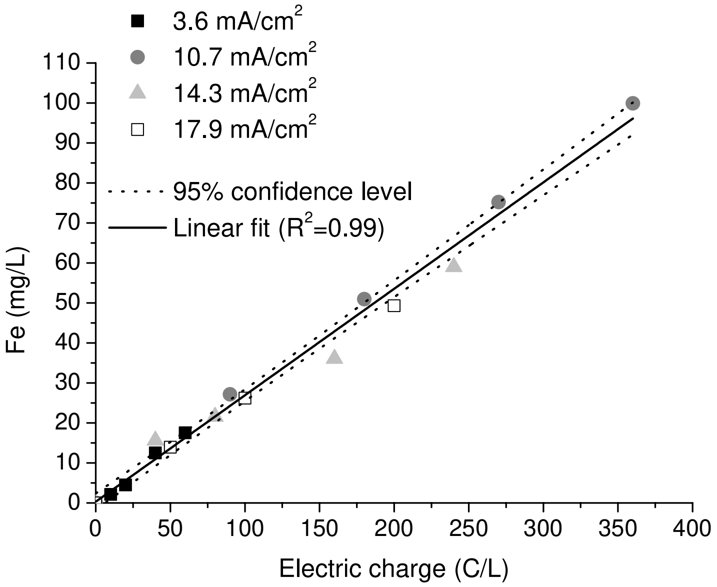


Figure 9. Dissolving of iron electrodes in various current densities (**IV**).

4.3 Change of pH and conductivity

Change of pH during the EC treatment is a well-known side effect of EC [76, 127, 194]. The effects of initial pH, temperature, electric charge and electrolysis cell construction on pH change were studied (**II, III**). When initial pH was highly acidic (pH 3), the alkalinity produced by electrochemical reaction was not sufficient to neutralise pH and final pH was 3.3–4.4 when the electric charge was 48–144 C/L. When initial pH was 4–6, the final pH was neutralised to pH 5.6–7.8. According to the results, the pH increment was higher when initial pH was acidic (except in very acidic initial pH 3) and therefore, it could be concluded that less HO^- ions were bound to the sludge produced in water having low initial pH. This may have an effect on sludge properties.

Tests with different cell constructions indicate that final pH also depended on the cell construction (**II**). This effect was due to different Al/HO^- ratios produced by different cell constructions. In initial pH 5 and electric charge 144 C/L the final pHs of waters treated with Cell T, Cell C and Cell A were 6.83, 7.47 and 7.76, respectively. Respective aluminium concentrations were 18.42 mg/L, 16.26 mg/L and 12.04 mg/L. The amount of HO^- ions produced by electrolysis followed Faraday's law. Aluminium, on the other hand, dissolved from both electrodes but chemical dissolution of cathodes did not follow Faraday's law. A higher concentration of free HO^- ions led to higher final pH. The effect was similar in other tested initial pHs. Decreasing temperature slightly increased the final pH due to this same effect; aluminium cathodes dissolved at a lower rate at lower temperatures and therefore, there were more free HO^- ions in the solution.

Water pH also increased when iron electrodes were used (**IV, V**), except at initial pH 8 when short treatment times were used. When DOC and COD removals were studied with high electric charges (4500 C/L) the final pH of the wastewater increased as high as 10.4. It was expected that pH increases faster and higher with iron electrodes than with aluminium electrodes because less coagulant was produced per produced HO^- ions, because iron did not dissolve on cathodes. Produced Fe(II) bound less HO^- ions compared to Al(III) and therefore pH increased to a higher level because sludge contained less HO^- ions. Al(III) form $Al(OH)_4^-$ species at high pH, which stabilises pH change. The transformation of Fe(II) to Fe(III) at high pH and oxidising conditions decreased pH because Fe(III) bound more HO^- ions.

Conductivities of samples depended on the concentration of residual metal coagulant and final pH. When initial pH was acidic, conductivity was naturally higher than in neutral initial pH because more ions were added into the solution. In temperature tests, water conductivity without EC treatments was 2.8 mS/m and after small pH correction (initial pH 6) and treatment with 144 C/L at 295.15 K the final conductivity was 3.0 mS/m. Water conductivity was 3.5 mS/m and 3.3 mS/m when waters having initial pH 4 and 5 were treated with the same parameters, respectively. It could be concluded that optimised EC treatment had a negligible effect on water conductivity. This differs from metal salt coagulants, which significantly increase the concentration of salts, such as chlorides or sulphates, in water.

4.4 Surface water treatment

4.4.1 Organic matter removal

The effects of current density, electric charge, initial pH, temperature and electrolysis cell construction on NOM removal from surface water samples were studied (**I–III**). In addition, the removal of NOM by combined chemical coagulation and EC was investigated (**I**).

When current density increased, the same amount of organic matter was removed in a shorter treatment time as when the production rate of coagulant increased (**I**). However, when organic matter removal was observed as a function of electric charge, low current density was more effective. According to Mouedhen et al. [78], the dissolution rate of cathodes does not increase as a function of current density in contrast to the dissolution of anodes. Even low current density initiated chemical dissolution of cathodes and therefore, more aluminium was produced per electric charge in low current density, which in turn meant that low current density was more energy efficient.

DOC or TOC removal increased when added electric charge per volume increased. Initial pH had a significant effect on the removal of organic matter. At initial pH 3, there was no significant effect whether aluminium originated from anodes or cathodes (**II**). The TOC removal rate was 0.83 mgTOC per mgAl added into the solution. TOC concentration depended linearly on the aluminium concentration added into the solution. The statistical model showed somewhat false results at this initial pH, especially for Cell C (Fig. 10). At low pH, the mechanism of NOM removal was mainly charge neutralisation and compression of double layer, because hydroxides were not stable in this environment [3, 10]. It is noteworthy that the TOC removal rate as a function of aluminium concentration did not decrease, even at low TOC concentrations at this initial pH. Therefore, it is possible that even higher TOC removal could be obtained if even higher aluminium concentrations would be used.

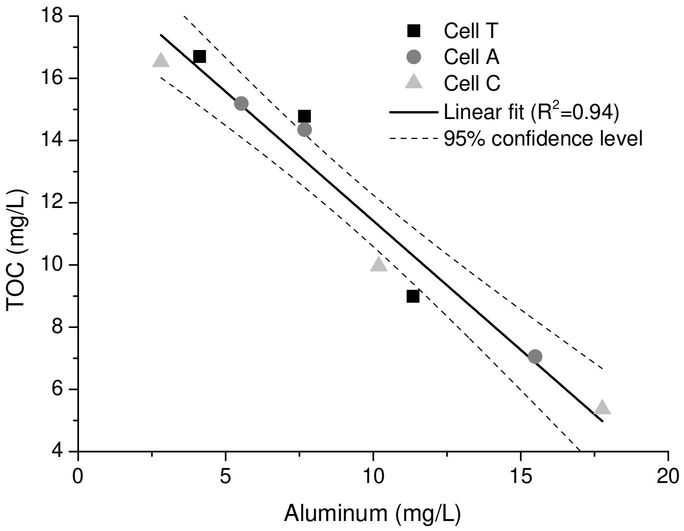


Figure 10. TOC concentrations of the samples treated with different cell constructions at initial pH 3 (**II**).

When initial pH was 4–6, the removal efficiency increased when initial pH decreased, as seen in Fig. 11 (**III**). Significantly higher aluminium concentrations were required per removed DOC at initial pH 6 than at initial pH 4 or 5. At initial pH 4–5, even the lowest obtained aluminium concentration removed most of the organic matter from water. When pH increased, aluminium species lost charge because they bound more hydroxyl ions and therefore more aluminium was required for charge neutralisation. The primary mechanism of NOM removal at near neutral pHs was therefore, precipitation and enmeshment, which required a higher concentration of aluminium compared to charge neutralisation [2, 3]. Similar results were obtained when the effect of cell constructions was studied at initial pH 4 and 5 (**II**). When initial pH was 6, the NOM concentration of water did not decrease linearly as a function of aluminium concentration, rather it followed logarithmic or asymptotic fit. Similar results have been reported in literature by other researchers [160, 161, 163]. According to their results, the efficiency of the NOM removal increased when initial pH decreased. At near neutral initial pH 6.2 there was a short time lag before any organic matter was removed by EC (**I**). According to this, a threshold aluminium concentration exists at neutral pH which has to be passed before enmeshment mechanism initiates.

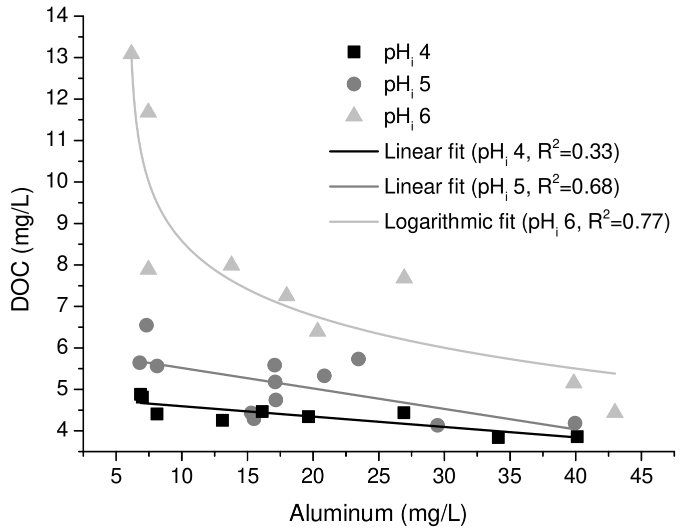


Figure 11. DOC concentration of samples treated at different initial pHs (pH$_i$). Temperature during the treatment was 275–295 K (**III**).

TOC removal stabilised at approximately 4 mg/L or 5 mg/L when initial pH was 4 or 5, respectively (**II**, **III**). It seemed that residual NOM was not easily removed by EC at these pHs. Water temperature and cell construction affected through aluminium concentration but besides that they did not have a major effect on NOM removal. For example, at 295 K more NOM was removed than at 275 K or 285 K (Fig. 12) as more aluminium was dissolved into the solution. Chemical coagulant additions reduced the required electric charge per volume for optimum organic matter removal (**I**).

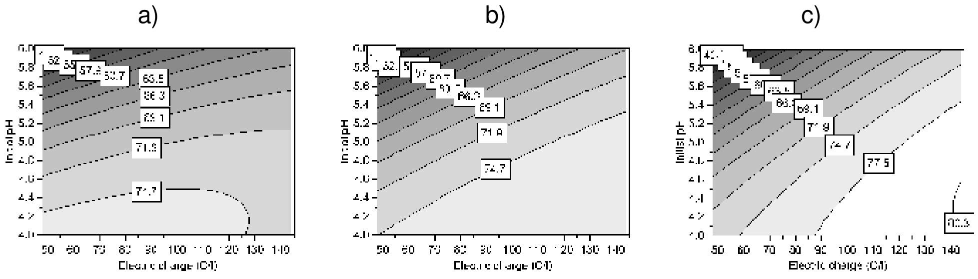


Figure 12. Contour plots of DOC concentration (mg/L) in a) 275 K, b) 285 K and c) 295 K according to statistical model (**III**).

The apparent colour of surface water was due to NOM, and both organic matter and apparent colour were removed simultaneously during the treatment (**I–III**). However, the colour intensity of water also varied with pH. Increasing pH increases the colour intensity [3]. The lowest measured colour value was 3 mg/L PtCo (96.4% removal) (**III**) when water having initial pH 4 was treated with 144 C/L at 295.15 K. Aluminium originating from anodes and cathodes had similar colour removal efficiency as can be seen in Fig. 13. At initial pH 3, colour was removed linearly with increasing aluminium concentration, whereas at initial pHs 4 and 5 the colour removal followed asymptotic or logarithmic fit. More colour was removed per electric charge when low current density was used, because more aluminium was produced per electric charge in low current density (**I**). In all tested current densities, cell configurations, temperatures and initial pHs high colour removal could be obtained when aluminium dosage was sufficient.

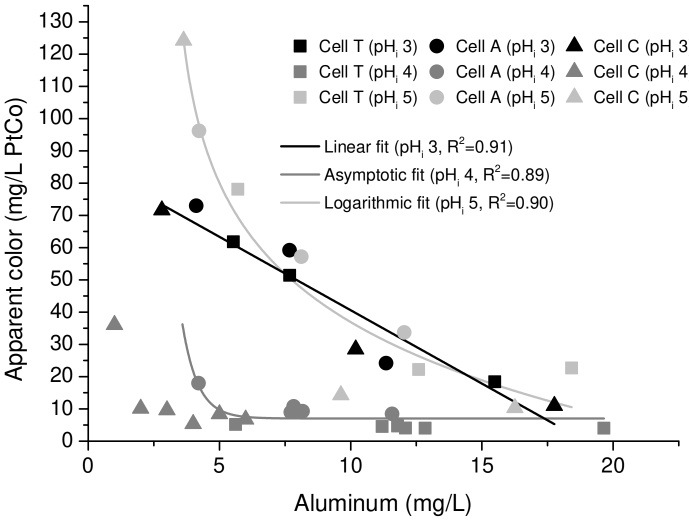


Figure 13. Apparent colour of samples treated in different initial pHs (pH$_i$) and cell constructions (**II**).

The initial SUVA value of surface water was 4.52 L/(m mg) (**II**) or 3.51 L/(m mg) (**III**). According to this, the water contained mainly hydrophobic humic material. The SUVA value decreased during the treatment simultaneously with DOC or TOC and colour. Temperature or cell constructions did not have a significant effect on SUVA values besides their effect on the dissolving of electrodes. The SUVA value decreased to 1.5–2.5 L/(m mg) during the treatment, except at two points at initial pH 6 and one point at initial pH 4 where SUVA values were higher (**III**). The effects of aluminium concentration and initial pH on SUVA values were also studied with different cell constructions (Fig. 14). SUVA values exhibited similar behaviour to apparent colour values. At initial pH 3 the SUVA value decreased linearly with aluminium concentration, whereas at initial pH 4 it followed asymptotic fit. At initial pH 5 there was more variation in the results. However, according to the results, EC removed mainly hydrophobic material and residual NOM fraction was composed mostly of hydrophilic non-humic material which was low in aromatic chemical structures.

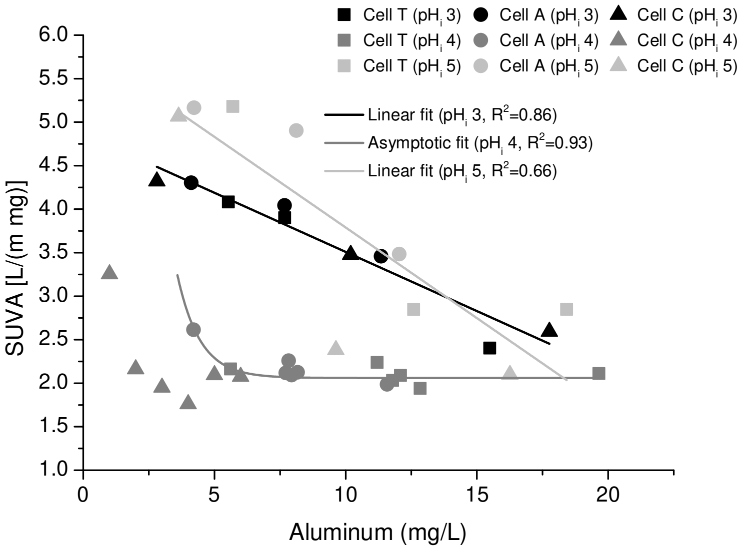


Figure 14. SUVA values of samples treated in different initial pHs (pH$_i$) and cell constructions (**II**).

When these results were compared with other studies it could be concluded that EC and chemical coagulation are similar in terms of aluminium doses per TOC or DOC removed, optimum pH of the treatment and fractions remaining in water after the coagulation [11, 19, 195]. Chow et al. [19] studied DOC removal with alum from four different surface waters. They obtained optimum DOC removal at pH 5, which was between the optimum initial pH and final pH of the EC treatment, according to this study. Alum treatment decreased the SUVA value of waters and recalcitrant DOC was found to have smaller molecular weight and lower SUVA value compared with the DOC of the raw water. Shi et al. [195] studied the coagulation of humic acid by preformed and non-preformed aluminium species. According to their results, decreasing pH reduces the coagulant dosage required for complete UV$_{254nm}$ removal. Large molecular and hydrophobic humic material was more effectively removed with non-preformed aluminium species, which are also released during the EC treatment.

The ζ-potential of the untreated water samples was -15.2 mV (**II**) or -17.1 mV (**III**). The results indicated that temperature affected zeta-potential, due to its effect on the dissolving speed of the aluminium electrodes, as reflected by the contour plots of the model (Fig. 15). The ζ-potential of the residual organic matter decreased when more aluminium was added to the solution. Water pH also had a significant effect on the ζ-potential of pollutants and metal hydroxides as discussed in Section 1.1.1. However, the model quality terms were low for the ζ-potential at the temperature studies. This was probably due to other non-controlled parameters which affected ζ-potential values. Indeed, there was correlation between residual aluminium concentrations and ζ-potential values. At low initial pHs 4 and 5 the ζ-potential increased as a function of residual aluminium concentration, whereas at initial pH 6 it decreased slightly. These results also indicated that aluminium species had a more positive charge when they were formed in acidic initial pH than in neutral initial pH, even when the final pH of water was similar.

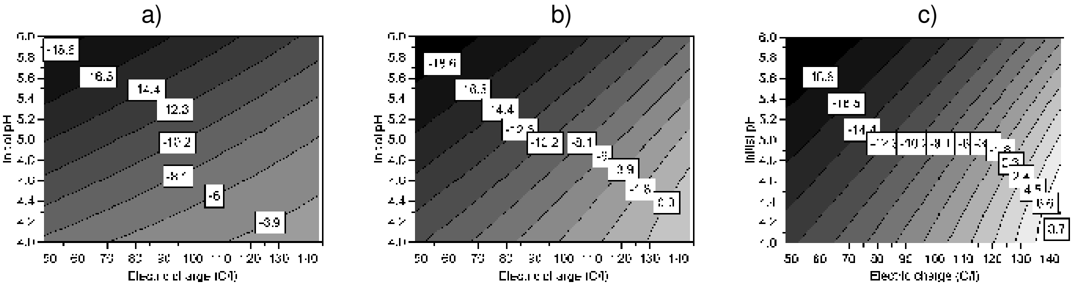


Figure 15. Contour plots of ζ-potential (mV) in a) 275 K, b) 285 K and b) 295 K according to statistical model (**III**).

The effect of initial pH on the ζ-potential was also studied with different cell constructions (**II**). At initial pH 3, the aluminium had a higher charge (Al^{3+}) due to lack of hydrolysis, and the ζ-potential of residual aluminium increased linearly with increasing aluminium concentration (Fig. 16). At this pH, small precipitates were formed that were not easily removed with sedimentation, flotation or filtration and therefore the residual metal concentration in water was higher than at initial pH 4 or 5. When the aluminium concentration was over 12 mg/L, the ζ-potential exceeded 0 mV, which may cause restabilisation of colloids. ζ-potentials of the samples at initial pHs 4 and 5 were similar after filtration. At these pHs, aluminium existed predominantly as hydroxides and easily settleable or filterable flocs were formed and therefore, residual aluminium did not have a significant effect on the ζ-potential of the samples. It was interesting that residual organic matter had more negative ζ-potential values at initial pH 4 and 5 than that measured from the untreated samples. According to this, some highly charged fraction of NOM was not removed by EC.

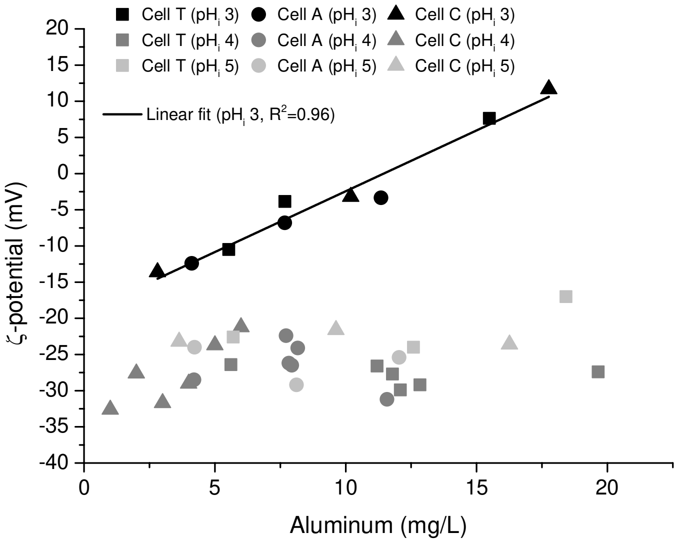


Figure 16. ζ-potential as a function of aluminium concentration at different initial pHs (pH_i) and cell constructions.

4.4.2 Residual metals and turbidity

Residual metals may cause problems, such as deposition and process chemical decomposition, in processes where water is consumed. There are also concerns that residual aluminium in drinking water may cause Alzheimer's disease [21]. The effects of current density, temperature, initial pH and cell construction on concentrations of residual metals were studied. The water had low initial turbidity and therefore turbidity was mostly associated with residual aluminium concentration as aluminium hydroxides form milky gel precipitates in water.

Residual aluminium concentration depended on water pH and aluminium added to the solution. When aluminium concentrations were low there was more residual aluminium in water, probably because floc size was small and passed more easily through the filters. At highly acidic initial pH 3 the residual aluminium concentrations were high (2.5–8.3 mg/L) because final pH remained acidic and more soluble aluminium and small flocs were present than at higher initial pHs (**II**). When initial pH was 4.0–6.2 and added aluminium concentrations were high, the residual aluminium concentrations were low (**I–III**). Negligible aluminium concentrations were measured in these conditions (< 0.1 mg/L). Temperature and cell constructions did not have a significant effect on residual aluminium concentration besides their effect on the dissolving rate of aluminium electrodes. According to Chow et al. [19], minimum residual aluminium concentrations following alum treatment were obtained between pH 6 and 7. They concluded that optimum DOC removal and minimum residual aluminium concentration cannot be obtained at the same pH. However, according to results of this study optimum DOC removal and low residual aluminium could be obtained simultaneously with EC when initial pH was 4–5. This could be a significant benefit of EC in surface water treatment compared to chemical coagulation.

Untreated surface water also contained a relatively high concentration of iron (0.35–0.88 mg/L) and also low concentrations of manganese (0.12 mg/L). Both of these metals can cause coloured deposits. Iron was removed simultaneously with residual aluminium. Negligible iron concentrations (< 0.1 mg/L) were measured from electrocoagulated waters when the final pH of water was close to neutral and a sufficient concentration of aluminium was produced by electrolysis. Similar results were obtained by Ghosh et al. [137] when they studied Fe(II) removal from tap water by EC. In contrast to iron removal, manganese removal seemed to depend on cell construction as the lowest manganese concentrations were measured from samples which were treated with Cell T. However, manganese concentration in all samples, including the untreated samples, was low. High removal efficiencies of manganese have been reported by other researchers [89, 104]. It has been suggested that a direct reduction of Mn^{2+} would occur at the cathode surface.

4.5 Wastewater treatment

Two possible applications of EC in wastewater treatment, sulphide precipitation and toxicity removal, were studied. The effects of treatment parameters, such as initial pH, current density and added electric charge per volume were investigated. The simultaneous removal of organic matter, colour and phosphorus were also studied. Iron was selected for the material of electrodes.

4.5.1 Organic matter removal

Organic matter removal by EC was investigated during the sulphide precipitation tests and toxicity tests. The removal of organic matter by iron EC required high electric charge per volume and iron concentration. This confirms that iron dissolved from anodes in Fe(II) form and was not effectively oxidised to Fe(III) in the studied conditions. Other researchers have also concluded that iron electrodes dissolve in Fe(II) form [72, 95, 96]

It was possible that simultaneous hydrogen formation during the treatment kept ORP of the water in the reducing range and therefore, oxidation of Fe(II) was slow.

ORP of the electrocoagulated samples confirmed this conclusion, as ORP decreased slightly during the sulphide treatment, even when ORP was already highly reducing in the untreated water (**IV**). Ricordel et al. [165] studied the change of oxygen concentration of water during the EC treatment with aluminium electrodes. According to their results, EC treatment reduced O_2 concentration of water to less than 1 mg/L at long treatment times. It seemed that the reduction of oxygen and the evolution of hydrogen during the EC treatment inhibited oxidation of Fe(II).

Removal efficiencies of organic matter were low in the tested range of treatment parameters. Removal of DOC from the wastewater was approximately 0.03 mgDOC removed per 1 C or 0.1 mgDOC removed per 1 mgFe dissolved (**IV**). Removal rate of DOC from the debarking effluent was approximately 0.1 mg DOC removed per 1 C (**V**). Initial pH had only a minor effect on the removal efficiency in the tested range (Fig. 17). There are studies where high removal of organic matter has been obtained with iron electrodes, such as [97, 153]. However, electric charges per volume have been typically high. For example Perng et al. [153] measured 70.5% removal (from 254 mg/L to 75 mg/L) of COD from paper mill effluent when they used 17280 C/L. Electric charge consumption was very high and would result in high electricity and electrode consumption and therefore high operating costs of the treatment. Katal and Pahlavanzadeh [97] studied a different combination of aluminium and iron electrodes on the treatment of paper mill wastewater. According to their results, a Fe-Fe electrode pair removed COD more efficiently than an Al-Al electrode pair. However, they also observed high removal efficiencies (50–90%) only at very high electric charges per volume (approximately 3 000–14 000 C/L).

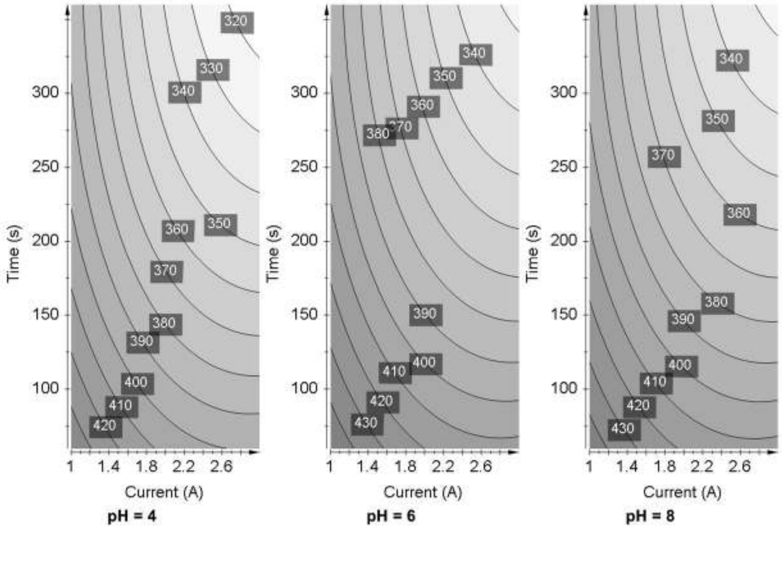


Figure 17. Contour plots DOC (mg/L) in debarking effluent in initial pHs 4, 6 and 8 (**V**).

EC removed the colour of debarking effluent with high efficiency (Fig. 18). Colour removal increased as a function of treatment time. However, the effect of current density was not as straightforward as with DOC removal as medium current density (14.3 mA/cm^2) provided highest removal efficiency. The initial apparent colour of the effluent was 1910 mg/L PtCo, while colour after the treatment varied from 93 mg/L PtCo to 6110 mg/L PtCo. The colour of debarking effluents is mainly caused by tannins, which are known to exhibit toxicity to microbes [196]. However, also residual iron affected the colour of the effluent. EC treatment is known to be able to remove polyphenols (tannins) from olive mill wastewaters with high efficiency, reducing toxicity of these wastewaters to microbes [155, 156, 197]. EC has also been used to recover tannins from tree bark [198].

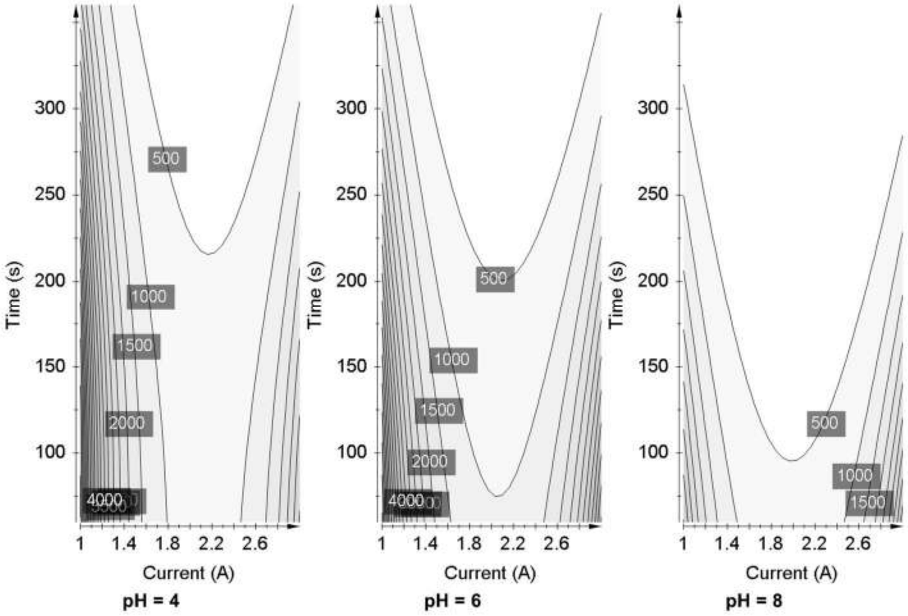


Figure 18. Contour plots of apparent colour (mg/L PtCo) of debarking effluent in initial pHs 4, 6 and 8 (**V**).

The ζ-potential of electrocoagulated samples was measured after filtration (**V**). According to results, ζ-potentials of the samples were -15.9-(-4.66) mV when initial pH was 4. At initial pH 6 and 8 the ζ-potentials varied from -23.4 mV to -18.4 mV. At low initial pH the final pH was also low and therefore, more soluble iron passed through the filter, which increased the ζ-potential of the samples in the same way as in aluminium EC during the NOM removal. Water pH also affected the hydrolysis of iron and ζ-potential of colloids in water. In acidic pH iron species were more positive, whereas typical colloidal pollutants had less negative charge.

Phosphorus removal from wastewater during the coagulation treatment can be beneficial or harmful depending on effluent being treated. Some wastewaters, such as pulp and paper mill wastewaters, contain low concentrations of phosphorus and therefore additional nutrients are added to the water before biological wastewater treatment to enhance microbial activity. Phosphorus removal from wastewater by EC during the sulphide precipitation was studied (**IV**). Phosphorus concentration decreased as a function of electric charge per volume and iron concentration. Regression followed asymptotic fit and approached 0.53 mg/L at high electric charges per volume. Current density did not show significant effect on the phosphorous removal rate at 3.6 mA/cm^2, 7.1 mA/cm^2 and 10.7 mA/cm^2. However, current efficiency of the treatment decreased slightly when current density was 14.3 mA/cm^2 or 17.9 mA/cm^2. According to Vasudevan et al. [113], aluminium electrodes remove phosphates more effectively than iron electrodes. Complete removal is possible at high electric charges. However, in these tests electric charges were low because sulphide removal did not require high concentration of coagulant.

4.5.2 Sulphide precipitation

Hydrogen sulphide is a volatile, malodorous, reduced sulphurous substance, which forms in long pipelines and pipeline facilities typically as a result of metabolic activity of anaerobic sulphate-reducing bacteria. It has adverse effects on human health and can deteriorate sewer systems. Hydrogen sulphide concentration in the air is regulated by laws in several countries.

Sulphide precipitation by EC system was studied in various current densities (**IV**). Sulphide reduction as a function of electric charge per volume followed asymptotic fit (Fig. 19). Precipitation reaction seems to follow second-order reaction kinetics. According to the regression, an EC process applying 10 C/L consumed 3.92 C per 1 mgS^{2-} while a process applying 60 C/L consumed 7.99 C per 1 mgS^{2}. Respective iron consumptions were 1.06 mgFe per 1 mgS^{2-} and 2.16 mgFe per 1 mgS^{2-}. A slight decrease in ORP as a function of electric charge was observed, which was due to the formation of ferrous iron and hydrogen during the process. Iron sulphide formation is a simple reaction which proceeds according to Eq. 7 and is not a coagulation reaction but rather a precipitation reaction. Sulphurous ion removal from tannery wastewaters by EC has been studied by Murugananthan et al. [199] and Feng et al. [148]. Sulphide ions were precipitated as metals sulphides during the treatment, whereas sulphites and sulphates were enmeshed into the metal hydroxides.

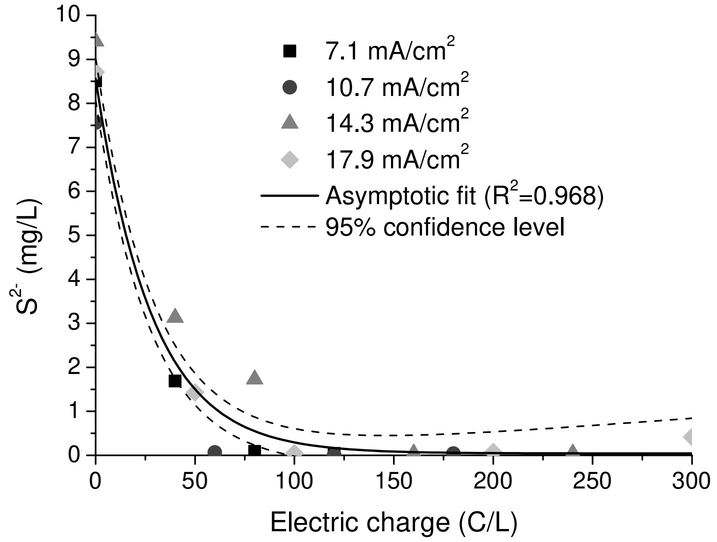


Figure 19. Sulphide concentration in wastewater as a function of electric charge per volume in different current densities of the treatment (**IV**).

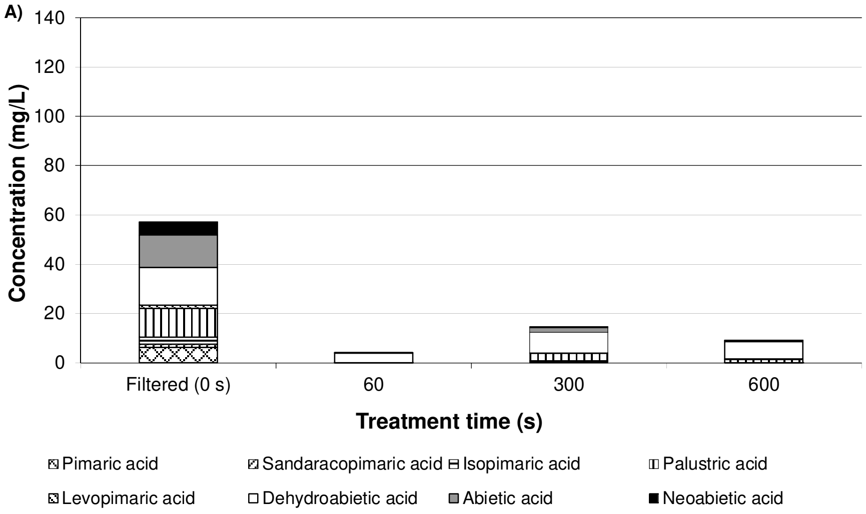
4.5.3 Resin acids, copper and toxicity removal

The removal of resin acids and toxicity was studied using synthetic resin acid solutions and debarking effluent (**V**). Water pH had a significant effect on the solubility of resin acids. At initial pH 4, simple filtration removed 54–74% of resin acids from synthetic solutions, whereas at initial pH 9, 2–64% of resin acids were removed (Table 12). EC further enhanced resin acid removal. Resin acid removals were higher at pH 5 and pH 7 than at pH 9, especially when the initial resin acid concentration was high. The highest removal yield (97%) was thus obtained when initial pH was 5, the treatment time was 60 seconds and the initial concentration was 125 mg/L.

Table 12. Removal percentages of resin acids and copper in EC and following filtration.

		Initial resin concentration			Initial Cu concentration		
Initial pH	**Treatment time (s)**	**25 mg/L**	**75 mg/L**	**125 mg/L**	**0.25 mg/L**	**0.75 mg/L**	**1.25 mg/L**
5	0 (filtration)	74	66	54	19	36	1
	60	86	94	97	80	95	96
	300	84	92	88	91	98	100
	600		86	93		98	99
7	0 (filtration)	63	63	57	21	25	0
	60	93	93	93	72	94	97
	300	90	87	85	89	99	100
	600	74	86	86	84	100	99
9	0 (filtration)	64	46	2	27	31	0
	60	83	92	77	78	95	97
	300	85	83	55	91	99	100
	600	59	95	62	99	99	100

EC removed pimarane-type resin acids with higher efficiency than abietane-type resin acids (Fig. 20). According to Peng et al. [200], abietane-type acids have higher water solubility than pimarane-type resin acids. The most soluble and least toxic resin acid in their studies was DHAA. It is expected that pimaric-type acids are more in colloidal form than abetic-type acids and can be destabilised by coagulants. Additional tests were carried out with pure DHAA and IPA, the results of which support this conclusion, as IPA was removed with higher efficiency than DHAA.



