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Sähkösaostus teollisuuden jätevesien puhdistuksessa ja vaihtelevassa vedenlaadussa

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Sähkökemialliset vedenpuhdistustekniikat mahdollistavat jäteveden puhdistuksen ilman saostuskemikaaleja ja niistä syntyviä jäännöspitoisuuksia. Työn aiheena on selvittää sähkösaostuksen toimivuus teollisuuden kaatopaikan suotovesissä keskittyen erityisesti sulfaattien ja kloridien poistoon.

Diplomityön teoriaosuudessa käydään läpi teollisuuden jätevesien puhdistamisen tarpeellisuutta lainsäädännön ja esimerkkien avulla. Osuudessa käydään läpi myös yleisimmät teollisuuden jätevesissä esiintyvät haitta-aineet ja niiden vaikutukset ympäristöön, sekä ihmisiin. Sähkökoagulaation soveltuvuutta arvioidaan kirjallisuuslähteiden kautta käymällä läpi kaikki tärkeimmät toimintaan vaikuttavat parametrit ja mahdollisuudet vaikuttaa niihin kustannustehokkaasti.

Teoriaosuudessa selvitettyjen tulosten perusteella suoritettiin pilot -mittakaavan testiajoja sähkösaostus laitteistolla hyödyntäen eri elektrodimateriaaleja. Testitulosten perusteella laitteiston parametrejä säädettiin suurempien reduktioiden saavuttamiseksi keskittyen erityisesti sulfaattien ja kloridien poistoon. Työn perusteella havaittiin, että tulosten epävarmuus ja laitteiston herkkyys vaihtelevalle pH:lle tekevät siitä epävarman ja täten lisäävät riskiä investoitaessa suuremman mittaluokan laitteistoon.

ABSTRACT

Lappeenranta-Lahti University of Technology LUT
School of Energy Systems
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Suitability of electrocoagulation for industrial wastewaters and changing water quality

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85 pages, 24 tables, 13 figures, 7 appendices

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Electrochemical water treatment methods are well suited for treatment of wastewater without a need for coagulation chemicals thus eliminating residual concentrations. The target of this master thesis is to evaluate the functionality of electrocoagulation for treatment of effluents from industrial waste treatment centre containing high concentrations of sulfates and chlorides.

The theoretical part of this paper explains the need for industrial wastewater treatment and the legislation concerning it. Also, most common elements in industrial effluents are explained and the effect for environment and human health clarified. Suitability of electrocoagulation is examined by going through literary sources around the topic and finding parameters that can be altered for better results cost-effectively.

Based on the theory, pilot -scale test runs are executed by utilizing different electrode materials. Parameters are changed based on the results for optimizing sulfate and chloride removal. Findings show that proper removal of sulfates and chlorides was uncertain, and sensitive for pH changes. This would increase the risk of a major industrial investment for types of waters tested.

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In Lahti 13 October 2019

Valtteri Visakorpi

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LIST OF SYMBOLS

Me	electrode material	, -
Z	number of electrons	, -
e	electron	, -
m	mass of dissolved electrode material	, g
I	current	, A
t	contact time	, s
M	molecular weight	, g/mol
F	faraday's constant	, 96,500
C/mol		
C	concentration	, %
V	volume	, m ³
RedOx	reduction-oxidation potential	, mV
DGS	disinfection by-products	
EC	electrocoagulation	
EF	electroflotation	
COD	chemical oxygen demand	

BOD	biological oxygen demand
TOC	total organic carbon
RuO ₂	ruthenium oxide
Pt	platinum
IrO ₂	iridium oxide
BDD	boron doped diamond
TDS	total dissolved solids
PbO ₂	lead oxide
SnO ₂	tin oxide

1 INTRODUCTION

1.1 Background

Lack of clean and safe water is one of the biggest challenges that people around the globe will face in coming years. Water systems are being polluted, especially, from anthropogenic activities such as industrial effluents. Together with increasing population, urbanization and climate change, the reuse of water in parts of the world becomes a necessity thus adding pressure for developing efficient water treatment technologies for variety of different pollutants. (Mollah et al. 2000). Landfill leachate is one of the most challenging types of industrial wastewater due to its high concentration of organic compounds, ammonia, heavy metals and salts. Typical feature is, also, the high variability in quantity and quality which makes the efficient treatment difficult. (Silva et al. 2016). Hence the hierarchy of environmental pollution presented in figure 1 controls the water management and it should direct the actions and strategies in every industrial activity.

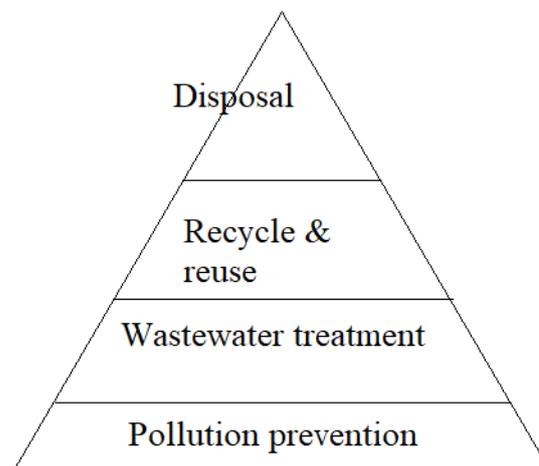


Figure 1. Hierarchy of environmental pollution (Ranade & Bhandari 2014).

Base of the pyramid refers to a ZERO waste scenario where industrial processes generate, as the name suggests, zero effluents. As this is almost never the case, the next two steps are the most important and most relevant. Produced wastewater should be treated and reused whenever possible. In industrial settings this can be done by purifying the water enough for a reuse in other processes, like for cooling water or wash water. Hence, the strategy for industrial water treatment can be presented as 3R -model, reduce-recycle-reuse. The last and most unwanted option is the disposal. The amount of disposed material should be minimized following the 3Rs. Still, some material that cannot be utilised again and waste is always generated and should be disposed in safe manner. The 3R -model is relevant is both, solid and/or liquid pollutants. (Ranade & Bhandari 2014, 19-22).

Most commonly used methods for treatment of wastewaters include variation of different physico-chemical processes such as, filtration, air stripping, ion-exchange, chemical precipitation, chemical oxidation, carbon absorption, ultrafiltration, reverse osmosis, volatilization and gas stripping. (Mollah et al. 2000). Even tough chemical methods are widely used, they involve major disadvantages relating to a formation of disinfection by-products generated species (DGSs) and high cost of excessive chemical consumption. (Hakizimana et al. 2017).

Electrochemical water treatment technologies have been proposed as an alternative since they are free from such problems and provide more efficient, reliable and versatile option for chemical treatment. Electrochemical methods consist of different technologies that are electrocoagulation (EC) /electroflotation (EF), electrodialysis, electrooxidation, electroreduction, photoassisted electrochemical methods and sonoelectrolysis methods. (Feng et al. 2016). Electrochemical treatments have gained popularity mostly due to decrease of electricity prices and increasing awareness towards environmental issues by encouraging “green development” (Samer 2015).

Electrocoagulation is one of the most widely commercially used electrochemical technologies and it has been proven to remove wide range of pollutants. Still, the lack of scientific attention has left some mechanics of EC unsolved, for example, very little consideration has been given to factors that affect the effective removal of certain ionic species, or parameters for systematic cell design which, both, limit the universal usability for all wastewater types. (Hakizimana et al. 2016; Mollah et al. 2000).

1.2 Research Problem

This study is about the utilization and correct cell design of electrocoagulation pilot equipment in industrial wastewater treatment. The work is carried out by the request of Fortum Waste Solutions Oy, and the waters to be tested are gathered from Fortum's waste treatment centre in Hausjärvi area, near Riihimäki. The collection area is receiving wide range of different wastes, which are listed below:

- Industrial waste
- Wastes from the treatment of municipal waste
- Contaminated soil
- Ash from incineration of municipal and hazardous waste
- Contaminated sludge
- Used vehicle tires
- Waste from car shredding
- Concrete waste
- Construction/demolition waste
- Asbestos waste
- Digestate from biorefineries
- Impregnated wood

Resulting runoff waters are complex mix of changing water quality and pollutant concentrations. Due to the heterogenous nature of resulting wastewaters, it is important to find working parameters to meet the requirements of the environmental permit and to evaluate the need of aftertreatment.

Waters from Fortum's treatment centres comprises of high concentrations of chlorides (Cl^-) and sulfates (SO_4^{2-}). Also, concentration of other harmful pollutants, such as heavy metals and COD, will be monitored to ensure sufficient water quality.

Objectives to be fulfilled are listed below:

- Evaluating the suitability for electrocoagulation to work in larger scale industrial design for types of waters containing high concentrations of sulfates and chlorides
- Defining parameters to ensure uninterrupted treatment of wastewaters containing high concentration of sulfates and chlorides. Main parameters that can be altered are initial/during/after pH, addition of polyelectrolytes, current at the electrodes and electrode material
- Reviewing literature researches around the topic and summary of similar tests conducted for variety of wastewaters using electrocoagulation and/or similar methods. Based on the literature review, preliminary forecast of the suitability can be made
- Performing test runs using pilot equipment with different water compositions to gather data for future use, and to obtain clear picture of the dissolution of anode material and the possible passivation of electrodes. Also, the formation of chlorine gas will be monitored and treated as required.

2 LEGISLATION CONCERNING INDUSTRIAL WASTEWATERS

2.1 Demand for Industrial Wastewater Treatment

In the late summer 2017, Viikinmäki wastewater treatment plant, which is the largest wastewater treatment facility in Finland, suffered severe disturbance that resulted for increased amounts of nitrogen concentration in effluents that eventually flowed to Gulf of Finland. Viikinmäki treatment plant uses biological nitrogen removal and suffered from unknown source of industrial activity that disrupted the bacterial balance needed for efficient nitrogen removal. Elevated nitrogen loadings were observed in the vicinity of wastewater discharge point. (Niemi 2018).

Above mentioned scenario is an example of why functioning industrial wastewater treatment is needed. In Finland, water services act requires municipal water utilities to treat waters that are similar as household waters (Finnish Water Utilities Association. 2018, 1). Hence, industrial effluent containing high concentrations of pollutants can disrupt the normal operation of wastewater plants designed to treat only household waters. In addition to disruption in processes, some areas in the world discharge industrial effluents straight to nature, even though, water treatment plant exists. For example, the non-existing pre-treatment of industrial wastewater in Kasur, Pakistan, has caused deteriorating surface and ground water quality as the local water treatment plant can not handle industrial scale effluents. (Nafees et al. 2015, 1). Contaminated waters and climate change together aggravate the water scarcity, especially in developing countries, bringing wastewater management being one of the most crucial problems to be solved in coming years by promoting water reuse and recycling. (Ranade & Bhandari 2014, 521).

2.2 General terms

Industrial wastewaters typically include wide variety of different waters originating from many different operations. Finnish Water Utilities Association (2018) defines industrial

wastewaters as “wastewater that is conveyed to sewers and differs from normal domestic wastewater in its quality”. These waters are from industrial processes like, for example, textile and paint industry and waters from landfills or runoffs from contaminated soil remediation. Industrial wastewater treatment is technically, administratively and legislatively complex matter which requires working exchange of information between parties. Main parties included in the industrial wastewater treatment are municipality, water utility, operator and the authorities granting permits and supervising. (Finnish Water Utilities Association. 2018, 1).

Water utilities and operators are the most important parties when it comes to defining the industrial wastewater agreement. Water utility is responsible for providing household water for customers and to organize sewerage and treatment of wastewater. These requirements are written in the water services act. Property that is located on the operational area of water utility, which is determined by municipality, must be connected to the sewer of that utility. However, water utilities can decline to connect a certain property into the sewage network if the conveyed water would affect negatively for the wastewater treatment processes. Utilities can also decline to provide water for the operator if its consumption would negatively affect the operation. Water service act does not require water utility to treat such waters from operator that produces large amounts of difficult waters. Agreement can be still made between operator and utility which is based on civil law and is called industrial wastewater agreement. (Finnish Water Utilities Association. 2018, 18).

Industrial wastewater agreement is implemented when an operator conveys non-household wastewater into utilities sewage networks. The agreement is usually made with operator that falls under environmental permit. If, however, operator does not hold environmental permit, the agreement is specifically decided in every case by the water utility. (Finnish Water Utilities Association. 2018, 21).

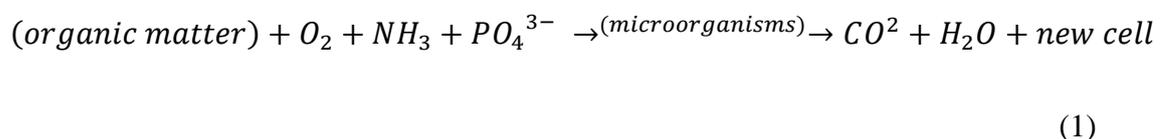
3 CHEMICAL AND BIOLOGICAL WASTEWATER TREATMENT

Most common wastewater treatment options can be divided into two segments which are chemical and biological treatment. Biological treatment refers to a secondary treatment of water where organic matter is treated in aerobic or anaerobic conditions by microorganisms or algae and fungi. Biological options include oxidation ponds, aeration lagoons, aerobic bioreactors and activated sludge. (Samer 2015).

Chemical treatment refers to a process where chemicals are added in order to remove inorganic components and is usually used as tertiary treatment with biological processes. Chemical treatment methods include chemical precipitation, ion exchange, neutralization, absorption and disinfection. (Samer 2015).

3.1 Treatment with microorganisms

Treatment with microorganisms is a biological way to oxidize dissolved biodegradable constituents into acceptable form and capture colloidal solids into a biological floc or biofilm. In industrial waters pre-treatment may be needed as municipal wastewater plants commonly utilize biological treatment options and a release of large quantities of toxic waters could potentially disrupt the functionality of wastewater plant. The basic principle of biological treatment by microorganisms is the oxidation of organic species into water and carbon dioxide which can be seen in simplified equation 1.



(1)

(Tchobanoglous et al. 2014, 555).

Ammonia and phosphate are presented as the nutrients that are required for a microorganism to work. As the organics are converted, a new biomass i.e. sludge is created (new cell) together with water and carbon dioxide. (Tchobanoglous et al. 2014, 556).

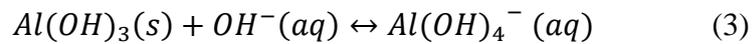
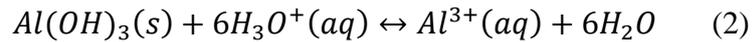
In biological treatment the C: N: P (BOD:TN:Ptot) ratio is crucial for the system to work. The nutrient concentrations should correspond the needs of the microorganisms as otherwise the bacteria will not convert the biological matter efficiently. Correct ratio is between 100:10:1 and 100:5:1. The varying quality of wastewater results for different ratios in the influent water. Usually so that excess nitrogen and phosphorus is present but can be eliminated from the water without difficulties. If the ratio of, for example, BOD and nitrogen goes widely out of range, the efficiency of denitrification process is impaired. This will result for high nitrate concentration in the outflow if not corrected. For increasing the organic matter, the accumulated sludge can be circulated back to the beginning of the process, or by adding it from external sources. In the same way, nutrients can be added externally if a deficiency is detected. (Treatment plant operator 2018).

3.2 Chemical flocculation

As chemical precipitation is close to electrocoagulation, it is explained more thoroughly compared to other chemical treatments. Chemical precipitation means coagulation and flocculation process that can be done with different coagulant chemicals. The resulting sludge can be removed by, for example, sedimentation or flotation. Chemical precipitation is a widely used technique, but as current trend is to reduce chemical use other alternatives like electrocoagulation and supplementary non-chemical options are increasing in value. (Samer 2015).

In more detail, chemical coagulation refers to aggregation of pollutants by addition of alum or ferric compounds which result for metal ion hydrolysis products. These species trap impurities and form solid flocs which will then be precipitated. (Tchobanoglous 2014, 460-468). The working principle follows two different methods: Adsorption and charge neutralization and enmeshment in sweep floc. Adsorption and charge neutralization refers to a adsorption of mononuclear and polynuclear metal species on the colloidal particle. Charge neutralization might occur simultaneously as the negative surface charge of pollutants is neutralized by metal salts. If enough metal coagulant is added, large amount of amorphous metal hydroxide flocs will be formed and cause a “sweep floc” phenomena. Large floc particles will exceed the buoyancy of water and result for rapid settling while descending flocs sweep through the medium and entrap colloidal particles. (Saukkoriipi 2010, 20).

The formation of correct metal hydrolysis species is highly influenced by the pH of the medium. For example, aluminium will form soluble outcomes in, acidic water by equation 2 and also in highly alkaline surroundings by equation 3.



(Tchobanoglous 2014, 468)

The solubility of aluminium and iron hydrolysis products follows the pH of the water. Figure 2 represents solubility diagram for aluminium hydroxyl. The operation range, where most insoluble aluminium exists, is pH range of 5 to 7 with minimum solubility at 6. For iron, it has been found that minimum solubility happens between 7 to 9. (Tchobanoglous 2014, 460-468).

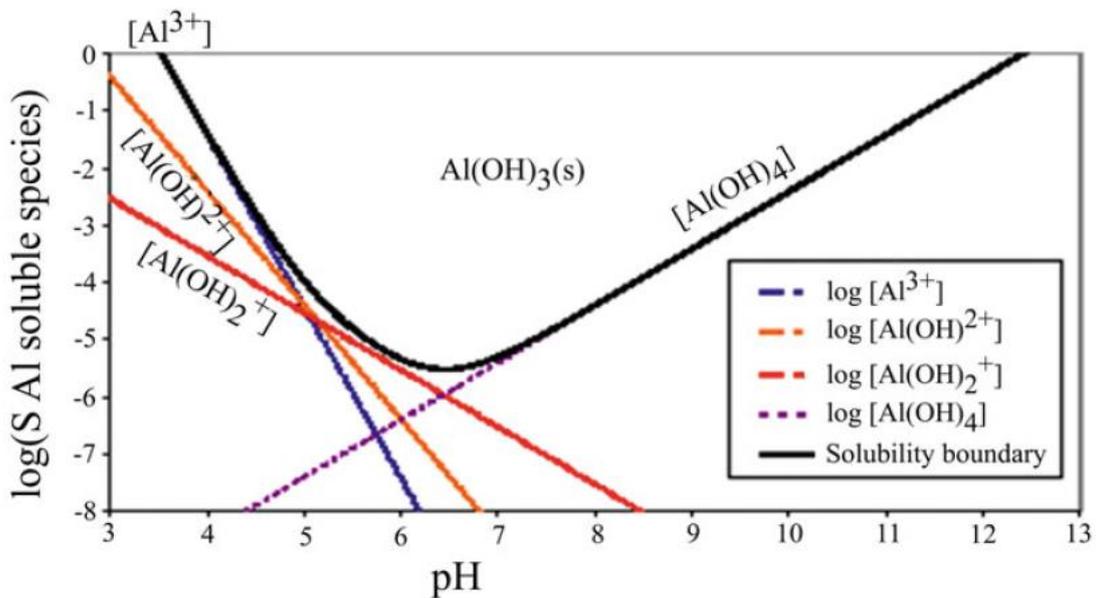


Figure 2. Solubility of aluminium hydroxyls in different pH (Mondal 2018)

The major downside of chemical flocculation is, in addition of increased cost, the resulting counter ion of added chemical. Most commonly used inorganic metallic chemicals are different aluminium chloride/sulfate compounds or ferric chloride/sulfate. Trace elements limit the usability in waters that contain already high concentrations of sulfates and/or chlorides, and which have to reach tight limits from wastewater permits.

4 ELECTROCOAGULATION AND PARAMETERS AFFECTING EFFICIENCY

4.1 Description of the technology

Electrochemical water treatment methods have gained popularity due to their potential to eliminate the shortcomings of more classical treatment options. Electrocoagulation is one of those technologies that could replace traditional, in this case chemical coagulation, in many places. Some of the advantages compared to it are presented below:

- Ease of operation
- Resistance to variable reactions and species in wastewater
- Simple equipment
- Less retention time
- Rapid sedimentation and formation of flocks
- Less sludge is formed during the process
- Less space is needed
- No need for chemicals

(Ogedey & Tanyol 2017).

Electrocoagulation encompasses also some disadvantages that should be noted before implementing it in a larger scale. Dissolution of sacrificial electrodes into wastewater as a result of oxidation leads to a need for replacing electrodes once in a while which, depending on the material, might become expensive. Also, places with high electricity prices, the cost of operation will be a substantial expenditure and reduce the benefits compared to chemical treatment. Furthermore, impermeable oxide film may be formed on the electrode which leads to a poor efficiency and increased energy consumption. Naturally, high conductivity of wastewater is, also, needed as electrocoagulation relies on electric current between electrodes. If the conductivity is not high enough, electrolytes like NaCl, BaCl₂, KCl can be used to increase it, but it will again increase the operating expenditures of the system and results for increased salt concentration. (Yosuf et al. 2000).

Inert or dissolving materials can be used in electrocoagulation which will lead to a different results and working mechanisms. When electric current is routed through electrodes, oxidation occurs at anode and reduction at cathode. In a case of dissolving material, usually aluminium or iron, metal cations are generated at the anode as the equations 4 suggests.



Me = anode material

Z = number of electrons transferred

e = electron

(Katal & Pahlavanzadeh. 2010).

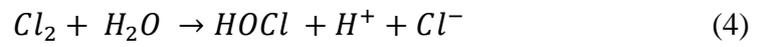
The produced metal cations will then hydrolyse and form metal hydroxyls with free hydroxyl radicals produced at the cathode, which will then destabilise and aggregate or precipitate/absorb suspended and dissolved particles. Due to electrophoresis, negatively charged pollutants and hydroxyl radicals migrate toward anode and positively charged metal cations and separate the water-contaminant mixture into floating layer, sediment layer and clear water which can be extracted from the EC unit by traditional methods. Prevailing hydrolysis product is a result of pH of the water and the electrode material used. (Katal & Pahlavanzadeh. 2010).