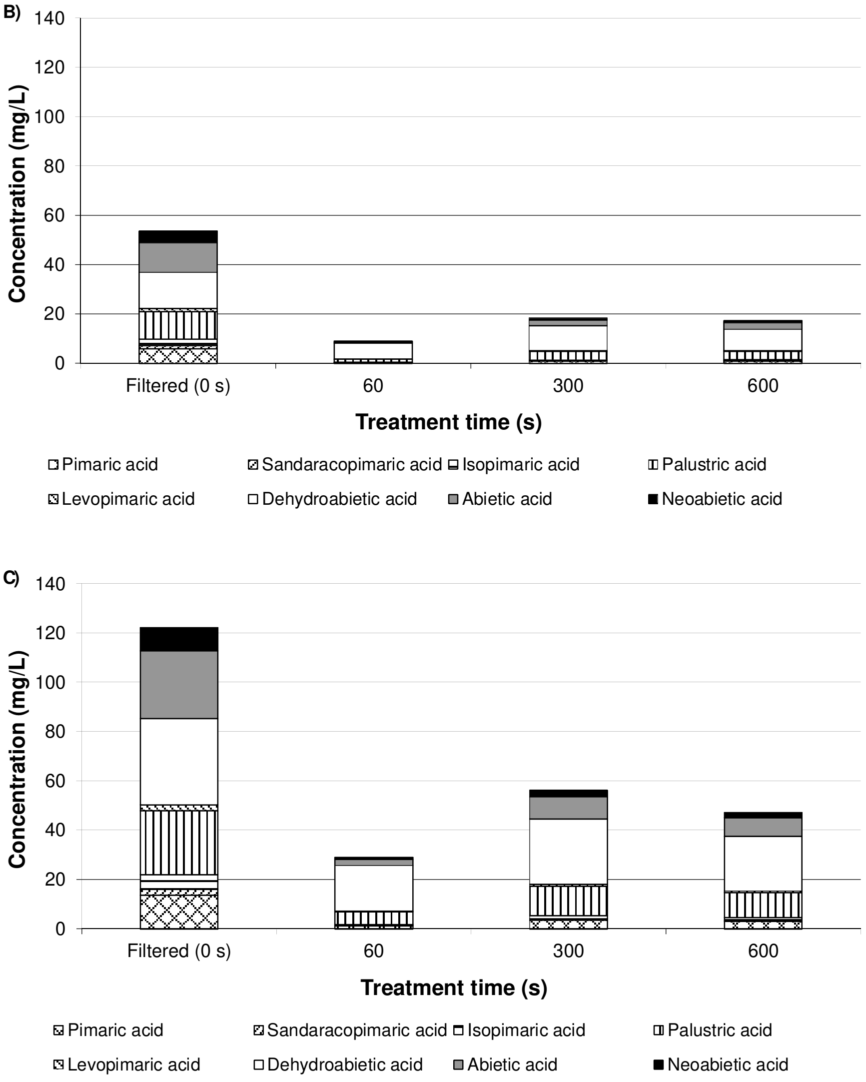


Figure 20. Concentrations of resin acids after the treatment at a) initial pH 5, b) initial pH 7 and c) initial pH 9. Initial total concentration of resin acids was 125 mg/L.

EC also removed copper from the solution with very high efficiency. Some copper was also removed by filtration only (0–36%). Short EC treatment of 60 s (200 C/L) treatment removed 72–97% of copper. Hanay and Hasar [104] studied mixed metal solution purification by EC. They obtained high removal of copper when they treated a mixed metal solution with aluminium EC. Highest residual iron concentrations were measured at low initial pH 5 and short treatment time. As previously mentioned, at low initial pH there were more soluble iron species and also oxidation of Fe(II) to Fe(III) was slow when pH was acidic or neutral.

EC had a minor effect on the toxicity of synthetic resin acid solutions. At initial pH 5, the solution strength causing 50% reduction in bioluminescence (EC_{50}) increased by 7–14%, which indicated a small reduction in toxicity. At initial pH of 9, toxicity slightly decreased with the shortest treatment time (60 seconds) but increased with longer treatment times. The effect of initial pH on toxicity was not due to protons alone, because the pH was adjusted to 7 prior to assay measurement. However, pH adjustment may have affected the solubility or speciation of resin acids and metals in the solution, and could partially explain the lack of correlation. However, toxicity to algae decreased as the function of copper concentration. Filtered samples which were not treated with EC were highly toxic to algae (EC_{50} with 3.7% solution). EC removed toxicity completely (EC_{50} with 95–110% solution) and, according to cell count measurements, electrocoagulated samples stimulated algal growth when compared to control algae tests. Wood rosin had only low toxicity to algae (EC_{50} 142 mg/L).

The removal of bacterial toxicity from debarking effluents was more effective than removal from synthetic solutions. The initial EC_{50} value of the filtered debarking effluent sample was 7.6%. Toxicities of the filtered reference samples at pH 4, 6 and 8 were also measured, and the EC_{50} values were 7.7%, 8.4% and 13.8%, respectively. It seems that simple pH adjustment prior to filtration significantly decreased the toxicity of the samples, even when pH was adjusted again to 7 prior to toxicity measurement. Toxicity change was also related to colour removal of the samples. The colour of debarking effluents is mainly caused by tannins, which are known to exhibit toxicity to microbes [196]. The highest colour removal was observed at high initial pH, whereas high toxicity removal was observed both at low and high initial pH. This was probably due to the effect of iron on colour values at low initial pH. The model predicts minimum toxicity, EC_{50}, at 43% solution in the tested factors ranges at 1.4 A, 360 seconds and initial pH 8. It is possible that this value is unrealistically high due to the model error, as the lowest measured toxicity (EC_{50}) was 21.9%. However, according to the results, EC enhanced toxicity removal. Longer treatment times could increase toxicity removal, but they would raise the operating cost of treatment. It should be noted that prior to the EC treatment, resin acids were minor toxic species in the debarking effluents compared to tannins. According to the results of synthetic wastewaters, the toxicity of the effluents after EC treatment could be caused by residual resin acids or toxic compounds formed during EC treatment. Khoufi et al. [156] studied olive mill wastewater treatment by iron EC. According to their results, long settling (3–6 days) enhanced toxicity removal. It is possible that this could also further enhance toxicity removal from debarking effluents.

5. Conclusions and recommendations

EC is suitable for the removal of various pollutants from surface water and wastewaters. It can produce high quality fresh water from highly coloured surface water having high concentrations of organic matter. Produced fresh water could be used as potable water or industrial fresh water. Optimum DOC removal and low residual aluminium can be obtained simultaneously with EC, which could be of significant benefit to EC in surface water treatment compared to chemical coagulation. In wastewater treatment applications, EC can be used to precipitate malodorous sulphides to prevent their release into air. Technology seems to be able to remove some toxic pollutants from wastewater and could be used as pretreatment prior to treatment at a biological wastewater treatment plant. However, organic matter removal from wastewaters with iron electrodes was poor in these studies.

Aluminium seems to be a more suitable electrode material for EC applications because it produces Al(III) species. Metal ions and hydroxides produced by iron electrodes are less effective in the destabilisation of pollutants because iron electrodes produce more soluble and less charged Fe(II) species. Iron electrodes could be suitable for some special applications, such as sulphide precipitation where Fe(II) is effective. Possible addition of oxidants could enhance pollutant removal due to oxidation of Fe(II) to Fe(III) form and this should be studied further. It is also possible that Fe(III) production could be enhanced by optimum water chemistry and electrochemical treatment parameters, for example, by increasing water pH and current density.

There are several published articles in the field where the coagulant concentration dissolved from the electrodes has not been measured. According to our studies, produced metal concentration is the main parameter affecting destabilisation of pollutants. Dissolution of aluminium electrodes cannot be calculated according to Faraday's law as aluminium cathodes dissolve chemically in local high pH environments at the electrode surface. Current density, treatment time, temperature and electrolysis cell construction affect the dissolution of electrodes and hence also the removal of pollutants. However, it seems that these parameters have low significance besides this effect (in the studied range of parameters). Initial pH and final pH have an effect through the dissolution of electrodes but they also define what aluminium or iron species are formed in the solution and affect the ζ-potential of all charged species in the solution. According to the results of this study, the destabilisation mechanisms of pollutants by EC and chemical coagulation are similar. Aluminium consumption in EC seems to be in the same order as used in chemical coagulation when our results are compared with values obtained from the literature.

Thorough economical and ecological comparison of chemical coagulation and EC is suggested as these methods seem to be similar to pollutant destabilisation mechanisms, metal consumption and removal efficiency in most applications. This investigation should contain operating and investment costs including coagulation, mixing and separation phases of the treatment. Side reactions of EC, such as flotation due to hydrogen bubble production, should also be considered. These calculations would show what the economically viable applications of EC are. If EC is more expensive than chemical coagulation, it may still have applications in small water treatment systems, for example, emergency water treatment systems or small communities as it could be simpler to operate than chemical coagulation, especially if electroflotation is used for particle separation. In addition to economic and ecological studies, new technological innovations and studies are also required to prevent passivation and fouling of electrodes and to further optimise treatment parameters. It is probable that possible full-scale systems operate in continuous-flow mode and therefore it is suggested that future studies are made in bench-scale continuous-flow systems.

References

[1] T. Cosgrove, Colloid science – Principles, methods and applications (Knovel ebook), Blackwell Publishing, UK, 2005.

[2] J.C. Crittenden, R.R. Trussell, D.W. Hand, K.J. Howe, G. Tchobanoglous, Water treatment – Principles and design (2nd ed.) (Knovel ebook), John Wiley & Sons, USA, 2005.

[3] J. Bratby, Coagulation and flocculation in water and wastewater treatment, 2nd ed., IWA Publishing, UK, 2006.

[4] F. Scholtz (Ed.), Electroanalytical Methods, 2^{nd} ed., Springer-Verlag, Germany, 2010, pp. 3–9.

[5] B.V. Derjaguin, L. Landau, Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes, Acta Phys.Chim.URSS. 14 (1941) 633–662.

[6] E.J.W. Verwey, Theory of the stability of lyophobic colloids, J. Phys. Chem. 51 (1947) 631–636.

[7] O. J.Th.G. Overbeek, Recent developments in the understanding of colloid stability, J. Colloid Interface Sci. 58 (1977) 408–422.

[8] J. Lyklema, Quest for ion–ion correlations in electric double layers and over-charging phenomena, Adv. Colloid Interface Sci. 147–148 (2009) 205–213.

[9] J. Lyklema, Overcharging, charge reversal: Chemistry or physics?, Colloids Surf. Physicochem. Eng. Aspects. 291 (2006) 3–12.

[10] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100–102 (2003) 475–502.

[11] M. Yan, D. Wang, J. Ni, J. Qu, C.W.K. Chow, H. Liu, Mechanism of natural organic matter removal by polyaluminum chloride: Effect of coagulant particle size and hydrolysis kinetics, Water Res. 42 (2008) 3361–3370.

[12] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: A review, Adv. Colloid Interface Sci. 159 (2010) 189–197.

[13] E. Smith, Y. Kamal, Optimizing treatment for reduction of disinfection by-product (DBP) formation, Water Sci. Technol. Water Supply 9 (2009) 191–198.

[14] C.W.K. Chow, R. Fabris, J. Van Leeuwen, D. Wang, M. Drikas, Assessing natural organic matter treatability using high performance size exclusion chromatography, Environ. Sci. Technol. 42 (2008) 6683–6689.

[15] J. Yu, D. Wang, M. Yan, C. Ye, M. Yang, X. Ge, Optimized coagulation of high alkalinity, low temperature and particle water: pH adjustment and polyelectrolytes as coagulant aids, Environ. Monit. Assess. 131 (2007) 377–386.

[16] C.S. Uyguner, M. Bekbolet, H. Selcuk, A comparative approach to the application of a physico-chemical and advanced oxidation combined system to natural water samples, Sep. Sci. Technol. 42 (2007) 1405–1419.

[17] J.J. Qin, M.H. Oo, K.A. Kekre, F. Knops, P. Miller, Impact of coagulation pH on enhanced removal of natural organic matter in treatment of reservoir water, Sep. Purif. Technol. 49 (2006) 295–298.

[18] Y.C. Soh, F. Roddick, J. van Leeuwen, The impact of alum coagulation on the character, biodegradability and disinfection by-product formation potential of reservoir natural organic matter (NOM) fractions, Water Sci. Technol. 58 (2008) 1173–1179.

[19] C.W.K. Chow, J.A. van Leeuwen, R. Fabris, M. Drikas, Optimised coagulation using aluminium sulfate for the removal of dissolved organic carbon, Desalination 245 (2009) 120–134.

[20] V. Uyak, I. Toroz, Disinfection by-product precursors reduction by various coagulation techniques in Istanbul water supplies, J. Hazard. Mater. 141 (2007) 320–328.

[21] T.P. Flaten, Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water, Brain Res. Bull. 55 (2001) 187–196.

[22] S. Matsukawa, S. Itoho, S. Habuthu, T. Aizawa, An approach to residual aluminium control at Nisiya purification plant, Water Sci. Technol. Water Supply 6 (2006) 67–74.

[23] D. Bérubé, C.C. Dorea, Optimizing alum coagulation for turbidity, organics, and residual Al reductions, Water Sci. Technol. Water Supply. 8 (2008) 505–511.

[24] J.Y. Shin, R.F. Spinette, C.R. O'Melia, Stoichiometry of coagulation revisited, Environ. Sci. Technol. 42 (2008) 2582–2589.

[25] L. Rizzo, A. Di Gennaro, M. Gallo, V. Belgiorno, Coagulation/chlorination of surface water: A comparison between chitosan and metal salts, Sep. Purif. Technol. 62 (2008) 79–85.

[26] M. Yan, D. Wang, S. You, J. Qu, H. Tang, Enhanced coagulation in a typical North-China water treatment plant, Water Res. 40 (2006) 3621–3627.

[27] E.L. Sharp, S.A. Parsons, B. Jefferson, The impact of seasonal variations in DOC arising from a moorland peat catchment on coagulation with iron and aluminium salts, Environ. Pollut. 140 (2006) 436–443.

[28] G.C. Budd, A.F. Hess, H. Shorney-Darby, J.J. Neemann, C.M. Spencer, J.D. Bellamy, P.H. Hargette, Coagulation applications for new treatment goals, J. Am. Water Works Assoc. 96 (2004) 102–113.

[29] W. Bellamy, K. Carlson, D. Pier, J. Ducoste, M. Carlson, Determining disinfection needs, J. Am. Water Works Assoc. 92 (2000) 44–52.

[30] M. Yan, H. Liu, D. Wang, J. Ni, J. Qu, Natural organic matter removal by coagulation: Effect of kinetics and hydraulic power, Water Sci. Technol. Water Supply. 9 (2009) 21–30.

[31] W.P. Cheng, F.H. Chi, C.C. Li, R.F. Yu, A study on the removal of organic substances from low-turbidity and low-alkalinity water with metal-polysilicate coagulants, Colloids Surf. Physicochem. Eng. Aspects. 312 (2008) 238–244.

[32] M. Yan, D. Wang, J. Yu, J. Ni, M. Edwards, J. Qu, Enhanced coagulation with polyaluminum chlorides: Role of pH/Alkalinity and speciation, Chemosphere. 71 (2008) 1665–1673.

[33] W. Dongsheng, L. Hong, L. Chunhua, T. Hongxiao, Removal of humic acid by coagulation with nano-Al_{13}, Water Sci. Technol. Water Supply. 6 (2006) 59–67.

[34] T.K. Liu, C.J.M. Chin, Improved coagulation performance using preformed polymeric iron chloride (PICl), Colloids Surf. Physicochem. Eng. Aspects. 339 (2009) 192–198.

[35] J.C. Wei, B.Y. Gao, Q.Y. Yue, Y. Wang, L. Lu, Performance and mechanism of polyferric-quaternary ammonium salt composite flocculants in treating high organic matter and high alkalinity surface water, J. Hazard. Mater. 165 (2009) 789–795.

[36] G. Lei, J. Ma, X. Guan, A. Song, Y. Cui, Effect of basicity on coagulation performance of polyferric chloride applied in eutrophicated raw water, Desalination 247 (2009) 518–529.

[37] A.I. Zouboulis, P.A. Moussas, F. Vasilakou, Polyferric sulphate: Preparation, characterisation and application in coagulation experiments, J. Hazard. Mater. 155 (2008) 459–468.

[38] M. Yan, D. Wang, J. Qu, J. Ni, C.W.K. Chow, Enhanced coagulation for high alkalinity and micro-polluted water: The third way through coagulant optimization, Water Res. 42 (2008) 2278–2286.

[39] A.I. Zouboulis, P.A. Moussas, Polyferric silicate sulphate (PFSiS): Preparation, characterisation and coagulation behaviour, Desalination 224 (2008) 307–316.

[40] F. Li, A. Yuasa, Y. Ando, Characterization of micro-flocs of NOM coagulated by PACl, alum and polysilicate-iron in terms of molecular weight and floc size, Water Sci. Technol. 57 (2008) 83–90.

[41] A.I. Zouboulis, N.D. Tzoupanos, Polyaluminium silicate chloride-A systematic study for the preparation and application of an efficient coagulant for water or wastewater treatment, J. Hazard. Mater. 162 (2009) 1379–1389.

[42] Y. Fu, S.L. Yu, Characterization and coagulation performance of solid polysilicic-ferric (PSF) coagulant, J. Non Cryst. Solids. 353 (2007) 2206–2213.

[43] Y. Fu, S. Yu, C. Han, Morphology and coagulation performance during preparation of poly-silicic-ferric (PSF) coagulant, Chem. Eng. J. 149 (2009) 1–10.

[44] P.A. Moussas, A.I. Zouboulis, A study on the properties and coagulation behaviour of modified inorganic polymeric coagulant-Polyferric silicate sulphate (PFSiS), Sep. Purif. Technol. 63 (2008) 475–483.

[45] X. Xu, S. Yu, W. Shi, Z. Jiang, C. Wu, Effect of acid medium on the coagulation efficiency of polysilicate-ferric (PSF) – A new kind of inorganic polymer coagulant, Sep. Purif. Technol. 66 (2009) 486–491.

[46] M. Yan, D. Wang, J. Ni, J. Qu, W. Ni, J. van Leeuwen, Natural organic matter (NOM) removal in a typical North-China water plant by enhanced coagulation: Targets and techniques, Sep. Purif. Technol. 68 (2009) 320–327.

[47] M. Yan, D. Wang, B. Shi, M. Wang, Y. Yan, Effect of Pre-ozonation on optimized coagulation of a typical North-China source water, Chemosphere. 69 (2007) 1695–1702.

[48] B.Y. Gao, Y. Wang, Q.Y. Yue, J.C. Wei, Q. Li, The size and coagulation behavior of a novel composite inorganic-organic coagulant, Sep. Purif. Technol. 62 (2008) 544–550.

[49] Y. Wang, B. Gao, Q. Yue, J. Wei, Q. Li, The characterization and flocculation efficiency of composite flocculant iron salts-polydimethyldiallylammonium chloride, Chem. Eng. J. 142 (2008) 175–181.

[50] J. Wei, B. Gao, Q. Yue, Y. Wang, W. Li, X. Zhu, Comparison of coagulation behavior and floc structure characteristic of different polyferric-cationic polymer dual-coagulants in humic acid solution, Water Res. 43 (2009) 724–732.

[51] J.C. Wei, B.Y. Gao, Q.Y. Yue, Y. Wang, Strength and regrowth properties of polyferric-polymer dual-coagulant flocs in surface water treatment, J. Hazard. Mater. 175 (2010) 949–954.

[52] E.L. Sharp, S.A. Parsons, B. Jefferson, Seasonal variations in natural organic matter and its impact on coagulation in water treatment, Sci. Total Environ. 363 (2006) 183–194.

[53] E.L. Sharp, P. Jarvis, S.A. Parsons, B. Jefferson, Impact of fractional character on the coagulation of NOM, Colloids Surf. Physicochem. Eng. Aspects. 286 (2006) 104–111.

[54] J. Świetlik, A. Dąbrowska, U. Raczyk-Stanisławiak, J. Nawrocki, Reactivity of natural organic matter fractions with chlorine dioxide and ozone, Water Res. 38 (2004) 547–558.

[55] R. Fabris, C.W.K. Chow, M. Drikas, B. Eikebrokk, Comparison of NOM character in selected Australian and Norwegian drinking waters, Water Res. 42 (2008) 4188–4196.

[56] Woodard & Curran Inc., Industrial Waste Treatment Handbook (2nd ed.) (Knovel ebook), Elsevier, USA, 2006.

[57] R.J. Stephenson, S.J.B. Duff, Coagulation and precipitation of a mechanical pulping effluent—II. Toxicity removal and metal salt recovery, Water Res. 30 (1996) 793–798.

[58] R. Reiffenstein, W. Hulbert, S. Roth, Toxicology of hydrogen sulfide, Annu. Rev. Pharmacol. Toxicol. 32 (1992) 109–134.

[59] T. Yamanaka, I. Aso, S. Togashi, M. Tanigawa, K. Shoji, T. Watanabe, N. Watanabe, K. Maki, H. Suzuki, Corrosion by bacteria of concrete in sewerage systems and inhibitory effects of formates on their growth, Water Res. 36 (2002) 2636–2642.

[60] J.L. Davis, D. Nica, K. Shields, D.J. Roberts, Analysis of concrete from corroded sewer pipe, Int. Biodeterior. Biodegrad. 42 (1998) 75–84.

[61] A.H. Nielsen, J. Vollertsen, H.S. Jensen, T. Wium-Andersen, T. Hvitved-Jacobsen, Influence of pipe material and surfaces on sulfide related odor and corrosion in sewers, Water Res. 42 (2008) 4206–4214.

[62] W. Sand, E. Bock, Concrete corrosion in the Hamburg Sewer system, Environmental Technology Letters. 5 (1984) 517–528.

[63] A.H. Nielsen, T. Hvitved-Jacobsen, J. Vollertsen, Effects of pH and Iron Concentrations on Sulfide Precipitation in Wastewater Collection Systems, Water Environ. Res. 80 (2008) 380–380.

[64] D. Firer, E. Friedler, O. Lahav, Control of sulfide in sewer systems by dosage of iron salts: Comparison between theoretical and experimental results, and practical implications, Sci. Total Environ. 392 (2008) 145–156.

[65] A.H. Nielsen, P. Lens, J. Vollertsen, T. Hvitved-Jacobsen, Sulfide-iron interactions in domestic wastewater from a gravity sewer, Water Res. 39 (2005) 2747–2755.

[66] R. Stuetz, F.B. Frechen (Eds.), Odours in Wastewater Treatment: Measurement, Modelling and Control, IWA Publishing, UK, 2001.

[67] H. Moreno, D. Cocke, J. Gomes, P. Morkovsky, J. Parga, E. Peterson, C. Garcia, Electrochemical reactions for electrocoagulation using iron electrodes, Ind. Eng. Chem. Res. 48 (2009) 2275–2282.

[68] E.A. Vik, D.A. Carlson, A.S. Eikum, E.T. Gjessing, Electrocoagulation of potable water, Water Res. 18 (1984) 1355–1360.

[69] B. Morgan, O. Lahav, The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O_2 in aqueous solution – basic principles and a simple heuristic description, Chemosphere 68 (2007) 2080–2084.

[70] J. Parga, D. Cocke, V. Valverde, J. Gomes, M. Kesmez, H. Moreno, M. Weir, D. Mencer, Characterization of electrocoagulation for removal of chromium and arsenic, Chem. Eng. Technol. 28 (2005) 605–612.

[71] J.A.G. Gomes, P. Daida, M. Kesmez, M. Weir, H. Moreno, J.R. Parga, G. Irwin, H. McWhinney, T. Grady, E. Peterson, D.L. Cocke, Arsenic removal by electrocoagulation using combined Al–Fe electrode system and characterization of products, J. Hazard. Mater. 139 (2007) 220–231.

[72] M.B. Sasson, W. Calmano, A. Adin, Iron-oxidation processes in an electroflocculation (electrocoagulation) cell, J. Hazard. Mater. 171 (2009) 704–709.

[73] T. Picard, G. Cathalifaud-Feuillade, M. Mazet, C. Vandensteendam, Cathodic dissolution in the electrocoagulation process using aluminium electrodes, J. Environ. Monit. 2 (2000) 77–80.

[74] P. Refait, J.M.R. Genin, Mechanisms of oxidation of Ni(II)-Fe(II) hydroxides in chloride-containing aqueous media: Role of the pyroaurite-type Ni-Fe hydroxychlorides, Clay Miner. 32 (1997) 597–613.

[75] P. Refait, H. Drissi, Y. Marie, J.M.R. Génin, The substitution of Fe^{2+} ions by Ni^{2+} ions in green rust one compounds, Hyperfine Interact. 90 (1994) 389–394.

[76] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.

[77] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. 114 (2004) 199–210.

[78] G. Mouedhen, M. Feki, M.D.P. Wery, H.F. Ayedi, Behavior of aluminum electrodes in electrocoagulation process, J. Hazard. Mater. 150 (2008) 124–135.

[79] K.A. Matis, E.N. Peleka, Alternative flotation techniques for wastewater treatment: Focus on electroflotation, Sep. Sci. Technol. 45 (2010) 2465–2474.

[80] C. Comninellis, Electrochemistry for the Environment, Springer, USA, 2010.

[81] L. Mansour, S. Chalbi, I. Kesentini, Experimental study of hydrodynamic and bubble size distributions in electroflotation process, Indian J. Chem. Technol. 14 (2007) 253–257.

[82] M.S.K.A. Sarkar, G.M. Evans, S.W. Donne, Bubble size measurement in electroflotation, Minerals Eng. 23 (2010) 1058–1065.

[83] X. Chen, G. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Sep. Purif. Technol. 19 (2000) 65–76.

[84] M. Kobya, H. Hiz, E. Senturk, C. Aydiner, E. Demirbas, Treatment of potato chips manufacturing wastewater by electrocoagulation, Desalination. 190 (2006) 201–211.

[85] J.L. Trompette, H. Vergnes, On the crucial influence of some supporting electrolytes during electrocoagulation in the presence of aluminum electrodes, J. Hazard. Mater. 163 (2009) 1282–1288.

[86] D. Hasson, V. Lumelsky, G. Greenberg, Y. Pinhas, R. Semiat, Development of the electrochemical scale removal technique for desalination applications, Desalination 230 (2008) 329–342.

[87] I. Heidmann, W. Calmano, Removal of Zn(II), Cu(II), Ni(II), Ag(I) and Cr(VI) present in aqueous solutions by aluminium electrocoagulation, J. Hazard. Mater. 152 (2008) 934–941.

[88] M.M. Emamjomeh, M. Sivakumar, Fluoride removal by a continuous flow electrocoagulation reactor, J. Environ. Manage. 90 (2009) 1204–1212.

[89] A. Shafaei, M. Rezayee, M. Arami, M. Nikazar, Removal of Mn^{2+} ions from synthetic wastewater by electrocoagulation process, Desalination 260 (2010) 23–28.

[90] S. Zodi, J. Louvet, C. Michon, O. Potier, M. Pons, F. Lapicque, J. Leclerc, Electrocoagulation as a tertiary treatment for paper mill wastewater: Removal of non-biodegradable organic pollution and arsenic, Sep. Purif. Technol. 81 (2011) 62–68.

[91] S. Zodi, O. Potier, F. Lapicque, J. Leclerc, Treatment of the textile wastewaters by electrocoagulation: Effect of operating parameters on the sludge settling characteristics, Sep. Purif. Technol. 69 (2009) 29–36.

[92] C.L. Lai, S.H. Lin, Treatment of chemical mechanical polishing wastewater by electrocoagulation: system performances and sludge settling characteristics, Chemosphere 54 (2004) 235–242.

[93] M. Kumar, F.I.A. Ponselvan, J.R. Malviya, V.C. Srivastava, I.D. Mall, Treatment of bio-digester effluent by electrocoagulation using iron electrodes, J. Hazard. Mater. 165 (2009) 345–352.

[94] H. Shin, J. Lee, Performance evaluation of electrocoagulation and electrodewatering system for reduction of water content in sewage sludge, Korean J. Chem. Eng. 23 (2006) 188–193.

[95] I. Linares-Hernández, C. Barrera-Díaz, G. Roa-Morales, B. Bilyeu, F. Ureña-Núñez, Influence of the anodic material on electrocoagulation performance, Chem. Eng. J. 148 (2009) 97–105.

[96] A. Bagga, S. Chellam, D.A. Clifford, Evaluation of iron chemical coagulation and electrocoagulation pretreatment for surface water microfiltration, J. Membr. Sci. 309 (2008) 82–93.

[97] R. Katal, H. Pahlavanzadeh, Influence of different combinations of aluminum and iron electrode on electrocoagulation efficiency: Application to the treatment of paper mill wastewater, Desalination 265 (2011) 199–205.

[98] F. Akbal, S. Camcı, Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation, Desalination 269 (2011) 214–222.

[99] W. Chou, C. Wang, K. Huang, Effect of operating parameters on indium (III) ion removal by iron electrocoagulation and evaluation of specific energy consumption, J. Hazard. Mater. 167 (2009) 467–474.

[100] P. Cañizares, C. Jiménez, F. Martínez, M.A. Rodrigo, C. Sáez, The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters, J. Hazard. Mater. 163 (2009) 158–164.

[101] S. Irdemez, N. Demircioğlu, Y.S. Yildiz, The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes, J. Hazard. Mater. 137 (2006) 1231–1235.

[102] M.J. Yu, J.S. Koo, G.N. Myung, Y.K. Cho, Y.M. Cho, Evaluation of bipolar electrocoagulation applied to biofiltration for phosphorus removal, Water Sci. Technol. 51 (2005) 231–239.

[103] F. Janpoor, A. Torabian, V. Khatibikamal, Treatment of laundry wastewater by electrocoagulation, J. Chem. Technol. Biotechnol. 86 (2011) 1113–1120.

[104] Ö. Hanay, H. Hasar, Effect of anions on removing Cu^{2+}, Mn^{2+} and Zn^{2+} in electrocoagulation process using aluminum electrodes, J. Hazard. Mater. 189 (2011) 572–576.

[105] A. Shafaei, E. Pajootan, M. Nikazar, M. Arami, Removal of Co(II) from aqueous solution by electrocoagulation process using aluminum electrodes, Desalination 279 (2011) 121–126.

[106] N. Balasubramanian, T. Kojima, C.A. Basha, C. Srinivasakannan, Removal of arsenic from aqueous solution using electrocoagulation, J. Hazard. Mater. 167 (2009) 966–969.

[107] C. Escobar, C. Soto-Salazar, M.I. Toral, Optimization of the electrocoagulation process for the removal of copper, lead and cadmium in natural waters and simulated wastewater, J. Environ. Manage. 81 (2006) 384–391.

[108] B. Al Aji, Y. Yavuz, A.S. Koparal, Electrocoagulation of heavy metals containing model wastewater using monopolar iron electrodes, Sep. Purif. Technol. 86 (2012) 248–254.

[109] A.K. Golder, A.N. Samanta, S. Ray, Removal of trivalent chromium by electrocoagulation, Sep. Purif. Technol. 53 (2006) 33–41.

[110] C.P. Nanseu-Njiki, S.R. Tchamango, P.C. Ngom, A. Darchen, E. Ngameni, Mercury(II) removal from water by electrocoagulation using aluminium and iron electrodes, J. Hazard. Mater. 168 (2009) 1430–1436.

[111] A. Kolics, J.C. Polkinghorne, A. Wieckowski, Adsorption of sulfate and chloride ions on aluminum, Electrochim. Acta. 43 (1998) 2605–2618.

[112] C.Y. Hu, S.L. Lo, W.H. Kuan, Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes, Water Res. 37 (2003) 4513–4523.

[113] S. Vasudevan, J. Lakshmi, J. Jayaraj, G. Sozhan, Remediation of phosphate-contaminated water by electrocoagulation with aluminium, aluminium alloy and mild steel anodes, J. Hazard. Mater. 164 (2009) 1480–1486.

[114] A.E. Yilmaz, R. Boncukcuoğlu, M.M. Kocakerim, M.T. Yilmaz, C. Paluluoğlu, Boron removal from geothermal waters by electrocoagulation, J. Hazard. Mater. 153 (2008) 146–151.

[115] M.G. Kiliç, Ç. Hosten, S. Demirci, A parametric comparative study of electrocoagulation and coagulation using ultrafine quartz suspensions, J. Hazard. Mater. 171 (2009) 247–252.

[116] A. Golder, A. Chanda, A. Samanta, S. Ray, Removal of Cr(VI) from aqueous solution: Electrocoagulation vs chemical coagulation, Sep. Sci. Technol. 42 (2007) 2177–2193.

[117] B. Zhu, D.A. Clifford, S. Chellam, Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes, Water Res. 39 (2005) 3098–3108.

[118] T.L. Theis, P.C. Singer, Complexation of iron(II) by organic matter and its effect on iron(II) oxygenation, Environ. Sci. Technol. 8 (1974) 569–573.

[119] A.K. Golder, A.N. Samanta, S. Ray, Removal of Cr^{3+} by electrocoagulation with multiple electrodes: Bipolar and monopolar configurations, J. Hazard. Mater. 141 (2007) 653–661.

[120] D. Ghosh, C.R. Medhi, M.K. Purkait, Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections, Chemosphere 73 (2008) 1393–1400.

[121] C. Wang, W. Chou, Y. Kuo, Removal of COD from laundry wastewater by electrocoagulation/electroflotation, J. Hazard. Mater. 164 (2009) 81–86.

[122] M. Asselin, P. Drogui, S.K. Brar, H. Benmoussa, J. Blais, Organics removal in oily bilgewater by electrocoagulation process, J. Hazard. Mater. 151 (2008) 446–455.

[123] M. Asselin, P. Drogui, H. Benmoussa, J. Blais, Effectiveness of electrocoagulation process in removing organic compounds from slaughterhouse wastewater using monopolar and bipolar electrolytic cells, Chemosphere 72 (2008) 1727–1733.

[124] M. Bayramoglu, M. Eyvaz, M. Kobya, Treatment of the textile wastewater by electrocoagulation, Chem. Eng. J. 128 (2007) 155–161.

[125] S. Vasudevan, B.S. Kannan, J. Lakshmi, S. Mohanraj, G. Sozhan, Effects of alternating and direct current in electrocoagulation process on the removal of fluoride from water, J. Chem. Technol. Biotechnol. 86 (2011) 428–436.

[126] M. Eyvaz, M. Kirlaroglu, T.S. Aktas, E. Yuksel, The effects of alternating current electrocoagulation on dye removal from aqueous solutions, Chem. Eng. J. 153 (2009) 16–22.

[127] L.K. Wang, Y. Hung, N.K. Shammas (Eds.), Advanced Physicochemical Treatment Technologies, Humana Press, USA, 2007, pp. 57–106.

[128] M.M. Emamjomeh, M. Sivakumar, Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes, J. Environ. Manage. 90 (2009) 1663–1679.

[129] J.R. Parga, D.L. Cocke, J.L. Valenzuela, J.A. Gomes, M. Kesmez, G. Irwin, H. Moreno, M. Weir, Arsenic removal via electrocoagulation from heavy metal contaminated groundwater in La Comarca Lagunera México, J. Hazard. Mater. 124 (2005) 247–254.

[130] N. Balasubramanian, T. Kojima, C. Srinivasakannan, Arsenic removal through electrocoagulation: Kinetic and statistical modeling, Chem. Eng. J. 155 (2009) 76–82.

[131] H.K. Hansen, P. Nuñez, D. Raboy, I. Schippacasse, R. Grandon, Electrocoagulation in wastewater containing arsenic: Comparing different process designs, Electrochim. Acta 52 (2007) 3464–3470.

[132] M.S. Bhatti, A.S. Reddy, A.K. Thukral, Electrocoagulation removal of Cr(VI) from simulated wastewater using response surface methodology, J. Hazard. Mater. 172 (2009) 839–846.

[133] T. Ölmez, The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology, J. Hazard. Mater. 162 (2009) 1371–1378.

[134] N. Meunier, P. Drogui, C. Montané, R. Hausler, G. Mercier, J. Blais, Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate, J. Hazard. Mater. 137 (2006) 581–590.

[135] N. Meunier, P. Drogui, G. Mercier, J. Blais, Treatment of metal-loaded soil leachates by electrocoagulation, Sep. Purif. Technol. 67 (2009) 110–116.

[136] I. Heidmann, W. Calmano, Removal of Ni, Cu and Cr from a galvanic wastewater in an electrocoagulation system with Fe- and Al-electrodes, Sep. Purif. Technol. 71 (2010) 308–314.