In a case of high anode potential, secondary reactions, like oxidation of Cl^{-} , H_2O and organic compounds following equations 2 and 3, may occur. Chlorine (Cl_2) will then hydrolyse and form hypochlorous acid (HOCl) by equation 4 which can then be ionized to hypochlorite ion (OCl^{-}) seen in equation 5 based on the pH of the solution as figure 3 shows. Furthermore, the formation of oxygen generates bubbles that will raise the coagulated pollutants to the surface of the unit.





(Hakizimana et al. 2016)



(Tchobanoglous et al. 2014, 8)

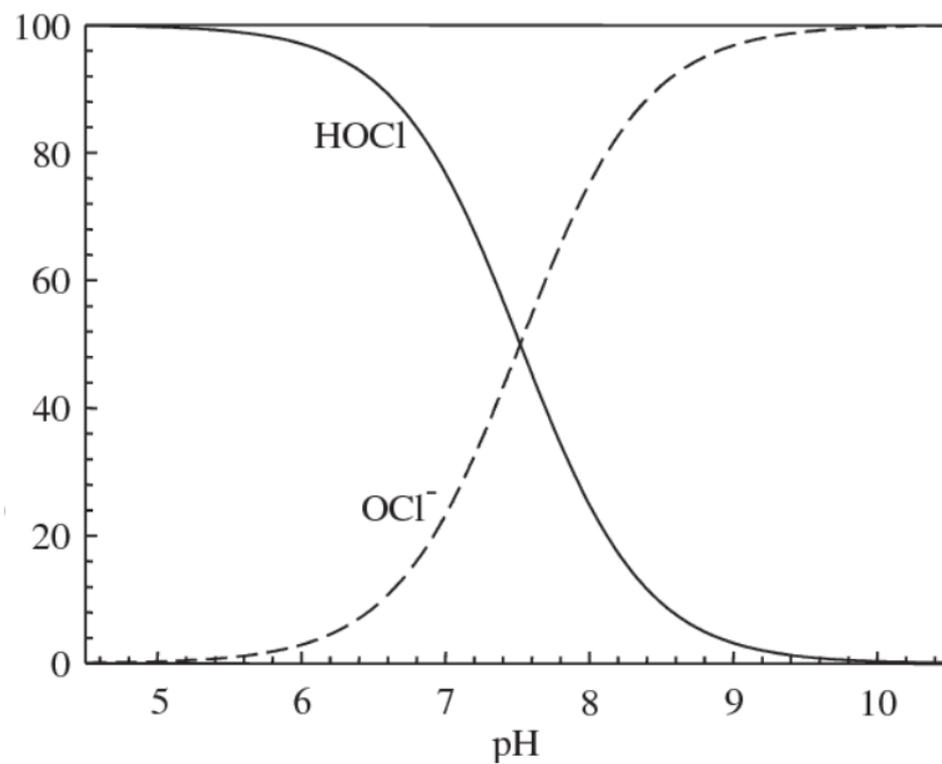
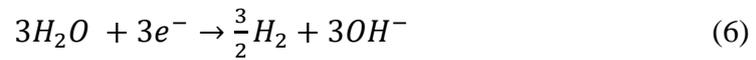


Figure 3 Hydrolysis of HOCl and OCl⁻ based on the pH of the water (Tchobanoglous et al. 2014, 8)

At the cathode water is reduced into hydrogen gas and hydroxyl anions as equations 6 shows. The formation of hydrogen will result for bubbling which will rise the coagulants to the

surface. The release of hydrogen gas will, also, increase the solution pH which leads to tendency for EC to neutralise highly acidic waters.



(Hakizimana et al. 2016)

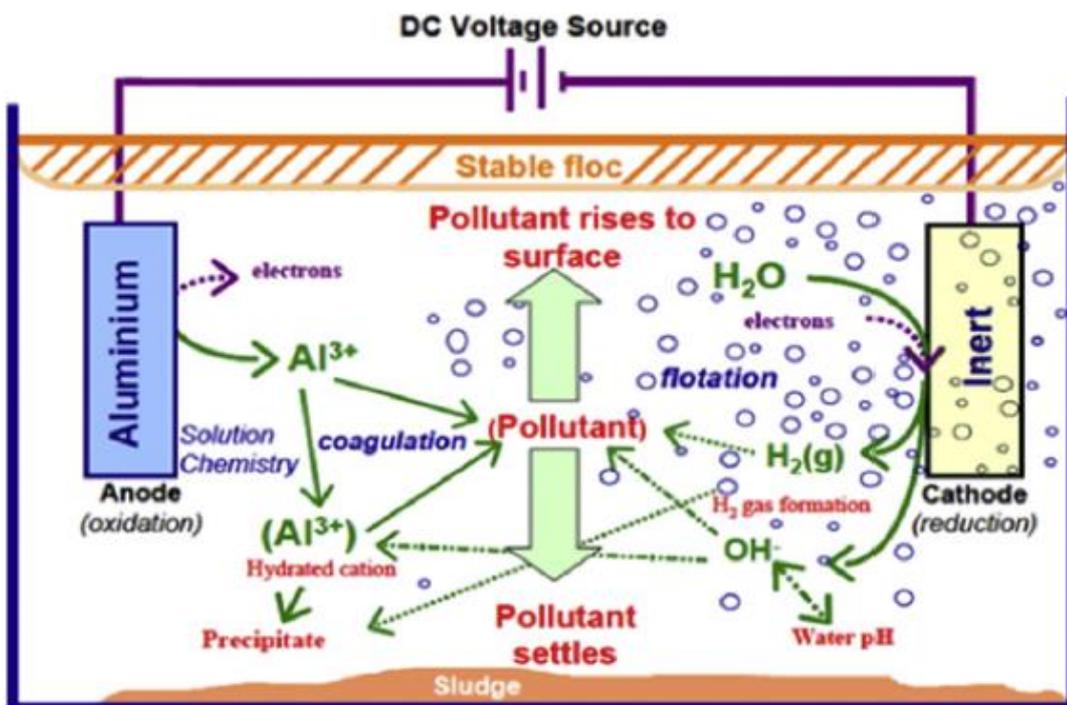


Figure 4. Simplified working principle of electrocoagulation unit (Hakizimana 2016).

Figure 4 presents simplified picture of electrocoagulation unit. Different cell designs and electrode materials are explained in more detail in relevant chapters. The amount of dissolved metal at the anode can be calculated with faradays law by the equation 7.

$$m = \frac{itM}{ZF} \quad (7)$$

m = mass of the dissolved electrode material [g]

i = current [A]

t = contact time [s]

M = molecular weight of electrode [g/mol]

Z = number of electrons involved in the reaction

F = faraday's constant [96,500 C/mol]

(Katal & Pahlavanzadeh 2010)

Faradays law is valid when all electrons participate only in the metal dissolution at the anode. Correction factor called, current efficiency or faradic yield, can be used if parallel reactions occur in the system simultaneously. Faradic yield can be under 1 if electrodes suffer from insulating layer or, in cases where chemical and electrochemical dissolution happen simultaneously, over 1. Faradic yields over one are common when using aluminum electrodes, which is due to additional dissolution at the cathode. (Hakizimana 2016).

In addition to colloidal particles, oils and other contaminants may be ionized, electrolyzed, hydrolyzed or altered by free radicals so the physical and chemical properties are changed. This can result for some contaminants to be released from water and be destroyed or made less soluble. (Mollah 2004).

4.2 Current density

One of the main factors affecting electrochemical treatment is current density [I/A]. It is the amount of current applied to a cross-sectional area of the electrode and is the main factor that defines which electrochemical reactions take place on the electrode surface. It also determines the rate of electrode dissolution, bubble generation, and electric potential in the cell, so it greatly affects the economics of the treatment. (Outotec 2019). Typical current

densities range from 1 mA/cm² to 15 mA/cm², even though, the required current is heavily based on the targeted pollutant. (Mondal et al. 2018). Muruganathan et al (2003) compared the removal of sulfates, sulfides and sulfites with different currents. They noticed that sulfides were removed almost completely with currents as low as 20 mA/cm², whereas, sulfates required at least 50 mA/cm² which resulted for 50% removal with iron anode.

Koby et al. (2003) observed that notably smaller current densities were needed for COD and turbidity removal, than for sulfuric compounds. The study concluded that for iron electrodes just 8 mA/cm² was enough for good removals and the removal efficiency did not increase further even with higher current. However, aluminium electrodes required 16 mA/cm² to reach the same efficiency in turbidity removal. COD never reached as good reductions with aluminium as with iron plates but still the results got better with higher currents.

Additional important parameter concerning scale-up of electrocoagulators is the ratio between surface area and volume (A/V). It is the only parameter affecting when designed bigger units while keeping the same inter electrode distance. Typically, ratios of 15 m²/m³ to 45 m²/m³ are being used. Increasing the ratio will lead to reduced treatment time and lower current density. Furthermore, when the area is high enough, current concentration (I/V) will become the most important parameter. The current concentration can be used together with faradays law to calculate concentration of coagulants at given time by equation 8.

$$c = \frac{M}{ZF} \times \left(\frac{I}{V}\right) \times t \quad (8)$$

c = concentration of metal cations [g/m³]

V = volume [m³]

t = time [s]

Under continuous mode, the volume of the basin makes it possible to define residence time for a considered flowrate and so the amount of released coagulants can be surmised. (Hakizimana 2016).

4.3 Electric conductivity

The electrical conductivity of water is a unit that expresses the water's capability to conduct an electric current and as electricity is conducted by ions in the solution, the conductivity is a direct measure of ion concentration in the water. Thus, electric conductivity can be used as a replacement for measuring total dissolved solids when more precise measurements are not available. Electric conductivity can be presented either in SI units as $\mu\text{S}/\text{cm}$ or as US customary units, $\mu\text{mho}/\text{cm}$. Equation for the estimate of dissolved solids is presented in equation 9.

$$TDS \cong \text{Electric conductivity} * (0.55 - 0.70) \quad (9)$$

TDS = total dissolved solids [mg/l]

(Tchobanoglous et al. 2014, 89)

The ionic strength of water affects all electrochemical processes. When the voltage is fixed, the current density increases with conductivity. In the same way, voltage decreases when current is kept the same while conductivity increases. Relatively high electric conductivity helps to achieve low voltage while maintaining high current thus reducing the total energy consumption. In addition to lower power requirement, addition of salts for better conductivity helps to create strong oxidant in situ in a form of chlorine. As the current affects the amount of generated metal cations, high current and low voltage is usually preferred. (Mondal et al. 2018).

Even though, high conductivity is usually connected to a better outcome of EC process, it mostly affects only the cost of operation. For example, Chavalparit & Ongwandee (2009) reached good results in suspended solids, COD and oil removal with a conductivity of just $350 \mu\text{S}/\text{cm}$. Chen et al (1999) discovered similar results from restaurant wastewater with conductivities ranging from $300 \mu\text{S}/\text{cm}$ to $500 \mu\text{S}/\text{cm}$. In addition, they concluded that conductivity did not have a notable difference for the removal efficiency in the range of $443 \mu\text{S}/\text{cm}$ to $2850 \mu\text{S}/\text{cm}$. Kobya et al. (2003) concluded that electric conductivity had a negative

effect in COD removal with aluminium electrodes when it was increased to over 3500 $\mu\text{S}/\text{cm}$. Between 1000 $\mu\text{S}/\text{cm}$ and 3500 $\mu\text{S}/\text{cm}$ removal efficiency was around 70%, but as it was increased further the efficiency decreased to 50%. The same experiment was repeated with iron electrodes but decrease in efficiency was not observed resulting for a conclusion that the efficiency drop can be related only to aluminium electrodes at highly conductive waters.

4.4 pH

One of the most important parameters affecting the efficiency of electrocoagulation is the pH of the solution. It affects the current efficiency, dissolution of electrodes and the resulting hydrolysis products. The formation of hydroxide precipitates from electrodes was presented in a study by Adelaide (2003). Figure 5 shows that poor coagulants, $\text{Al}(\text{OH})_4^-$ and $\text{Fe}(\text{OH})_4^-$, are formed in alkaline conditions. Also, the formation of Fe hydroxyls occurs in wider pH range than Al hydroxyls.

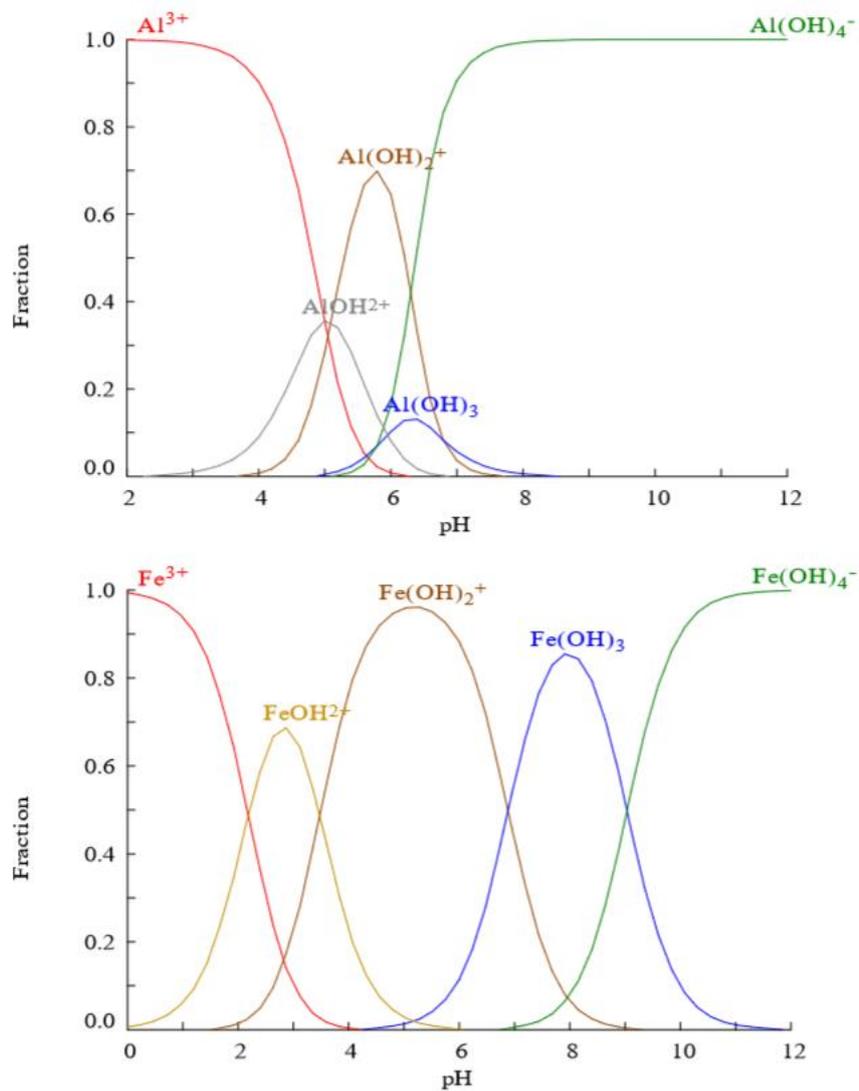


Figure 5. Different hydroxyl products based on the pH (Adelaide 2013, 20)

Other study by Chen et al (2000) noticed that the optimal pH for COD removal when using iron or aluminium electrode, was 7, although the reduction stayed relatively same in the pH range of 3 - 10. Dramatic drop in efficiency was observed only after pH going over 10. It was also observed that pH increased during the electrocoagulation when influent pH was acidic and decreased when initial pH was higher than 9. This means that EC act as pH neutralizer and would allow the effluent to be discharged into sewers without chemical adjustment. Also, some anions like SO_4^{2-} and Cl^- can exchange with OH^- in Al(OH)_3 to free OH^- which leads to an increase in pH. The decrease of pH at alkaline conditions was found to

originate from coprecipitation of Ca^{2+} and Mg^{2+} with $\text{Al}(\text{OH})_3$ in the form of hydroxide. Ogedey & Tanyol (2017) investigated, also, treatment of COD from landfill leachate with electrocoagulation. In their study, iron and aluminium electrodes were used and they found out that best COD removal happened between pH 6,5 - 8,5. This supports the findings from Chen et al. (2000) and states the best range for COD removal.

Muruganathan et al (2003) investigated the removal of sulfide, sulfate and sulfite ions from leather industry with electrocoagulation. They tested three different anode materials, Aluminium, iron and titanium in different solution pH and pollutant concentrations. They noticed that sulfates were removed most efficiently in acidic pH with Fe or Al anodes. Best efficiencies were 68% and 72% for Fe and Al respectively when the pH was 5,5. At pH 10,5 the reductions were only 22% and 20% which shows the importance of correct pH when removing sulfuric elements. The Al anode showed significant efficiency drop after pH 8,5 while Fe anode was drastically affected after pH 9,5. For both materials, the efficiency stayed relatively constant in pH range of 5,5 – 7,0 facing only 3 - 5% drop in reduction. Titanium anode was found to be inferior choice as it only oxidized sulfides into sulfates without removing them. During tests, sulfate concentration of 100 mg/l, current density 62 mA/cm² and 10 min coagulation time were used. Chloride reduction was non existing while COD was removed almost completely, from 1314 mg/l to 75 mg/l with Al anode.

Mamelkina et al (2017) investigated the removal of sulfates from acidic mining waters with electrocoagulation. The removal efficiency was highest at initial pH 2, and current density 12.4 Ah/dm³, they used once-through mode electro cell, i.e. water was channelled through cell without circulation. The study also concluded that even as high as 70 mA/cm² current density would be needed in order to reach good sulfate removals with EC. In addition, continuous electrocoagulation unit was found to be better solution than batch, as there was flocculation tank and a possibility to alter pH after EC.

4.5 Cell design

Electrocoagulator can be designed in different ways. In its simplest form, the unit consists of one anode and one cathode connected with external power source. Wastewater treatment involves large water volumes, thus making the correct cell design important parameter as

the sufficient rate of metal dissolution requires large electrode surface area. This can be achieved by having cells containing monopolar electrodes either in parallel or series connection. in some cases, even bipolar electrodes in parallel connection can be used. (Yousuf et al. 2000).

In monopolar parallel configuration anode and cathode are placed, as the name suggests, parallel to each other forming many individual cells in one unit. Each pair has its own voltage and current based on the resistivity between anode and cathode. This means that the output current from the power source is divided between all the electrodes in relation to the resistance of each cell. Figure 6 presents a simple monopolar parallel electrocoagulation unit. Number of electrodes can be increased based on the flowrate and volume of water to be treated in order for reaching sufficient ratio between surface area and volume. (Mollah et al. 2004).

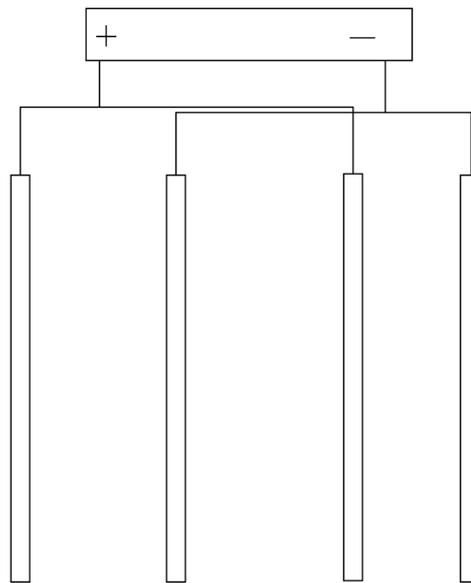


Figure 6. Monopolar parallel configuration

In monopolar series connection seen in figure 7, each pair of internal electrodes is connected to each other, while the outermost electrodes are only connected to the power source. The electric current passing through the electrodes is the same, but the total voltage is the sum of each individual cell. When compared to parallel configuration, higher potential is needed for a given current as the resistance is higher in series connection. (Mollah et al. 2004).

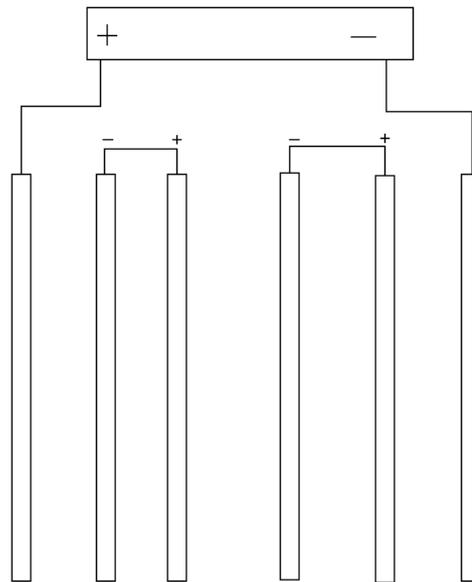


Figure 7. Monopolar series configuration

Bipolar parallel connection seen in figure 8 uses two outer electrodes connected to power supply while bipolar sacrificial electrodes are placed between them. Outer electrodes are monopolar and inner electrodes are bipolar. Bipolar electrodes are not interconnected, and each side has opposite charge compared to the parallel side besides it. The anodic dissolution happens at positive side, while negative side goes through cathodic reactions. Bipolar parallel system offers simple set-up and easy maintenance. (Mollah et al. 2004).

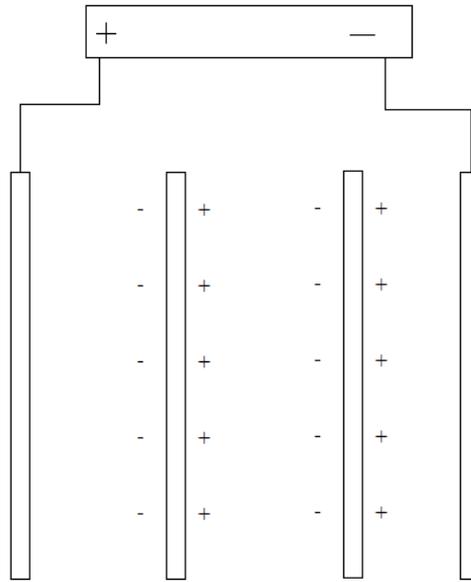


Figure 8. Bipolar parallel configuration

4.6 Electrode material

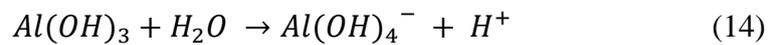
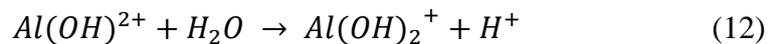
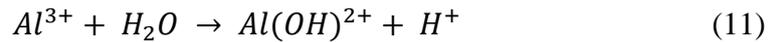
Electrode material can be either soluble sacrificial, like aluminium and iron or inert non-sacrificial like graphite or titanium. Soluble materials release metal cations as described previously, whereas, inert materials can remove metal ions from the solution and start coagulation of suspended solids or oxidise species based on the oxidation potentials. (Yosuf et al. 2000).