[137] D. Ghosh, H. Solanki, M.K. Purkait, Removal of Fe(II) from tap water by electrocoagulation technique, J. Hazard. Mater. 155 (2008) 135–143.

[138] I. Kabdaşli, T. Arslan, T. Olmez-Hanci, I. Arslan-Alaton, O. Tünay, Complexing agent and heavy metal removals from metal plating effluent by electrocoagulation with stainless steel electrodes, J. Hazard. Mater. 165 (2009) 838–845.

[139] Z. Zaroual, M. Azzi, N. Saib, E. Chainet, Contribution to the study of electrocoagulation mechanism in basic textile effluent, J. Hazard. Mater. 131 (2006) 73–78.

[140] A. Aleboyeh, N. Daneshvar, M.B. Kasiri, Optimization of C.I. Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology, Chem. Eng. Process. 47 (2008) 827–832.

[141] I. Kabdaşli, B. Vardar, I. Arslan-Alaton, O. Tünay, Effect of dye auxiliaries on color and COD removal from simulated reactive dyebath effluent by electrocoagulation, Chem. Eng. J. 148 (2009) 89–96.

[142] C. Phalakornkule, P. Sukkasem, C. Mutchimsattha, Hydrogen recovery from the electrocoagulation treatment of dye-containing wastewater, Int. J. Hydrogen Energy 35 (2010) 10934–10943.

[143] K. Yetilmezsoy, F. Ilhan, Z. Sapci-Zengin, S. Sakar, M.T. Gonullu, Decolorization and COD reduction of UASB pretreated poultry manure wastewater by electrocoagulation process: A post-treatment study, J. Hazard. Mater. 162 (2009) 120–132.

[144] M. Kobya, E. Senturk, M. Bayramoglu, Treatment of poultry slaughterhouse wastewaters by electrocoagulation, J. Hazard. Mater. 133 (2006) 172–176.

[145] I.A. Dengil, S. Kulaç, M. Özacar, Treatment of tannery liming drum wastewater by electrocoagulation, J. Hazard. Mater. 167 (2009) 940–946.

[146] A. Benhadji, M. Ahmed, R. Maachi, Electrocoagulation and effect of cathode materials on the removal of pollutants from tannery wastewater of Rouiba, Desalination 277 (2011) 128–134.

[147] S. Kongjao, S. Damronglerd, M. Hunsom, Simultaneous removal of organic and inorganic pollutants in tannery wastewater using electrocoagulation technique, Korean J. Chem. Eng. 25 (2008) 703–709.

[148] J. Feng, Y. Sun, Z. Zheng, J. Zhang, S. Li, Y. Tian, Treatment of tannery wastewater by electrocoagulation, J. Environ. Sci. 19 (2007) 1409–1415.

[149] F.R. Espinoza-Quiñones, M.M.T. Fornari, A.N. Módenes, S.M. Palácio, F.G. da Silva, N. Szymanski, A.D. Kroumov, D.E.G. Trigueros, Pollutant removal from tannery effluent by electrocoagulation, Chem. Eng. J. 151 (2009) 59–65.

[150] M. Zaied, N. Bellakhal, Electrocoagulation treatment of black liquor from paper industry, J. Hazard. Mater. 163 (2009) 995–1000.

[151] R. Sridhar, V. Sivakumar, V. Prince Immanuel, J. Prakash Maran, Treatment of pulp and paper industry bleaching effluent by electrocoagulant process, J. Hazard. Mater. 186 (2011) 1495–1502.

[152] M. Uğurlu, A. Gürses, C. Doğar, M. Yalçin, The removal of lignin and phenol from paper mill effluents by electrocoagulation, J. Environ. Manage. 87 (2008) 420–428.

[153] Y. Perng, E. Wang, S. Yu, A. Chang, Application of a pilot-scale pulsed electrocoagulation system to OCC-based paper mill effluent, Tappi J. 8 (2009) 14–20.

[154] S. Mahesh, B. Prasad, I. Mall, I. Mishra, Electrochemical degradation of pulp and paper mill wastewater. Part 1. COD and color removal, Ind. Eng. Chem. Res. 45 (2006) 2830–2839.

[155] F. Hanafi, O. Assobhei, M. Mountadar, Detoxification and discoloration of Moroccan olive mill wastewater by electrocoagulation, J. Hazard. Mater. 174 (2010) 807–812.

[156] S. Khoufi, F. Feki, S. Sayadi, Detoxification of olive mill wastewater by electrocoagulation and sedimentation processes, J. Hazard. Mater. 142 (2007) 58–67.

[157] Ü. Tezcan Ün, S. Uğur, A.S. Koparal, Ü. Bakır Öğütveren, Electrocoagulation of olive mill wastewaters, Sep. Purif. Technol. 52 (2006) 136–141.

[158] M. Tir, N. Moulai-Mostefa, Optimization of oil removal from oily wastewater by electrocoagulation using response surface method, J. Hazard. Mater. 158 (2008) 107–115.

[159] M.H. El-Naas, S. Al-Zuhair, A. Al-Lobaney, S. Makhlouf, Assessment of electrocoagulation for the treatment of petroleum refinery wastewater, J. Environ. Manage. 91 (2009) 180–185.

[160] A.S. Koparal, Y.Ş. Yildiz, B. Keskinler, N. Demircioğlu, Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation, Sep. Purif. Technol. 59 (2008) 175–182.

[161] Y.Ş. Yıldız, A.S. Koparal, B. Keskinler, Effect of initial pH and supporting electrolyte on the treatment of water containing high concentration of humic substances by electrocoagulation, Chem. Eng. J. 138 (2008) 63–72.

[162] Y.Ş. Yildiz, A.S. Koparal, Ş. İrdemez, B. Keskinler, Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes, J. Hazard. Mater. 139 (2007) 373–380.

[163] Q. Feng, X. Li, Y. Cheng, L. Meng, Q. Meng, Removal of humic acid from groundwater by electrocoagulation, J. China Univ. Mining Technol. 17 (2007) 513,520–515,520.

[164] M.H. El-Masry, O.M. Sadek, W.K. Mekhemer, Purification of raw surface water using electro-coagulation method, Water Air Soil Pollut. 158 (2004) 373–385.

[165] C. Ricordel, A. Darchen, D. Hadjiev, Electrocoagulation–electroflotation as a surface water treatment for industrial uses, Sep. Purif. Technol. 74 (2010) 342–347.

[166] J. Zhu, H. Zhao, J. Ni, Fluoride distribution in electrocoagulation defluoridation process, Sep. Purif. Technol. 56 (2007) 184–191.

[167] D. Ghernaout, A. Badis, A. Kellil, B. Ghernaout, Application of electrocoagulation in *Escherichia coli* culture and two surface waters, Desalination 219 (2008) 118–125.

[168] N. Uduman, V. Bourniquel, M.K. Danquah, A.F.A. Hoadley, A parametric study of electrocoagulation as a recovery process of marine microalgae for biodiesel production, Chem. Eng. J. 174 (2011) 249–257.

[169] E. Lacasa, P. Cañizares, C. Sáez, F.J. Fernández, M.A. Rodrigo, Removal of nitrates from groundwater by electrocoagulation, Chem. Eng. J. 171 (2011) 1012–1017.

[170] M.M. Emamjomeh, M. Sivakumar, Denitrification using a monopolar electrocoagulation/flotation (ECF) process, J. Environ. Manage. 91 (2009) 516–522.

[171] Ş. İrdemez, N. Demircioğlu, Y.Ş. Yıldız, Z. Bingül, The effects of current density and phosphate concentration on phosphate removal from wastewater by electrocoagulation using aluminum and iron plate electrodes, Sep. Purif. Technol. 52 (2006) 218–223.

[172] Ş. İrdemez, Y.Ş. Yildiz, V. Tosunoğlu, Optimization of phosphate removal from wastewater by electrocoagulation with aluminum plate electrodes, Sep. Purif. Technol. 52 (2006) 394–401.

[173] O.T. Can, M. Kobya, E. Demirbas, M. Bayramoglu, Treatment of the textile wastewater by combined electrocoagulation, Chemosphere 62 (2006) 181–187.

[174] I. Kabdaşli, T. Arslan, I. Arslan-Alaton, T. Olmez-Hanci, O. Tünay, Organic matter and heavy metal removals from complexed metal plating effluent by the combined electrocoagulation/Fenton process, Water Sci. Technol. 61 (2010) 2617–2624.

[175] C. Barrera-Diaz, B. Bilyeu, G. Roa-Morales, P. Balderas-Hernandez, A comparison of iron and aluminium electrodes in hydrogen peroxide-assisted electrocoagulation of organic pollutants, Environ. Eng. Sci. 25 (2008) 529–537.

[176] G. Roa-Morales, E. Campos-Medina, J. Aguilera-Cotero, B. Bilyeu, C. Barrera-Díaz, Aluminum electrocoagulation with peroxide applied to wastewater from pasta and cookie processing, Sep. Purif. Technol. 54 (2007) 124–129.

[177] M. Hernández-Ortega, T. Ponziak, C. Barrera-Díaz, M.A. Rodrigo, G. Roa-Morales, B. Bilyeu, Use of a combined electrocoagulation–ozone process as a pre-treatment for industrial wastewater, Desalination. 250 (2010) 144–149.

[178] M. Boroski, A.C. Rodrigues, J.C. Garcia, A.P. Gerola, J. Nozaki, N. Hioka, The effect of operational parameters on electrocoagulation-flotation process fol-

lowed by photocatalysis applied to the decontamination of water effluents from cellulose and paper factories, J. Hazard. Mater. 160 (2008) 135–141.

[179] M. Boroski, A.C. Rodrigues, J.C. Garcia, L.C. Sampaio, J. Nozaki, N. Hioka, Combined electrocoagulation and TiO_2 photoassisted treatment applied to wastewater effluents from pharmaceutical and cosmetic industries, J. Hazard. Mater. 162 (2009) 448–454.

[180] S. Vilhunen, M. Vilve, M. Vepsäläinen, M. Sillanpää, Removal of organic matter from a variety of water matrices by UV photolysis and UV/H_2O_2 method, J. Hazard. Mater. 179 (2010) 776–782.

[181] M. Kobya, C. Ciftci, M. Bayramoglu, M.T. Sensoy, Study on the treatment of waste metal cutting fluids using electrocoagulation, Sep. Purif. Technol. 60 (2007) 285–291.

[182] J. Emsley, Nature's building blocks: an A–Z guide to the elements, Oxford University Press, UK, 2003.

[183] J.A. Field, S. Kortekaas, G. Lettinga, The tannin theory of methanogenic toxicity, Biological Wastes. 29 (1989) 241–262.

[184] J.A. Field, M.J.H. Leyendekers, R. Sierra Alvarez, G. Lettinga, L.H.A. Habets, Methanogenic toxicity of bark tannins and the anaerobic biodegradability of water soluble bark matter, Water Sci. Technol. 20 (1988) 219–240.

[185] M.K. Korczak, S. Koziarski, B. Komorowska, Anaerobic treatment of pulp mill effluents, Water Sci. Technol. 24 (1991) 203–206.

[186] J.H.M. Temmink, J.A. Field, J.C. Van Haastrecht, R.C.M. Merkelbach, Acute and sub-acute toxicity of bark tannins in carp (*Cyprinus carpio* L.), Water Res. 23 (1989) 341–344.

[187] L.T.K. Chung, H.P. Meier, J.M. Leach, Can pulp mill effluent toxicity be estimated from chemical analyses?, Tappi 62 (1979) 71–75.

[188] J.M. Leach, A.N. Thakore, Toxic constituents in mechanical pulping effluents, Tappi 59 (1976) 129–132.

[189] A. Oikari, B.E. Lonn, M. Castren, Toxicological effects of dehydroabietic acid (DHAA) on the trout, *Salmo gairdneri* Richardson, in fresh water, Water Res. 17 (1983) 81–89.

[190] M.R. Soimasuo, A.E. Karels, H. Leppänen, R. Santti, A.O.J. Oikari, Biomarker responses in whitefish (*Coregonus lavaretus* L. s.l.) experimentally exposed in a large lake receiving effluents from pulp and paper industry, Arch. Environ. Contam. Toxicol. 34 (1998) 69–80.

[191] J. Lappalainen, R. Juvonen, K. Vaajasaari, M. Karp, A new flash method for measuring the toxicity of solid and colored samples, Chemosphere 38 (1999) 1069–1083.

[192] R.G. Brereton, Applied Chemometrics for Scientists, John Wiley & Sons Ltd, UK, 2007.

[193] R. Pina, C. Cervantes, Microbial interactions with aluminium, Biometals 9 (1996) 311–316.

[194] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC) – science and applications, J. Hazard. Mater. 84 (2001) 29–41.

[195] B. Shi, Q. Wei, D. Wang, Z. Zhu, H. Tang, Coagulation of humic acid: The performance of preformed and non-preformed Al species, Colloids Surf. Physicochem. Eng. Aspects 296 (2007) 141–148.

[196] M. Ali, T.R. Sreekrishnan, Aquatic toxicity from pulp and paper mill effluents: A review, Adv. Environ. Res. 5 (2001) 175–196.

[197] S. Khoufi, F. Aloui, S. Sayadi, Extraction of antioxidants from olive mill wastewater and electro-coagulation of exhausted fraction to reduce its toxicity on anaerobic digestion, J. Hazard. Mater. 151 (2008) 531–539.

[198] S. Chowwanapoonpohn, S. Chewchanwuttiwong, M.J. Garson, D. Buddhasukh, Electrocoagulation and recovery of tannins from tree barks, J. Appl. Electrochem. 33 (2003) 647–650.

[199] M. Murugananthan, G. Bhaskar Raju, S. Prabhakar, Removal of sulfide, sulfate and sulfite ions by electro coagulation, J. Hazard. Mater. 109 (2004) 37–44.

[200] G. Peng, J.C. Roberts, Solubility and toxicity of resin acids, Water Res. 34 (2000) 2779–2785.

PUBLICATION I

Combined electrocoagulation and chemical coagulation of paper mill mechanically cleaned water

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Combined Electrocoagulation and Chemical Coagulation of Paper Mill Mechanically Cleaned Water

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This paper presents a study on the removal of natural organic matter (NOM) from paper mill mechanically treated water by integrating electrocoagulation (EC) with chemical coagulation (CC). The EC cell was made from monopolar aluminum plates and samples were pipetted, filtered or floated after CC and EC. It was found that the combination method was efficient in removing NOM even with small electric charges per litre. Colour and permanganate removals of 91 and 88%, respectively, were achieved by the combination of coagulation methods and dissolved air flotation treatment. Permanganate removal in the combination treatment exceeded pure CC. Residual aluminum levels were below 0.05 mg/L in filtered samples. EC also raised the pH and lowered the conductivities of the samples. The best current efficiency for removal of NOM from water was achieved with the smallest current density and the highest removal rate with the highest current density.

Nous avons procédé à une étude sur l'élimination des matières organiques naturelles de l'eau d'une usine de papier mécaniquement traitée en combinant l'électrocoagulation (EC) et la coagulation chimique (CC). Nous avons préparé une cellule à l'aide de plaques d'aluminium monopolaires, et pipetté, filtré et fait flotter des échantillons après la CC et l'EC. Nous avons trouvé que la méthode combinée pouvait efficacement éliminer les matières organiques naturelles, même à de très petites charges électriques par litre. Nous avons pu éliminer 91 % de la couleur et 88 % du permanganate en combinant les méthodes de coagulation et en procédant à un traitement de flottation par air dissous. L'élimination du permanganate dans le traitement combiné a dépassé la coagulation chimique pure. La quantité de résidus d'aluminium était inférieure à 0,05 mg/L dans les échantillons filtrés. L'électrocoagulation a aussi élevé le pH et réduit la conductivité des échantillons. L'élimination des matières organiques résiduelles de l'eau a été le plus efficace avec le courant de la densité la plus faible, et la vitesse d'élimination la plus rapide avec le courant de la densité la plus élevée.

INTRODUCTION

Large quantities of water are used in pulp and paper mills. Finnish surface waters usually contain high amounts of natural organic matter (NOM). Organic matter inflicts various problems on the paper machine and pulp bleaching. NOM and metals that bind to it can cause colour changes in the end product and fouling and corrosion. In addition, the presence of the metals catalyzes the decomposition of pulp bleaching chemicals.

Chemical coagulation (CC), together with flotation and/or filtration, is used commonly in water treatment for pulp and papermaking processes. Coagulants, such as alum and polyaluminum chloride (PAC), have difficulties in removing the smallest NOM particles from water [1], whereas electrocoagulation (EC) has proven to be a more effective method in removing dissolved organic carbon (DOC) from synthetic natural water [2].

EC has been tested on several waters, such as synthetic natural waters [3], laundry wastewaters [4], pasta and cookie processing wastewaters [5], dairy wastewater [6], alcohol distillery wastewaters [7] and distillery efflu-

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ents [8]. There are several types of EC apparatus used in the experiments [9,10]. EC electrodes are made from aluminum, iron or a combination of these. Iron or aluminum cations are produced on the surface of the electrodes (Eq. 1) and cause destabilization of the target compounds.

At the aluminum anode, the reaction is aluminum dissolution:

$$Al \rightarrow Al^{3+} + 3e^- \quad (1)$$

And, at the cathode, hydrogen formation:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

Hydrogen formation on the cathode (Eq. 2) is desirable if flotation is used for separating flocculated material from water. Hydrogen bubble size distribution depends on pH, current density, electrode material and cell arrangement. The hydrogen bubble size at pH 7 at platinum electrodes is 5–30 µm, at iron electrodes 5–45 µm and at carbon electrodes 5–80 µm, while the bubble size for dissolved air flotation (DAF) usually is 50–70 µm [9].

Together with hydrogen formation, the pH of the cathode surface increases, which hastens the chemical dissolution of aluminum (Eq. 3) [11,12]. Chemical dissolution can make an important contribution to the total dissolving rate. A change in pH in the course of electrolysis also affects the aluminum hydrolyzation species [13,14]. Aluminum can have various monomeric, oligomeric and polymeric species in aqueous solutions.

Chemical dissolution of aluminum:

$$2Al + 6H_2O \rightarrow 2Al^{3+} + 3H_2 + 6OH^- \quad (3)$$

There are also other competing reactions occurring at the electrodes that depend on electrolysis conditions such as electrode potential, electrolyte concentrations and pH. Possible side-reactions are chlorine and hypochlorous acid formation, cathodic dissolution, oxygen formation and precipitation reactions [4]. Hypochlorous acid or hypochlorites formation can cause disinfection but can also lead to the formation of disinfection byproducts [15]. Precipitation reactions create a passive layer on the electrodes, and this raises ohmic resistance on the electrodes.

CC and EC treatments have been compared to removing viruses [16], metals [17] and clay [18] from water. EC enhanced virus removal during microfiltration, and a better reduction was achieved than with CC pretreatment. This is due to electrophoretic movement, pH changes at the electrode surfaces and a higher local concentration of coagulant on the electrode surface [16]. Electrophoretic movement was also seen to be important in the EC of ultrafine kaolin particles [19]. Metal removal from acidic soil leachate was effective by EC, and researchers achieved good removal efficiencies of Pb, Ni, Cd, Cr, Cu and Zn [17]. Metal removal was also cost effective when compared to chemical precipitation. Turbidity removal associated with clay pollutants was more effective with EC than with alum. This might be due to the lower sulphate concentration and the formation of hydroxyl ions [18].

There are several advantages of EC when compared to CC, as discussed in review articles [10,20]. Some of the important advantages for paper and pulp mill raw water treatment are:

- EC produces low amounts of sludge, and the sludge is dewatered easily.
- Flocs formed in EC are larger and more stable than flocs formed in CC.
- Due to electrophoretic movement, the removal of DOC from water is better with EC than with CC [2].
- Competing reactions, such as hydrogen and hypochlorite formation, can be beneficial in water treatment.
- No harmful anions, such as sulphate and chloride, are added to water when EC is used.

The disadvantages of EC in industrial water treatment are the passivation of electrodes due to the presence of oxides and of precipitation layers on the electrode surfaces, the dissolving of the electrodes and the low conductivity of the surface waters [20]. High voltages can be avoided by reducing the distance between electrodes. The dissolving of the electrode material requires regular replacement of electrodes, which results in additional maintenance costs.

A study concerning the treatment of textile wastewaters shows that combined chemical and electrochemical coagulation (CEC) has beneficial effects [21]. CEC was faster than CC with PAC or with alum. PAC or alum addition also lowered the pH, while EC treatment raised it, so that effluent pH values can be adjusted with CC and EC treatments. Also, PAC addition can remove, at least partially, passivation problems due to a high chloride concentration [22].

EC has proven to be an efficient technology for the removal of several harmful substances from water. However, there are no studies concerning pulp and paper raw water treatment. In addition, there is little information about the possibilities of combined EC and CC. The aim of this research was to investigate the feasibility of combining EC with CC. In this study, CEC was applied for the first time to pulp and paper mill raw water treatment.

TABLE I
MECHANICALLY TREATED WATER PARAMETERS

Date	Conductivity (mS/m)	pH	Colour (mg/L PtCo)	$KMnO_4$ (mg/L)
31.5.2006		6.21	149	71
1.6.2006	3.34	6.16	151	78
11.9.2006	3.54	6.52	121	56
25.9.2006	3.56	6.60	117	61

MATERIALS AND METHODS

Materials

Mechanically treated water used for the experiments was gathered from a Finnish paper mill raw water treatment plant. The quality of raw water was analyzed on a daily basis in the paper mill laboratory, and the analysis results are presented in Table I. Water quality changed significantly during the course of time. Organic matter content was much higher in May and June than in September.

PAC solutions added to the samples were diluted from the 38% solution used in the paper mill raw water treatment. Due to the acidic nature of PAC, the pH was adjusted using 1 mol/L NaOH (J.T. Baker, Phillipsburg, NJ, USA) and the doses were selected on the basis of preliminary tests. The initial pH was adjusted to 6.2 for pipetted samples and to 6.0 for floated samples. NaCl (J.T. Baker) was added to some samples to get better conductivity.

All chemicals were added to the samples before the EC treatment. Chemical additions are shown in Table II. For floated samples in the series DR and D1, dispersion water dilution was taken into account and concentrations were calculated for the initial volume of sample without dispersion water.

Experimental Setup and Procedure

EC was done in standard 1 L glass beakers. Both the anode and the cathode plates were made of aluminum. The monopolar EC cell was composed of two anode and two cathode plates with dimensions 120 x 70 mm, and the gap between electrode plates was 10 mm. The

TABLE II
CHEMICAL ADDITIONS AND CURRENT DENSITIES

	Date	Series	PAC (mg/L)	NaOH (mg/L)	NaCl (mg/L)	Current density (mA/cm^2)
Pipetted	31.5.2006	P1	0.0	0.0	49.8	1.79
	31.5.2006	P2	4.5	2.0	49.7	1.79
	1.6.2006	P3	12.0	5.2	49.6	1.79
Filtered	11.9.2006	F1	14.4	6.4	0.0	0.36
	11.9.2006	F2	14.4	6.4	0.0	0.71
	11.9.2006	F3	14.4	6.4	0.0	1.07
DAF	25.9.2006	D1	14.4	6.4	0.0	0.71
	25.9.2006	DR1	17.8	8.8	0.0	0.71

Concentrations for DAF-treated samples are calculated for the initial volumes of the samples.

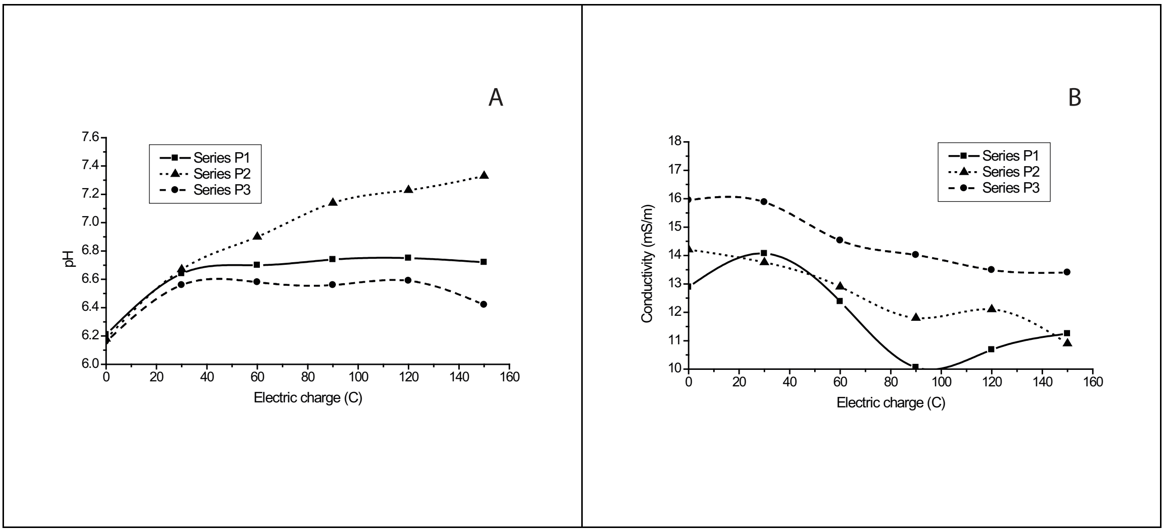

Fig. 1. Variation of the (A) pH and (B) conductivity of pipetted samples with electric charge. The results of the analyses are presented as a function of time or of electric charge. One coulomb is the same as an electric charge of one ampere in one second. The chemical coagulant concentration in the sample series was 4.5 mg/L in P2 and 12.0 mg/L in P3.

direct current power supply used in the experiments was an Instek GPC-3030DQ (Chino, CA, USA). The experiments were done galvanostatically, so that the current was adjusted to the desired level. Current densities used in the series are presented in Table I. Water was stirred during EC with a magnetic stirrer at a speed of 500 rpm.

In the series P1, P2 and P3, samples were transferred to a programmable stirrer and flocculator after EC treatment. The flocculator speeds were: 350 rpm for 10 s, 10 rpm for 5 min, and settling time 30 min. After settling, samples were pipetted from the glass beakers using 100 mL glass pipettes. Pipetting was done from the centre of the beaker to avoid getting floating material in the sample.

In the filtered sample series F1, F2 and F3, samples were transferred to a flocculator after EC treatment. The flocculator had the same speed setup that was used with the pipetted samples. After flocculation, samples were filtered using 589/1 black ribbon filter paper (Whatman, Maidstone, Kent, UK). The chemical additions of the samples are listed in Table II. The chemical additions were ~80% of the water treatment plant chemical dose.

Some samples were floated using a laboratory-scale DAF. The equipment used was DAFSEP's bench-scale DAF kit (Sciental Supply & Equipment, Monument, CO, USA). The pressure in the saturation tank was 483 kPa and the stabilization time was 10 min. In the series D1 and DR, the amount of dispersion water added to the sample was 200 mL. Water used in the saturation tank was ion-exchanged water used in the paper mill laboratory. Flotation time was 30 min. After flotation, water was filtered using a 589/1 black ribbon filter. Chemical additions of the D1 series were 80% of the water treatment plant's chemical additions. There were two samples, shown as DR, for which the chemical additions equaled the water treatment plant usages.

Analyses were done on filtered or pipetted samples, except for pH and conductivity measurements, which were analyzed from the whole sample. The permanganate index was measured as stated in Standard EN ISO 8467:1995 [23]. Apparent colour was measured as stated in Standard EN ISO 7887:1994 [24] using a Hach 2100AN IS photometer (Loveland, CO, USA). Residual aluminum was measured using the Merck (Darmstad, Germany) aluminum photometric test. The photometer used for the aluminum and turbidity measurements was the Spectroquant NOVA60 (Merck).

The results of the analyses are presented as a function of time or of electric charge. The

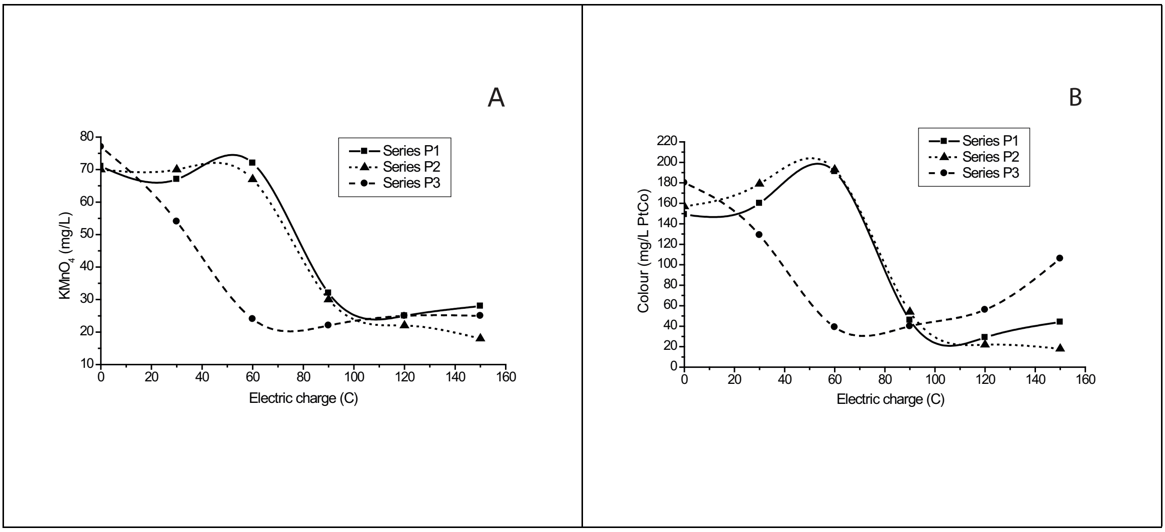

Fig. 2. Variation of the (A) permanganate index and (B) apparent colour of pipetted samples with electric charge. The chemical coagulant concentration in the sample series was 4.5 mg/L in P2 and 12.0 mg/L in P3.

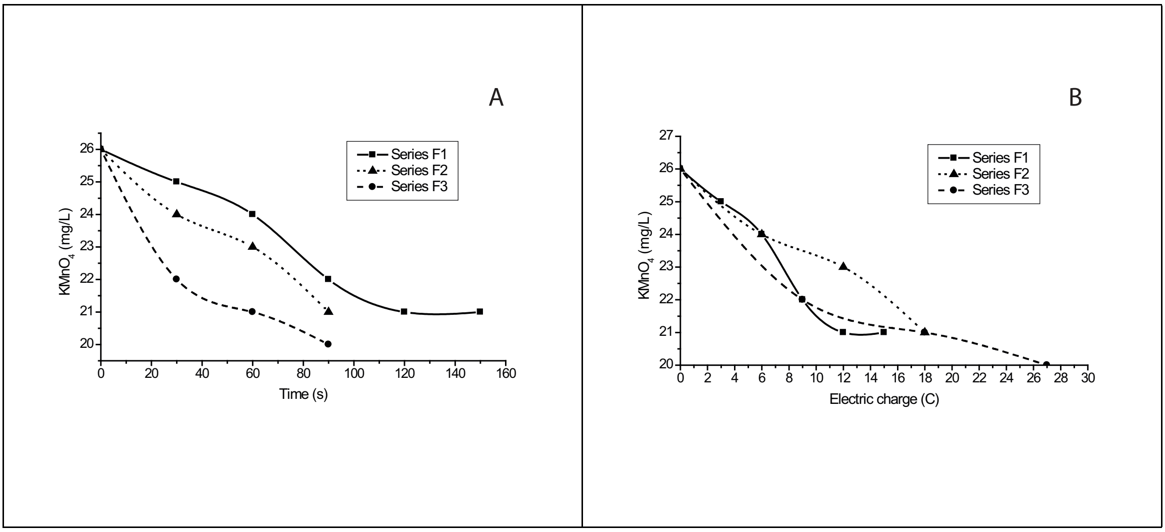

Fig. 3. Variation of the permanganate index of filtered samples with (A) time and (B) electric charge. The current densities in the series were 0.36 mA/cm^2 in F1, 0.71 mA/cm^2 in F2 and 1.07 mA/cm^2 in F3.

current efficiencies during various EC treatments are presented using electric charges. Electric charges are reported in coulombs, equal to an electric charge of one ampere in one second.

RESULTS AND DISCUSSION

Pipetted Samples

The initial pH of the series P1, P2 and P3 was adjusted to 6.2. Cathodic hydroxide ion formation raised the pH of EC-treated samples, as can be seen from Fig. 1A. In the series P1, in which no chemical coagulant was added, the pH rose to 6.8. In the series P2 with 4.5 mg/L coagulant addition, the pH rise was higher than in the series P1 and P3. A change of pH in EC is a widely known phenomenon [9]. For CEC, pH reactions are complicated due to a change in chloride concentration. A higher chloride concentration accelerates the dissolving of the electrode material and accelerates chlorine evolution.

The pH affects the zeta potential of humic and fulvic acids and the state of aluminum in solution. Higher amounts of aluminum and its hydrolysation products slow down the rise of pH, as can be seen from the series P3. The aluminum species in CC and in EC has been found to be equal to each other, and it has been concluded that the water pH change is the major difference between CC and EC [13]. How-

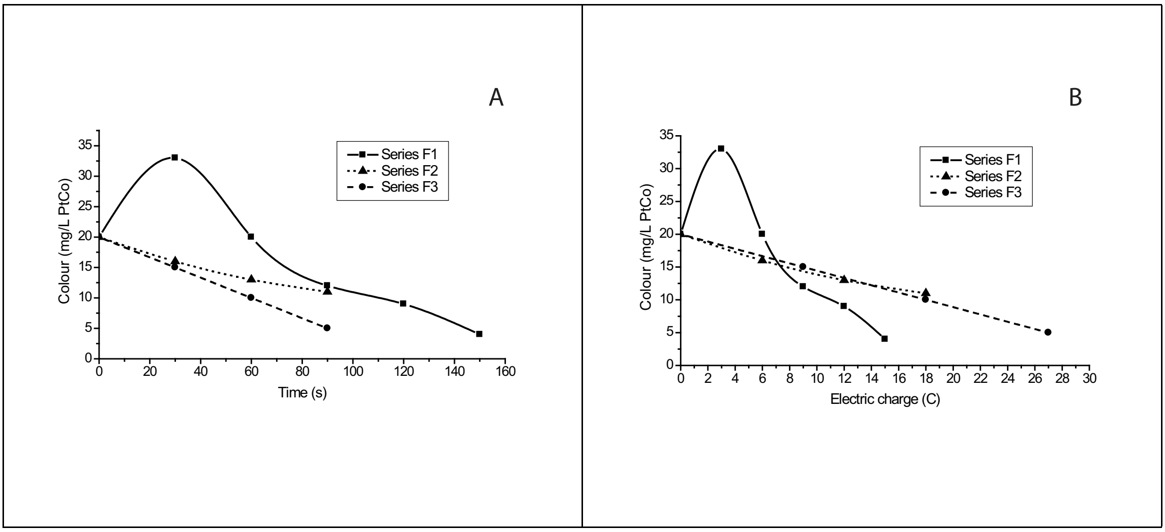

Fig. 4. Variation of apparent colour of filtered samples with (A) time and (B) electric charge. The current densities in the series were 0.36 mA/cm^2 in F1, 0.71 mA/cm^2 in F2 and 1.07 mA/cm^2 in F3.

ever, speciation on the electrode surface, where pH change is most significant, may still differ between EC and CC. After EC treatment, the speciation may change and lead to the formation of species similar to those after chemical treatment.

The conductivities of EC-treated samples were lower than untreated samples for electric charges greater than 30 C in EC (Fig. 1B). This is due partly to a change in pH during EC treatment. Conductivity values of untreated samples depended on chemical additions.

The effect of EC on the permanganate index of pipetted samples is depicted in Fig. 2A and apparent colour in Fig. 2B. The lowest permanganate index and apparent colour were achieved in series P2, which had a chemical coagulant dose of 4.5 mg/L. The fastest permanganate index and apparent colour reduction was achieved in the series P3, which had a chemical coagulant dose of 12.0 mg/L. The apparent colour in the series P3 started to rise after an electric charge of 90 C. This is probably due to the overdosing of coagulant, which causes the restabilization of particles in the solution.

Filtered Samples

The effect of EC on the permanganate index in the series F1, F2 and F3 is shown in Fig. 3. The fastest reduction occurred when the highest current density was used. When the permanganate index is a function of electric charge, it can be seen that the lowest current density is the most effective. This can be explained by the smaller amount of side reactions, such as hypochlorite and oxygen formation. Higher current densities on the electrode surfaces result in a higher electrode potential, which leads to different reactions. Side reactions are desirable when disinfection or flotation is needed.

Apparent colour reduction was fastest at the highest current density, as seen in Fig. 4A. Initially, there was a slight increase in apparent colour values in the F1 series with 30 s EC treatment time but, after this, colour reduction was fast. The effect of EC treatment on colour values as a function of electric charge is depicted in Fig. 4B. Colour reduction as a function of electric charge is similar for the series F2 and F3. The best current efficiency was achieved in the series F1, where the lowest current density was used. Again, this is probably due to the smaller amount of side reactions. It can be seen from Fig. 4 that colour reduction was faster than permanganate index reduction, especially in series F3. This might be due to the fast reduction of small NOM particles that contribute a large fraction of colour [25]. In previous studies, EC has proven to be superior in removing DOC compared to CC in model coloured water [2]. According to these results, current density has a significant impact on the removal efficiency of small NOM particles and of colour.