4.6.1 Aluminium

Aluminium electrodes have been widely used in electrocoagulation in many different occasions. The resulting hydroxyl group is based on the pH of the solution like figure 5 shows. The main reaction when using aluminium anode is shown in equation 10:



According to acid/base reactions aluminium cations forms different aluminium hydroxyl species by equations 11-14.



(Hakizimana et al. 2016).

The prevailing species can be deduced from figure 5, but in practise soluble Al^3 will prevail if pH is under 4 and equally soluble $Al(OH)_4^-$ aluminate will prevail with pH higher than 10. Otherwise, Insoluble $Al(OH)_3$ is observed to be predominant (Hakizimana et al. 2016).

Picard et al (1999) proved in their research the cathodic dissolution of aluminium and formation of aluminium hydroxyls which happens as the equation 15 shows. The paper compared hydrogen evolution with stainless steel (SS) and aluminium (Al) cathodes and noticed excess hydrogen evolution when using aluminium. This proved that the hypothesis based on equation 15 to only work with aluminium and not with stainless steel.



(Picard et al. 1999)

As a consequence, the amount of dissolved Al exceeds the calculated amount with Faradays law and a correction factor has to be used and the actual value can reach as high as 200% increase to theoretical value. (Hakizimana et al. 2016).

4.6.2 Iron

In a case of iron electrodes, the electrocoagulation forms iron hydroxides via different methods. Iron can be oxidised to ferric iron by single step process as equation 16 shows.



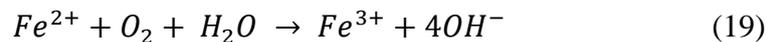
(Hansen et al. 2006)

A twostep process is, also, possible based on the anode potential. In equations 17 and 18 iron is first oxidised to ferrous iron and then to ferric iron.



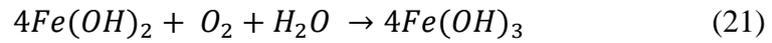
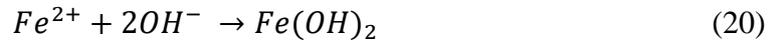
(Hansen et al. 2006)

Many studies assume that the anodic oxidation releases mostly Fe^{2+} due to poor dissolution of Fe^{3+} . Also, the transformation of Fe^{2+} to Fe^{3+} depends highly on the pH and amount of dissolved oxygen in the water. Hence, the oxidation of Fe^{2+} in acid conditions is very slow and follows the equation 19.



(Hakizimana et al. 2016)

In alkaline medium Fe^{2+} hydrolyzes rapidly into ferrous hydroxide which then turns into ferric hydroxide due to dissolved oxygen as seen in the equations 20 and 21.



(Hakizimana et al. 2016).

In oxygen depleted mediums the formation of green rust happens which consists mostly of $Fe(OH)_2$ after which partial oxidation can turn the precipitant into greenish-black. Additional access to dissolved oxygen will convert the ferrous oxide into hydrous ferric oxide or ferric hydroxide which can be noticed by the orange or red-brown appearance. (Moreno et al. 2007).

In addition, Fe^{2+} being a highly soluble it results for poor EC performance and usually Fe^{3+} is preferred in iron-based electrocoagulation. However, Electrocoagulation with iron electrodes requires more optimization for Fe^{3+} production than when using aluminium electrodes where the produced metal is always in Me^{3+} form. Hakizimana et al (2016) introduced four techniques, which are listed below, that can be used for improving Fe^{3+} formation:

- Water aeration to improve Fe^{2+} oxidation
- pH control to 7.5 or higher to improve oxidation of Fe^{2+}
- Increasing the residence time to promote complete oxidation of Fe^{2+}
- Having chloride in the water to gain oxidant in a form of chlorine

Chlorine from chlorides can be either achieved by direct oxidation at iron anode or in additional electrolysis cell with inert electrodes such as graphite, titanium or BDD. Chlorine will then oxidize Fe^{2+} as equation 22 shows. The concentration of chlorides should still be more than 600 mg/l in order for the process to be efficient.



(Alkan et a. 2004).

Additional advantages of iron include the cheap price compared to aluminium. Iron is also nontoxic, however, limits based on aesthetic and organoleptic reasons might exist. (Hakizimana et al. 2016). Ferric hydroxide can be detected by the red-orange precipitant whereas ferrous hydroxide forms greenish precipitant (Hansen et al. 2006).

4.6.3 Graphite

Graphite electrode is usually used as cathode material in electrocoagulation as it is inert and does not release metal hydroxyls in a same way as iron and aluminium as described in previous chapters, which makes it unsuitable for coagulation purposes.

When using graphite as anode, the process turns more into a form of electrooxidation (EO), as the main reaction happening is oxidation of water based and different constituents in the water based and the oxidation potential of them. Electrooxidation can occur indirectly with the help of different oxidising species or directly at the anode surface. At high chloride concentrations, typically over 3g/l, the formation of chlorinated species helps to oxidise organic pollutants. (Chen 2003).

Direct electrooxidation refers to formation of hydroxyl radicals at the anode surface. As OH^\cdot is more effective oxidant than O_2 , the oxygen evolution at anode is unwanted reaction that lowers the efficiency of electrooxidation. Thus, electrode materials with high oxygen overpotentials is usually preferred because otherwise most of the supplied current is wasted to split water. Table 1 presents the most common anode materials and their oxygen evolution potentials. (Chen 2003).

Table 1. Different oxygen evolution potentials for different anode materials (Chen 2003)

Anode	Value (V)
Pt	1.3
IrO ₂	1.6
Graphite	1.7
PbO ₂	1.9

SnO ₂	1.9
Pb-Sn	2.5
Titanium oxides	2.2
Si/BDD	2.3
Ti/BDD	2.7
DiaChem	2.8

Electrode materials with low oxygen evolution potential indicates better removal efficiency at lower current or with high concentrations of chemical reactants as, otherwise, the formation of oxygen causes significant decrease of efficiency. In addition, the formation potential of most common oxidants will determine what will occur at the anode. (Chen 2003).

Dbira et al. (2019) investigated the fate of chloride ions in electrooxidation when using either RuO₂, Pt, IrO₂ or BDD electrodes. Based on their findings, chlorides turned into higher oxidation species such as hypochlorite, chlorate, perchlorate and other volatile chlorine derivatives.

4.7 Coexisting ions

The electrolyte solutions have big effect for the proper functioning of the system and lifespan of electrodes. Electrocoagulation follows pseudo first and pseudo second kinetics which means that high concentrations competing anions might have negative effect for the performance of the EC. Also, it has been noted that some contaminants may compete with other, which lowers the efficiency of EC if high concentrations of competing anions exist in the electrolyte solution. For example, sulfate ions compete with fluoride ions which reduces the removal efficiency of fluoride. Also, fluoride and arsenate concentrations have been noticed to have negative effect on phosphate removal. (Adelaide 2013).

Arroyo et al (2008) discovered that high chloride concentrations enhanced the anode dissolution by corrosion on the surface of the electrode. It was supported with a study by Haki-zimana et al (2016) which stated that chloride ions promote the corrosion and removes the aluminum oxide film which helps the additional dissolution of aluminum. The positive effect of anions was declared to be in descending order: Cl^- , Br^- , I^- , F^- , ClO_4^- , OH^- , SO_4^{2-} . Also, Adelaide (2013, 25) found out that to ensure the breakdown of passive film, $\text{Cl}^-/\text{SO}_4^{2-}$ ratio should be higher than 0.1.

The presence of chloride ions, also, reduce the negative effect of SO_4^{2-} and HCO_3^- in second way, as the existence of those ions lead to a precipitation of Ca^{2+} or Mg^{2+} that will form insulating layer on surface of electrodes. Studies suggest that at least 20% of the anions in the water should be chlorides in order to reach normal long-lasting operating conditions. (Chen 2003,18)

Roa-Morales et al (2006) noticed how addition of H_2SO_4 and the resulting SO_4^{2-} affected the chemical equilibrium of the EC process with aluminium anode by formation of new insoluble chemical species at acidic waters. Most of the compounds were AlOHSO_4 , but also $\text{Al}(\text{SO}_4)_2^-$, AlSO_4^+ and $\text{Al}(\text{OH})_2^+$ were present in the solution.

When inert anodes are used in electrocoagulation, selective discharge of anions affects how they are discharged during electrolysis. The main factors are the concentration of anions and ease of discharge, if more than one type of anion is present in the solution. Ease of discharge of different anions is presented below:

- Sulfate ion, SO_4^{2-}
- Nitrate ion, NO_3^-
- Chloride ion, Cl^-
- Bromide ion, Br^-
- Iodide ion, I^-
- Hydroxide ion, OH^-

Ions at the bottom of the list discharge more easily at the anode, whereas, sulfate and nitrate ions are not discharged at all as they are positioned high up in the list. The concentration of

anions affects, also, which is oxidized even if that type of anion is higher at the list. In dilute aqueous solution OH^- ions forms water and oxygen, whereas, if concentration of iodide, bromide or chloride is higher, they will discharge more easily and form either iodine, bromine or chlorine molecule. (Jain 2016).

4.8 Temperature

Effect of temperature is not widely studied even though it affects the generation rate of hydroxyl radicals, dissolving of electrodes and solubility of the precipitants (Hashim et al. 2015). Katal & Pahlavanzadeh (2010) noticed that temperature had an effect for colour, phenol and COD removal. Temperature was evaluated at 10, 20, 30, 40 and 50 degrees of Celsius at constant current. Removal efficiencies were better at low temperature as the aluminium and iron were more soluble at higher degrees. Removal decreased between 10-20% when temperature was raised from 20 °C to 60 °C. However, some researches have reached opposite results so that removals increased as temperature increased.

Vepsäläinen (2018, 37) summarised different papers about the effect of temperature and concluded that if temperature is too high, dense flocs will form which will deposit on the electrode surface. Also, increasing temperature enhances the solubility of aluminium species. Still, as some studies found better performance at higher temperatures, only proven fact was that temperature might have positive or negative effect depending on the removal mechanism of pollutants.

5 INDUSTRIAL WASTEWATER CHARACTERISTICS

5.1 Metals

Several industries discharge heavy metals as a result of their production. Table 2 summarises most common industries and the resulting constituents. It is visible that chromium is the most common discharged product as it is a by-product of every presented industry. However, toxicity of different heavy metals changes based on the element. For example, even though chromium is most widely discharged, cadmium, copper, lead and mercury are notably more severe for living organism. These elements disrupt enzyme function by forming sulfur bonds in enzymes. They also bind to cell membrane stopping the movement through cell wall. (Munter 2019).

Table 2. Metal pollutants from most common industries (Munter 2019).

Industry	Al	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn
Pulp and paper				x	x	x	x	x	x
Organic chemistry	x	x	x	x		x	x		x
Alcalies, Chlorine		x	x	x		x	x		x
Fertilizers	x	x	x	x	x	x	x	x	x
Petroleum refineries	x	x	x	x	x		x	x	x
Steelworks		x	x	x	x	x	x	x	x
Aircraft plating, finishing	x		x	x	x	x		x	
Flat glass, cement				x					
Textile mill				x					
Tanning				x					
Power plants				x					

As heavy metals are extremely toxic even at low concentrations, the accurate monitoring and treatment should be utilised whenever the possibility for even small discharge exist. In 1956, the largest heavy metal poisoning was discovered in the city of Minamata in Japan. A local chemical plant discharged waste that contained mercury into Minamata Bay. As a result, 43

people died from consuming seafood from the contaminated bay. As of March 2001, some sources suggest even as many as 2265 victims had been recognised of which 1784 had died. Symptoms from mercury poisoning included paralysis, blindness, insanity, chromosome breakage, depression and different sort of birth defects. The discharged mercury accumulated and concentrated into fish fat tissue and caused poisoning when eaten. (Munter 2019).

5.2 Inorganic compounds causing corrosion

Inorganic non-metallic compounds derive from background levels in water and from domestic and industrial actions. Inorganic elements in industrial wastewater consist of nitrogen, phosphorus, chlorides and sulfates. Chlorides and sulfur compounds are those that are highly corrosive to pumps and sewages.

Halogen group consist of chlorine, fluorine, bromine, iodine and astatine. Halogens are strongly electronegative metalloids that are good oxidizers. Due to their electronegativities, the prominent oxidation state for halogens is - I. Most common halogen is chlorine and most of it is in inorganic form as chloride and stored in seawater and salt stocks. The circulating amounts of sea salt provide chloride to all parts of the world, due to this, Cl^- is found in all-natural waters. High concentrations of chloride are corrosive for the sewers and pumping stations if they are near the concrete's surface so that chlorides in water can be in direct contact with it. Thus, industrial wastewater permits usually set limits for chloride effluents. Also, as the conventional wastewater treatment technologies are not enough for chloride removal and a need for efficient pre-treatment is usually at place (Tshobanoglous et al. 2014, 92).

Sulfur compounds are common in industrial water as well, and they create different corrosion causing substances in sewages. Sulfur exists in nature in sulphide- and sulfate minerals and as elemental sulfur in different oxidation states, of which sulfates (+VI) is largest and sulfides (-II) lowest. In anaerobic conditions sulfur compounds are decomposed to hydrogen sulphide gas by bacterial action which is then absorbed into the humid wall of concrete pipes. As the water reaches aerobic conditions, hydrogen sulphide gas turns into sulfuric acid, which is highly corrosive to the pipes. (Finnish Water Utilities Association 2018).

Sulfides, which are derivatives of hydrogen sulfide, are harmful to concrete structures as they are in hydrogen sulfide form in pH of under 7. Sulfides as bound, soluble salt are not harmful, but should be controlled as they turn easily into hydrogen sulfide as seen in figure 9, which shows the percentage of hydrogen sulfide release from sulfide in different pH. (Finnish Water Utilities Association. 2018)

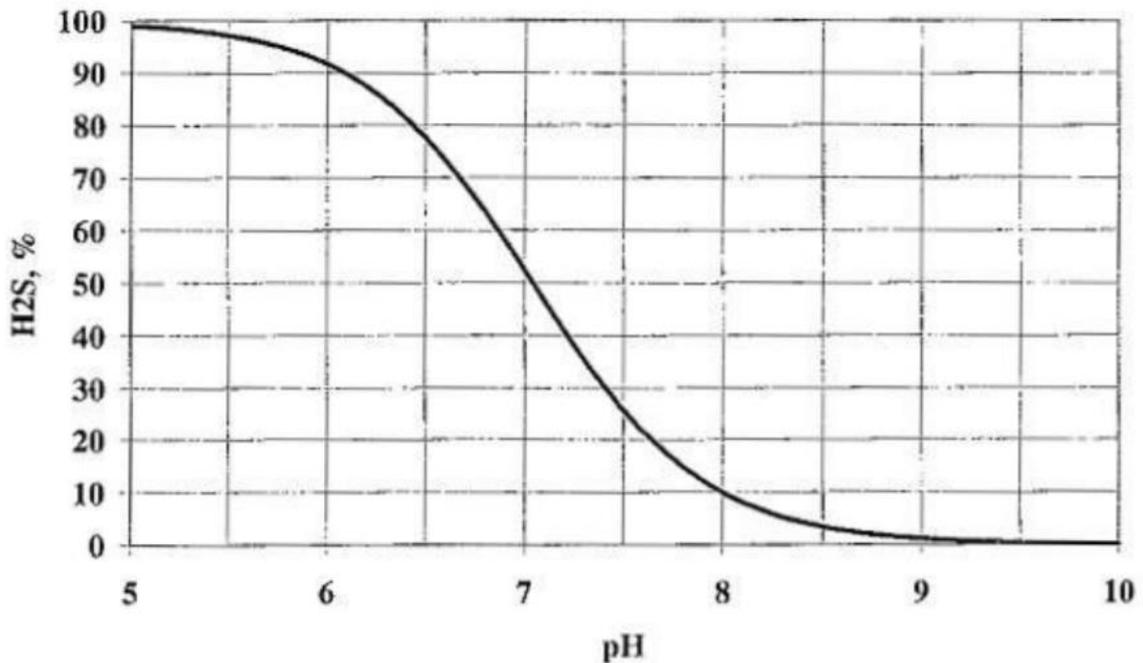


Figure 9. Formation of hydrogen sulfide from sulfide in different pH (Finnish Water Utilities Association 2018)

Sulfates, thiosulfates and sulfites cause corrosion in high concentrations by swelling of concrete or intrusion into concrete by reacting with different components in the cement. Usually the limit value for wastewater is given as sulfates which is a composite of value of sulfate, thiosulfate and sulfite because reliable analysis only for thiosulfate and sulfite is difficult. (Finnish Water Utilities Association. 2018).

5.3 Organic compounds

Organic constituents are a combination of carbon, hydrogen, oxygen and sometimes nitrogen. Due to the complex nature organic compounds, they can be classified as aggregate or

individual pollutants. Aggregate constituents are a mix of individual components that cannot be explained or presented separately as opposed to independently distinguished particles. Organic loading can originate from many different sources like unused medicine, personal care products and cleaning products. In addition, proteins, carbohydrates, fats/oils and urea are contributing factor for organic load. (Tshobanoglous et al. 2014, 114).

Measurement of organic content is usually done by three different methods:

- biochemical oxygen demand (BOD)
- chemical oxygen demand (COD)
- total organic carbon (TOC)

BOD is the most widely used parameter when measuring aggregate organic content and it involves the measurement of dissolved oxygen that is used by the microorganisms in the water. In principle, BOD shows the difference in the dissolved oxygen concentration values after certain incubation times, which is most commonly 5 days. BOD measurement involves certain constraints which limits the usability as only method for organic estimates. Limiting factors are the following:

- high concentration of bacteria seed is required in water
- pre-treatment of water is needed if highly toxic waters are used
- only biodegradable organics are measured
- BOD test has no stoichiometric validity after soluble organics are consumed

The biggest limitations occur from the long time required for measuring BOD. The most widely used time, five days, may or may not corresponds for the actual time that it takes to microorganisms use all soluble organic matter. (Tshobanoglous et al. 2014, 114-122).

Chemical oxygen demand is a measurement of the oxygen equivalent of the organic matter that can be oxidised chemically. COD usually shows higher values than BOD as many organic substances can be oxidised chemically but not biologically. Also, some organic constituents can be toxic to microorganisms and are oxidised only chemically. Lastly, dichromate that is used in COD test can react with some inorganic pollutants, like chlorides, and thus show higher values. Anyway, main advantage of COD compared to BOD is the short

time that it takes to have a result. Rapid COD tests take around 15 minutes, whereas, more traditional versions can be completed in 2,5 hours. Relatively short time compared to five days of BOD. (Tshobanoglous et al. 2014, 123).

Total organic carbon is used to determine total organic carbon by heat, oxygen, ultraviolet radiation and chemical oxidants that convert organic carbon into carbon dioxide. TOC is usually used to measure pollution characteristics of water, and sometimes it is possible to relate TOC to BOD and COD. Total organic carbon analysis is, also, very fast to do taking only 5 to 10 minutes. If relationship with TOC and BOD/COD can be found, TOC test can be used for process control as it is faster to complete. Even continuous TOC analysers have been developed which can be used to detect residual organics after different processes. (Tshobanoglous et al. 2014, 124).

As the explained methods all measure organic content, relationships between them can be drawn. Typical ratio between BOD and COD in untreated water varies between 0,3 - 0,8 and for treated water between 0,1 – 0,3. Whereas the ratio between BOD and TOC in untreated water is from 1,2 to 2,0 and in final effluent from 0,2 to 0,5. Although, the relationship between different methods is not always consistent and it changes between degree or treatment. However, in some cases, conclusions can be made based on one method alone. (Tshobanoglous et al. 2014, 125).

6 METHODS

The electrocoagulation tests were carried out in pilot scale electrolysis unit. All tests were done in batch mode in order to define right parameters before working in continuous mode. sulfate and chloride concentrations were analysed in situ together with pH, conductivity, temperature and, later, RedOx potential. Test runs that showed best results, were taken to Fortum's laboratory for further analysis of rest of the pollutants which are presented in table 3. The in-situ analysis for sulfates and chlorides were done with Hach DR1900 spectrophotometer.

Electrocoagulation unit consisted of 500 litres EC tank, flocculation basin and filter press equipped with filter paper for the separation of resulting sludge. Electrocoagulation tank was equipped with a mixing pump for faster reaction time and for better contact for pollutants. The basin was, also, equipped with gate valve for easier gathering of samples when working in batch mode. Two dosing pumps were used for pH control and addition of polyelectrolytes for better settling when it was needed. The generator that was used, had maximum output power of 300A – 24 V. It was also possible to change the polarity without changing the position of electrodes. This gave an opportunity to have automated polarity changes in pre-determined time intervals and made it possible to utilise full potential of electrode materials as anode and cathode.

The electrolysis cell was equipped with 10 pair of electrodes measuring (80 cm x 40 cm) each having inter electrode distance of 5 cm. Tested electrode materials were:

- Aluminium alloy
- Graphite
- Iron

All the experiments were conducted in galvanostatic mode so that a constant current was applied, and the voltage changed based on the electric conductivity of water, and resistance of chosen electrodes. This was done to achieve more consistent results and to observe the difference between electrode materials. The pH of the solution was controlled with either HCl (33%), H₃PO₄ (87%), Ca(OH) or citric acid (C₆H₈O₇). Experiments were done outside,

and the temperature changed based on the prevailing weather. Also, the quality of water changed throughout the experiment phase, as the water in the treatment ponds were a result of runoff waters from the treatment centre. The electrodes were installed in monopolar parallel style as figure 10 presents.