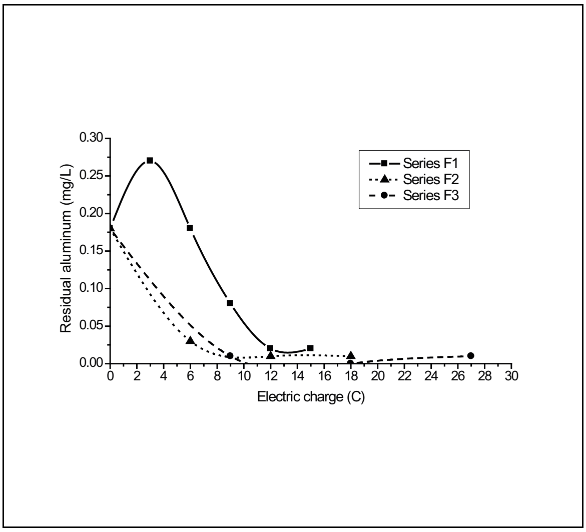

Fig. 5. Variation of residual aluminum with electric charge. The current densities in the series were 0.36 mA/cm^2 in F1, 0.71 mA/cm^2 in F2 and 1.07 mA/cm^2 in F3.

A residual aluminum concentration in treated water is harmful, as it causes deposits and disturbs the manufacturing process. The residual aluminum concentration in EC-treated water was very low in all series beyond treat-

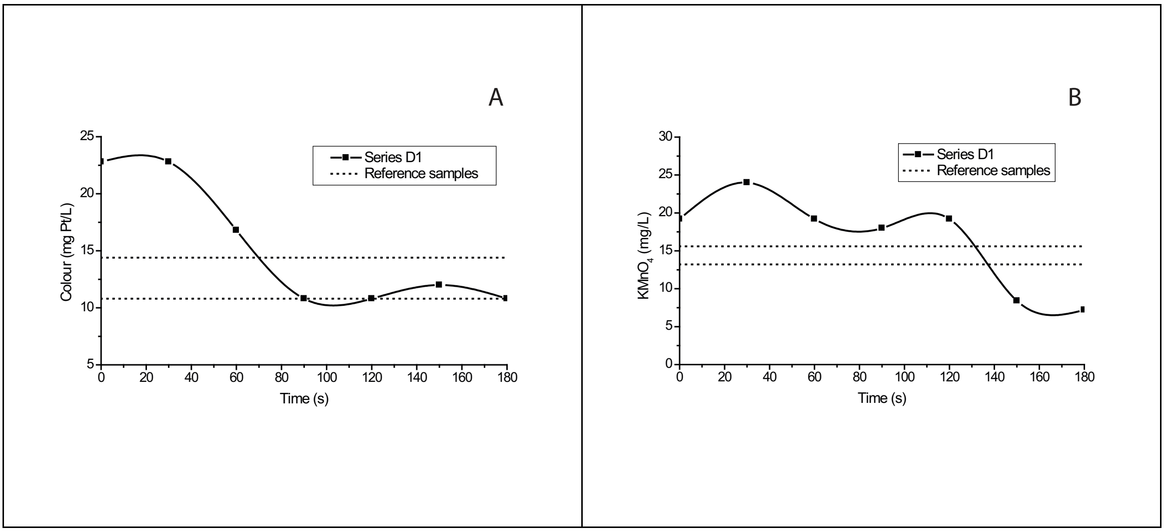

Fig. 6. Variation of (A) apparent colour and (B) permanganate index of DAF-treated samples with electric charge. The values are calculated for the original volume of sample, which does not include dispersion water.

ments of 12 C, as seen in Fig. 5. Current density had an impact on the removal of residual aluminum. The best current efficiency for residual aluminum removal was achieved when high current densities were used. This may be due to a higher rate of hydrogen formation and faster flotation. Faster flotation can also have an impact on the contact time of NOM particles and aluminum flocs, which can decrease the removal efficiency of NOM at high current densities.

Floated Samples

In the D1 and DR series, EC-treated samples were floated using a DAF bench-scale kit. The current density was the same as in the series F2. DR samples were reference samples in which coagulant and NaOH doses equaled those in the water treatment plant. The EC treatment removed colour, but the maximum colour reduction obtained was similar to that obtained with CC (Fig. 6A). The permanganate index was lower in EC-treated samples with treatments at 30 C and 36 C than in reference samples (Fig. 6B.). The total reduction of colour using CC and EC was 91% at 18 C/L and the permanganate index reduction was 88% at 36 C/L. Colour reductions of the reference samples were 88 and 91%, and the permanganate index reductions were 74 and 78%. The turbidities of all samples were below 5 FAU (Formacin Attenuation Unit).

Operating Cost

According to the literature, the price of aluminum in PAC is 7.83–9.40 US$/kg (9.00–10.8 AU$/kg) and the price of aluminum as a metal is ~2.4 US$/kg (25.9.2007) [26]. The true price of the electrode material depends also on the work needed to make electrodes and on the aluminum alloy used as a material of construction. In the EC treatment, electricity is needed for dissolving aluminum. The theoretical value for dissolving aluminum is 0.093 mg/C, according to Faraday's law and, for 10 V voltage, the electricity needed is 30 kWh/kg. As an estimate, if the price of electricity is 0.07 US$/kWh, then the cost of electricity needed for dissolving aluminum is 2.10 US$/kg. According to these calculations, EC can be a cost-effective method for water treatment.

CONCLUSIONS

Electrocoagulation with chemical coagulation was studied in this research. The effects of chemical coagulant dose, current density and various post-treatments were investigated.

- The dose of CC affects the electrical charge per litre needed for maximal NOM removal from mechanically treated water. Maximal removal reduces the size of the EC equipment and results in a lower investment cost.
- Combining EC with CC leads to a better removal of NOM and better water quality. PAC addition lowers the pH and EC raises the pH, thus lowering the need for chemicals required for pH adjustment.
- The fastest reduction in apparent colour and permanganate index is achieved at the highest current density. On the other hand, the best current efficiency is realized when the lowest current density is used. Consequently, optimization of investment and operation costs is needed. Residual aluminum reduction was fastest when the highest current density was used.

According to these results, EC can be used together with chemical coagulants. Beneficial effects are achieved when these two methods are combined. The best removal rate was realized at the smallest current density used (0.37 mA/cm^2) and therefore also at the lowest voltage and power consumption.

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REFERENCES

1. NISSINEN, T.K., MIETTINEN, I.T., MARTIKAINEN, P.J. and VARTIAINEN, T., "Molecular Size Distribution of Natural Organic Matter in Raw and Drinking Waters", *Chemosphere* 45(6–7):J867–873 (2001).
2. JIANG, J.-Q., GRAHAM, N., ANDRÉ, C., KELSALL, G.H. and BRANDON, N., "Laboratory Study of Electro-Coagulation-Flotation for Water Treatment", *Water Res.* 36(16):J4046–4078 (2002).
3. YILDIZ, Y.Ş., KOPARAL, A.S., İRDAMEZ, Ş. and KESKINLER, B., "Electrocoagulation of Synthetically Prepared Waters Containing High Concentration of NOM Using Iron Cast Electrodes", *J. Hazard. Mater.* 139(2):373–380 (2007).
4. GE, J., QU, J., LEI, P. and LIU, H., "New Bipolar Electrocoagulation-Electroflotation Process for the Treatment of Laundry Wastewater", *Sep. Pur. Technol.* 36(1):J33–39 (2004).
5. ROA-MORALES, G., CAMPOS-MEDINA, E., AGUILERA-COTERO, J., BILYEU, B. and

BARRERA-DÍAZ, C., “Aluminium Electrocoagulation with Peroxide Applied to Wastewater from Pasta and Cookie Processing”, *Sep. Pur. Technol.* 54(1):J124–129 (2007).

6. ŞENGIL, İ.A. and ÖZACAR, M., “Treatment of Dairy Wastewater by Electrocoagulation Using Mild Steel Electrodes”, *J. Hazard. Mater.* 137(2):J1197–1205 (2006).
7. YAVUZ, Y., “EC and EF Processes for the Treatment of Alcohol Distillery Wastewater”, *Sep. Pur. Technol.* 53(1):J135–140 (2007).
8. KANNAN, N., KARTHIKEYAN, G. and TAMILSELVAN, N., “Comparison of Treatment Potential of Electrocoagulation of Distillery Effluent with and without Activated *Areca catechu* Nut Carbon”, *J. Hazard. Mater.* 137(3):J1803–1809 (2006).
9. CHEN, G., “Electrochemical Technologies in Wastewater Treatment”, *Sep. Pur. Technol.* 38(1):J11–41 (2004).
10. MOLLAH, M.Y.A., MORKOVSKY, P., GOMES, J.A.G., KESMEZ, M., PARGA, J. and COCKE, D.L., “Fundamentals, Present and Future Perspectives of Electrocoagulation”, *J. Hazard. Mater.* 114(1–3):199–210 (2004).
11. CAÑIZARES, P., CARMONA, M., LOBATO, J., MARTÍNEZ, F. and RODRIGO, M.A., “Electrodissolution of Aluminum Electrodes in Electrocoagulation Process”, *Ind. Engin. Chem. Res.* 44(12):J4178–4185 (2005).
12. CAÑIZARES, P., MARTINEZ, F., CARMONA, M., LOBATO, J. and RODRIGO, M.A., “Continuous Electrocoagulation of Synthetic Colloid-Polluted Wastes”, *Ind. Engin. Chem. Res.* 44(22):J8171–8177 (2005).
13. CAÑIZARES, P., MARTINEZ, F., JIMÉNEZ, C., LOBATO, J. and RODRIGO, M., “Comparison of the Aluminum Speciation in Chemical and Electrochemical Dosing Processes”, *Ind. Engin. Chem. Res.* 45(26):J8749–8756 (2006).
14. DUAN, J. and GREGORY, J., “Coagulation by Hydrolysing Metal Salts”, *Adv. Coll. Interface Sci.* (100–102):J475–502 (2003).
15. NISSINEN, T.K., MIETTINEN, I.T., MARTIKAINEN, P.J. and VARTIANEN, T., “Disinfection By-Products in Finnish Drinking Waters”, *Chemosphere* 48(1):9–20 (2002).
16. ZHU, B., CLIFFORD, D.A. and CHELLAM, S., “Comparison of Electrocoagulation and Chemical Coagulation Pretreatment for Enhanced Virus Removal Using Microfiltration Membranes”, *Water Res.* 39(13):J3098–3108 (2005).
17. MEUNIER, N., DROGUI, P., MONTANÉ, C., HAUSLER, R., MERCIER, G. and BLAIS, J.-F., “Comparison between Electrocoagulation and Chemical Precipitation for Metals Removal from Acidic Soil Leachate.”, *J. Hazard. Mater.* 137(1):J581–590 (2006).
18. HOLT, P.K., BARTON, G.W., WARK, M. and MITCHELL, C.A., “A Quantitative Comparison between Chemical Dosing and Electrocoagulation”, *Coll. Surf. A* 211(2–3):233–248 (2002).
19. MATTESON, M.J., DOBSON, R.L., GLENN Jr., R.W., KUKUNOOR, N.S., WAITS III, W.H. and CLAYFIELD, E.J., “Electrocoagulation and Separation of Aqueous Suspensions of Ultrafine Particles”, *Coll. Surf. A* 104(1):101–109 (1995).
20. MOLLAH, M.Y.A., SCHENNACH, R., PARGA, J.R. and COCKE, D.L., “Electrocoagulation (EC) – Science and Applications”, *J. Hazard. Mater.* 84(1):29–41 (2001).
21. CAN, O.T., KOBYA, M., DEMIRBAS, E. and BAYRAMOGLU, M., “Treatment of the Textile Wastewater by Combined Electrocoagulation”, *Chemosphere* 62(2):J181–187 (2006).
22. HU, C.Y., LO, S.L. and KUAN, W.H., “Effects of Co-Existing Anions on Fluoride Removal in Electrocoagulation (EC) Process Using Aluminum Electrodes”, *Water Res.* 37(18):J4513–4523 (2003).
23. “Water Quality – Determination of Permanganate Index”, ISO 8467:1993, Intl. Org. Standardiz., Geneva, Switzerland (1993).
24. Water Quality – Examination and Determination of Colour”, ISO 7887:1994, Intl. Org. Standardiz., Geneva, Switzerland (1994).
25. RATNAWEERA, H., HILLER, N. and BUNSE, U., “Comparison of the Coagulation Behavior of Different Norwegian Aquatic NOM Sources”, *Env. Int.* 25(2–3):J347–355 (1999).
26. GEBBIE, P., “Using Polyaluminium Coagulants in Water Treatment”, Proc. 64th Ann. Water Industry Engineers Operators’ Conf., Australian Water Wastewater Operators Assoc., 39–47 (2001).

REFERENCE: VEPSÄLÄINEN, M., SELIN, J., PULLIAINEN, M. and SILLANPÄÄ, M., Combined Electrocoagulation and Chemical Coagulation of Paper Mill Mechanically Cleaned Water, Journal of Pulp and Paper Science, 33(4):233–239 October/November/December 2007. Paper offered as a contribution to the Journal of Pulp and Paper Science. Not to be reproduced without permission from the Pulp and Paper Technical Association of Canada. Manuscript received February 19, 2007; revised manuscript approved for publication by the Review Panel October 16, 2007.

KEYWORDS: WATER RECLAMATION, WATER TREATMENT, COAGULATION, ELECTRICITY.

2007 JPPS Best Paper Award

Congratulations to James Olson, Richard Kerekes and David Goosen, University of British Columbia, Vancouver, BC for winning the 2007 JPPS Best Paper Award. Their winning paper is "The Role of Heterogeneity in Compression Refining", published in the April/May/June 2007 issue of JPPS.

The award is conferred in recognition of the best paper published in the Journal of Pulp and Paper Science. The awards were presented during the PAPTAC Awards Ceremony at the 94th Annual Meeting, February 7, 2008 in Montreal. The Scientific Editor and the Associate Scientific Editors judged the papers.

PUBLICATION II

Effect of electrochemical cell structure on natural organic matter (NOM) removal from surface water through electrocoagulation (EC)

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Effect of electrochemical cell structure on natural organic matter (NOM) removal from surface water through electrocoagulation (EC)

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ABSTRACT

This study analyzed the effect of electrocoagulation cell construction on NOM removal from Finnish surface water. Three types of cells were used in this research: one that only had aluminum electrodes, one that had aluminum anodes and inert cathodes, and one that had inert anodes and aluminum cathodes. Main water quality parameters such as TOC, apparent color, and concentrations of residual metals were measured from the samples. A statistical model was made from the results using partial least squares (PLSs) regression. According to the results, electrocoagulation was able to produce high quality water with low NOM concentration. Lowest measured TOC concentration was 4.02 mg/l (78% removal). The potential applications of water after the treatment could be potable water or industrial fresh water. Aluminum originating from the anodes or cathodes had similar NOM removal efficiency. According to TOC and ζ-Potential results, the mechanism of NOM removal was similar to chemical coagulation in different pHs. It seems that in low pH, double layer compression was the main destabilization mechanism whereas in higher pH, adsorption and bridging dominated.

1. Introduction

Electrocoagulation has been suggested to be a promising alternative to chemical coagulation for removing various pollutants from freshwaters and wastewaters [1–3]. Sacrificial metal anodes or cathodes produce metal ions or metal hydroxides into solution. Metal cations and hydroxides interact with pollutants by several mechanisms, including charge neutralization, precipitation, and enmeshment. Pollutants can be removed from water by electroflotation, which can occur simultaneously with electrocoagulation, or by sedimentation, or filtration. Electroflotation is caused by micrometer-sized bubbles (15–23 μm diameter), which are produced on the cathode surface [4]. Other mechanisms that may affect pollution removal are electromigration of ions towards electrodes and reduction of metals on the cathode surface. These reactions, as well as well-known advantages and disadvantages and applications of electrocoagulation, are presented in review articles [1–3,5,6].

It is well known that aluminum in the electrocoagulation process can be dissolved from aluminum anodes and cathode electrodes. Aluminum dissolves from anodes according to simple electrochemical reaction Eq. (1) and forms hydroxides in water Eq. (2). Meanwhile, aluminum cathodes dissolve due to high pH on the cathode surface Eq. (4), which is caused by OH^- that is produced by an electrochemical reaction Eq. (3). Aluminate also forms various hydroxides in water Eq. (2) depending on the water pH.

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^- \tag{1}$$

$$Al^{3+}(aq) + nH_2O \leftrightarrow Al(OH)_n^{3-n+} + nH^+(aq) \tag{2}$$

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \tag{3}$$

$$2Al(s) + 6H_2O + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g) \tag{4}$$

Electrocoagulation treatment of surface waters and removal of NOM from waters has been studied in several articles [7–16]. Jiang et al. applied a laboratory flow-through system, which they tested with model-colored water and lowland surface water [8]. Electrocoagulation performed better for DOC removal than chemical coagulation for the model-colored water, but for the lowland surface water both processes had similar performance. Yildiz et al. studied the effect of initial pH, supporting electrolyte, applied potential and initial humic substance concentration on NOM removal from synthetically prepared waters containing a high concentration of NOM [14,15]. According to their results, the optimum initial pH is 5 for electrocoagulation using aluminum plate electrodes. They concluded that Na_2SO_4 was the most favorable supporting

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electrolyte. However, it should be noted that applying supporting electrolyte takes away one advantage of electrocoagulation: lower salt concentration of produced water. The effect of temperature and initial pH of surface water on removing natural organic matter (NOM) was studied in our earlier research [11]. According to our results, temperature had a minor effect on removal of NOM in temperature range 275.15–295.15 K. The greatest NOM removal (80.4%) in the tested range of parameters, according to dissolved organic carbon results, was obtained when the initial pH was 4.3 and the maximum electric charge was applied (144 C/l).

Response surface method (RSM) is a statistical method that is used to study the relationship of the factors and responses. It has been used in several studies where factors affecting electrocoagulation efficiency have been studied and optimized. We have successfully used RMS in our previous studies [11,17]. RSM has also been used to optimize oil removal from oily wastewater [18], azo dye removal from simulated wastewater [19] and Cr(VI) from simulated wastewater [20] and real wastewater [21]. In this study RSM with partial least squares regression (PLS) was used to optimize the electrocoagulation treatment of surface water. Additional tests were done with optimized parameters to verify the empirical model.

It is possible that aluminum ions and hydroxides produced on the anodes and the cathodes have different properties if they react with pollutants on the electrode surface before they are stabilized in bulk water to similar hydroxides. The aim of this study was to investigate if aluminum dissolved from anodes and cathodes has different properties in NOM removal from surface water. This was conducted by using three different cell constructions: a cell with aluminum anodes and cathodes, a cell with aluminum anodes and inert cathodes, and a cell with inert anodes and aluminum cathodes.

2. Experimental

2.1. Electrochemical treatment

Water samples were collected from a Finnish river and stored in a cold room. The untreated samples had high NOM concentration according to photometric and DOC measurements. The physicochemical properties of the samples before and after EC treatment are presented in Table 1. Water pH was adjusted before treatment to the desired level using 0.1 M, 0.01 M and 0.001 M sulfuric acid solutions (analytical grade). Studies were made in acidic initial

Table 1
Factor and response values used in the model and initial water quality parameters.

Turbidity (NTU)	Apparent color (mg/l PtCo)	TOC (mg/l)	ζ-Potential (mV)	Residual Al (mg/l)	Residual Fe (mg/l)
Initial water quality parameters					
0.34	102.0	18.29	−15.2	0.3145	0.8838

Factors		Responses								
Electric charge (C/l)	Initial pH	Final pH	Turbidity (NTU)	Apparent color (mg/l PtCo)	TOC (mg/l)	ζ-Potential (mV)	Dissolved Al (mg/l)	Residual Al (mg/l)	Residual Fe (mg/l)	Residual Mn (mg/l)
Cell A+C: Aluminium anodes and aluminium cathodes										
48	3.0	3.50	1.24	61.8	15.19	−10.5	5.531	5.2770	0.2030	0.0842
96	3.0	3.80	1.01	51.4	14.35	−3.9	7.675	7.2800	0.1848	0.0863
144	3.0	4.36	1.52	18.4	7.06	7.6	15.490	8.4020	0.0754	0.0781
48	4.0	6.56	1.51	12.4	5.20	−26.4	5.613	0.0364	0.0068	0.0407
96	4.0	6.73	1.72	11.3	4.04	−29.2	12.840	0.0163	0.0000	0.0397
144	4.0	6.82	2.05	11.8	4.02	−27.4	19.650	0.0462	0.0015	0.0319
48	5.0	6.42	2.75	78.1	13.23	−22.6	5.703	2.7960	0.3990	0.0248
96	5.0	6.81	1.98	22.2	7.45	−24.0	12.590	0.5711	0.0324	0.0118
144	5.0	6.83	3.46	22.7	6.54	−17.0	18.420	0.7860	0.0047	0.0073
96	4.0	6.62	1.42	11.0	4.07	−29.9	12.090	0.0156	0.0000	0.0409
96	4.0	6.61	1.18	8.1	4.72	−27.7	11.790	0.0224	0.0017	0.0420
96	4.0	6.54	1.38	9.2	4.53	−26.6	11.200	0.0288	0.0046	0.0413
Cell A: Aluminium anodes and DSA cathodes										
48	3.0	3.53	1.08	73.0	16.70	−12.4	4.115	3.9600	0.2984	0.1694
96	3.0	3.97	0.80	59.2	14.78	−6.8	7.672	7.1710	0.2538	0.1650
144	3.0	4.39	0.76	24.2	8.99	−3.4	11.350	8.3230	0.1519	0.1390
48	4.0	6.98	1.19	18.0	7.77	−28.5	4.201	0.1319	0.0355	0.1190
96	4.0	7.02	1.24	9.3	5.45	−24.1	8.167	0.0240	0.0072	0.1086
144	4.0	7.13	1.00	8.5	5.38	−31.2	11.578	0.0310	0.0017	0.0874
48	5.0	7.18	2.70	96.2	15.69	−24.0	4.224	2.6940	0.5336	0.1169
96	5.0	7.68	3.96	57.2	11.01	−29.2	8.118	2.0170	0.2115	0.0805
144	5.0	7.76	3.22	33.7	8.81	−25.4	12.040	1.2270	0.0760	0.0515
96	4.0	6.65	1.53	10.8	6.10	−26.2	7.826	0.0535	0.0205	0.0874
96	4.0	6.94	1.29	9.0	5.45	−22.4	7.722	0.0395	0.0225	0.0822
96	4.0	6.75	1.29	9.1	5.36	−26.5	7.940	0.0358	0.0229	0.0884
Cell C: DSA anodes and aluminium cathodes										
48	3.0	3.27	1.17	71.6	16.53	−13.6	2.806	2.5370	0.3475	0.1465
96	3.0	4.09	1.17	28.5	9.96	−3.2	10.190	7.0370	0.1653	0.1427
144	3.0	4.43	0.88	11.0	5.37	11.7	17.764	6.2580	0.0652	0.1337
48	4.0	7.08	2.06	36.1	10.44	−32.6	3.590	0.2531	0.0912	0.1338
96	4.0	6.89	1.21	10.1	5.02	−27.6	7.744	0.0316	0.0046	0.1064
144	4.0	7.23	1.61	9.7	4.84	−31.7	11.160	0.0262	0.0157	0.0828
48	5.0	7.21	2.15	124.2	18.42	−23.2	3.633	3.2670	0.7600	0.0999
96	5.0	7.23	1.32	14.3	6.67	−21.6	9.627	0.0857	0.0111	0.0656
144	5.0	7.47	1.52	10.3	5.14	−23.6	16.258	0.0802	0.0114	0.0517
96	4.0	7.28	0.96	5.4	4.10	−29.0	10.070	0.0207	0.0003	0.0526
96	4.0	6.49	1.52	8.4	4.57	−23.7	6.672	0.0318	0.0025	0.0641
96	4.0	6.30	1.15	6.8	4.54	−21.2	6.670	0.0536	0.0102	0.0664

pH because our previous study shows that low initial pH enhances NOM removal [11]. Surface waters in Scandinavia are typically soft and therefore a low amount of acid is required for the pH adjustment.

In this study, three EC cells were constructed. Cells A + C was made of 6 aluminum plates; 3 anodes and 3 cathodes. Cell A was made of aluminum anodes (3 plates) and inert cathodes (3 plates). Cell C was similar to Cell A, but inert plates were used as anodes and aluminum plates as cathodes. Inert electrode material used in this study was commercially available dimensionally stable anode (DSA) electrodes. These electrodes were made of titanium that was coated with a mixed metal oxide layer (iridium and ruthenium oxides). Aluminum alloy 1050 (99.5% Al) was used in the experiments. All electrode plates were 7 cm long and 5 cm wide. Distance between electrode plates was 1 cm. EC treatment was done in batch cells where electrodes were arranged into monopolar configuration. Water volume during the treatment was 500 ml.

GW Instek PSM-6003 was used as a power source throughout the experiments. The current used in this study was 0.100 A. Low current density 0.48 mA/cm^2 was selected on the basis of our previous studies [12]. Treatment time varied from 4 (48 C/l) to 12 min (144 C/l). Electrode plates were washed thoroughly with 4% HCl, tap water, and MilliQ-water after treatments.

Samples were magnetically stirred during the EC treatment at the speed of 300 rpm. After the treatment, samples were stirred with an overhead stirrer at the speed of 40 rpm for 10 min to facilitate flocculation. Settling time after flocculation was 30 min. Water samples were filtered through a glass fiber filter (GF/C Whatman, nominal pore size 1.2 μm) and stored in a cold room before further analysis.

2.2. Chemical analysis

Metal concentrations were determined using iCAP 6000 series ICP-OES (Thermo Electron) from samples in which 0.2 ml of 37% HNO_3 (analytical grade) was added to 10 ml of sample. Dissolved aluminum samples were taken right after electrochemical treatment before slow stirring stage. Residual metals were analyzed

Table 2
The fraction of the variation of the response explained by the model (R^2) and the fraction of the variation of the response predicted by the model according to cross validation (Q^2).

Term	Final pH	Turbidity	Apparent color	TOC	ζ-Potential	Dissolved Al	Residual Al	Residual Fe	Residual Mn
Cell A+C									
R^2	0.98	0.93	0.86	0.93	0.94	0.97	0.98	0.80	0.98
Q^2	0.85	0.53	0.52	0.62	0.70	0.70	0.82	0.57	0.80
Cell A									
R^2	0.99	0.97	0.98	0.96	0.94	1.00	0.98	0.93	0.94
Q^2	0.92	0.75	0.87	0.77	0.71	0.92	0.88	0.77	0.71
Cell C									
R^2	0.96	0.70	0.91	0.93	0.93	0.92	0.96	0.81	0.79
Q^2	0.84	0.12	0.40	0.46	0.58	0.41	0.74	0.43	0.32

Table 3
Coefficients of the model terms (X_1 is electric charge and X_2 is initial pH).

Response	Unit	Constant	X_1	X_2	X_1^2	X_2^2	$X_1{}^*X_2$
Cell A+C							
Final pH		−2.07E+01	−1.55E−02	1.26E+01	5.19E−05	−1.43E+00	2.66E−03
Turbidity[a]	NTU	4.86E−01	−1.05E−02	−1.14E−01	5.70E−05	3.30E−02	1.61E−04
App. Color[a]	PtCo mg/l	1.01E+01	−1.10E−02	−4.15E+00	3.27E−05	5.11E−01	2.50E−04
TOC[a]	mg/l	6.91E+00	−3.80E−03	−2.91E+00	1.03E−06	3.53E−01	2.47E−04
ζ-Potential[b]	mV	−1.09E+00	−3.71E−04	−4.71E−01	5.71E−06	5.53E−02	−1.01E−04
Dissolved Al	mg/l	−2.42E+01	3.62E−02	1.27E+01	3.29E−04	−1.50E+00	7.10E−03
Residual Al[a]	mg/l	3.18E+01	−2.92E−02	−1.56E+01	1.43E−04	1.89E+00	1.66E−04
Residual Fe[c]	mg/l	2.74E+01	−4.79E−02	−1.36E+01	2.22E−04	1.67E+00	−1.34E−03
Residual Mn[a]	mg/l	−1.63E+00	6.25E−03	4.29E−01	−3.54E−06	−8.09E−02	−1.98E−03
Cell A							
Final pH		−2.00E+01	6.94E−03	1.14E+01	2.28E−05	−1.18E+00	−1.45E−03
Turbidity[a]	NTU	1.64E+00	−1.30E−04	−1.03E+00	−2.69E−05	1.51E−01	1.19E−03
App. Color[a]	PtCo mg/l	1.25E+01	−6.42E−03	−5.51E+00	7.98E−06	6.92E−01	1.25E−04
TOC[a]	mg/l	6.23E+00	−4.29E−03	−2.55E+00	8.09E−06	3.14E−01	9.38E−05
ζ-Potential[b]	mV	−1.47E+00	1.42E−03	−3.16E−01	−2.50E−06	3.77E−02	−2.15E−04
Dissolved Al	mg/l	9.77E−01	6.52E−02	−1.79E−01	2.82E−06	1.20E−02	3.03E−03
Residual Al[a]	mg/l	2.86E+01	4.49E−03	−1.48E+01	3.69E−05	1.86E+00	−3.46E−03
Residual Fe[c]	mg/l	1.77E+01	1.84E−02	−9.96E+00	−8.00E−05	1.28E+00	−2.88E−03
Residual Mn[a]	mg/l	3.27E−01	2.58E−03	−5.41E−01	5.45E−06	6.57E−02	−1.41E−03
Cell C							
Final pH		−2.26E+01	9.60E−03	1.27E+01	7.57E−05	−1.32E+00	−4.67E−03
Turbidity[a]	NTU	−6.42E−01	−9.96E−03	5.50E−01	4.79E−05	−5.56E−02	−1.40E−04
App. Color[a]	PtCo mg/l	7.74E+00	−2.78E−02	−2.53E+00	1.29E−04	3.31E−01	−1.39E−03
TOC[a]	mg/l	4.70E+00	−1.44E−02	−1.52E+00	5.73E−05	1.92E−01	−3.43E−04
ζ-Potential[b]	mV	−1.24E+00	3.51E−03	−4.82E−01	−4.27E−06	6.19E−02	−5.77E−04
Dissolved Al	mg/l	3.06E+01	1.79E−01	−1.85E+01	−4.50E−05	2.43E+00	−1.22E−02
Residual Al[a]	mg/l	2.00E+01	6.41E−03	−1.01E+01	1.44E−04	1.31E+00	−1.04E−02
Residual Fe[c]	mg/l	1.43E+01	−5.51E−02	−6.53E+00	3.46E−04	8.52E−01	−5.70E−03
Residual Mn[a]	mg/l	5.18E−01	−4.79E−03	−5.11E−01	4.20E−05	6.02E−02	−1.28E−03

[a] Logarithmic transformation Log 10(Y).
[b] Negative logarithmic transformation –Log 10(100 − Y).
[c] Logarithmic transformation Log 10(Y+0.001).

from samples that were taken after filtration. DOC was measured using TOC analyzer (Shimadzu) after filtering the samples through 0.45 μm pore size membrane.

Apparent color was analyzed with DR 2800 photometer (Hach), and turbidity with Model 2100P ISO turbidimeter (Hach). Conductivity was determined using a CON6 Conductivity Meter (Ecoscan), and pH with Multiline P3 (WTW). Absorbance of the samples at 254 nm wavelength was measured with a Lambda 45 UV/VIS spectrophotometer (Perkin-Elmer), while the zeta potential was determined using a Zetasizer Nano ZS (Malvern).

2.3. Design of experiments and response surface method (RSM)

Factors of the experiments were electric charge added per volume and initial pH. Due to the small number of factors, full factorial design was carried out for three electrochemical cell constructions. Responses included in the model were final pH, turbidity, apparent color, TOC, ζ-Potential, aluminum dissolved, residual aluminum, residual iron, and residual manganese. The experimental design contained 12 tests for each electrochemical cell construction, including the 3 repeating tests at the center point. Three additional tests were conducted using Cells A + C to verify the water quality at the predicted optimum region. The range and levels of the factors and measured values of responses are shown in Table 1.

The first method used in the modeling was partial least squares regression (PLS). PLS is a statistical method that finds the relationship between response variables (matrix Y) and the predictor of factor variables (matrix X). As with other statistical regression methods, such as multiple linear regression (MLR), an equation describing the relationship between the response variable and predictor variables (factors) is gained. The general form of the regression equation including single terms, square terms, and interaction terms is shown in Eq. (5), where Y is the response variable, b are the coefficients of the model, and X are the factor variables.

$$Y = b_0 + \underbrace{\sum_{i=1}^{k} b_i X_i}_{\text{single terms}} + \underbrace{\sum_{i=1}^{k} b_{ii} X_i^2}_{\text{square terms}} + \underbrace{\sum_{i}^{i<j}\sum_{j} b_{ij} X_i X_j}_{\text{interaction terms}} \tag{5}$$

The quality of the regression equation can be evaluated using analysis of variance (ANOVA). However, due to the high number of responses in this study only R^2 and Q^2 are presented for each response in Table 2. R^2 is the amount of variance explained by the model whereas Q^2 is an estimate of the model's predictive ability. Q^2 is calculated by cross-validation. Model terms are presented in Table 3.

3. Results and discussion

3.1. RSM model quality

According to R^2 values of the model responses (Table 2) all models explain the variance of final pH, apparent color, TOC, ζ-Potential, dissolved Al, and residual Al and Fe with high accuracy ($R^2 > 0.8$). Lower R^2 values were obtained for turbidity and residual Mn with Cell C. According to Q^2 values of the model responses, the predictive ability of the model made for Cell C is significantly lower than the predictive ability of the models made for Cells A + C and Cell A. This can be due to the mechanism of aluminum dissolving from the cathodes, which does not behave linearly at the initial stage of the electrocoagulation process.

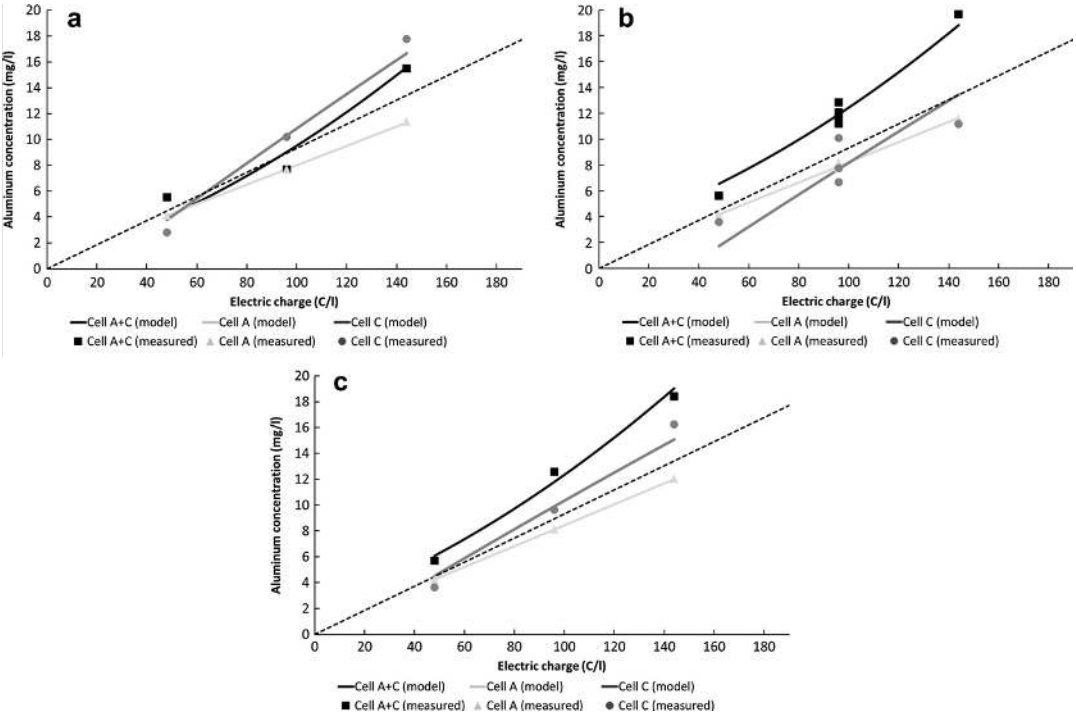

Fig. 1. Measured and predicted (statistical model) dissolving rates of the aluminum electrodes in different electrode constructions in (a) initial pH 3, (b) initial pH 4 and (c) initial pH 5.