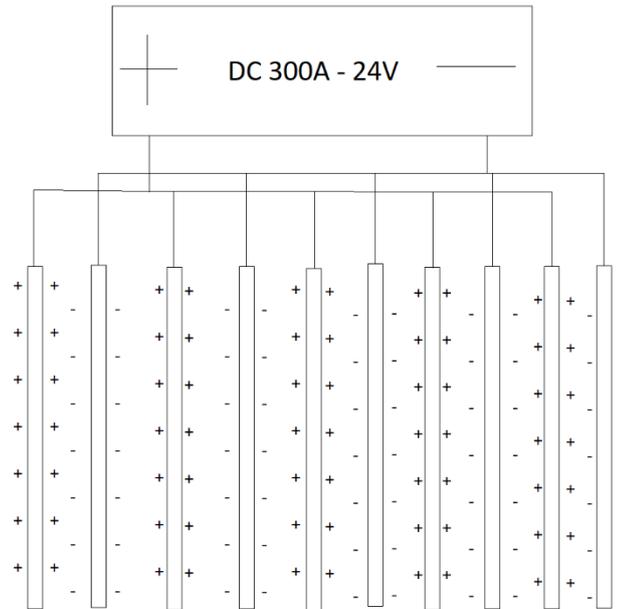


Figure 10. Simplified schematic of the EC unit. Actual unit consisted of 10 anodes and 10 cathodes

The efficiency of the pollutant removal was calculated with equation 21.

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (21)$$

C_0 = initial concentration [mg/l]

C_t = concentration at time t [mg/l]

Other operating settings are given later in relevant chapters, these include pH, addition of chemicals and the current used. Samples were first taken every 30 min for 2 hours, but as more information was gathered the time intervals were spaced out for once in an hour. The formation of chlorine gas and hydrogen sulphide gas were monitored before and during treatment with GasAlert extreme single gas detector and GasAlert micro 5 multi-gas meter respectively.

The first tests were done with aluminium and graphite electrodes. Experiments were done by changing one parameter at a time to obtain best possible results. The polarity was changed between experiment runs so that while aluminium worked as anode, graphite was cathode and vice versa. Also, few tests were made so that the polarity changed automatically in chosen time intervals, but those tests were not continued as the results were unsatisfactory and they resulted for non-existing reduction percentages. Aeration was used in all test runs before and/or after the treatment if removal of volatile gases was deemed necessary. After aluminium and graphite pairs, aluminium and iron electrodes were installed, and tests were performed in the same manner with a goal of reaching as good or better results than in previous experiments. Lastly, iron and graphite pairs were used, and tests repeated.

The laboratory analysis included most important constituents that should be treated based on the industrial wastewater permit for the area. Due to the changing nature of wastes inside the treatment centre, it is impossible to determine all the elements in the water at all time. Hence, the list of elements seen in table 3 are chosen as they represent the most important and probable pollutants that should be followed. Based on the data from previous years it was known, that concentration of sulfates and chlorides are close to the discharge limits most of the year, thus making them most important elements of interest.

Table 3. Pollutants included in full analyses

COD	Mercury, Hg	Silver, Ag	Aluminium, Al	Arsenic, As
Barium, Ba	Cadmium, Cd	Cobalt, Co	Chromium, Cr	Copper, Cu

Iron, Fe	Potassium, K	Lithium, Li	Magnesium, Mg	Manganese, Mn
Molybdenum, Mo	Sodium, Na	Nickel, Ni	Phosphorus, P	Lead, Pb
Sulfur, S	Antimony, Sb	Tin, Sn	Vanadium, V	Zinc, Zn
Fluoride, F ⁻	Chloride, Cl ⁻	Bromide, Br ⁻	Sulfate, SO ₄ ²⁻	Ammonical Nitrogen, NH ₄ -N
pH, 25°C	Conductivity, 25°C	TOC		

7 PERFORMANCE OF ALUMINIUM AND GRAPHITE ELECTRODES

7.1 Aluminium anode with graphite cathode

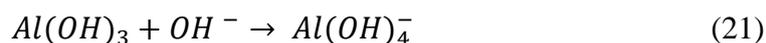
Experiments were started with maximum power without changing the pH before, during or after the treatment. Samples for sulfates were taken every 30 minutes, and for chlorides, once in an hour. Results are listed in table 4. Aluminium was used as anode and graphite as cathode. Current was set to 300A and the voltage stayed between 7,0 - 7,2V throughout the test.

Table 4. Results with aluminium anode and 300A and without pH control

Time, min	pH	Conductivity, $\mu\text{S}/\text{cm}$	$^{\circ}\text{C}$	Sulfate, mg/l	Chloride, mg/l	Reduction sulfate, %	Reduction Chloride, %
0	7,9	2700	7,8	785	399	-	-
30	9,6	2450	12,0	700	-	11	-
60	11,8	2350	15,3	638	309	19	23
90	9,4	2200	17,0	618	-	22	-
120	9,4	2300	17,4	590	333	25	17

From the table above, the rapid increase of pH can be observed. This is consistent with other, previously mentioned, researches around the topic. It is a result of formation of excess OH^- ions at the cathode and a release of CO_2 originating from the release of hydrogen at cathode. Chen et al (1999, 70) observed, also, a partial Cl^- and SO_4^{2-} exchange with OH^- in $\text{Al}(\text{OH})_3$ which could increase the rate of overall pH change. Jing- Wei et al (2007, 1411) supported this theory in their research as well. The problem with alkaline pH is visible in figure 5. Most of the dissolved aluminium is in $\text{Al}(\text{OH})_4^-$ form which is a poor coagulant and results for unsatisfactory performance. pH also increases to its maximum value after first hour before

decreasing. Based on the researches around the topic, this is due to two different reactions which are coprecipitation of Ca^{2+} and Mg^{2+} with $\text{Al}(\text{OH})_3$, and the formation of $\text{Al}(\text{OH})_4^-$ according to equation 21. (Chen et al. 1999, 70).



The most probable reason for the removal of chlorides was due to direct oxidation resulting from sufficient potential difference at anode and is explained in equation 2. The partial exchange of Cl^- with OH^- in resulting hydrolysis products could, also, be a reason for reduction of chlorides. The third reason for reduction of chlorides was explained by Vepsäläinen (2012, 13) who concluded that during electrocoagulation there might be deposition of salts on the surface of the electrode.

Increasing temperature have been noticed to have a negative influence for the removal efficiency. However, range of temperature and its effect is commonly investigated at higher values than 20 degrees and still, the decreasing efficiency played a minor role.

7.1.1 Effect of pH for the performance

In addition to bad coagulation performance of aluminium hydroxyls in alkaline conditions, sulfate removal has been observed to work better in acidic conditions. Murugananathan et al (2003) observed different pH levels with aluminium anode and iron cathode. They noticed that lower initial pH increased the removal rate of sulfates. The same results were observed in study by Mamelkina et al. (2017). In their paper, iron electrodes were used, and best reduction occurred at acidic pH.

In the next phase of tests, the pace of increasing pH was observed by testing different output powers by lowering the current and measuring the pH every 5 minutes for the first 30 minutes, and then once in 30 minutes. Figure 11 shows the rate of pH change during electrocoagulation with different currents.

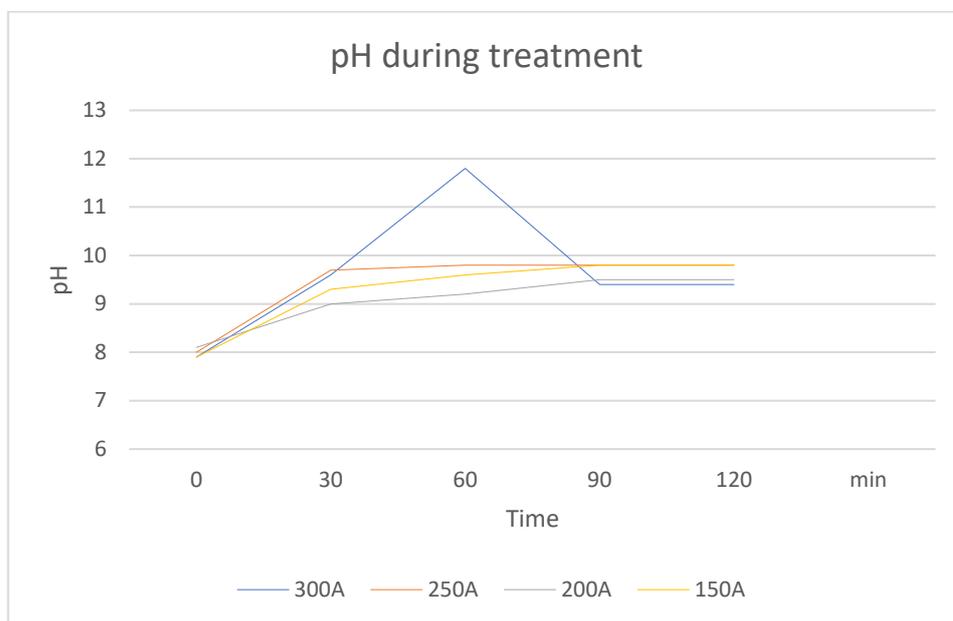


Figure 11. The change of pH during electrocoagulation using aluminium anode and graphite cathode using different currents.

At lower currents, the pH stayed under 10 for the whole duration on treatment. Still, based on the figure 2 and previous researches around the topic, conditions were too alkaline for ideal efficiency. The rise of pH was faster with higher current, which is seen as spike in the figure at one-hour mark, but the final pH was almost the same in all of the experiments. Vainio (2017, 67) observed the same results when using aluminium electrodes in his study. He concluded that the faster pH rise from higher current is from more effective OH^- and H_2 generation at the cathode. Next experiments were conducted without pH control and with lower currents in order to observe more closely its affect for the performance. The experiments were done in consecutive days so that the water matrix was as similar in all tests as possible. Sulfate concentrations at the beginning were: 590 mg/l, 478 mg/l, 500 mg/l and 605 mg/l for 300A, 250A, 200A and 150A experiments. Chloride concentrations were: 399 mg/l, 400 mg/l, 423 mg/l and 409 mg/l. As the EC basin was 500 litres, the current concentrations (I/V) were $150\text{A}/\text{m}^3$, $125\text{A}/\text{m}^3$, $100\text{A}/\text{m}^3$ and $75\text{A}/\text{m}^3$.

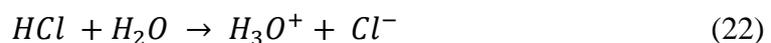
Table 5. Reductions of Cl^- and SO_4^{2-} with different output currents

Current (A)	Reduction after 1h, (%)		Reduction after 2h, (%)	
	SO_4^{2-}	Cl^-	SO_4^{2-}	Cl^-
150	10	15	16	20
200	29	3	35	15
250	33	22	35	18
300	19	23	25	17

From table above, the effect of pH for the results becomes apparent. The variation in removed chlorides is only few percentages in all tests and it can be assumed to originate from measuring error, or from other variables, so the pH of the water or the current seems to have no effect for chloride removal during the treatment when aluminium is anode. Results show a difference in better removal efficiency after first hour when using currents of 200 or 250 amperes compared to 300 or 150 amperes. During the second hour, reduction efficiency gets worse which is due to treatment being in high pH for the whole time. The low efficiency for 300 ampere test resulted from too alkaline pH after first hour.