3.2. Aluminum dissolved from the electrodes and metal residuals after treatment

Measured and predicted aluminum concentrations of the samples after EC treatment are shown in Fig. 1. The highest aluminum concentrations per electric charge were measured for Cells A + C when initial pH was 4 and 5. However, in initial pH 3 the highest dissolved aluminum concentrations with 96 C/l and 144 C/l were measured for Cell C. It is possible that at very low pH the chemical dissolution of aluminum from all electrode plates (Eq. (6)) occurs simultaneously with Eq. (1).

$$2\mathrm{Al(s)} + 6\mathrm{H}^+ \rightarrow 2\mathrm{Al}^{3+}\mathrm{(aq)} + 3\mathrm{H_2} \tag{6}$$

There were small variations in the initial delay before the electric current was switched on, but the fact that the electrodes were immersed in the solution or on the metal surface state could explain the difference measured between the aluminum concentrations obtained with Cells A + C and Cell C in pH 3. According to Sasson et al. iron electrodes are significantly corroded without electricity at pH < 8 [22]. In this study, aluminum electrodes were used and dissolution rate of electrodes in the solution without electricity was not measured. However, it is well known that aluminum corrodes when pH is either acidic or alkaline [23]. Aluminum is naturally passive because continuous protecting alumina (Al_2O_3) layer is formed on the surface. This layer protects aluminum efficiently at the pH range 4–8. In higher and lower pH environment, alumina layer dissolves at considerable rate. The corrosion behavior of aluminum depends also on the other parameters of solution, such as the concentration of anions. Sulphate anions are passivating agents and therefore reduce the production of metal cations [24]. Chlorides, on the other hand, induce the breakdown of the passive layer and therefore cause pitting corrosion [23,25]. It is known that passivation and formation of deposits on electrodes increases the voltage of electrocoagulation system when current density is kept constant and hence reduces the power efficiency [1]. However, this was not observed in these short batch studies.

The dissolving of Cell A follows theoretical values calculated according to Faraday's law of electrolysis (Eq. (7)).

$$m = \frac{ItM_w}{zF} \tag{7}$$

where I is the current density, t is the operation time (s), M_w is molecular weight of the substance, F is Faraday's constant (96485 C/mol), z is the number of electrons involved in the reaction (3 for Al^{3+}) and m is the mass of the aluminum dissolved.

When the initial pH was 3, aluminum concentrations dissolved from Cells A + C and Cell C were close to theoretical values (Fig. 1a). With the higher initial pH, theoretical values were different to measured values for Cells A + C and Cell C (Fig. 1b and c). Faraday's law only considers direct electrolysis reactions occurring at the electrodes, e.g. dissolving of aluminum from anodes. The dissolution reaction rate is nearly constant in all cases in the range of variables studied, except in pH 3 with Cells A + C. With initial pH 3 and 4, linear fits of Cell C and Cells A + C results cross the *X*-axis at 0–10 C/l range, whereas linear fits of Cell A cross the *X*-axis almost at the 0 C/l (origin). This indicates that there is a short lag period before aluminum dissolving at the cathodes initiates in low pH. Aluminum cathodes dissolve chemically due to local high pH environment at the electrode surface that is formed when hydroxyl-ions form according to Eq. (3). Hence in low pH environment at the initial stage, hydroxyl ions are consumed by acidic water close the electrode surface which may cause this lag period in acidic solution. It is interesting that the aluminum concentration obtained with Cells A + C is not the sum of concentrations of Cell A and Cell C. It is unclear what mechanism inhibits the dissolving reactions of Cells A + C.

Our results support the conclusion made by Mouedhen et al. [26]. According to their results, no secondary reactions such as oxygen evolution took place at the aluminum anodes. Our results verify that the proportion of side-reaction on the aluminum anodes is low or negligible. Moudhen et al. concluded that chemical dissolution of cathodes contributed significantly to the total amount of aluminum dissolved into solution. Solution pH increased during the treatment. However, in very low pH environment (initial pH 2) the alkalinity produced during by cathodic reaction was not sufficient to increase the pH of the solution. Solution pH 9 was stable during treatment. When the initial pH was very low (pH < 3), less aluminum was produced on the cathode surface. Current density also had a significant influence on the aluminum produced on the cathode surface. The highest current efficiencies were measured with the lowest current densities. Aluminum dissolved from the anode was practically equal to theoretical values and insensitive to current density (in the range tested).

Residual metals can cause problems, such as deposition and process chemical decomposition, in processes where water is consumed. Concentration of residual metals (Al, Fe and Mn) was high in EC treated samples when the final pH of water was low. These metals are highly soluble in acidic and alkaline pH. Neutral amorphous metal hydroxides, such as $Al(OH)_3$ and $Fe(OH)_3$ are poorly soluble species [27]. Minimum solubility for $Al(OH)_3$ and $Fe(OH)_3$ is in neutral to slightly alkaline pH region. In addition to monomeric hydrolysis products, also polynuclear species, e.g. Al_{13} $[AlO_4Al_{12}(OH)_{24}^{7+}]$ are formed in water. The formation of the hydrolysis products of Al(III) and Fe(III) are gone through in detail in [27]. Insoluble hydroxides can be removed by sedimentation or filtration. The residual manganese concentration was low in

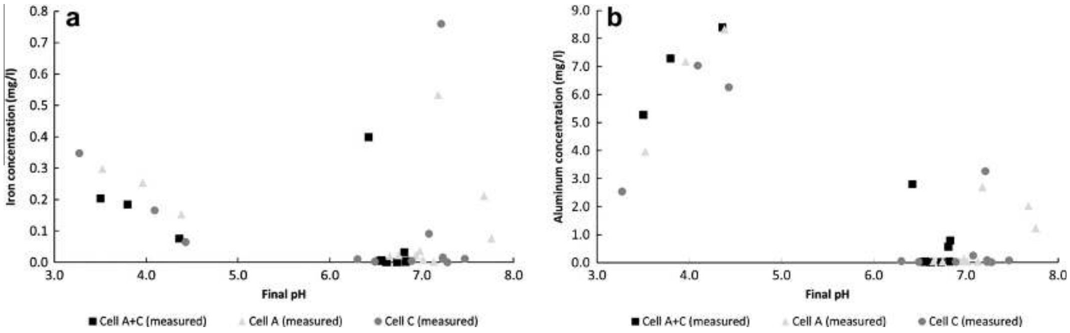

Fig. 2. Measured concentration of residual metals (a) iron and (b) aluminum in the samples after electrocoagulation.

untreated water and was still reduced due to treatment. The lowest manganese concentrations were measured from samples treated with Cells A + C. The lowest residual aluminum and iron concentrations were measured from samples that had high final pH and were treated longer (Fig. 2). High pH and aluminum concentration promote the formation of larger flocs in water, as was visually observed, and therefore more metals were removed from the solution.

According to our results optimum organic matter removal can be obtained simultaneously with minimum residual metal concentrations when acidified surface water is treated with electrocoagulation. This could be a significant benefit of electrocoagulation in surface water treatment compared to chemical coagulation. According to Chow et al. minimum residual aluminum concentration following alum treatment was obtained between pH 6 and 7 whereas optimum DOC removal was obtained at pH 5 [28]. They concluded that optimum DOC removal and minimum residual aluminum concentration cannot be obtained in same pH when alum is used. In electrocoagulation treatment initial pH can be acidic and in these conditions optimum DOC removal occurs. Neutral final pH, on the other hand, is optimum for metal removal because they form insoluble precipitates in these conditions.

3.3. Organic matter removal during treatment

Apparent color and TOC was measured from the samples after the treatment. Color was removed from the water with high efficiency, and the lowest measured color value, 5.4 mg/l PtCo, was obtained with Cell C. According to the results and model, color removal was slightly higher with Cell C than Cell A or Cells A + C. However, all cell constructions were able to remove more than 90% of the color with optimum parameters. Jiang et al. achieved comparable efficiency in their article [8]. According to WHO guidelines for drinking water, drinking water should ideally have no visible color [29]. Levels of color below 15 as true color units (TCO) are acceptable to consumers. However, WHO does not give health-based guideline for color in drinking water.

TOC removal with different cell constructions can be compared when TOC concentration of the samples is presented as a function of aluminum concentration dissolved from the electrodes (Fig. 3). With pH 3, there was no significant effect if the aluminum originated from either the anodes or the cathodes. TOC concentration depended linearly on the aluminum concentration added to the solution. In low pH (typically at pH < 6), the mechanisms of NOM removal are mainly charge neutralization and compression of double layer because hydroxides are not stable in this environment [3,30]. It is interesting that TOC removal did not show any stabilization at low concentrations, and it is possible that even lower TOC concentrations could be achieved with longer treatment times. Models show some errors for this pH, especially with Cell C, which predicts stabilization of TOC concentration at approximately 6 mg/l.

Also, with pH 4 electrode construction did not have a significant effect on the TOC removal per aluminum added. With pH 4, TOC removal was not linear as a function of aluminum, but rather asymptotic, and TOC removal stabilized at approximately 4 mg/l concentration with the cell constructions tested. It seems that aluminum concentrations higher than 8 mg/l were not effective. Final pH was near neutral, and therefore metal hydroxides are the predominant form of aluminum in the solution. Hydroxides form flocs, and sweep coagulation and bridging are the predominant mechanisms of the NOM removal. In adsorption, mechanism charged

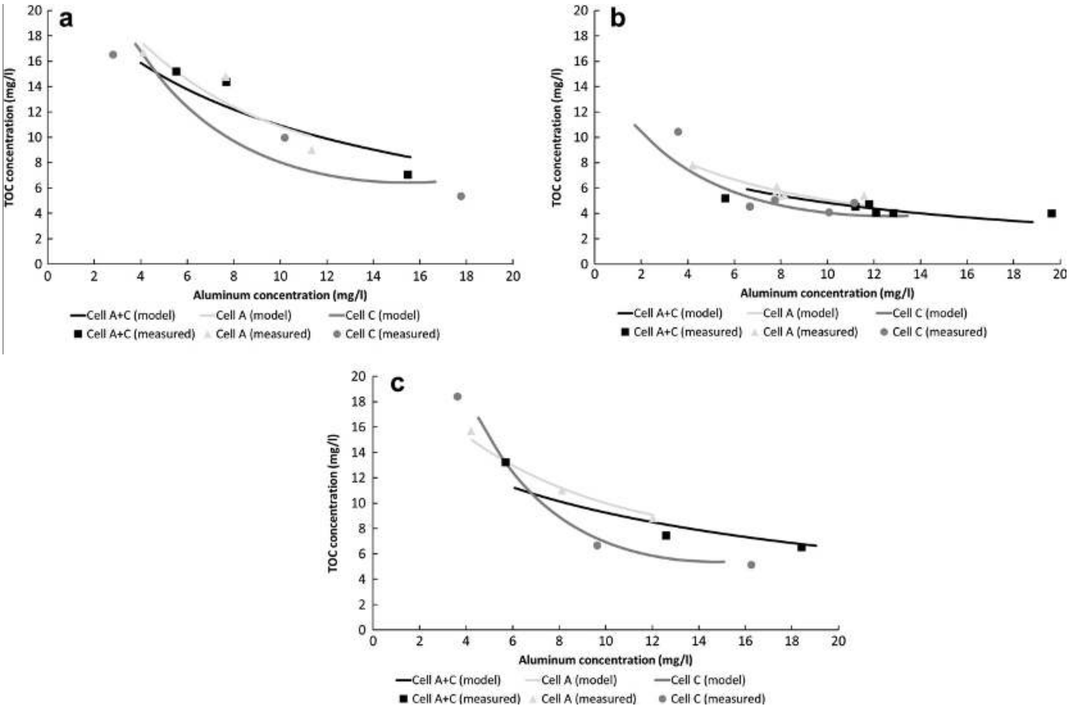

Fig. 3. Measured and predicted (statistical model) TOC concentrations of electrocoagulation treated samples as a function of aluminum concentration dissolved from the electrodes in (a) initial pH 3, (b) initial pH 4, and (c) initial pH 5.

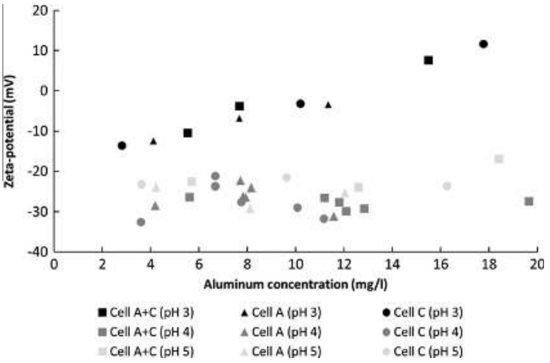

Fig. 4. Measured ζ-Potentials of the samples after electrocoagulation and filtration.

coagulant species are adsorbed onto the particle surface and the effective surface charge is reduced. Bridging mechanism occurs when polynuclear metal hydroxides form bridges between particles, and thus promote the destabilization of NOM. It is likely that residual TOC (4 mg/l) is composed mainly of hydrophilic substances, such as fulvic acids, which are not easily removed in neutral pH [30].

With pH 5, there was more variation in the results of the different cells. Slightly better TOC removal per aluminum added was measured from the samples that were treated with Cell C. However, the efficiency of EC treatment was lower with this pH in all cell constructions when compared to pH 4, and more aluminum was required for the same TOC removal. It also seems that the TOC level stabilizes to a slightly higher TOC level (5 mg/l) than with pH 4 (4 mg/l). It possible that the mechanism of NOM removal changed even further from charge neutralization and double layer compression to adsorption and bridging mechanisms, which were unable to remove hydrophilic colloids from the water.

ζ-Potential of the filtered samples was measured (Fig. 4). These results support the previously mentioned findings. With pH 3, the aluminum has a higher charge (Al^{3+}) due to lack of hydrolysis. This affects NOM destabilization through double layer repression. ζ-Potential in initial pH 3 increased linearly with increasing aluminum concentration. With this pH, small precipitates are formed that are not easily removed with sedimentation, flotation, or filtration. According to ζ-Potential results, it seems that with this pH no specific NOM fraction was enriched to filtered samples. When aluminum concentration was over 12 mg/l ζ-Potential was over 0 mV, which may cause restabilization of colloids. ζ-Potentials of the samples with initial pH 4 and 5 were similar after filtration. In these pH's aluminum exists predominantly as hydroxides and easily settleable or filterable flocs are formed. It seems that highly charged, and probably hydrophilic, NOM fraction was enriched into the samples during the treatment. According to ζ-Potential results, the same NOM fractions were removed whether aluminum was dissolved from the anodes or the cathodes. However, this should be verified with research where composition of the remaining NOM fraction is studied.

Three additional tests were done with optimum parameters of Cell C (Table 4). The initial pH in these tests was 4.1 and the electric charge per volume was 115 C/l. Results were similar to results at the center point of the mode, which was expected because the factor values were close to each other. The model predicts a TOC value of 4.04 mg/l, which is slightly lower than the measured value. The predicted final pH was 7.1, which is slightly higher than the measured value. The predicted aluminum concentration dissolved from the electrodes was 9.97 mg/l, whereas the measured aluminum concentration was 7.90–9.52 mg/l. Turbidity, color, and residual metal concentrations were close to predicted values. According to the results of these verification tests, the model predicts water quality parameters with high accuracy.

4. Conclusions

This study analyzed the effect of electrocoagulation cell construction on NOM removal. Three types of cells were studied: one that only had aluminum electrodes, one that had aluminum anodes and inert cathodes, and one that had inert anodes and aluminum cathodes. Besides the TOC concentration of the water, the other main parameters measured were final pH, turbidity, color, and concentration of residual metals of the water produced. A model was made from the results of each cell construction using PLS regression. The model quality was high for the most of the responses. The following conclusions can be made from the results:

- Aluminum dissolved from the Cells A + Chat was constructed from aluminum anodes and inert cathodes followed theoretical values calculated according to Faraday's law.
- Aluminum dissolved from the cathodes did not follow electric charge per volume linearly. Low initial pH (pH 3) decreased the dissolving reaction rate, probably because the hydroxyl ions produced were consumed by the acidic water.
- Low residual metals concentrations (Al, Fe, Mn) were measured from the samples when the final pH was high and treatment time was long and hence aluminum concentration was high.
- The efficiency of aluminum in TOC removal was similar in all cell constructions in the pH range tested. According to these results, the efficiency of electrocoagulation cannot be enhanced significantly by using either aluminum anodes or cathodes or both. High TOC removal was measured with all constructions tested.
- When the initial pH was 3, the TOC concentration of the treated samples depended linearly on aluminum added to the solution. In pH 4 and 5, the TOC removal per added aluminum followed asymptotic regression. This is probably due to the transition of the destabilization mechanism of colloids from double layer compression to adsorption and bridging. This conclusion was supported by the ζ-Potential results.

The results of this research indicate that reactions between NOM and aluminum occur in the bulk water and not on the electrode surface. It seems that destabilization mechanisms of NOM are similar compared to chemical coagulation. According to our results, optimum organic matter can be obtained simultaneously

Table 4
Measured water quality parameters of the samples from the additional repeating tests. Initial pH was 4.1 and electric charge per volume was 115 C/l.

Responses							
Final pH	Turbidity (NTU)	Apparent color (mg/l PtCo)	TOC (mg/l)	Dissolved Al (mg/l)	Residual Al (mg/l)	Residual Fe (mg/l)	Residual Mn (mg/l)
5.95	0.92	6.1	4.61	7.904	0.0518	0.0018	0.0187
6.39	1.22	7.3	4.48	9.520	0.0235	0.0024	0.0210
6.29	1.09	6.6	4.29	8.357	0.0184	0.0015	0.0228

with minimum residual metal concentrations when surface water is treated with electrocoagulation. The potential applications of water after the treatment could be potable water or industrial fresh water.

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References

[1] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.
[2] M.M. Emamjomeh, M. Sivakumar, Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes, J. Environ. Manage. 90 (2009) 1663–1679.
[3] H. Liu, X. Zhao, J. Qu, Electrocoagulation in Water Treatment, in: C. Comninellis, G. Chen (Eds.), Electrochemistry for the Environment, Springer, New York, 2010, pp. 245–262.
[4] M.S.K.A. Sarkar, G.M. Evans, S.W. Donne, Bubble size measurement in electroflotation, Miner. Eng. 23 (2010) 1058–1065.
[5] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC) – science and applications, J. Hazard. Mater. 84 (2001) 29–41.
[6] G. Chen, Y. Hung, Electrochemical Wastewater Treatment Processes, in: L.K. Wang, Y. Hung, N.K. Shammas (Eds.), Advanced Physicochemical Treatment Technologies, Humana Press, 2007, pp. 57–106.
[7] M.H. El-Masry, O.M. Sadek, W.K. Mekhemer, Purification of raw surface water using electro-coagulation method, Water, Air, Soil, Pollut. 158 (2004) 373–385.
[8] J. Jiang, N. Graham, C. André, G.H. Kelsall, N. Brandon, Laboratory study of electro-coagulation–flotation for water treatment, Water Res. 36 (2002) 4064–4078.
[9] A.S. Koparal, Y.Ş. Yildiz, B. Keskinler, N. Demircioğlu, Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation, Sep. Purif. Technol. 59 (2008) 175–182.
[10] C. Ricordel, A. Darchen, D. Hadjiev, Electrocoagulation–electroflotation as a surface water treatment for industrial uses, Sep. Purif. Technol. 74 (2010) 342–347.
[11] M. Vepsäläinen, M. Ghiasvand, J. Selin, J. Pienimaa, E. Repo, M. Pulliainen, M. Sillanpää, Investigations of the effects of temperature and initial sample pH on natural organic matter (NOM) removal with electrocoagulation using response surface method (RSM), Sep. Purif. Technol. 69 (2009) 255–261.
[12] M. Vepsäläinen, J. Selin, M. Pulliainen, M. Sillanpää, Combined electrocoagulation and chemical coagulation of paper mill mechanically cleaned water, J. Pulp Pap. Sci. 33 (2007) 233–239.
[13] E.A. Vik, D.A. Carlson, A.S. Eikum, E.T. Gjessing, Electrocoagulation of potable water, Water Res. 18 (1984) 1355–1360.
[14] Y.S. Yildiz, A.S. Koparal, B. Keskinler, Effect of initial pH and supporting electrolyte on the treatment of water containing high concentration of humic substances by electrocoagulation, Chem. Eng. J. 138 (2008) 63–72.
[15] Y.S. Yildiz, A.S. Koparal, S. Irdemez, B. Keskinler, Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes, J. Hazard. Mater. 139 (2007) 373–380.
[16] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: a review, Adv. Colloid Interface Sci. 159 (2010) 189–197.
[17] M. Vepsäläinen, H. Kivisaari, M. Pulliainen, A. Oikari, M. Sillanpää, Removal of toxic pollutants from pulp mill effluents by electrocoagulation, Sep. Purif. Technol. 81 (2011) 141–150.
[18] M. Tir, N. Moulai-Mostefa, Optimization of oil removal from oily wastewater by electrocoagulation using response surface method, J. Hazard. Mater. 158 (2008) 107–115.
[19] A. Aleboyeh, N. Daneshvar, M.B. Kasiri, Optimization of C.I. Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology, Chem. Eng. Process. 47 (2007) 827–832.
[20] M.S. Bhatti, A.S. Reddy, A.K. Thukral, Electrocoagulation removal of Cr(VI) from simulated wastewater using response surface methodology, J. Hazard. Mater. 172 (2009) 839–846.
[21] T. Ölmez, The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology, J. Hazard. Mater. 162 (2008) 1371–1378.
[22] M.B. Sasson, W. Calmano, A. Adin, Iron-oxidation processes in an electroflocculation (electrocoagulation) cell, J. Hazard. Mater. 171 (2009) 704–709.
[23] C. Vargel, Corrosion of Aluminium, Elsevier Ltd., The Netherlands, 2004.
[24] A. Kolics, J.C. Polkinghorne, A. Wieckowski, Adsorption of sulfate and chloride ions on aluminum, Electrochim. Acta 43 (1998) 2605–2618.
[25] J.L. Trompette, H. Vergnes, On the crucial influence of some supporting electrolytes during electrocoagulation in the presence of aluminum electrodes, J. Hazard. Mater. 163 (2009) 1282–1288.
[26] G. Mouedhen, M. Feki, M.D.P. Wery, H.F. Ayedi, Behavior of aluminum electrodes in electrocoagulation process, J. Hazard. Mater. 150 (2008) 124–135.
[27] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100–102 (2003) 475–502.
[28] C.W.K. Chow, J.A. van Leeuwen, R. Fabris, M. Drikas, Optimised coagulation using aluminium sulfate for the removal of dissolved organic carbon, Desalination 245 (2009) 120–134.
[29] Guidelines for Drinking-Water Quality, fourth ed., World Health Organization, Malta, 2011.
[30] J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, second ed., IWA Publishing, London, 2006.

PUBLICATION III

Investigations of the effects of temperature and initial sample pH on natural organic matter (NOM) removal with electrocoagulation using response surface method (RSM)

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Investigations of the effects of temperature and initial sample pH on natural organic matter (NOM) removal with electrocoagulation using response surface method (RSM)

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ABSTRACT

The removal of natural organic matter (NOM) from surface water by electrocoagulation (EC) was studied using response surface method (RSM). Factors used in the empirical model were electric charge per liter, initial pH and temperature. Relevant square and interaction terms of factors were studied. Based on analysis of variance (ANOVA), the model fitted well with dissolved organic carbon (DOC) reduction, aluminum dissolving and pH changes. UV 254 nm absorbance removal was moderately predicted. According to results, temperature affected significantly the dissolving rate of aluminum electrodes. Initial DOC concentration of the surface water was 18.35 mg/l. Maximum DOC removal of 80.4% was obtained when high electric charge per liter (144 C/l), low pH (4.3) and high temperature (295.15 K) were used. However, high DOC removal of 76.2% was predicted also when water temperature was only 275.15 K. Effect of temperature on NOM removal was minor as compared to the effects of electric charge per volume and the initial pH. EC neutralized pH during the EC treatment and had little impact on the conductivity of the water. According to the results, EC can be used for NOM removal during cold water period in Nordic countries.

1. Introduction

Surface water in Nordic region typically contains a high concentration of natural organic matter (NOM), which gives water its brown color. Efficient removal of NOM is required for drinking and industrial water applications. In the drinking water, high NOM concentration causes formation of disinfection by-products (DBP) that are carcinogenic. In the industrial applications, such as paper making process, NOM can cause fouling of the surfaces, resulting in the defects in the end-product quality [1].

Basically, NOM is a complex mixture of different organic materials such as bacteria, viruses, humic acids, fulvic acids, polysaccharides and proteins. Dissolved organic matter (DOM) is defined to be a part of the NOM that passes through 0.45 μm pore size membrane. Normal coagulation process in combination with flotation or sedimentation can easily remove the high molecular weight fraction but it has limited effect on small molecular weight fraction [2,3]. Hydrophopic NOM has a higher charge density than hydrophilic NOM and is therefore more easily removed during coagulation treatment [4]. Humic acid fraction (HAF) of NOM has a higher amount of aromatic structures and therefore, is more hydrophobic than fulvic acid fraction (FAF) [5,6]. Typically water containing high DOM concentration is commonly treated with enhanced coagulation where a high dose of coagulant is used together with acidic pH [7].

In electrocoagulation (EC), coagulant is added from electrodes and concurrently beneficial side-reactions, such as pH change and hydrogen bubble formation, take place. Near electrode surface pH differs from the solution pH. Aluminum ions formed during the corrosion of the aluminum at the anode [Eq. (1)] go through hydrolysis reactions [Eq. (2)] and pH at the vicinity of the anode surface decreases.

$$\mathrm{Al(s)} \rightarrow \mathrm{Al^{3+}(aq)} + 3\mathrm{e^-} \tag{1}$$

$$\mathrm{Al^{3+}(aq)} + n\mathrm{H_2O} \leftrightarrow \mathrm{Al(OH)}_n{}^{3-n} + n\mathrm{H^+(aq)} \tag{2}$$

At the cathode, surface pH increases due to hydrogen evolution [Eq. (3)]. The increment of the pH at the cathode surface leads to the

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Table 1
Initial water quality.

DOC (mg/l)	UV 254 nm	Al (mg/l)	pH	ζ-potential (mV)	SUVA (l/(m mg))	Turbidity (NTU)	Conductivity (mS/m)
18.35	0.644	0.257	5.8	−17.1	3.51	0.51	2.8

corrosion of the aluminum [Eq. (4)], thus facilitating the formation of aluminate, $Al(OH)_4^-$ [Eq. (5)].

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad (3)$$

$$2Al(s) + 6H_2O + 2OH^-(aq) \rightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g) \quad (4)$$

$$Al(OH)_3(s) + OH^-(aq) \leftrightarrow Al(OH)_4{}^-(aq) \quad (5)$$

Faraday's law calculations take consideration only reactions at the anode surface. According to literature, there is no significant difference in anodic dissolving reaction and theoretical dissolving speeds calculated using the Faraday's law when current density is in the range of 0–4 A/dm^2 [8]. Dissolving of the aluminum at the cathode is chemical dissolution facilitated by the pH change at the electrode surface and current efficiency for this reaction is affected by the current density. When aluminum cathodes having low current density are used in the EC process, a high current efficiency is achieved. Solution pH has small effect on dissolving rate when pH is near neutral region [9]. Highly alkaline solution pH increases chemical dissolving.

Hydrophilic humic fraction is not easily removed by coagulation. Therefore it needs different coagulation conditions as compared to hydrophobic fraction [7]. In chemical coagulation with metal coagulants destabilization of NOM can occur either by enmeshment mechanism or by the formation of insoluble complexes and precipitation reactions. In an acidic pH range, precipitation and charge neutralization are favored and the removal of hydrophilic colloids takes place. At neutral pH, hydrophobic NOM is mostly removed by adsorption to metal hydroxides and bridging mechanism. During EC treatment, pH changes in course of time, affecting to the mechanism of NOM destabilization. When treatment is carried out at low initial pH, hydrophilic NOM could be removed. At the end of the treatment, when pH is neutralized, adsorption and bridging of hydrophobic NOM takes occurs. According to literature, to acquire simultaneously good microfloc and macrofloc formation during water treatment, pH control is an important factor [10]. The effect of initial pH on NOM removal in EC has been studied in the range of 5–9.6 [11]. At low humic substance concentration, pH did not have significant effect on EC efficiency on studied range. However, the effect of initial pH was not studied at lower than pH 5.

Temperature also affects the activity of coagulation treatment. Normally optimum operating pH increases when pH decreases [7]. Temperature affects especially in low-turbidity water when aluminum sulfate is used as a coagulant chemical. To date, the effect of temperature on EC efficiency is not widely studied [12]. The increment of the solution temperature has positive effect on EC efficiency on azo dye and boron removal to certain extent [13,14]. However, so far there is no information about the effect of the solution temperature on NOM removal from surface waters during EC treatment. This factor is important if EC is employed for NOM removal in Nordic water during winter season.

Response surface method (RSM) is a statistical method that is used to study the relationship of the factors and responses [15]. It can be employed to evaluate the relative significance of the factors. RSM has also been used to optimize the removal of oil and azo dye by electrocoagulation [16,17]. High coefficients of determination values were gained for regression models. According to results, RSM is suitable method to study and optimize pertinent parameters of EC treatment.

In this study, EC was employed for treating highly colored surface water. The effects of electric charge, initial pH and temperature on NOM removal were investigated. RSM was used as a tool to study the effect of factors and their interactions on responses.

2. Experimental

2.1. Electrochemical treatment

Water samples were collected from a Finnish paper mill surface water inlet flow and were stored in a cold room. The untreated samples had a high NOM concentration according to photometric and DOC measurements. Physicochemical properties of the samples before EC treatment are presented in Table 1. Normally mill uses chemical coagulation treatment to remove NOM from the surface water before using it in the following processes.

In this case, initial pH values were selected based on preliminary tests. Temperature adjustment during the tests was undertaken at 295.15 K using heating plate, at 285.15 K using water flow and at 275.15 K with ice bath. The temperatures were adjusted to values stated in test plan before treatment and maintained constant during EC treatment, flocculation, sedimentation and filtration. According to measurements, temperature was maintained within ±1 K range of set temperature during all stages.

In this study, EC cell was made from three aluminum anodes and three aluminum cathodes with dimensions of 7 cm in length and 5 cm in width. GW Instek PSM-6003 was used as a power source throughout the experiments. Experimental setup is shown in Fig. 1. Current used in this study was 0.100 A. Low current density of 0.48 mA/cm^2 was selected based on the preliminary studies [18]. Electrode plates were washed thoroughly with 4% HCl, tap water and MilliQ-water after treatments.

Samples were magnetically stirred during the EC treatment at the speed of 300 rpm. After the treatment, samples were stirred with overhead stirrer at the speed of 40 rpm for 10 min to facilitate flocculation. Settling time after flocculation was 30 min. Water samples were filtrated using Whatman 589/1 filter paper and then stored in the cold room before further analysis.

2.2. Chemical analysis

Metal concentrations were determined using iCAP 6000 series ICP-AES (Thermo Electron) from samples in which 0.2 ml of 37%

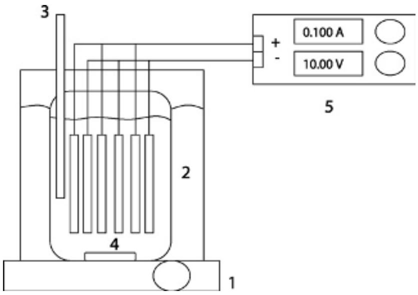

Fig. 1. Schematic diagram of the experimental setup: (1) magnetic stirrer; (2) water or ice bath; (3) temperature meter; (4) electrochemical cell; (5) DC power supply.

HNO_3 (analytical grade) was added to 10 ml of sample. DOC was measured using TOC analyzer (Shimadzu) after filtering the samples through 0.45 μm pore size membrane.

Apparent color was analyzed with DR 2800 photometer (Hach) and turbidity with Model 2100P ISO turbidimeter (Hach). Conductivity was determined using CON6 conductivity-meter (Ecoscan) and pH with Multiline P3 (WTW). Absorbance of the samples at 254 nm wavelength was measured with Lambda 45 UV/VIS-spectrophotometer (PerkinElmer), while the zeta-potential was determined using Zetasizer Nano ZS (Malvern).

2.3. Design of experiments and response surface method (RSM)

Multiple linear regression (MLR) was selected as regression method (Umetrics MODDE 8.0) in this study. Design of the experiments was done using full factorial design. Factors of the RSM model were electric charge added per volume, temperature and initial pH. Electric charge per volume controls the amount of electrochemical reactions taking place on the electrode surface. Initial pH was selected because pH has significant effect on coagulation efficiency and optimum coagulation pH may vary with temperature as stated in Section 1. Effect of temperature is important factor because water temperature changes significantly especially in the Nordic countries. Flocculation parameters were not included in the factors to keep the amount of samples in reasonable level. Range and levels of factors are presented in Table 2.

Responses included in the model were removal efficiency (R%) of DOC and UV 254 nm absorbance, total aluminum added, pH change during the EC treatment and zeta-potential of the filtered samples after treatment. Removal efficiencies were calculated according to Eq. (6).

$$\text{Removal efficiency (R\%)} = \left(\frac{C_0 - C_{EC}}{C_0}\right) \times 100 \qquad (6)$$

Table 2
Factor levels of full factorial design.

Variable	Factor range and levels		
	−1	0	1
X_1, Electric charge (C/l)	48	96	144
X_2, Initial pH	4	5	6
X_3, Temperature (K)	275.15	285.15	295.15

C_0 and C_{EC} are the initial and the final concentration before and after the EC treatment.

Current efficiency for aluminum dissolving was calculated according to Eq. (7).

$$\text{Current efficiency(CE\%)} = \frac{C_{EC}}{C_{FL}} \times 100 \qquad (7)$$

C_{EC} is the concentration of aluminum predicted by the RSM model, while C_{FL} is the concentration of aluminum added according to the Faraday's law. Accuracy of the RSM prediction of aluminum dissolving is presented in Section 3.

Q^2 was calculated using a predicted sum of the squares (PRESS) from the cross-validation and the total sum of the squares of Y corrected for the mean (SS) [Eq. (8)].

$$Q^2 = 1 - \frac{\text{PRESS}}{\text{SS}} \qquad (8)$$

R^2 was the amount of variance explained by the model and 'R^2 adjusted' was adjusted for the degrees of freedom. Model validity compared model error to pure error. If model validity was larger than 0.25, there was no significant lack of fit in the model. Reproducibility was calculated from the replications at the center points according to Eq. (9).

$$\text{Reproducibility} = 1 - \frac{\text{MS}_{\text{Pure error}}}{\text{MS}_{\text{Total corrected}}} \qquad (9)$$

Table 3
Factors and response values of full factorial design.

Factors			Responses					Not included in the model			
Electric charge	Initial pH	Temperature	DOC (R%)	UV 254 nm (R%)	Al (mg/l)	pH change	ζ-potential (mV)	SUVA (l/(m mg))	Turbidity (NTU)	Residual Al (mg/l)	Conductivity (mS/m)
−1	−1	1	76.0	89.2	8.1	1.64	−11.6	1.59	0.09	0.054	3.6
0	−1	1	76.3	89.0	19.7	2.40	−9.9	1.63	0.36	0.273	3.3
1	−1	1	79.0	91.3	40.1	2.52	6.1	1.45	0.19	0.455	3.5
−1	0	1	64.3	78.5	7.3	1.49	−16.4	2.12	0.27	0.239	3.6
0	0	1	71.0	84.9	20.9	1.88	−10.1	1.83	0.36	0.401	3.9
1	0	1	77.2	89.6	39.9	1.99	3.9	1.60	0.49	0.858	3.3
−1	1	1	28.7	6.0	6.2	−0.12	−20.9	4.63	3.96	5.184	5.2
0	1	1	65.2	81.9	20.3	0.02	−11.8	1.82	0.49	0.580	3.4
1	1	1	75.8	88.1	43.0	0.75	1.4	1.73	0.93	1.784	3.0
−1	−1	0	73.8	88.8	7.0	2.48	−12.1	1.50	0.34	0.053	3.4
0	−1	0	75.7	88.2	16.1	2.94	−12.6	1.71	0.94	0.398	3.1
1	−1	0	79.1	79.3	34.1	2.65	16.1	3.47	8.88	5.168	3.2
−1	0	0	69.7	87.0	8.1	1.36	−12.2	1.51	0.13	0.027	3.4
0	0	0	71.8	87.6	17.1	1.38	−14.0	1.55	0.15	0.062	3.0
1	0	0	77.5	90.2	29.5	2.26	−0.1	1.53	0.42	0.311	3.0
−1	1	0	57.0	69.0	7.5	0.22	−19.4	2.53	1.7	1.107	4.0
0	1	0	60.5	80.6	18.0	0.73	−18.1	1.73	0.39	0.266	3.0
1	1	0	71.9	86.4	39.9	0.04	−5.3	1.70	0.96	0.909	3.0
0	0	0	76.6	85.7	15.5	0.72	2.17	2.15	2.32	1.457	4.4
0	0	0	74.1	88.6	17.2	0.68	−17.7	1.55	0.56	0.230	3.3
0	0	0	69.6	85.8	17.1	0.66	−14.4	1.64	0.2	0.070	3.2
−1	−1	−1	73.4	88.1	6.9	1.82	−10.7	1.58	0.45	0.169	3.8
0	−1	−1	76.8	86.7	13.1	2.08	12.9	2.02	2.41	2.013	3.4
1	−1	−1	75.8	88.3	26.9	1.85	1.2	1.70	1.71	1.005	3.1
−1	0	−1	69.3	86.2	6.8	0.78	−12.9	1.58	0.14	0.060	3.2
0	0	−1	75.9	87.1	15.3	1.70	10.9	1.88	2.33	1.804	3.3
1	0	−1	68.8	85.4	23.5	0.94	−14.8	1.64	0.32	0.141	2.9
−1	1	−1	36.3	31.7	7.5	0.37	−21.2	3.77	2.56	4.023	3.6
0	1	−1	56.5	69.2	13.8	0.42	−14.3	2.48	1.73	1.962	3.0
1	1	−1	58.1	84.8	26.9	0.30	−14.2	1.28	0.15	0.132	3.3

Table 4
ANOVA of the model.

Variable	DOC	UV 245 nm	Al added	pH increase	ζ-potential
R^2	0.87	0.82	0.98	0.81	0.68
R^2 adjusted	0.82	0.76	0.98	0.75	0.58
Q^2	0.72	0.60	0.97	0.68	0.45
Regression (degrees of freedom = 7)					
Sum of squares	0.44	1.27	3673.93	18.60	2.27
Mean square	0.06	0.18	524.85	2.66	0.32
P-value	0.00	0.00	0.00	0.00	0.00
F-value	20.27	13.91	186.25	13.14	6.67
Lack of fit (degrees of freedom = 19)					
Sum of squares	0.06	0.28	60.02	4.08	0.83
Mean square	0.00	0.01	3.16	0.21	0.04
P-value of lack of fit	0.466	0.075	0.111	0.353	0.829
F-value of lack of fit	1.33	6.45	4.78	1.78	0.54
Pure error (degrees of freedom = 3)					
Sum of squares	0.01	0.01	1.98	0.36	0.24
Mean square	0.00	0.00	0.66	0.12	0.08

Table 5
Coefficients of the model terms.

Response	Unit	Constant	X_1	X_2	X_3	X_1^2	X_2^2	$X_1 \times X_2$	$X_1 \times X_3$
DOC[a]	R%	2.01E−02	−2.73E−02	2.76E−01	−6.35E−03	−9.07E−06	−5.02E−02	1.11 E−03	8.77E−05
UV 254 nm[a]	R%	8.40E−01	−4.62E−02	6.49E−01	−9.31E−03	−1.34E−05	−1.16E−01	3.60E−03	1.17E−04
Al added	mg/l	1.45E+02	−2.33E+00	−1.09E+01	−3.94E−01	1.45E−03	9.88E−01	1.66E−02	7.86E−03
pH increase		1.10E+01	−9.78E−02	−5.40E−01	−2.27E−02	8.27E−07	-3.64E−02	−7.99E−04	3.70E−04
ζ-potential[b]	mV	6.58E+00	−6.19E−02	1.61 E−01	−1.91 E−02	−1.11E−05	−5.78E−02	2.07E−03	2.07E−04

[a] Negative logarithmic transformation $-\log_{10}(100 - Y)$.

[b] Logarithmic transformation $\log_{10}(Y + 24)$.

$MS_{\text{Pure error}}$ is the mean square of the pure error, while $MS_{\text{Total corrected}}$ is the mean square of the total sum of the squares where the constants sum of the squares was subtracted.

3. Results and discussion

3.1. RSM model quality

All the results used in RSM model are presented in Table 3. Turbidity, residual aluminum and conductivity were measured but not included in the RSM model. Model terms were not able to explain the variance of these responses adequately. However, these responses are important for water quality and give valuable information when applications of EC and need for additional research are considered. Therefore they are gone through separately in Section 3.2. Specific UV absorbance (SUVA) values were calculated from DOC and UV 254 nm absorbance results. It can be seen from the results that efficient organic matter removal can be achieved with EC treatment.

According to the analysis of variance (ANOVA) in Table 4, the RSM model accurately predicted DOC reduction, aluminum dissolving and changes in pH. UV 254 nm absorbance was moderately predicted according to R^2, R^2 adjusted and Q^2. Zeta-potential had low R^2 and Q^2 values, due to the pure error of the measurements based on to the reproducibility values. Model validities were good for all the responses, suggesting that the lacks of fit of the responses were not significantly larger than that of the pure errors. According to the model quality values, RSM was suitable method to study the effects of electric charge per volume, temperature and initial pH on NOM removal during the EC treatment.

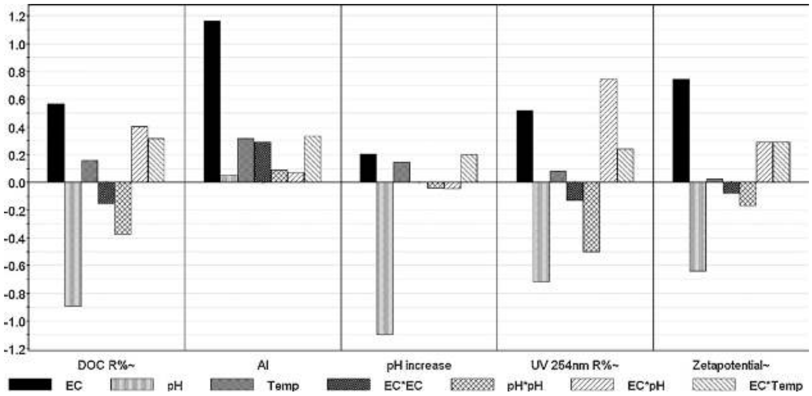

Fig. 2. Normalized coefficients of the model.

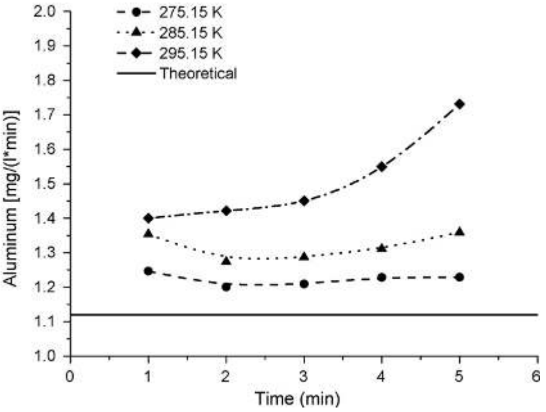

Fig. 3. Dissolving rate of the electrodes in different water temperatures. Theoretical values are calculated according to Faraday's law for anodic dissolving reaction.

Coefficients of the model terms are listed in Table 5 and normalized coefficients are presented in Fig. 2. The effects of the terms to responses could be easily seen from the normalized coefficients. Square terms of electric charge per liter and initial pH and interaction terms of electric charge per liter with initial pH and temperature were included in the model. Square terms or interaction terms that were not significant at 95% confidence level to any of the responses were not included in the model.

3.2. Reactions during the EC treatment

Dissolving speed at different temperatures was tested prior to the preparation of the model. Temperature had significant effect on the dissolving speed of the aluminum. In Fig. 3, theoretical rates of aluminum dissolving, calculated according to Faraday's law, and measured aluminum dissolving rates are plotted. Rate of the dissolving increased during the tests especially at 295.15 K.

Accuracy of the aluminum dissolving was high according to RSM model R^2 and Q^2 values (0.98 and 0.97 respectively). Rate of the aluminum dissolving exceeded theoretical values in the factors range as can be seen from Fig. 4. Over-Faradic current efficiency is attributed to the dissolving of the aluminum at the cathode surface due to hydroxyl ion generation [8,9,19].

According to RSM model, temperature, electric charge per liter, square term of electric charge per liter and interaction term of temperature and electric charge per liter were terms that affect on speed of the dissolving of the aluminum at 95% confidence level. It was reflected from the contours plot in Fig. 4 that at higher electric charge per liter treatments, temperature had significant effect on amount of aluminum that was dissolved to the samples. It is apparent that chemical dissolving reaction at the cathode surface was affected by water temperature. According to current efficiencies, dissolving reaction rate did not attained equilibrium during the batch experiments even at the highest temperature. Initial pH of the samples did not have significant effect on the dissolving speed of the electrodes at the studied range.

It is evident that initial pH affects on the change of pH during the EC treatment. All other RSM model terms are insignificant at 95% confidence level. Lower initial pH leads to higher pH increment during the EC treatment. Final pH of all of the samples after filtration ranged between 5.6 and 7.3. At this pH range, flocculation was efficient and flocs were easily removed by settling or flotation. This suggests that after EC treatment of the surface water no pH adjustment is required to facilitate flocculation.

When aluminum was produced at a low initial pH at the beginning of the EC treatment, NOM probably reacted through the formation of insoluble aluminum humate complexes and charge neutralization. Less hydroxyl ions were bound to aluminum when low initial pH was used according to results of pH change. When pH increased during the treatment and aluminum hydrolysed, removal mechanism of NOM changed from complex formation to adsorption and enmeshment. When high initial pH is used, aluminum hydrolysis increased as compared to low initial pH and the adsorption and enmeshment of NOM is prevalent mechanism during the whole treatment time.

Zeta-potential was measured from the filtered samples from which flocculated materials were removed during settling and filtration stages. According to RSM model, electric charge per volume and initial pH were primary terms that affected on zeta-potential of the NOM in the filtered samples. Results indicate that temperature affected on zeta-potential through the dissolving speed of the aluminum electrodes, as reflected by the coefficients of the zeta-potential and the contour plots in Fig. 5. The zeta-potential of the NOM in the filtered samples was higher when the initial pH of the water was acidic. Increased charge neutralization at samples indicates that the formation of aluminum humates and charge neutralization occurred, when EC treatment was initiated at acidic pH range. It seems that the final pH of the samples after the EC treatment did not have significant effect on the zeta-potential of the NOM in the samples. This might be related to small difference in final pH between the samples.

Water conductivity was not included in the model. Conductivities of the EC treated samples varied from 2.9 mS/m to 5.2 mS/m. Conductivity was affected by the residual aluminum and final pH. According to results, EC has little impact on water conductivity. This differs from inorganic coagulation chemicals, such as aluminum sulfate and iron(III) sulfate, that increase salt concentration of the

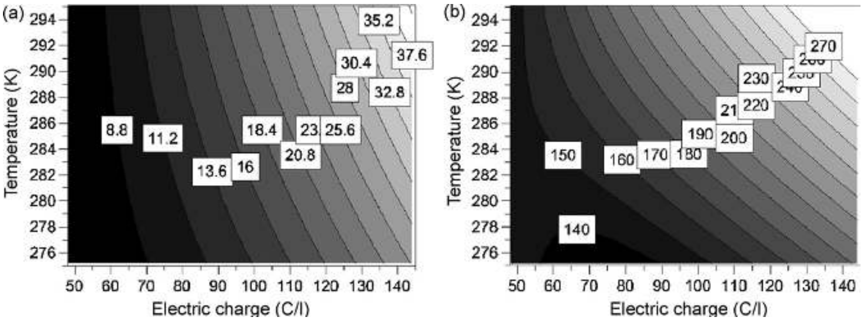

Fig. 4. Contour plots of (a) dissolved aluminum (mg/l) and (b) current efficiency (%) of aluminum dissolving at pH 5.

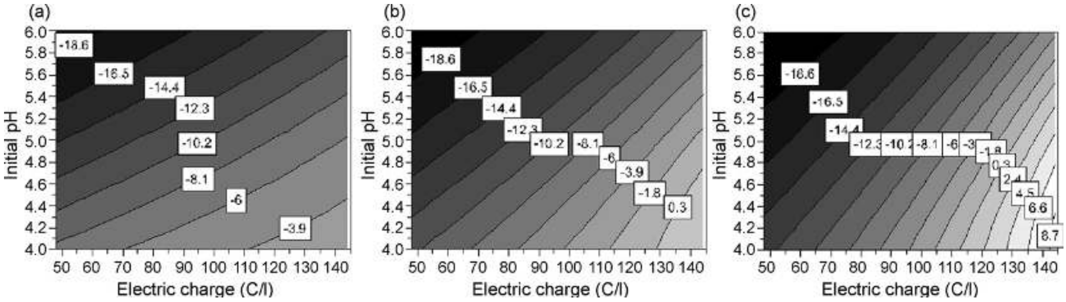

Fig. 5. Contour plots of ζ-potential at (a) 275.15 K, (b) 285.15 K and (c) 295.15 K.

water. This indicates that EC treatment could be suitable method for pretreatment of water before deionizing.

3.3. Removal efficiencies

Main RSM model terms affecting on the removal of DOC were electric charge per liter, initial pH, square term of initial pH and interaction terms of electric charge per liter with initial pH and temperature. Temperature and square term of electric charge per liter were not significant at the 95% confidence level. Temperature affected on DOC removal through the dissolving rate of the electrodes which is seen in the coefficient of interaction term of electric charge and temperature.

High DOC removal efficiencies were achieved in all temperatures. The lowest residual DOC concentration was attained when water temperature and electric charge per volume were high, while the initial pH was low as can be seen from Fig. 6. On the other hand, the removal efficiency per aluminum added was the highest when temperature was low. This might be attributed to formation of various hydrolysis products in different temperatures. However, the effect of the temperature in studied range was relatively low when compared to the effect of the electric charge per liter and initial pH on DOC removal.

Aluminum dissolved from the cathode surface was present in the form of aluminate ion, $Al(OH)_4^-$, which did not coagulate humic material unless it went through dehydrolysis to less hydrated aluminum species. Dehydrolysis occurred at the solution when aluminate moved from the high pH at the surface of the electrode to lower pH at the solution. Aluminum sulfate, PACl and sodium aluminate were compared in the coagulation pretreatment of ultrafiltration and it was found that aluminate did not gave good results at pH higher than 5 [20]. For this reason, aluminate formation at the cathode might have significant effects on the removal of organic matter depending on solution pH. Formation of aluminate could be controlled using non-dissolving materials on the cathode.

UV 254 nm removal had corresponding terms affecting the removal of DOC. Interaction term of electric charge and initial pH had stronger influences on UV 254 nm removal than on DOC removal according to RSM model coefficients. Maximum UV 254 nm removal was obtained at pH 5 at highest temperature (Fig. 7). To SUVA values, temperature did not have significant effect. Initial SUVA value of the samples was 3.5 and decreased to less than 1.5 after EC treatment. Model predicted that SUVA values were small when low pH and low electric charge or high pH and high electric charge were used. Results suggest that, using EC it is possible to reach low SUVA values, thus facilitating low DBP formation in disinfection [7].

Residual aluminum and turbidity after filtration were measured. Turbidity was affected by residual aluminum and high turbidities and residual aluminum values were measured from the same samples. Although residual aluminum concentration correlated to initial pH and electric charge, model terms could not predict the residual aluminum concentration in sufficient accuracy. Because bubbles form during EC treatment, normal flocculation may be inefficient and cause high turbidities and aluminum residuals in few samples. Flocs start to rise at the surface during the flocculation which shortens the time for adsorption and enmeshment.

Voltage in the experiments varied between 9 V and 21 V. Sample temperature had the greatest influence on the voltage. Voltage affected energy consumption and hence, the operational cost of the treatment. According to the RSM model, a maximum DOC removal of 80.4% in the factors ranges (Table 1) was predicted when electric charge of 144 C/l, initial pH of 4.3 and temperature of 295.15 K were used. A maximum UV 254 nm absorbance removal of 91.2% was predicted when same electric charge and temperature at initial pH of 5.0 were used. Energy consumption in 144 C/l treatment with 10 V was 0.4 kWh/m^3 and the corresponding aluminum consumption according to RSM model was 40 mg/l. However, such high concentration can lead to high operational cost. With more economical 10 mg/l concentration 76.2% DOC reduction and 89.2% UV 254 nm reduction were predicted.

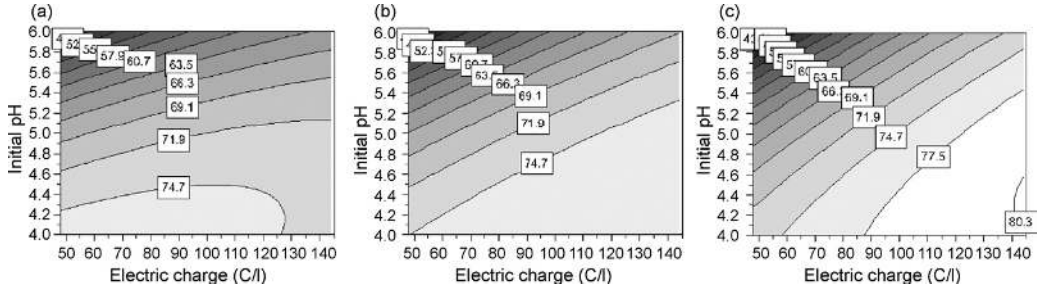

Fig. 6. Contour plots of DOC reduction at (a) 275.15 K, (b) 285.15 K and (c) 295.15 K.

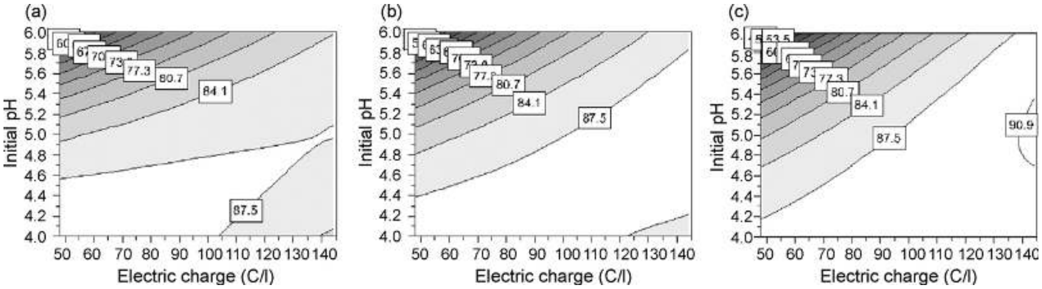

Fig. 7. Contour plots of UV 254 nm reduction at (a) 275.15 K, (b) 285.15 K and (c) 295.15 K.

4. Conclusions

In this study, the effects of temperature and initial sample pH on the NOM removal from surface water by EC process have been investigated using RSM. Aluminum added, DOC and UV 254 nm absorbance removal and pH change during electrochemical treatment well correlated with the predicted values of the RSM model.

- Dissolving speed of the aluminum electrodes increased when temperature of the samples increased. Reaction rate of the dissolving was not balanced during the batch experiments. With flow-through cell aluminum concentration could be controlled more easily and used as factor when making design of experiments.
- Change of the pH during EC treatment was mainly affected by the initial pH. Final pHs of the samples were in the range of 5.6–7.3.
- Electrocoagulation had little impact on the conductivity of the water. Conductivities of the samples varied from 2.9 mS/m to 5.2 mS/m.
- High NOM removal was obtained in EC treatment. Maximum NOM removal, according to DOC and UV 254 nm measurements, was achieved when low pH of 4.3, high temperature of 295.15 K and high electric charge of 144 C/l were applied. Energy consumption in maximum DOC and UV 254 nm absorbance removal in the factors range was 0.4 kWh/m^3 and aluminum consumption was 40 mg/l.
- Temperature had minor effect on the removal of NOM in studied range when compared to effect of electric charge per liter and initial pH. Temperature affected mainly through the different dissolving rate of the electrodes.

According to results, EC treatment can be used for efficient removal of NOM from surface waters also during the cold water period. According to results, EC could be suitable method for pretreatment of surface water before deionizing process. Lower salt concentration may also reduce corrosion in the water systems and have positive effects to following industrial processes.

In future studies, more information about the effects of different aluminum species formed during the EC treatment on the anode and the cathode surface is needed to optimize NOM removal. Simultaneous bubble formation during EC treatment may need further development of flocculation to have good floc formation and separation simultaneously.

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References

[1] P. Hynninen, Papermaking Science and Technology: Environmental Control, Fapet Oy, Helsinki, 1998, pp. 43–55.
[2] A. Matilainen, N. Lindqvist, S. Korhonen, T. Tuhkanen, Removal of NOM in the different stages of the water treatment process, Environ. Int. 28 (2002) 457–465.
[3] T.K. Nissinen, I.T. Miettinen, P.J. Martikainen, T. Vartiainen, Molecular size distribution of natural organic matter in raw and drinking waters, Chemosphere 45 (2001) 865–873.
[4] E.M. Sharp, S.A. Parsons, B. Jefferson, Seasonal variations in natural organic matter and its impact on coagulation in water treatment, Sci. Total Environ. 363 (2006) 183–194.
[5] M.J. Scott, M.N. Jones, C. Woof, B. Simon, E. Tipping, The molecular properties of humic substances isolated from a UK upland peat system: a temporal investigation, Environ. Int. 27 (2001) 449–462.
[6] E.L. Sharp, P. Jarvis, S.A. Parsons, B. Jefferson, Impact of fractional character on the coagulation of NOM, Colloids Surf. A 286 (2006) 104–111.
[7] J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, second ed., IWA Publishing, London, 2006.
[8] G. Mouedhen, M. Feki, M. De Petris Wery, H.F. Ayedi, Behavior of aluminium electrodes in electrocoagulation process, J. Hazard. Mater. 150 (2008) 124–135.
[9] P. Gañizares, M. Garmona, J. Lobato, F. Martínez, M.A. Rodrigo, Electrodissolution of aluminium electrodes in electrocoagulation processes, Ind. Eng. Chem. Res. 44 (2005) 4178–4185.
[10] J.E. Gregor, C.J. Nokes, E. Fenton, Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation, Water Res. 31 (12) (1997) 2949–2958.
[11] A.S. Koparal, Y. Ş Yildiz, B. Keskinler, N. Demircioğlu, Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation, Sep. Purif. Technol. 59 (2008) 175–182.
[12] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.
[13] N. Daneshvar, H. Ashassi Sorkhabi, M.B. Kasiri, Decolorization of dye solution containing Acid Red 14 by electrocoagulation with a comparative investigation of different electrode connections, J. Hazard. Mater. B112 (2004) 55–62.
[14] A.E. Yilmaz, R. Boncukcuoğlu, M.M. Kocakerim, M.T. Yilmaz, C. Paluluoğlu, Boron removal from geothermal waters by electrocoagulation, J. Hazard. Mater. 153 (2008) 146–151.
[15] R. Myers, D. Montgomery, Response Surface Methodology: Process and Product Optimization Using Designed Experiments, second ed., John Wiley & Sons Inc., NY, 2002.
[16] A. Aleboyeh, N. Daneshvar, M.B. Kasiri, Optimization of C.I. Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology, Chem. Eng. Process 47 (2008) 827–832.
[17] M. Tir, N. Moulai-Mostefa, Optimization of oil removal from oily wastewater by electrocoagulation using response surface method, J. Hazard. Mater. 158 (2008) 107–115.
[18] M. Vepsäläinen, J. Selin, M. Pulliainen, M. Sillanpää, Combined electrocoagulation and chemical coagulation of paper mill mechanically cleaned water, J. Pulp Pap. Sci. 33 (2007) 233–239.
[19] T. Picard, G. Cathalifaud-Feuillade, M. Mazet, C. Vandensteendam, Cathodic dissolution in the electrocoagulation process using aluminium electrodes, J. Environ. Monit. 2 (2000) 77–80.
[20] M. Kabsch-Korbutowicz, Effect of Al coagulant type on natural organic matter removal efficiency in coagulation/ultrafiltration process, Desalination 185 (2005) 327–333.

PUBLICATION IV

Precipitation of dissolved sulphide in pulp and paper mill wastewater by electrocoagulation

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Precipitation of dissolved sulphide in pulp and paper mill wastewater by electrocoagulation

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The precipitation of dissolved sulphide ions by electrocoagulation was studied at laboratory scale using pulp and paper mill wastewaters. Concentrations of dissolved organic carbon and phosphorus were analysed before and after the electrocoagulation process to examine the suitability of the process for treatment of sulphide odour from pulp and paper mill wastewater. The electrochemical cell used in this study was constructed from monopolar dissolving iron electrodes. The dissolved iron concentration was directly proportional to the applied electric charge (C/L) at the tested current densities. Electrochemically produced ferrous iron (Fe^{2+}) precipitated dissolved sulphide ions efficiently. Electricity consumption of the treatment was 4–8 C/mg S^{2-} while iron consumption was 1.1–2.2 mg/mg S^{2-} during the initial phase of the sulphide precipitation when the applied electric charge was 10–60 C/L. When 60 C/L was applied, 88% of dissolved sulphides and 40% of phosphorus was precipitated. The reduction in DOC was low during the sulphide precipitation. According to these results, electrocoagulation can precipitate dissolved sulphides effectively and thereby reduce sulphide odours of pulp and paper mill wastewaters.

Keywords: electrocoagulation; sulphide precipitation; odour treatment; pulp and paper mill wastewater; iron dissolution

1. Introduction

Disturbing odours originating from pulp and paper mills have received increasing public attention during recent years. Pulp and paper mill effluents usually contain high concentrations of sulphurous compounds that can change into malodorous reduced sulphur molecules in a low oxygen environment. The most commonly found malodorous sulphurous substance is hydrogen sulphide, which forms in the long pipelines and pipeline facilities. It can be formed within biofilms, where sulphates (present in the wastewater) can be converted to sulphides as a result of the metabolic activity of anaerobic sulphate-reducing bacteria (SRB) [1]. Odours, and especially hydrogen sulphide, are regulated by laws in many countries, such as the US, the UK, Germany and Japan [2].

Hydrogen sulphide (H_2S) has an odour threshold of 0.5 μg/L. Air above wastewater treatment lagoons can contain 100 or even 1000 times this threshold concentration, resulting in odour problems in the vicinity of wastewater treatment facilities [3]. Besides common odour problems, H_2S also has adverse effects on human health. It penetrates biological membranes, and several cases of poisoning of industrial workers have been reported [4]. Hydrogen sulphide concentrations in the range of 250–500 mg/L can cause pulmonary oedema, and concentrations over 500 mg/L cause unconsciousness, respiratory paralysis and even death. Hydrogen sulphide also accelerates corrosion of concrete and iron [5,8]. In the moist sewer atmosphere, a thin water layer containing a high concentration of hydrogen sulphide forms on the surfaces of the gas space. Sulphur-oxidizing bacteria can oxidize sulphides to sulphuric acid in the anaerobic regions of the biofilms covering submerged and wet sewer walls [9]. The surface pH of the concrete can decrease to below 2.0 after one month of exposure to high hydrogen sulphide concentrations.

Several chemical and biological technologies have been proposed for hydrogen sulphide emission control, such as catalytic oxidation, adsorption and biological oxidation diffusion into activated sludge [10–12]. Commonly used chemical oxidants, such as hydrogen

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peroxide, chlorine, hypochlorite and potassium permanganate, oxidize sulphides, thereby decreasing the amount of malodorous sulphides present in wastewater [10,11]. Biological oxidation of sulphides through the addition of nitrate and nitrite is also a technique that can be used to control sulphide odours. The formation of H_2S is also controlled by increasing the pH, which leads to a smaller proportion of volatile sulphides (Equation (1)).

$$H_2S_{(g)} \leftrightarrow H^+ + HS^-_{(aq)} \quad (pK_a = 7.04) \qquad (1)$$

$$HS^-_{(aq)} \leftrightarrow H^+ + S^{2-}_{(aq)} \quad (pK_a = 11.96) \qquad (2)$$

Electrochemical processes can oxidize sulphides to other sulphurous compounds, such as elemental sulphur or sulphates. However, electrochemical oxidation of sulphides may require a high electric charge per volume, which can make this process uneconomical for large-scale use [13]. Dutta *et al.* recovered sulphides from the effluent from anaerobic paper mill treatment, using an electrochemical process [14]. The sulphide removed was recovered as pure, concentrated alkaline sulphide/polysulphide solution, from which elemental sulphur can be obtained.

Precipitation of dissolved sulphides is normally performed using iron salts, such as ferric chloride or ferrous sulphate. Iron salts can be added prior to sulphide formation or to wastewater already containing sulphides. A higher concentration of iron salt is required if dosing is conducted before sulphide formation, because iron hydroxides and carbonates are formed, and iron cations only partially react with dissolved sulphide ions [15]. Sulphides form black ferrous sulphide (FeS) according to Equation (3) in the presence of Fe^{2+}. Fe^{3+} can remove sulphides by chemically oxidizing them to elemental sulphur (Equation (4)), while the Fe^{2+} formed during the reaction can subsequently produce FeS (Equation (3)). According to Firer *et al.*, the stoichiometry of the reaction with Fe^{2+} is approximately 1.3 mole of Fe^{2+} per 1 mole of S^{2-} removed, and with Fe^{3+}, 0.9 mole is required per 1 mole of S^{2-} removed [16]. According to the results of Zhang *et al.* [17] the addition of Fe^{3+} also inhibits SRB activity of anaerobic sewer biofilms, which is beneficial if ferric salt is dosed upstream of sewers.

$$Fe^{2+}_{(aq)} + HS^-_{(aq)} \rightarrow FeS_{(s)} + H^+ \qquad (3)$$

$$2Fe^{3+}_{(aq)} + HS^-_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + S^0_s + H^+ \qquad (4)$$

Common issues that arise when iron chemicals are used include the corrosion of equipment and a localized decrease in the pH at the feeding point, which can release hydrogen sulphide into the sewer atmosphere. Because of the corrosive nature of the chemicals, special materials, such as titanium, are used in the tanks and piping, increasing capital costs of equipment [10,18].

Electrocoagulation (EC) is an evolving technology that has been effectively applied in the treatment of industrial wastewater containing various pollutants, such as textile wastewaters, chemical mechanical polishing wastewaters and olive mill wastewaters [19–21]. Anodes can be made of iron or aluminium, whereas cathodes can also be made of other materials, such as titanium or graphite, depending upon the wastewater to be treated and the contaminants to be removed [22,23]. Coagulants dissolved from the anodes during the electrochemical process cause destabilization of the pollutants. Iron anodes can produce ferrous or ferric ions according to Equation (5). Ferrous and ferric hydroxides are produced according to Equation (6), where m depends on the pH, and the value of m ranges from 0–2 for ferrous and 0–3 for ferric ions in the pulp and paper mill wastewater pH range [24]. Hydrogen formation on the cathode (Equation (7)) is usually the main reduction reaction occurring on the iron electrodes during EC treatment [23]. $Fe^{2+}$is oxidized to Fe^{3+}, according to Equation (8), in the presence of dissolved oxygen and neutral or high pH (above 7.0).

$$Fe_{(s)} \rightarrow Fe^{n+}_{(aq)} + ne^- \qquad (5)$$

$$Fe^{n+}_{(aq)} + mOH^- \leftrightarrow Fe(OH)^{(n-m)+}_m \qquad (6)$$

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \qquad (7)$$

$$4Fe^{2+}_{(aq)} + 10H_2O + O_{2(aq)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+ \qquad (8)$$

Hydrogen evolution can induce flotation of particles [23]. This electroflotation technology can be used for efficient separation of precipitated, coagulated or flocculated material. Utilization of electroflotation technology for the treatment of chemically coagulated paper mill wastewater has been studied by Mansour *et al.* [25].

Murugananthan *et al.* [26,27] and Feng *et al.* [28] have studied sulphurous ion removal from tannery wastewater by electrocoagulation. According to results of Murugananthan *et al.*, sulphide ions were precipitated as metal sulphides during the treatment, whereas sulphites and sulphates were enmeshed in the metal hydroxides [26,27]. Sulphides such as pyrite, marcasite, makhinawite, greigite as well as elemental sulphur were detected in the samples. According to Feng et al. [28], sulphide removal was significantly higher with iron electrodes than with aluminium electrodes. When aluminium electrodes were used, Al_2S_3 was produced, which is unstable in the solution and is converted to $Al(OH)_3$.Studies made with tannery wastewaters indicate that electrocoagulation can be used to precipitate sulphides present in wastewaters. However, sulphide removal as a function of iron consumption has not been studied. It is an important parameter when considering the efficiency of the treatment and operating costs in real applications.

Electrocoagulation is a widely studied technology that has several advantages over chemical coagulation. Because of the high conductivity of pulp and paper mill wastewaters and their high concentrations of sulphurous compounds, electrochemical technologies can be potential alternatives for treating pulp and paper mill effluents. Hydrogen sulphide gas formation can be prevented, prior to or after the sulphide formation, using precipitation or oxidation technologies. In this work, EC treatment of sulphide odour from pulp and paper mill wastewater was studied using samples in which sulphide formed due to the metabolic activity of anaerobic bacteria. The suitability of EC for sulphide precipitation after long transport in pipelines can be evaluated based on the results. The dissolved iron concentration was measured at various current densities to estimate the efficiency of the dissolving reaction, the required iron dosage per unit of sulphide precipitated and the amount of side reactions. These parameters have a major influence on the operating cost of the treatment.

Pulp and paper industry wastewaters are typically deficient in phosphorus and cannot be efficiently treated using conventional biological treatment processes without addition of supplementary nutrients, such as urea and phosphoric acid [29]. Precipitation of phosphorus was analysed in this research because its removal during the sulphide precipitation process would be undesirable. The reduction in dissolved organic carbon (DOC) was measured to estimate the coagulation of organic matter during the odour treatment.

2. Experimental

Wastewater was collected from a Finnish pulp and paper mill and stored in a cold room between experiments. It was filtered through a coarse sieve (mesh size 0.2 mm), and 5 L of the wastewater was slowly stirred for 2–4 days in a closed bottle at 40 °C to promote growth of SRB in the wastewater and to produce the required sulphide concentration. During the experiments nitrogen was supplied continuously to the bottle to prevent oxidation of sulphides. Reference samples were measured before and after electrochemical treatment to detect the possible oxidation of sulphides by atmospheric oxygen. Reference samples were treated similarly to the electrocoagulated samples to ensure that sulphides were not removed from the solutions by oxidation. The redox potential was measured from all the samples to further ensure that they were not significantly oxidized during the electrocoagulation and filtration steps. The composition of the wastewater before electrocoagulation treatment is presented in Table 1.

To ensure comparability of the results, the experimental set-up was similar to that used in our previous research [13]. The volume of wastewater used in electrocoagulation was 500 mL. Tests were conducted using an Agilent model 6555A power source in constant current mode. The electrocoagulation cell was constructed from four monopolar iron plates with surface areas of 70 cm^2 per plate and inter-electrode gaps of 5 mm. Water was stirred (250 rpm) with a magnetic stirrer during the treatment to keep the sample homogeneous. During the experiments wastewater was first pumped into the beaker with a tube pump, then the electrodes were immersed into the solution and finally the electricity was switched on. Table 2 presents experimental parameters of the study.

Phosphorous and dissolved sulphide concentrations were measured from samples that were filtered through filter paper (VWR 415) and through 0.45 μm pore size membrane filters. Dissolved sulphide was measured immediately after the treatment to minimize oxidation of the samples and the release of sulphide to the air. Sulphate and chloride concentrations were measured from the unfiltered samples. Dissolved sulphide and phosphorus measurements were done using a HACH Lange photometer (DR 2800 VIS spectrophotometer) using Lange cuvette tests.

Iron concentration was measured from acidified samples (nitric acid) using a Thermo Electron iCAP 6000 series ICP. Samples for DOC measurements were filtered through 0.45 μm pore size membranes, and the DOC was measured using a TOC-5000A Analyser. Chemical oxygen demand (COD) was measured from

Table 1. Composition of the pulp and paper mill wastewater before the experiments.

Parameter	
pH	6.5–7.1
Conductivity (mS/cm)	1.4–3.0
Redox (mV)	−300 to −200
Sulphate (mg/L)[a]	600
Dissolved oxygen (mg/L)	0.5–2.0
Dissolved sulphide (mg/L)	7.5–9.5
Phosphorus (mg PO_4/L)	1.3–1.5
COD (mg O_2/L)	800–1500
DOC (mg/L)	300–450

[a] Measured from one sample.

Table 2. Parameters of the experiments.

	Current (A)	Current density (mA/cm^2)	Voltage (V)	Time (s)
Sulphide and phosphorus tests	0.5	3.6	2.2–2.3	10–60
	1.0	7.1	4.6–5.2	20–60
	1.5	10.7	5.6–6.1	30–120
	2.0	14.3	6.7–7.0	10–60
	2.5	17.9	7.9–8.4	10–60
	1.0	7.1	6.7–7.3	120–600
DOC tests	2.0	14.3	10.2–11.2	120–600
	2.5	17.9	8.5–9.6	60–900

unfiltered samples as stated in the standard method SFS 5504 [30]. Dissolved oxygen, conductivity, pH and redox potential were measured using VWR DO200, VWR EC300, and VWR pH100 equipment, respectively.

3. Results and discussion

3.1. Dissolution of the iron electrodes

The concentration of dissolved iron was measured from the samples that were treated at various current densities to examine the influence of current density on the proportion of anodic side reactions. It can be seen (Figure 1) that the dissolved iron concentration was dependent on electric charge per volume added (C/L), and current density had a minor effect on the current efficiency of the reaction. The theoretical dissolution rate (mg Fe/C) can be calculated according to Faraday's law:

$$\frac{w}{It} = \frac{M_w}{nF}, \qquad (9)$$

where I is the current (A), t is the operation time (s), M_w is molecular weight of the substance, F is Faraday's constant (96,485 C/mol), n is the number of electrons involved in the reaction (2 for Fe^{2+} and 3 for Fe^{3+}) and w is the quantity of metal dissolved.

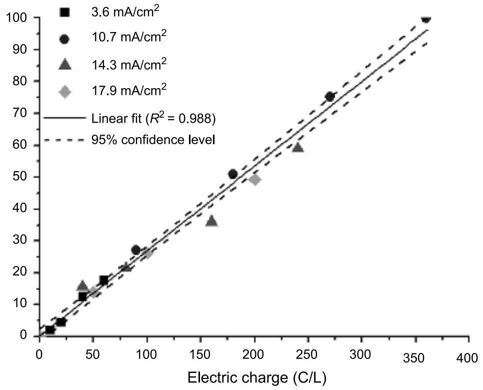

Figure 1. Iron dissolution during the tests as a function of electric charge per volume. Slope of the linear regression is 0.27 mg Fe/C. The 95% confidence interval of the linear regression is presented in the figure.

According to the linear regression presented in Figure 1, iron dissolved at a rate of 0.27 mg Fe/C. The theoretical dissolution rate for Fe^{2+} is 0.29 mg/C and for Fe^{3+} it is 0.19 mg/C. It can be concluded based on the current efficiency of the iron-dissolving reaction that iron dissolved from the anodes mostly in the ferrous (Fe^{2+}) form. The dissolving of ferric (Fe^{3+}) iron would require a higher electric charge per unit of produced coagulant. According to the R^2 and confidence interval values of the linear regression, iron concentration variance is explained predominantly by the applied electric charge per volume. However, the current efficiency of the iron-dissolving reaction was slightly lower at 14.3 mA/cm^2 and 17.9 mA/cm^2 than it was at 3.6 mA/cm^2 and 10.7 mA/cm^2. This indicates that the amount of side reactions or ferric ion formation increases when higher current densities are used.

Sasson *et al*. studied the behaviour of iron electrodes during electrocoagulation and concluded that iron dissolves from the electrodes in Fe^{2+} form [31]. The oxygen saturation level of the water remained stable or decreased during the treatment, which indicates that no significant amount of oxygen or chlorine is produced on the anodes. The results of our research support the conclusions of Sasson *et al*.

Dissolved iron can form various hydroxides in solution, according to Equation (6). Hydroxides can coagulate impurities in wastewater and form larger agglomerates. The iron concentration in filtered and unfiltered samples indicates that particle size increases when electric charge per volume increases (Figure 2).

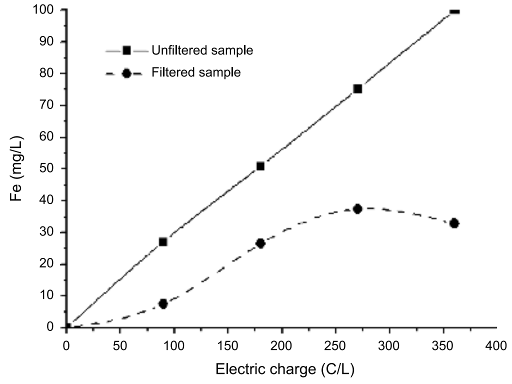

Figure 2. Iron concentration of the unfiltered and filtered samples as a function of electric charge per volume. Samples were electrocoagulated with a current density of 10.7 mA/cm^2.

Iron concentration decreased in the filtered samples when the electric charge per volume was higher than 250 C/L. Precipitation of sulphides as ferrous sulphides occurred at the beginning of the electrochemical treatment when the sulphide concentration in the wastewater was high. Iron hydroxide began to form and particle size increased significantly after most of the sulphide was precipitated. The concentration of dissolved oxygen in the samples was below 2 mg/L before electrochemical treatment, wastewater pH was in the neutral region, and the redox potential slightly decreased during the electrocoagulation. Based on these results, it can be concluded that no significant oxidation of Fe^{2+} to Fe^{3+} occurred during the electrocoagulation or filtration (Equation (8)).

Wastewater pH increased slightly during the sulphide odour treatment, with the maximum increase being 0.3 units (<300 C/L treatments). Hydroxyl ion formation occurs on the cathode simultaneously with hydrogen evolution, according to Equation (7), and the slight increase in pH indicates that the amount of hydroxide ions produced on the cathode is higher than the amount of hydroxide ions consumed by iron ions. This has also been confirmed by other researchers [22]. The release of CO_2 during hydrogen formation can also cause an increase in pH as the carbonic acid concentration of the wastewater decreases. A reduction in dissolved inorganic carbon in the electrocoagulated samples was noticed during total organic carbon (TOC) measurements (inorganic carbon content is measured simultaneously with TOC). The inorganic carbon concentration decreased from 41.15 mg/L to 7.79 mg/L when current density of the treatment was 14.3 mA/cm^2 and applied electric charge per volume was 2400 C/L.

3.2. *Precipitation of sulphides during electrochemical treatment*

After immersion of the electrodes in the wastewater and initiation of the experiment, the colour of the wastewater turned rapidly to dark grey and black, which was probably due to the formation of black iron sulphides. Bubble formation on the cathodes was vigorous but significant flotation occurred only when the highest electric charges per volume were used during the DOC reduction tests (>1000 C/L). A small amount of grey material remained in the filtrate after passage through a 0.45 μm pore size membrane filter. Therefore, some FeS particles were smaller than the membrane pores.

The initial dissolved sulphide concentration varied from 7.5 mg/L to 9.5 mg/L (Figure 3). The demand for electric charge and iron concentration per unit of precipitated sulphide was low at the beginning of the treatment and increased as the sulphide concentration decreased. Sulphide reduction as a function of electric charge per volume is explained in Figure 3 using asymptotic fitting. Regression predicts the initial sulphide value of the test series to be 8.55 mg/L (0 C/L). According to the regression, an electrocoagulation process applying 10 C/L consumes 3.92 C/mg S^{2-} while a process applying 60 C/L consumes 7.99 C/mg S^{2-}. Residual sulphide concentrations of the wastewaters are 6.00 mg/L (30% reduction) and 1.05 mg/L (88% reduction), respectively. The sulphide concentration approaches zero when high electric charges are used.

Iron consumption per unit of precipitated sulphide can be calculated using the linear correlation between iron concentration and electric charge (0.27 mg Fe/C). For a 10 C/L process, iron consumption per unit of precipitated sulphide is 1.06 mg Fe/mg S^{2-} and, for a

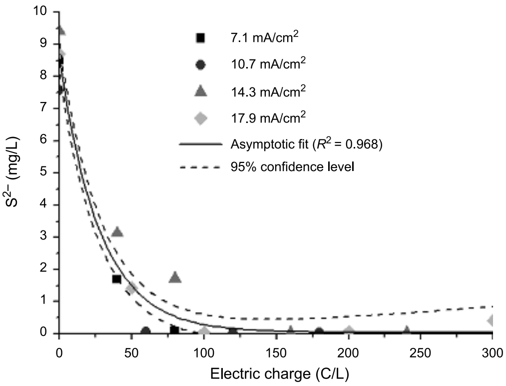

Figure 3. Sulphide concentrations plotted as a function of applied electric charge per volume. Asymptotic regression $Y = 0.043 + 8.51 \times 0.965^x$ was fitted to the results together with 95% confidence interval.

60 C/L process, it is 2.16 mg Fe/mg S^{2-}. According to these results, sulphides were precipitated efficiently by electrochemically produced iron. However, consumption of electricity and iron by the process depends greatly on the required level of purification.

Current density did not have a noticeable effect on the electric charge or iron concentration required per unit of sulphide precipitated. This is important when considering full-scale applications where the required electrode surface area of the system depends on the current (A) and current density (A/m^2) targets of the treatment. However, high current density increases voltage and power consumption of the system and also, therefore, the operating cost of the purification process.

Redox potentials of the solutions were in the range of −290 mV to −412 mV after electrocoagulation. A slight decrease in the redox potential as a function of electric charge was observed, which could be due to the formation of ferrous iron and hydrogen during the process. Based on redox potentials, no substantial amount of oxidants, such as chlorine or oxygen, was produced on the electrodes. It can also be concluded that oxidation of sulphides by atmospheric oxygen was insignificant.

3.3. *Phosphorous and organic matter removal*

Figure 4 shows the effect of electrocoagulation treatment on phosphorous precipitation. As seen with sulphide, the phosphorus precipitation as a function of electric charge per volume can be explained using an asymptotic fitting. The initial phosphorus concentration predicted by the regression is 1.38 mg/L. According to the regression, an electrocoagulation process applying 10 C/L consumes 75.0 C/mg PO_4 while a process applying 60 C/L consumes 110.4 C/mg PO_4. Predicted residual phosphorus concentrations of the wastewaters are 1.24 mg/L (10% reduction) and 0.83 mg/L (40% reduction), respectively. The regression curve approaches a value of 0.53 mg/L when high electric charge per volume is applied. According to this, some part of the phosphorus could not be removed during the process.

Current density did not show a significant effect on the phosphorous removal rate at 3.6 mA/cm^2, 7.1 mA/cm^2 and 10.7 mA/cm^2. However, current efficiency decreased slightly when current densities were 14. mA/cm^2 and 17.9 mA/cm^2. This can be attributed to a faster flotation and a shorter contact time between pollutants and the coagulants produced.

Based on the sulphide and phosphorus results, some phosphorus precipitation occurred simultaneously with sulphide precipitation. However, sulphide precipitation requires a lower electric charge per unit of pollutant, especially during the initial phase of the electrocoagulation (low electric charge per volume).

Coagulation of DOC by electrocoagulation required a high electric charge per volume and iron concentration. The current efficiency of the iron-dissolving reaction indicates that iron dissolved mainly in the ferrous form, and redox potentials of the samples showed that ferrous iron was not oxidized significantly to the ferric form during the tests. Ferrous iron produced from anodes does not coagulate organic matter well [24]. The removal rate increased slightly when current density decreased, as can be seen from Figure 5. However, no significant coagulation of organic matter occurred during the precipitation of sulphides when electric charge per volume was less than 300 C/L.

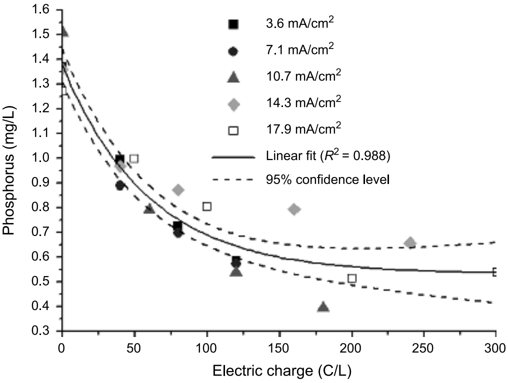

Figure 4. Phosphorus concentrations plotted as a function of electric charge per volume. Asymptotic regression $Y = 0.531 + 0.846 \times 0.983^x$ was fitted to the results together with 95% confidence interval.

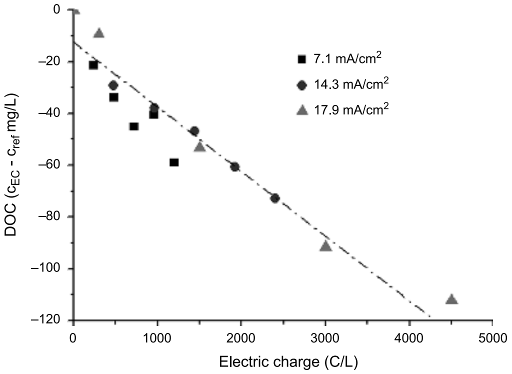

Figure 5. DOC concentration as a function of electric charge per volume. C_{EC} is the DOC concentration after electrocoagulation and C_{ref} is the DOC concentration of the reference sample (0 C/L).

Table 3. Comparison of dissolved sulfide removal by electrocoagulation and electro-oxidation. Similar experimental procedures were used in both studies.

	Electrocoagulation	Electro-oxidation
Electrode material	Iron	Mixed metal oxide
Surface area (per anode/cathode)	140 cm^2	70 cm^2
Mechanism of S^{2-} removal	Precipitation	Oxidation
Electricity consumption	~4–8 C/mg S^{2-}	25–67 C/mg S^{2-}
Electrode consumption	~1.1–2.2 mg Fe/mg S^{2-}	Negligible consumption
Cost of electrode material	Low	High
Other effects	Coagulation of organic matter Phosphorus precipitation Increased pH Gas formation	Increased redox potential Inhibits bacteria growth Gas formation

3.4. Comparison of electrocoagulation and electro-oxidation technologies for sulphide odour treatment

The main results for sulphide odour treatment by electro-oxidation [13] and electrocoagulation (present study) are summarized in Table 3. According to the results of these studies, both technologies can be employed for removal of dissolved sulphide from pulp and paper wastewater. However, electrocoagulation has a lower electricity consumption and lower material costs for the electrodes, which makes it a more economical solution than electro-oxidation.

4. Conclusions

The removal of dissolved sulphides from pulp and paper mill wastewater by electrocoagulation was found to be highly effective. The current efficiency of the dissolving reaction of the iron electrodes was close to theoretical values calculated according to Faraday's law. Iron was dissolved from the anodes mainly in the ferrous (Fe^{2+}) form and the proportion of anodic side reactions was low based on the current efficiency of the dissolving reaction. Electric charge per volume varied from 3.92 to 7.99 C/mg S^{2-}, while the sulphide removal rate ranged from 30% to 88%. Iron consumption, in the same range, varied from 1.06 to 2.16 mg Fe/mg S^{2-}.

Gas formation on the cathodes was vigorous. However, no significant flotation occurred during the precipitation of sulphides (<300 C/L). Some phosphorus was precipitated simultaneously with the sulphides. When sulphide removal was 88%, phosphorus removal was 40%. The DOC removal during the precipitation of sulphides was found to be negligible. According to the results of this study, electrocoagulation can be an economically viable solution for treatment of sulphide odour in pulp and paper wastewater

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References

[1] H. Satoh, M. Odagiri, T. Ito, and S. Okabe, *Microbial community structures and* in situ *sulfate-reducing and sulfur-oxidizing activities in biofilms developed on mortar specimens in a corroded sewer system,* Water Res. 43 (2009), pp. 4729–4739.

[2] L.K. Wang, N.C. Pereira, and Y.T. Hung (eds.), *Advanced Air and Noise Pollution Control,* Humana Press, Totowa, NJ, USA, 2005.

[3] C.R. Lange and J. Christiansen, *Characterization of odors originating from pulp and paper wastewater lagoons,* 2004 Paper Summit, Spring Technical & International Environmental Conference Proceedings, TAPPI, 2004.

[4] R.J. Reiffenstein, W.C. Hulbert, and S.H. Roth, *Toxicology of hydrogen sulfide,* Annu. Rev. Pharmocol. Toxicol. 32 (1992), pp. 109–134.

[5] T. Yamanaka, I. Aso, S. Togashi, M. Tanigawa, K. Shoji, T. Watanabe, K. Maki, and H. Suzuki, *Corrosion by bacteria of concrete in sewage systems and inhibitory effects of formates on their growth,* Water Res. 36 (2002), pp. 2636–2642.

[6] J.L. Davis, D. Nica, K. Shields, and D.J. Roberts, *Analysis of concrete from corroded sewer pipes,* Int. Biodeter. Biodegrad. 42 (1998), pp. 75–84.

[7] A.H. Nielsen, J. Vollertsen, H.S. Jensen, T. Wium-Andersen, and T. Hvitved-Jacobsen, *Influence of pipe material and surfaces on sulfide related odor and corrosion in sewers,* Water Res. 42 (2008), pp. 4206–4214.

[8] W. Sand and E. Bock, *Concrete corrosion in the Hamburg sewer system,* Environ. Technol. 5 (1984), pp. 517–528.

[9] D. Nica, J.L. Davis, L. Kirby, G. Zuo, and D.J. Roberts, *Isolation and characterization of microorganisms involved in the biodeterioration of concrete in sewers,* Int. Biodeter. Biodegrad. 46 (2000), pp. 61–68.

[10] R. Stuetz and F.-B. Frechen, *Odours in Wastewater Treatment: Measurement, Modelling and Control,* IWA Publishing, London, 2001.

[11] G. Moussavi, K. Naddafi, A. Mesdaghinia, and M.A. Deshusses, *The removal of H_2S from process air by diffusion into activated sludge,* Environ. Technol. 28 (2007), pp. 987–993.

[12] I. Devai and R.D. Delaune, *Effectiveness of selected chemicals for controlling emission of malodorous sulfur gases in sewage sludge,* Environ. Technol. 23 (2002), pp. 319–329.

[13] H. Särkkä, K. Kuhmonen, M. Vepsäläinen, M. Pulliainen, J. Selin, P. Rantala, E. Kukkamäki, and M. Sillanpää, *Electrochemical oxidation of sulphides in paper mill wastewater by using mixed oxide anodes,* Environ. Technol. 30 (2009), pp. 885–892.

[14] P.K. Dutta, K. Rabaey, Z. Yuan, R.A. Rozendal, and J. Keller, *Electrochemical sulphide removal and recovery from paper mill anaerobic treatment effluent,* Water Res. 44 (2010), pp. 2563–2571.

[15] A.H. Nielsen, P. Lens, J. Vollertsen, and T. Hvitved-Jacobsen, *Sulfide-iron interactions in domestic wastewater from a gravity sewer,* Water Res. 39 (2005), pp. 2747–2755.

[16] D. Firer, E. Friedler, and O. Lahav, *Control of sulfide in sewer systems by dosage of iron salts: comparison between theoretical and experimental results, and practical implications,* Sci. Total. Environ. 392 (2008), pp. 145–156.

[17] L. Zhang, J. Keller, and Z. Yuan, *Inhibition of sulfate-reducing and methanogenic activities of anaerobic sewer biofilms by ferric iron dosing,* Water Res. 43 (2009), pp. 4123–4132.

[18] J.R. Crowder, G.A. Tinti, and P.M. Niedenzu, *Wastewater odor control using ferric chloride,* TAPPI 1992 Environmental Conference Proceedings, 1992.

[19] M. Kobya, M. Bayramoglu, and M. Eyvaz, *Techno-economical evaluation of electrocoagulation for the textile wastewater using different electrode connections,* J. Hazard. Mater. 148 (2007), pp. 311–318.

[20] N. Drouiche, N. Ghaffour, H. Lounici, and M. Mameri, *Electrocoagulation of chemical mechanical polishing wastewater,* Desalination 214 (2007), pp. 31–37.

[21] S. Khoufi, F. Feki, and S. Sayadi, *Detoxification of olive mill wastewater by electrocoagulation and sedimentation processes,* J. Hazard. Mater. 142 (2007), pp. 58–67.

[22] M.Y.A. Mollah, R. Schennach, J.R. Parga, and D.L. Cocke, *Electrocoagulation (EC) – science and applications,* J. Hazard. Mater. 84 (2001), pp. 29–41.

[23] G. Chen, *Electrochemical applications in wastewater technologies,* Sep. Purif. Technol. 38 (2004), pp. 11–41.

[24] J. Bratby, *Coagulation and Flocculation in Water and Wastewater Treatment,* 2nd ed., IWA Publishing, London, 2006.

[25] L.B. Mansour, I. Ksentini, and B. Elleuch, *Treatment of wastewaters of paper industry by coagulation–electroflotation,* Desalination 208 (2007), pp. 34–41.

[26] M. Murugananthan, G.B. Raju, and S. Prabhakar, *Separation of pollutants from tannery effluents by electro flotation,* Sep. Purif. Technol. 40 (2004), pp. 69–75.

[27] M. Murugananthan, G.B. Raju, and S. Prabhakar, *Removal of sulfide, sulfate and sulfite ions by electro coagulation,* J. Hazard. Mater. 109 (2004), pp. 37–44.

[28] J. Feng, Y. Sun, Z. Zheng, J. Zhang, S. Shu, and Y. Tian, *Treatment of tannery wastewater by electrocoagulation,* J. Environ. Sci. 19 (2007), pp. 1409–1415.

[29] A.M. Springer, *Industrial Environmental Control: Pulp and Paper Industry,* 3rd ed., Tappi Press, Atlanta, GA, USA, 2000.

[30] *SFS 5504: Determination of chemical oxygen demand (COD Cr), in water with the closed tube method. Oxidation with dichromate,* Finnish Standards Association, Helsinki, 1988.

[31] M.B. Sasson, W. Calmano, and A. Adin, *Iron-oxidation processes in an electroflocculation (electrocoagulation) cell,* J. Hazard. Mater. 171 (2009), pp. 704–709.

PUBLICATION V

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Removal of toxic pollutants from pulp mill effluents by electrocoagulation

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Copper

ABSTRACT

This study investigated the effect of electrocoagulation treatment on toxic pollutant removal from pulp mill effluents. Synthetic wastewaters containing wood rosin and copper or pure resin acids were used to investigate the removal of resin acids and copper by electrocoagulation. Removal of pollutants by electrocoagulation was also tested with real debarking effluent. In this study, statistical experimental design and partial least squares modeling were used to investigate the effect of initial pH, current (current density) and treatment time. Electrocoagulation and subsequent filtration removed resin acids and copper from the synthetic wastewaters with high efficiency. Toxicity to algae (*Pseudokirchneriella subcapita*) was completely eliminated by the treatment, however reduction of bacterial toxicity (*Vibrio fischeri*) was more limited. While the initial EC_{50} value for bacteria in debarking effluent was around 8–14 vol%, toxicity was approximately halved by electrocoagulation. Toxicity removal from the debarking effluents was associated with color removal.

1. Introduction

Pulp and paper mills generate large amounts of wastewater in their manufacturing processes. Pollutants are produced during the wood debarking, digesting, pulp washing, pulp bleaching and papermaking processes. Effluents often contain high amounts of toxic chemicals which originate from raw materials, such as resin acids and tannins, or are produced during the manufacturing processes, such as chlorinated organic compounds. These pollutants can cause long-term toxic effects on animal life, such as respiratory stress, toxicity, mutagenicity and genotoxicity [1].

Soil, dirt and bark are removed from the wood raw material during the wood preparation stages [2]. Debarking can be carried out by means of wet processes [3]. Wet processes usually circulate water in order to reduce water consumption and produce lower effluent levels. Wet debarking processes remove large amounts of organic matter from the wood and transfer them into the circulating water. The effluents are highly colored due to their tannin content, which contributes to up to 50% of the COD of debarking wastewater [4]. The effluents are known to exhibit toxicity to bacteria and fish due to their interaction with enzymes [4–7].

Debarking waters also contain a high concentration of resin acids, which are weak hydrophobic acids. Commonly found resin acids in pulping wastewaters include isopimaric, sandacopimaric, levopimaric, abietic, dehydroabietic, neoabietic and palustric acids [1,8–10,14]. According to Peng et al., resin acid toxicity is strongly affected by wastewater pH which has an effect on the solubility of the resin acids [8]. Their toxicity correlates inversely with their solubility, the least soluble being the most toxic. According to the results of Peng et al. and Wilson et al. [8,11], in pulp and paper mill wastewaters isopimaric acid is the most toxic resin acid, although it is not the most prevalent. In studies with rainbow trout, acute lethal concentrations (LC_{50}) of individual resin acids have been found to be in the range of 0.4–1.1 mg/l [12–14]. Oikari et al. reported the minimum effective concentration of dehydroabietic acid to be as low as 20 μg/l [15].

Aerobic and anaerobic biological processes are able to remove resin acids from the effluent streams [1,9,10,17,18]. However, discharged residue can still be toxic to aquatic organisms [9,10]. Debarking effluents also cause problems in wastewater treatment due to their toxicity to microbes in the treatment process. Tannins have been found to be effective inhibitors of methanogens, which may in turn inhibit anaerobic biological treatment processes [4,19]. Oligomeric tannins have highest toxicity as they can form strong hydrogen bonds with proteins [6,20].

Chemical coagulation has been proposed as a treatment for toxic mechanical pulping effluents and bleaching filtrates [21,22]. Resin acids are poorly water soluble, in particular under acidic conditions, and are present as colloids, which could be destabilized by chemical coagulants. Stephenson et al. studied toxicity removal

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and metal salt recovery of a mechanical pulping effluent [21]. According to their results, chemical coagulation eliminated toxicity efficiently. Toxicity was completely eliminated from four-times diluted effluent at a ferric chloride dose of 5 g/l. Ferrous chloride was more effective than ferrous sulfate in decreasing Microtox toxicity. However, coagulants, especially ferrous sulfate, were themselves toxic at high concentration. It is possible that sulfate anions of the coagulant contributed to toxicity to some extent.

Electrocoagulation (EC) is an evolving technology which can be used to remove various chemical species of pollutants in effluents [23,24]. The EC cell consists of electrodes and an AC or DC power source. Anodes can be constructed from iron or aluminum, whereas the cathode material can also be inert, such as titanium. When sufficient external current flows in the cell, the iron anodes dissolve according to Eq. (1) producing iron cations ($n = 2$ for ferrous and 3 for ferric ions) which are further hydrolyzed according to Eq. (2), where m is the amount of hydroxyl anions bound with metal ions. According to this, the degree of hydrolysis depends on the pH of the solution.

$$\mathrm{Fe_{(s)}} \rightarrow \mathrm{Fe_{aq}^{n+}} + ne^- \tag{1}$$

$$\mathrm{Fe_{(aq)}^{n+}} + \mathrm{mOH^-} \leftrightarrow \mathrm{Fe(OH)}_n^{(n-m)+} \tag{2}$$

Iron cations and hydrolyzed species cause destabilization of the particles or chemical aggregates in the solution [23,24]. It is probable that EC mainly removes impurities that are in colloidal form, as in chemical coagulation, and the main mechanisms of particle removal are the same for electrocoagulation and inorganic chemical coagulants: double layer compression, adsorption destabilization, bridging and precipitation [16]. However, there are significant differences between chemical coagulation and electrocoagulation, such as:

- No anions, such as sulfate or chloride, are added together with metal cations and hydroxides during electrocoagulation.
- Hydrogen produced at the cathode induces flotation that can separate agglomerated particles from water.
- Water pH increases during electrocoagulation, whereas typical iron and aluminum coagulants decrease water pH.

Electrocoagulation can also remove toxic pollutants from effluents. Toxicity caused by Cr(VI) [25–27], dyes [28–31], olive mill wastewater pollutants [32–34] and poultry manure wastewater pollutants [35] have been successfully removed by EC. Polyphenolic substances are mainly responsible for the toxic effects of olive mill wastewaters. According to the findings of Khoufi et al., EC and subsequent sedimentation decreased the inhibition of *Vibrio fischeri* luminescence by 66%, and further increased the biotransformation of pollutants in the subsequent anaerobic treatment [32]. Yetilmezsoy et al. used EC with anaerobic sludge blanket treated poultry manure wastewaters [35]. According to their results, 90% of chemical oxygen demand (COD) and 92% of residual color were removed during the treatment. They tested the toxicity with guppy fish (*Lebistes reticulates*), revealing no mortality or behavioral changes after 48 h exposure to the EC treated wastewater.

Chowwanapoonpohn et al. studied the recovery of tannins from tree bark by EC [36]. They first elutriated tannins from the bark with water, treated this solution with electrocoagulation, dissolved the coagulum in hydrochloric acid, extracted the tannins with 1-butanol, and evaporated the solution. The procedure increased tannin enrichment by 0–48% when compared to simple aqueous extraction and evaporation. However, the effect of EC treatment on the toxicity of debarking effluents has not been studied. High removal of organic matter in the EC process could enable reuse of water in the debarking process. Reducing the amount of toxic compounds going to the biological wastewater plant could enhance the stability of the biological wastewater treatment operation and decrease pollution of the receiving water body.

In this study, the effect of EC treatment on the removal of toxic components from pulp mill effluents was investigated. Synthetic wastewaters containing softwood rosin and copper or exclusively pure resin acids were used to investigate the removal of resin acids and copper by EC. Toxic pollutant removal by EC was also assessed for debarking effluents. Statistical experimental designs and partial least squares modeling were used to investigate the effect of initial pH, current (current density) and treatment time on pollutant removal.

2. Experimental

2.1. Test solutions

Synthetic wastewaters were used in order to analytically study the removal of resin acids and a metal pollutant (Cu) and their toxicity by electrocoagulation. These solutions contained Polish wood rosin (Hercules Corporation, Wilmington, DE, USA) and copper nitrate $\mathrm{Cu(NO_3)_2}$. The main components of the Polish wood rosin are shown in Table 1. Additional tests were conducted using pure dehydroabietic acid (DHAA) and isopimaric acid (IPA) (purity 99.0%, Helix Biotechnologies, Canada).

Filtered Finnish oligotrophic lake water (Lake Palosjärvi, Toivakka) was used to dilute the mother solutions to final test concentrations. Lake water was used to obtain a realistic background, such as salts and metals concentration, for the electrocoagulation tests. Solution pHs were adjusted to 5, 7 or 9 using 0.5 M sulfuric acid or sodium hydroxide. To ensure adequate conductivity of the synthetic wastewaters, 20 ml of 0.5 M sodium sulfate (purity 99%, Merck) solution was added to the water.

Debarking effluent was collected from a Finnish pulp and paper mill and stored in a cold room. The effluent had a high organic matter content and dark color, and was filtered through a coarse sieve (0.2 mm mesh size) to remove bark fragments and needles prior to electrochemical treatment.

2.2. Electrochemical treatment

Electrochemical treatment was conducted in a standard 1000 ml glass beaker. For synthetic wastewaters, a volume of 600 ml was used during electrocoagulation treatment. The corresponding volume for debarking effluents was 400 ml. The electrochemical cell construction consisted of four iron electrodes which were connected to the power supply using a monopolar arrangement (Fig. 1). The plate dimensions were 70 × 50 mm and the iron electrode surface area 70 $\mathrm{cm^2}$ per plate (double-sided), totaling an anode surface area of 140 $\mathrm{cm^2}$. The distance between anodes and cathodes was 10 mm. A laboratory DC power source

Table 1
Breakdown of resin acids content of the Polish wood rosin (Hercules Corporation, USA) used in this study.

Resin acid	% (w/w)
Pimaric acid	8.0
Sandaracopimaric acid	1.7
Isopimaric acid	3.1
Palustric acid	20.7
Dehydroabietic acid	30.6
Abietic acid	22.4
Neoabietic acid	5.3
Levopimaric acid	8.2

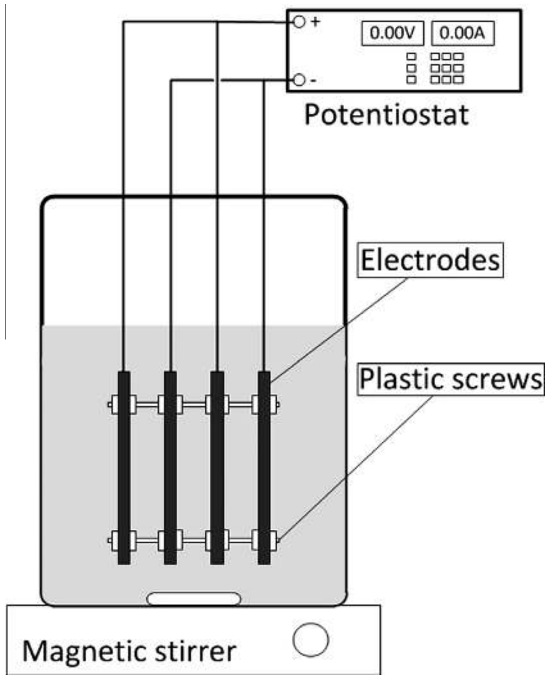

Fig. 1. Schematic diagram of the EC reactor with monopolar electrodes.

(Instek PSP-405, Taiwan) was used in constant current mode in all tests. The voltage varied in the tests between 19 and 28 V.

Synthetic wastewaters were treated at room temperature with a constant current of 2 A (current density 14.3 mA/cm^2). The applied current was a test variable in the tests with debarking effluent and varied from 1 A (7.1 mA/cm^2) to 3 A (21.4 mA/cm^2). Wastewater samples were stirred during the electrochemical treatments at a speed of 350 rpm using a standard magnetic stirrer. Electrodes were washed with 10% HCl acid solution between treatments and rinsed with tap water and distilled water. The treatment parameters for synthetic wastewaters are shown in Table 2.

After electrocoagulation treatment the samples were allowed to settle for 10 min and then filtered through a glass fiber filter (GF/C Whatman, nominal pore size 1.2 μm) to simulate particle separation by filtration, sedimentation or flotation.

2.3. Toxicity analysis

Bacterial toxicity was measured using a Microtox-Flash assay based on the bioluminescence of the marine bacterium *V. fischeri*. Physical and chemical interference (toxicity) affects the metabolism of the bacterial cells and can break down the cell structures, reducing their bioluminescence. The analysis was carried out using the BioTox™ method (Aboatox, BO1243-500, Turku, Finland) using a Sirius luminometer (Berrthold Detection Systems, Germany). Measurements were conducted according to the Aboatox manual, standard draft ISO/CD 2006b, and the method developed by Lappalainen et al. [37]. Luminescence was measured after 15 s, 5, 15 and 30 min exposure times at five different sample concentrations. The sample concentration required to reduce bioluminescence by 50% (EC_{50}) was calculated based on the results. The negative control solution was 2% NaCl, whereas $K_2Cr_2O_7$ was used as the positive reference chemical.

Toxicity to algae (*Pseudokirchneriella subcapita*) was analyzed according to standard ISO:8692 (1989). In contrast to the standard procedure, the sample size was reduced to fit 48-well microplates (Greiner bio-one GmbH, Germany). The average algal cell concentration prior to exposure to wastewaters was measured using a microscope (Olympus BX40, Japan) and cytometer (Assistant, Germany). Fluorescence emitted by the algae was measured prior to exposure and 24, 48 and 72 h after exposure to wastewaters using a fluorometer (Fluoroscan Ascent, Labsystems, Finland). A negative control was conducted with nutrient solutions. $K_2Cr_2O_7$ was used as the positive reference substance.

2.4. Chemical analysis

The metal concentrations of the acidified samples were measured using an ICP system (Thermo Electron Corporation, USA). DOC samples were filtered through 0.45 μm pore size PTFE membranes and analyzed using a TOC system (Shimadzu, Japan). Color (PtCo) was measured using a photometer (Hach Lange DR2800, Germany) and turbidity using a turbidimeter (Model 2100P ISO turbidimeter, Hach, Germany). Resin acids were measured according to the method described by Soimasuo et al. [38] using a GC–MS system (HP 6890, Hewlett-Packard, Germany) with an HP-5 capillary column. Z-potentials were measured using a Zetasizer Nano ZS (Malvern, USA).

2.5. Design of experiments and modeling

The design of experiments (DOE) and modeling of the results were performed using Umetrics MODDE 8.0. The DOE was carried out using a Central Composite Face (CCF) design. The model factors

Table 2
Removal percentages of resin acids and copper in electrocoagulation and filtration.

Initial pH	Treatment time (s)	Initial resin concentration			Initial Cu concentration		
		25 mg/l	75 mg/l	125 mg/l	0.25 mg/l	0.75 mg/l	1.25 mg/l
5	0 (filtration)	74	66	54	19	36	1
	60	86	94	97	80	95	96
	300	84	92	88	91	98	100
	600		86	93		98	99
7	0 (filtration)	63	63	57	21	25	0
	60	93	93	93	72	94	97
	300	90	87	85	89	99	100
	600	74	86	86	84	100	99
9	0 (filtration)	64	46	2	27	31	0
	60	83	92	77	78	95	97
	300	85	83	55	91	99	100
	600	59	95	62	99	99	100

Table 3
Factor range and levels of the experimental design for wood debarking effluent.

Variable	Factor range and levels		
	−1	0	1
X_1, Current (A)	1	2	3
X_2, Time (s)	60	210	360
X_3, Initial pH	4	6	8

used were current (X_1), treatment time (X_2) and initial pH (X_3). The range and levels of the factors are shown in Table 3. The DOE included 18 experiments, although one dataset was excluded from the model due to sampling error. The measured response variables were DOC, color (PtCo), iron, toxicity, final pH and zeta potential.

The fit method used in the modeling was Partial Least Squares regression (PLS). PLS is a statistical method which finds the relationship between response variables (matrix Y) and the predictor of factor variables (matrix X). The method is especially useful when dealing with a small number of observations and a high number of predictor variables. As with other statistical regression methods, such as multiple linear regression (MLR), an equation describing the relationship between the response variable and predictor variables (factors) is gained. The general form of the regression equation including single terms, square terms and interaction terms is shown in Eq. (3), where Y is the response variable, b are the coefficients of the model, and X are the factor variables.

$$Y = b_0 + \underbrace{\sum_{i=1}^{k} b_i X_i}_{\text{single terms}} + \underbrace{\sum_{i=1}^{k} b_{ii} X_i^2}_{\text{square terms}} + \underbrace{\sum_{i}^{i<j}\sum_{j} b_{ij} X_i X_j}_{\text{interaction terms}} \quad (3)$$

The quality of the regression equation can be evaluated using analysis of variance (ANOVA). R^2 is the amount of variance explained by the model whereas Q^2 is an estimate of the predictive ability of the model. Q^2 is calculated by cross-validation. Detailed descriptions of PLS regression and ANOVA are given elsewhere [39].

3. Results and discussion

3.1. Synthetic wastewaters

The effect of filtration alone on resin acid removal was studied by filtering untreated reference samples through a glass fiber filter (Table 2). Initial concentration and pH had a significant effect on the solubility of the resin acids and their corresponding removal by filtration, with the removal yield decreasing in line with increased pH, especially at the highest initial concentration. According to the results, pH had a significant effect on the solubility of the resin acids. At low pH, a higher proportion of resin acids was associated with particles and they were removed during filtration. Removal of pimaric-type acids was slightly higher than abietic-type resin acids. Filtration removed 0–36% of copper from the reference samples.

Electrocoagulation improved resin acid removal in all test conditions except when the initial concentration was 25 mg/l, the pH was 9 and the treatment time was 600 s (5% decrease in removal yield compared to filtration only). Resin acid removals were higher at pH 5 and pH 7 than at pH 9, especially when the initial resin acid concentration was high. The highest removal yield (97%) was thus obtained when the initial pH was 5, the treatment time was 60 s and the initial concentration was 125 mg/l. The lowest residual concentration (1.80 mg/l) was measured from samples which had an initial concentration of 25 mg/l, an initial pH of 7, and a electrocoagulation treatment time of 60 s. According to the results, long treatment may reduce resin acid removal. This may be due to restabilization of particles when the coagulant concentration is very high [16].

EC removed pimaric-type resin acids with higher efficiency than abietic-type acids. The proportion of pimaric acid in the samples decreased from 21% (unfiltered samples) to 0.87–14.7% in electrocoagulated samples. The lowest pimaric acid concentration (0.04 mg/l) was measured from samples which had an initial concentration of 125 mg/l, an initial pH of 5 and a treatment time of 60 s (Fig. 2a). Dehydroabietic acid was the main component in the samples after electrocoagulation (Fig. 2b). Overall, abietic-type resin acids had a lower removal percentage at all initial pHs. The results thus revealed that the soluble fraction contained a higher proportion of abietic-type resin acids, which were not as easily removed by EC as pimaric-type acids. According to Peng et al. [8], abietic-type acids have higher water solubility than pimaric-type resin acids. The most soluble, and least toxic, resin acid in their studies was dehydroabietic acid.

The effect of EC on resin acid removal was also studied with samples containing pure dehydroabietic and isopimaric acids. Removal yields with filtration after EC and sole filtration were significantly lower with pure chemicals than with Polish wood rosin (Fig. 3). This indicates that pure chemicals were more soluble or resin particles in the water were smaller (filter pore size 1.2 μm) than those formed from whole wood rosin. Electrocoagulation had

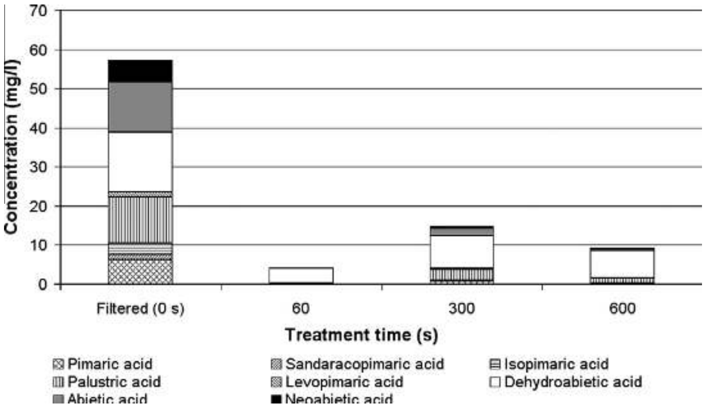

Fig. 2a. Concentration of resin acids in the experimental waters. Samples had an initial pH of 5 and initial resin acid concentration of 125 mg/l.

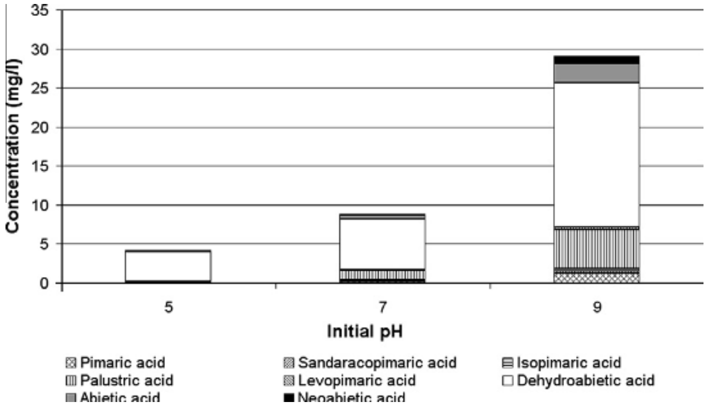

Fig. 2b. Concentration of resin acids in the water samples. Samples had an initial resin acid concentration of 125 mg/l and were treated with electrocoagulation for 60 s.

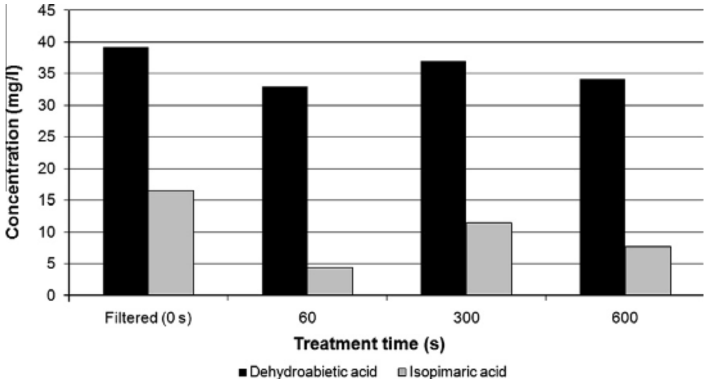

Fig. 3. Concentration of dehydroabietic acid and isopimaric acid in the samples after electrocoagulation and filtration.

a stronger effect on isopimaric acid removal than dehydroabietic acid removal, which is consistent with the results gained with Polish wood rosin.

Electrocoagulation and filtration removed copper from the solutions with very high efficiency. Treatment for 60 s followed by filtration removed 72–97% of copper from the solutions. Proportionally, the lowest reduction was measured from samples with the lowest initial concentration (0.25 mg/l). However, the residual concentration of the samples was similar for all samples after electrocoagulation (0.01–0.07 mg/l). As expected, iron concentrations in the electrocoagulated samples were higher than in the references. Iron concentrations were

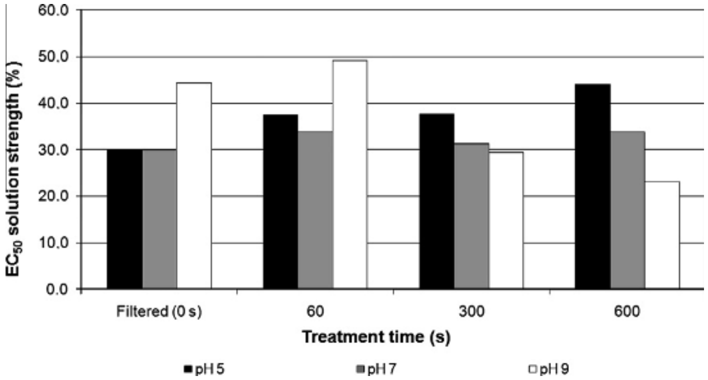

Fig. 4. Bacterial toxicity of the samples after electrocoagulation and filtration. EC_{50} values are based on the solution strength (%) causing a 50% reduction in bioluminescence.

Table 4
Factors and response values of the CCF design.

Run	Factor					Response			
	Current	Time	Initial pH	DOC (mg/l)	Zeta (mV)	Final pH	Color PtCo	Fe (mg/l)	Toxicity (%)
1	−1	−1	−1	excluded					
2	1	−1	−1	405.7	−15.4	5.12	2680	85.8	12.3
3	−1	1	−1	383.5	−15.9	4.94	2790	126.5	11.5
4	1	1	−1	322.2	−4.66	5.46	560	70.3	12
5	−1	−1	1	441.4	−20.1	7.60	3780	25.1	1.3
6	1	−1	1	409.8	−21.5	7.77	3490	56.1	18.5
7	−1	1	1	384.2	−21.5	8.48	368	4.6	21.9
8	1	1	1	335.2	−23.4	9.92	154	0.4	13.4
9	−1	0	0	420.6	−20.5	6.90	3680	70.8	0.4
10	1	0	0	348.4	−19.1	7.69	6110	1.4	1.1
11	0	−1	0	439.7	−18.4	7.03	2480	35.1	6.4
12	0	1	0	346.7	−20.6	8.19	93	1.0	14.7
13	0	0	−1	355.6	−15.4	5.27	946	98.7	11.4
14	0	0	1	377.7	−22.6	9.19	253	1.5	15.6
15	0	0	0	372.4	−19.5	7.40	379	12.6	13.2
16	0	0	0	369.3	−21	7.37	250	10.2	6.6
17	0	0	0	373.6	−20.2	7.34	258	8.5	16.4

Table 5
Analysis of variance (ANOVA) of the model.

Variable	DOC	Zeta potential	Final pH	Color	Fe	Toxicity
R^2	0.95	0.93	0.98	0.88	0.81	0.87
R^2 adjusted	0.86	0.83	0.96	0.70	0.53	0.67
Q^2	0.51	0.57	0.78	0.61	0.41	0.34
Regression (degrees of freedom = 9)						
Sum of squares	1.78E+04	1.68E+00	3.06E+01	4.63E+00	7.94E+00	3.71E+00
Mean square	1.98E+03	1.87E-01	3.40E+00	5.15E-01	8.82E-01	4.13E-01
P-value	0.004	0.007	0.000	0.032	0.108	0.045
F-value	11.47	8.97	36.49	4.96	2.85	4.31
Lack of fit (degrees of freedom = 4)						
Sum of squares	1.02E+03	1.10E-01	5.57E-01	6.02E-01	1.84E+00	4.67E-01
Mean square	2.56E+02	2.74E-02	1.39E-01	1.51E-01	4.61E-01	1.17E-01
P-value of lack of fit	0.019	0.234	0.007	0.064	0.016	0.337
F-value of lack of fit	52.03	3.50	144.71	14.88	62.33	2.19
Pure error (degrees of freedom = 2)						
Sum of squares	9.85E+00	1.56E-02	1.92E-03	2.02E-02	1.48E-02	1.07E-01
Mean square	4.92E+00	7.82E-03	9.62E-04	1.01E-02	7.40E-03	5.33E-02

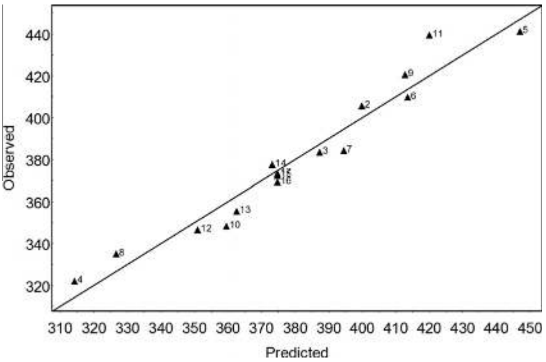

Fig. 5. Observed values versus predicted values of the PLS model for wastewater DOC (mg/l).

highest (1.59–10.59 mg/l) with shortest treatment times (60 s), decreasing as treatment time increased. The highest iron concentrations were measured in experiments with an initial pH of 5, apparently due to increased solubility of iron electrodes at acidic pH, a higher proportion of ionic iron, more soluble iron compounds, or slow oxidation of ferrous iron to ferric form [16,40]. Iron concentrations of samples which were treated with the shortest treatment times were unacceptably high for final effluent. Addition of oxidant and base to promote oxidation of ferrous iron to ferric form could reduce the concentration of soluble iron.

Bacterial toxicity (*V. fischeri*) was analyzed from pure chemicals and from samples having the highest concentration of Polish wood rosin and copper. For pure chemicals, the EC_{50} values for copper and wood rosin were 17.0 and 38.2 mg/l, respectively. The experimental combination of dehydroabietic and pimaric acids had an EC_{50} value of 28.1 mg/l. Toxicity to algae (*P. subcapita*) was measured from the samples having an initial wood rosin concentration of 125 mg/l and an initial pH of 9. In this study, the EC_{50} value of copper to algae was 0.1 mg/l. The toxicity of wood rosin to algae was thus significantly lower (EC_{50} = 142 mg/l) than its toxicity to bacteria.

The bacterial toxicity of the samples did not decrease directly as a function of wood rosin concentration, any specific resin acid concentration or copper concentration (Fig. 4). At an initial pH of 5, the solution strength causing a 50% reduction in bioluminescence (EC_{50}) increased by 7–14%, which indicates a small reduction in toxicity. At an initial pH of 9, toxicity slightly decreased with the

Table 6
Coefficients of the model.

Response	Constant	X_1	X_2	X_3	X_1^2	X_2^2	X_3^2	$X_1{*}X_2$	$X_1{*}X_3$	$X_2{*}X_3$
DOC	4.49E+02	−6.42E+01	−3.10E-01	2.18E+01	1.15E+01	4.81E-04	−1.68E+00	−5.75E-02	6.41E-01	−1.10E-03
Zeta potential[a]	−4.53E-02	6.09E-01	4.99E-03	1.52E-03	−1.39E-02	−7.28E-07	1.32E-02	−2.49E-04	−8.32E-02	−7.37E-04
Final pH	1.06E+00	5.58E-01	−1.30E-02	1.41E+00	−3.54E-01	5.73E-06	−9.22E-02	2.26E-03	1.09E-01	1.41E-03
Color[b]	5.81E+00	−3.83E+00	3.62E-03	3.83E-01	8.47E-01	−5.90E-06	−4.21E-02	−4.92E-04	6.32E-02	−5.61E-04
Fe[b]	4.21E+00	−9.44E-01	4.22E-03	−4.25E-01	3.33E-01	3.12E-06	3.34E-02	−1.54E-03	−5.62E-02	−9.01E-04
Toxicity[c]	−2.23E+00	4.43E+00	−1.60E-03	−1.27E+00	−8.52E-01	1.79E-05	1.15E-01	−2.26E-03	−3.94E-02	6.73E-05

[a] Logarithmic transformation $\mathrm{Log}_{10}(Y) + 24$.
[b] Logarithmic transformation $\mathrm{Log}_{10}(Y)$.
[c] Logit transformation $\mathrm{Log}_{10}[Y/(100 - Y)]$.

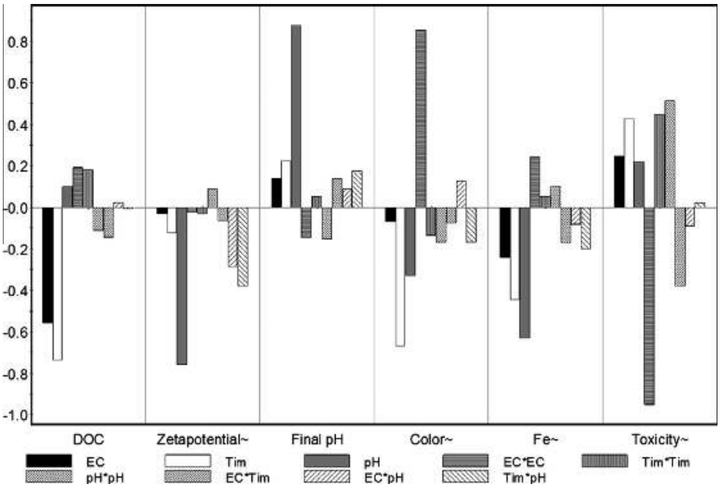

Fig. 6. Normalized coefficients of the PLS model. EC is electric current, Tim is treatment time and pH is the initial pH of the wastewater.

shortest treatment time (60 s) but increased with longer treatment times. The effect of initial pH on toxicity was not due to protons alone, because the pH was adjusted to 7 prior to assay measurement. However, pH adjustment may have affected the solubility or speciation of resin acids and metals in the solution, and could partially explain the lack of correlation.

Toxicity to algae decreased as a function of copper concentration. Filtered samples which were not treated with electrocoagulation were highly toxic to algae (EC_{50} with 3.7% solution). EC removed toxicity completely (EC_{50} with 95–110% solution) and, according to cell count measurements, electrocoagulated samples stimulated algal growth when compared to control algae tests. Due to the low toxicity of wood rosin to algae (EC_{50} 142 mg/l), removal of resin acids by EC did not have any further contribution in terms of algal toxicity.

3.2. Debarking effluents

The measured response values of the CCF design are shown in Table 4. According to the R^2 of the responses (Table 5), the model explained the response variance with good accuracy. However, iron concentration and toxicity had markedly low Q^2 values (<0.5), thus indicating poor cross-validation results and therefore low predictability of these responses. According to ANOVA, this is mainly related to model error. Examples of observed values versus predicted values of wastewater DOC are presented in Fig. 5.

The coefficients of the model terms are shown in Table 6 and the normalized coefficients in Fig. 6. The direction and magnitude of the normalized coefficients in the figure visualize the effect of single, square and interaction terms on the responses. Normalized coefficients (mean zero value and dataset variance of 1.0) enable simultaneous comparison of the effect of the terms on the responses. For example, it can be seen from Fig. 6 that current (current density) and time are the most important terms affecting DOC values, and both in the same direction. It should be noted that the statistical model is valid only within the limits of the experimental data obtained.

DOC removal was low in the tested factor ranges. As mentioned above, the main terms affecting DOC removal were electric current (current density) and treatment time. DOC concentration decreased as current density and treatment time increased. The minimum DOC value predicted by the model was 314 mg/l, while the minimum measured DOC value was 322 mg/l (26.3% removal). According to the model, color removal was not directly linked to DOC removal. Electrocoagulation removed color with high efficiency (Fig. 7). Color decreased as a function of treatment time while the other main term affecting color removal was the square term of electric current. The model predicts total color removal at intermediate current density, high treatment time, and high initial pH. At low pH, a high residual iron concentration may have increased color values. According to previous studies, EC treatment effectively removes color and toxicity caused mainly by polyphenols (tannins) from olive mill wastewaters [32–34].

Initial pH was the main parameter affecting the final pH and zeta potential of the samples. Current density and treatment time slightly increased the final pH. Electrocoagulation increases pH due

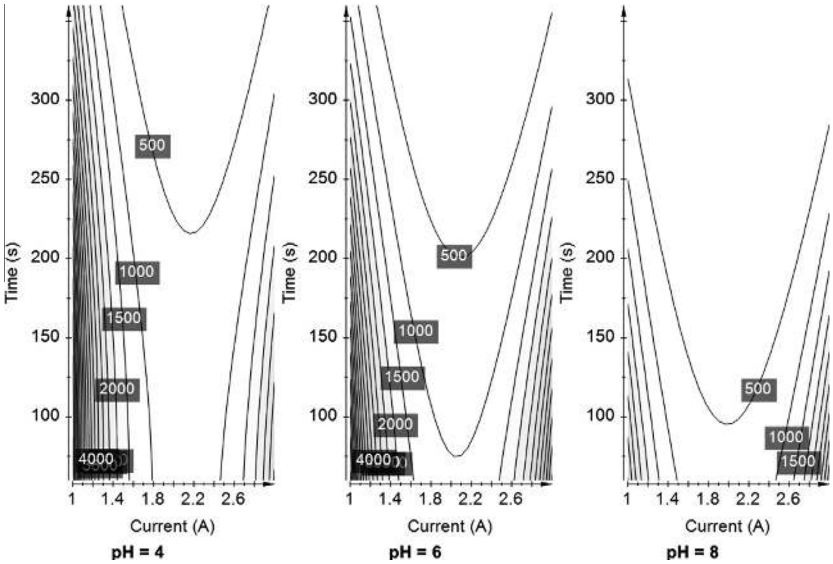

Fig. 7. Contour plots of debarking water color (mg/l PtCo) predicted by the PLS model.

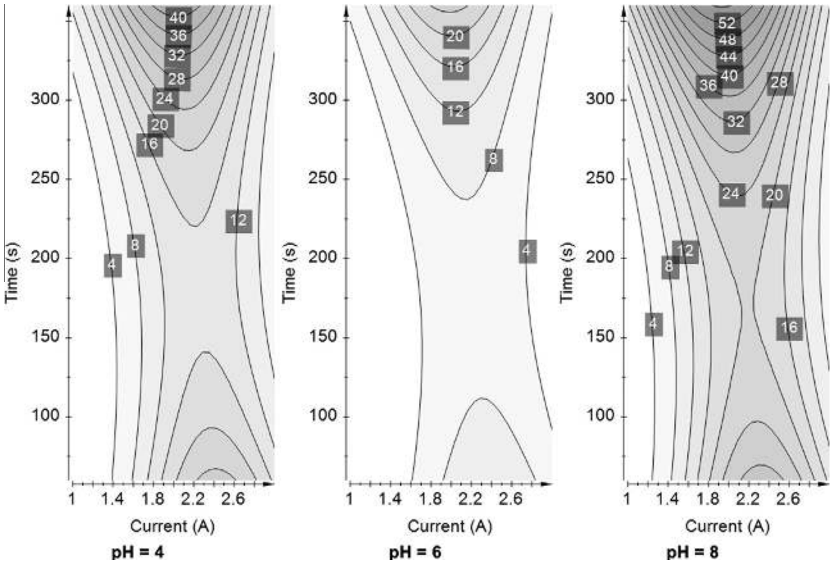

Fig. 8. Contour plots of debarking water bacterial toxicity (% based on solution strength) predicted by the PLS model.

to the production of hydroxyl ions at the cathodes, which are not totally consumed by formation of ferrous or ferric hydroxides. The zeta potential was measured from the filtered samples. At low pH, the zeta potential decreased as a function of electric charge and current density. This was not predicted at higher pH, where ferrous and ferric iron form flocs containing ferrous and ferric hydroxides and are easily separated during filtration. At low pH, ferrous and ferric ions and hydroxides are in more soluble form and also have higher charge, leading to more effective charge neutralization of pollutants by EC. This was confirmed by the residual iron concentrations, which were high at low initial pH.

The initial EC_{50} value of the filtered debarking effluent sample was 7.6%. Toxicity as inhibited bioluminence of the filtered reference samples at pH 4, 6 and 8 was also measured, and the EC_{50} values were 7.7%, 8.4% and 13.8%, respectively. It seems that simple pH adjustment prior to filtration significantly decreased the toxicity of the samples. According to the model, high toxicity removal is predicted when the initial pH is either low or high, the current density is intermediate and the treatment time is long (Fig. 8). Toxicity change was also related to color removal of the samples. The color of debarking effluents is mainly caused by tannins, which are known to exhibit toxicity to microbes [1]. Highest color removal was observed at high initial pH, whereas high toxicity removal was observed both at low and high initial pH. This is probably due to the effect of iron on color values at low initial pH. The model predicts minimum toxicity, EC_{50} at 43% solution in the tested factor ranges at 1.4 A, 360 s and initial pH 8. It is possible that these values are unrealistically high due to model error, as the lowest measured toxicity (EC_{50}) was 21.9%. However, according to the results, electrocoagulation enhanced toxicity removal. Longer treatment times could increase toxicity removal, but would raise the operating cost of treatment. It can be noted that prior the EC treatment, resin acids were minor toxic species in the debarking effluents compared to tannins. According to the results for synthetic wastewaters, the toxicity of the effluents after EC treatment could be caused by residual resin acids or toxic compounds formed during EC treatment.

4. Conclusions

This study investigated the effect of electrocoagulation treatment on toxic pollutant removal from pulp mill effluents. Synthetic wastewaters containing wood rosin and copper or pure resin acids were used to investigate the removal of resin acids by electrocoagulation. According to the results, the following conclusions can be drawn:

- Electrocoagulation enhanced resin acid removal in the subsequent filtration stage. Maximum removal (97%) was obtained with an initial pH of 5, a treatment time of 60 s, and an initial concentration of 125 mg/l. Pimaric-type acids were removed with higher efficiency than abietic-type resin acids.
- Copper was efficiently removed with a short treatment time. A 60 s treatment with 2 A current removed 72–97% of the copper from the experimental solution.
- EC_{50} values for copper and wood rosin to bacteria (*V. fischeri*) were 17.0 and 38.2 mg/l, respectively. Electrocoagulation had no significant effect on bacterial toxicity despite a high removal efficiency of resin acids and copper.
- Electrocoagulation and filtration completely eliminated the toxicity of synthetic wastewaters to algae (*P. subcapita*) even with the shortest treatment time (60 s).

Toxic pollutant removal by electrocoagulation was also studied with debarking effluents. Statistical experimental design and partial least squares modeling were used to investigate the effect of initial pH, current (current density) and treatment time on pollutant removal. According to the results:

- Electrocoagulation enhanced color removal. The model predicts optimum removal with intermediate current, long treatment time, and high initial pH. The lowest measured color value was 93 PtCo. Some DOC was removed with high current density and long treatment time.
- According to the model, toxicity was associated with sample color. Optimum toxicity removal is predicted with same parameters as optimum color removal. The lowest EC_{50} value based on the solution strength was 22%.

In summary, electrocoagulation combined with separation technologies such as filtration, sedimentation or flotation offers a potential method for the removal of toxic pollutants from pulp mill wastewaters. However, further studies are required to optimize the treatment. Addition of oxidants to mill wastewater could further increase the efficiency of coagulation due to enhanced oxidation of ferrous iron to ferric form, which is known to have better coagulation performance.

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References

[1] M. Ali, T.R. Sreekrishnan, Aquatic toxicity from pulp and paper mill effluents: a review, Adv. Environ. Res. 5 (2001) 175–196.
[2] D. Pokhrel, T. Viraraghavan, Treatment of pulp and paper mill wastewater – a review, Sci. Total Environ. 333 (2004) 37–58.
[3] P. Bajpai, Environmentally Friendly Production of Pulp and Paper, John Wiley & Sons, Hoboken, 2010.
[4] J.A. Field, M.J.H. Leyendeckers, R. Sierra-Alvarez, G. Lettinga, L.H.A. Habets, The methanogenic toxicity of bark tannins and the anaerobic biodegradability of water-soluble bark matter, Water Sci. Technol. 20 (1988) 219–240.
[5] M.K. Korczak, S. Koziarski, B. Komorowska, Anaerobic treatment of pulp and paper mill effluents, Water Sci. Technol. 24 (1991) 203–206.
[6] J.A. Field, S. Kortekaas, G. Lettinga, The tannin theory of methanogenic toxicity, Biol. Waste 29 (1989) 241–262.
[7] J.H.M. Temmink, J.A. Field, J.C. Haastrecht, R.C.M. van Merkelbach, Acute and sub-acute toxicity of bark tannins in carp (*Cyprinus carpio*, L.), Water Res. 23 (1989) 341–344.
[8] G. Peng, J.C. Roberts, Solubility and toxicity of resin acids, Water Res. 34 (2000) 2779–2785.
[9] A. Kostamo, B. Holmbom, J.V.K. Kukkonen, Fate of wood extractives in wastewater treatment plants at kraft pulp mills and mechanical pulp mills, Water Res. 38 (2004) 972–982.
[10] A. Kostamo, J.V.K. Kukkonen, Removal of resin acids and sterols from pulp mill effluents by activated sludge treatment, Water Res. 37 (2003) 2813–2820.
[11] A.E.J. Wilson, E.R.B. Moore, W.W. Mohn, Isolation and characterization of Isopimaric acid degrading bacteria from sequencing batch reactor, Appl. Environ. Mirobiol. 62 (1996) 3146–3151.
[12] L.T.K. Chung, H.P. Meier, J.M. Leach, Can pulp mill effluent toxicity be estimated from chemical analysis, Tappi 62 (1979) 71–74.
[13] J.M. Leach, A.N. Thakore, Toxic constituents in mechanical pulping effluents, Tappi 59 (1976) 129–132.
[14] J.M. Leach, L.T.K. Chung, Development of a chemical toxicity assay for pulp mill effluents, US EPA publication No EPA-600/2-80-206, Ohio, USA.
[15] A. Oikari, B. Lönn, M. Caastren, T. Nakari, B. Snickars-Nikinmaa, H. Bister, E. Virtanen, Toxicological effects of dehydroabietic acid (DHAA) on the Trout *Salmo Gairdneri* Richardsonin fresh water, Water Res. 17 (1983) 81–98.
[16] J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, second ed., IWA publishing, London, 2006.
[17] M. Belmonte, C. Xavier, J. Decap, M. Martinez, R. Sierra-Alvarez, G. Vidal, Improved aerobic biodegradation of abietic acid in ECF bleached kraft mill effluent due to biomass adaptation, J. Hazard. Mater. B135 (2006) 256–263.
[18] T. Leiviskä, J. Rämö, H. Nurmesniemi, R. Pöykiö, T. Kuokkanen, Size fractionation of wood extractives lignin and trace elements in pulp and paper mill wastewater before and after biological treatment, Water Res. 43 (2009) 3199–3206.
[19] J.A. Field, G. Lettinga, The methanogenic toxicity and anaerobic degradability of a hydrolysable tannin, Water Res. 21 (1987) 367–374.
[20] T. White, Tannins – their occurrence and significance, J. Food. Sci. Agric. 8 (1957) 377–384.
[21] R.J. Stephenson, S.J.B. Duff, Coagulation precipitation of a mechanical pulping effluent – II. Toxicity removal metal salt recovery, Water Res. 30 (1996) 793–798.
[22] T. Leiviskä, J. Rämö, Coagulation of wood extractives in chemical pulp bleaching filtrate by cationic polyelectrolytes, J. Hazard. Mater. 153 (2008) 525–531.
[23] M.Y. Mollah, R. Schennach, J. Parga, D.L. Cocke, Electrocoagulation (EC) – science and applications, J. Hazard. Mater. B84 (2001) 29–41.
[24] M.Y.A. Mollah, P. Morkovksy, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals present and future perspectives of electrocoagulation, J. Hazard. Mater. B114 (2001) 199–210.
[25] I. Zongo, J.P. Leclerc, H.A. Maïga, J. Wéthe, F. Lepicque, Removal of hexavalent chromium from industrial wastewater by electrocoagulation: a comprehensive comparison of aluminium and iron electrodes, Sep. Purif. Technol. 66 (2009) 159–166.
[26] S. Aber, A.R. Amani-Ghadim, V. Mirzajani, Removal of Cr(VI) from polluted solutions by electrocoagulation: Modeling of experimental results using artificial neural network, J. Hazard. Mater. 171 (2009) 484–490.
[27] I. Heidmann, W. Calmano, Removal of Zn(II), Cu(II), Ni(II), Ag(I) and Cr(VI) present in aqueous solutions by aluminium electrocoagulation, J. Hazard. Mater. 152 (2008) 934–941.

[28] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorisation of basic dye solution by electrocoagulation: an investigation of the effect of operational parameters, J. Hazard. Mater. B 129 (2006) 116–122.

[29] A. Alinsafi, M. Khemis, M.N. Pons, J.P. Leclerc, A. Yaccoubi, A. Benhammou, A. Nejmeddine, Electro-coagulation of reactive textile dyes and textile wastewater, Chem. Eng. Process. 44 (2005) 461–470.

[30] A. Aleboyeh, N. Daneshvar, M.B. Kasiri, Optimization of C.I. Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology, Chem. Eng. Process. 47 (2008) 827–832.

[31] S.M. Palácio, F.R. Espinoza-Guiñones, A.N. Módenes, C.C. Oliveira, F.H. Borba, F.G. Silva Jr., Toxicity assessment from electro-coagulation treated-textile dye wastewaters by bioassays, J. Hazard. Mater. 172 (2009) 330–337.

[32] S. Khoufi, F. Feki, S. Sayadi, Detoxification of olive mill wastewater by electrocoagulation and sedimentation processes, J. Hazard. Mater. 142 (2007) 58–67.

[33] S. Khoufi, F. Aloui, S. Sayadi, Extraction of antioxidants from olive mill wastewater and electro-coagulation of exhausted fraction to reduce its toxicity on anaerobic digestion, J. Hazard. Mater. 151 (2008) 531–539.

[34] F. Hanafi, O. Assobhei, M. Mountadar, Detoxification and discoloration of Moroccan olive mill wastewater by electrocoagulation, J. Hazard. Mater. 174 (2010) 807–812.

[35] K. Yetilmezsoy, F. Ilhan, Z. Sapci-Zengin, S. Sakar, S.T. Gonullu, Decolorization and COD reduction of UASB pretreated poultry manure wastewater by electrocoagulation process: a post-treatment study, J. Hazard. Mater. 162 (2009) 120–132.

[36] S. Chowwanapoonpohn, S. Chewchanwuttiwong, M.J. Garson, D. Buddhasukh, Electrocoagulation and recovery of tannins from tree barks, J. Appl. Electrochem. 33 (2003) 647–650.

[37] J. Lappalainen, R. Juvonen, K. Vaajasaari, M. Karp, A new flash method for measuring the toxicity of solid and colored samples, Chemosphere 38 (1999) 1069–1083.

[38] M.R. Soimasuo, A.E. Karels, H. Leppänen, R. Santti, A.O.J. Oikari, Biomarker responses in whitefish (*Coregonus lavaretus* L. s.l) experimentally exposed in a large lake receiving effluents from pulp paper industry, Arch. Environ. Contam. Toxicol. 34 (1998) 69–80.

[39] R.G. Brereton, Applied Chemometrics for Scientists, John Wiley & Sons Ltd., England, 2007.

[40] M.B. Sasson, W. Calmano, A. Adin, Iron-oxidation processes in an electroflocculation (electrocoagulation) cell, J. Hazard. Mater. 171 (2009) 704–709.

Series title and number
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Title	**Electrocoagulation in the treatment of industrial waters and wastewaters**
Author(s)	Mikko Vepsäläinen
Abstract	Chemical coagulation is commonly used in raw water and wastewater treatment plants for the destabilisation of pollutants so that they can be removed in the subsequent separation processes. The most commonly used coagulation chemicals are aluminium and iron metal salts. Electrocoagulation technology has also been proposed for the treatment of raw waters and wastewaters. With this technology, metal cations are produced on the electrodes via electrolysis and these cations form various hydroxides in the water. In addition to this main reaction, several side reactions, such as hydrogen bubble formation and the reduction of metals on cathodes, also take place in the cell. In this research, the applications of electrocoagulation were investigated in raw water treatment and wastewater applications. The surface water used in this research contained high concentrations of natural organic matter (NOM). The effect of the main parameters – current density, initial pH, electric charge per volume, temperature and electrolysis cell construction – on NOM removal were investigated. In the wastewater treatment studies, the removal of malodorous sulphides and toxic compounds from the wastewaters and debarking effluents were studied. Also, the main parameters of the treatment, such as initial pH and current density, were investigated. Aluminium electrodes were selected for the raw water treatment, whereas wastewaters and debarking effluent were treated with iron electrodes. Aluminium is more suitable electrode material for electrocoagulation applications because it produces Al(III) species. Metal ions and hydroxides produced by iron electrodes are less effective in the destabilisation of pollutants because iron electrodes produce more soluble and less charged Fe(II) species. However, Fe(II) can be effective in some special applications, such as sulphide removal. The resulting metal concentration is the main parameter affecting destabilisation of pollutants. Current density, treatment time, temperature and electrolysis cell construction affect the dissolution of electrodes and hence also the removal of pollutants. These parameters have minimal significance in the destabilization of the pollutants besides this effect (in the studied range of parameters). Initial pH and final pH have an effect on the dissolution of electrodes, but they also define what aluminium or iron species are formed in the solution and have an effect on the ζ-potential of all charged species in the solution. According to the results of this study, destabilisation mechanisms of pollutants by electrocoagulation and chemical coagulation are similar. Optimum DOC removal and low residual aluminium can be obtained simultaneously with electrocoagulation, which may be a significant benefit of electrocoagulation in surface water treatment compared to chemical coagulation. Surface water treatment with electrocoagulation can produce high quality water, which could be used as potable water or fresh water for industrial applications. In wastewater treatment applications, electrocoagulation can be used to precipitate malodorous sulphides to prevent their release into air. Technology seems to be able to remove some toxic pollutants from wastewater and could be used as pretreatment prior to treatment at a biological wastewater treatment plant. However, a thorough economic and ecological comparison of chemical coagulation and electrocoagulation is recommended, because these methods seem to be similar in pollutant destabilisation mechanisms, metal consumption and removal efficiency in most applications.
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