7.1.2 Controlling the pH before and after electrocoagulation

Controlling the pH was done in order to investigate its effect for electrocoagulation. Hydrochloric acid (HCl), 33%, was first used to lower the pH before, during and after the treatment. Initial pH has been proven to be important parameter in EC, especially, in sulfate removal. (Mamelkina et al. 2017; Murugananathan et al. 2003). As the removal of chlorides happens through anodic oxidation or via other reactions, the coagulation performance was not believed to have a major effect for it. Upon contact to water, HCl forms hydronium cations and chloride ions as seen in equation 22.



(Socratic 2019)

Because of the increasing concentration of chloride ions, the effect of pH was investigated from the viewpoint of sulfates only. HCl was chosen because of the easy acceptability, ease of usage and as it does not leave any additional competing ions that could impair the removal of other pollutants. Also, measuring the RedOx potential was included for the in-situ measurements at this point. First test was done with 300A and the pH was lowered to 5,7 before treatment. Results are presented in table 6.

Table 6. Result of low initial pH

Time, (min)	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Temp ($^{\circ}\text{C}$)	Sulfate, mg/l	Reduction sulfate, %	Redox, mV
0	5,7	3830	10,4	767	-	56,4
30	11,3	4250	11,0	628	18	-179
60	11,6	4250	15,0	546	29	-180
120	10,9	3950	18,0	531	31	-210

The rise of pH was even faster, when initial conditions were acidic leading only to slightly better removal. These results led to a new experiment with current of 250A and pH correction before and after electrocoagulation. Also, the decline of RedOx can be seen from both of the results.

Table 7. Results with 250A and pH correction before and after treatment

Time, min	pH, initial	pH, adjusted	Conductivity $\mu\text{S}/\text{cm}$	Temp., $^{\circ}\text{C}$	Sulfate mg/l	Reduction sulfate, %
0	3,6	-	3660	13,2	764	-
30	10,8	9,2	3540	16,8	579	24
60	10,4	4,7	3570	17,0	562	27
120	10,0	6,0	3590	17,4	393	49

The lower current did not slow down the rapid increase of pH which was even faster at acidic conditions and can be seen from table 7. However, reduction of sulfates was higher than in previous test which shows that the pH should be lowered after the electrocoagulation. RedOx of the water decreased from initial 162 mV to -47 mV.

Third experiment was done with just pH correction after electrocoagulation with maximum power, as the lower initial pH only accelerated the rise. Initial concentration of sulfates was 713 mg/l and the pH was lowered to different values in one and two hour samples with HCl to observe the difference.

Table 8. Effect of pH for reduction of sulfates

After 1 hour			After 2 hours		
pH	Sulfates, mg/l	Reduction, %	pH	Sulfates, mg/l	Reduction, %
9	605	15	9	433	39
6,8	560	21	4,8	379	47
4,8	531	26	-	-	-
2,8	507	29	-	-	-

Table 8 shows that the reduction is better in acidic conditions. Chloride concentrations were analysed before adding HCl and the reduction was 27%, after first hour, and 33% after second hours, both compared to initial value which was 527 mg/l. Due to discharge limits for waters conveyed to sewage, the pH should be around neutral after treatment. Previous test was done again with careful pH drop to 7,5 for both samples. For the first hour sample, 0,25 ml of HCL (33%) per 400 ml of sample was used to lower the pH from 11,3 to 7,5. For the second hour sample 0,5 ml HCl (33%) per 400 ml sample was used to drop pH from 10,7 to 7.5. This indicates that the buffer capacity of water increases as the treatment time is longer. Again, chlorides were measured before addition of HCl as it was important to observe whether the reduction stays the same.

Table 9. Results for 300A and pH control for pH 7,5

Time, min	pH, initial	pH, adjusted	Sulfate mg/l	Chloride mg/l	Reduction sulfate., %	Reduction Chloride., %
0	3,6	-	721	449	-	-
60	11,2	7,5	571	343	21	24
120	10,7	7,5	401	293	44	35

Results confirm that controlling the final pH results for better efficiency than changing it before treatment. The reduction of sulfates reached 44% after 2 hours. Reduction of chlorides stayed at around 30% in all experiments.

7.1.3 Controlling the pH during electrocoagulation

Next step was to investigate the possibility to control pH during electrocoagulation so that different chemicals were injected into the EC unit while the process was ongoing. HCl, citric acid and phosphorus acid were used in these tests and the results are explained below. Experiments were started with the use of HCl due to its dissolution to chlorides which seems to have no negative influence for the removal efficiency of other elements. On the contrary, various papers around the topics suggest that chloride ions are beneficial for the EC system as it increases conductivity and keeps the electrode plates from passivating. (Ayrroyo et al 2008; Hakizimana et al 2007; Adelaide 2013). The current in all tests was first set to maximum.

HCl

Table 10 shows the removal of sulfates and increase of chlorides during two hours of electrocoagulation with uninterrupted dosing of HCl, which was diluted to 9% for these experiments. Based on the results it was concluded that it is possible to control pH by dosing it straight into the EC basin. Coagulation performance was good as seen in appendix 1 and the samples were taken to laboratory in order to see reduction for rest of the pollutants also.

Table 10. Full analysis of the results with HCl addition during treatment. “<” refers to a lower limit for analysis telling that the concentration of that pollutant is less than what the value dictates

Element	Unit	0 min	60 min	120 min
COD	mgO ₂ /l	83,9	61,1	61,8
Mercury, Hg	µg/l	<1,0	<1,0	<1,0
Silver, Ag	mg/l	<0,013	<0,013	<0,013
Aluminium, Al	mg/l	8,2	0,82	0,4
Arsenic, As	mg/l	0,036	<0,013	<0,013
Barium, Ba	mg/l	0,11	0,034	0,039
Cadmium, Cd	mg/l	<0,0013	<0,0013	<0,0013
Cobalt, Co	mg/l	0,0084	<0,0013	<0,0013
Chromium, Cr	mg/l	0,025	<0,0063	<0,0063
Copper, Cu	mg/l	0,19	<0,0063	<0,0063
Iron, Fe	mg/l	2,4	0,011	0,034
Potassium, K	mg/l	110	130	120
Lithium, Li	mg/l	0,27	0,29	0,27
Magnesium, Mg	mg/l	7,3	0,14	0,43
manganese, Mn	mg/l	0,2	<0,013	0,029
Molybdenum, Mo	mg/l	0,41	0,24	0,11
Sodium, Na	mg/l	610	630	630
Nickel, Ni	mg/l	0,034	0,007	0,0069
Phosphorus, P	mg/l	0,3	<0,063	<0,063
Lead, Pb	mg/l	0,021	<0,013	<0,013
Sulfur, S	mg/l	350	240	180
Antimony, Sb	mg/l	<0,013	<0,013	<0,013
Tin, Sn	mg/l	<0,013	<0,013	<0,013
Vanadium, V	mg/l	<0,013	<0,013	<0,013
Zinc, Zn	mg/l	0,94	0,028	0,069

Fluoride, F ⁻	mg/l	<1,0	<1,0	<1,0
Chloride, Cl ⁻	mg/l	590	782	892
Bromide, Br ⁻	mg/l	3,3	2,3	2,1
Sulfate, SO ₄ ²⁻	mg/l	957	683	489
NH ₄ -N	mg/l	4,2	4,6	4,3
pH, 25°C		7,9	7,2	7,2
Conductivity, 25°C	µS/cm	3 840	3 880	3 890
TOC	mg/l	<50	<50	<50

Results show 49% reduction in sulfates while chloride concentration increases around 300 mg/l. Reduction in most of the metals is more than 90%, whereas COD is removed by 27%. Low concentration of aluminium at final sample demonstrates that in neutral pH most of the dissolved aluminium is in insoluble form and is removed with precipitant.

Citric acid

Next test included the use of citric acid, even though, it is known to be poor chemical if coagulation is required due to chelating effect. Chelation is a way of ions and molecules to bind metal ions by creating ligand bond around central ion. Chelation involves a ligand compound which is usually an organic, and most commonly called either chelant, chelators, chelating agents or sequestering agent. (Bassi 2019).

Citric acid is a low-molecular-mass (LMM) ligand. Citric acid and aluminium can form different Aluminium citrate complexes, of which some are presented in figure 12. (Caruso et al. 2005).

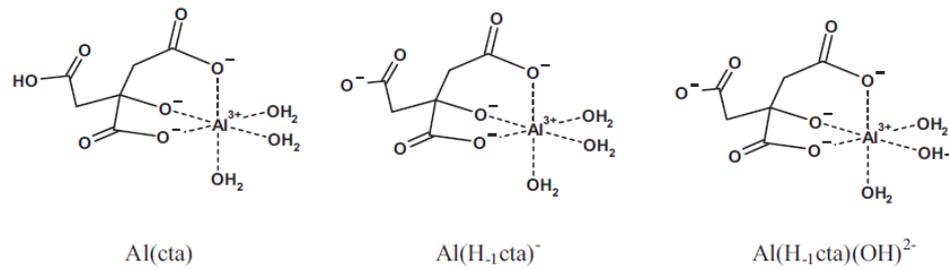


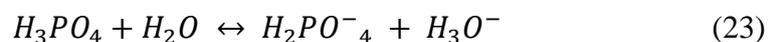
Figure 12. Different aluminium citrate compounds (Caruso et al 2005)

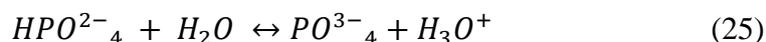
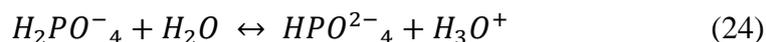
Chelate effect has been observed to hinder the coagulation and precipitation of Al(OH)_3 as the interaction of ligands with aluminium forms above mentioned complexes that prevent floc formation and thus hydrolysing aluminium precipitants. (Boyd 2011, 9-13).

Citric acid was still tested because it does not leave any unwanted constituents to the water, like chlorides, sulfates, nitrates or phosphorus. The usability of such acid could show great potential in areas with strict permit limits. However, the results were as expected, and the precipitation was non existing as can be seen from appendix 2. The test was terminated after 80 minutes due to unwanted results. Still, reduction of chlorides was 10% after first hour, and 28% after second hour. This supports the earlier observations about chloride removal without the need for precipitation or insoluble hydrolysis products.

Phosphorus acid

Final part of the pH control test included the use of phosphorus acid for maintaining suitable pH. In previous tests, the phosphorus levels showed good removal rates, hence it was chosen as control chemical for the final part of testing. Phosphorus acid reacts with water forming dihydrogen phosphate, hydrogen phosphate and phosphate through many phases following acid dissociation constant and is seen in equations 23-25.





(Anttila et al. 2013, 139)

During the first 30 minutes, the voltage showed values between 20-22 volts for 30 minutes after which it declined to 6,9 volts. This indicated that the surface of electrodes was passivated. The performance was rather poor as can be seen from appendix 3. The electrodes were changed to new ones and the test repeated with lower current. This time 250A was used and the results can be seen from table 11. Voltage was around 3 volts which was a result of high conductivity of water, lower current and good performance of new electrodes. The removal rates were again very poor with sulfates and chlorides while rest of the metals showed good reduction rates. The addition on phosphorus acid was seen as spike in phosphate concentration in one-hour sample, however, it decreased to initial value at two-hour sample which shows the good removal of phosphate with electrocoagulation. The reason for sharp increase in both tests in COD stayed unclear, but as it did not happen in previous tests. The formed phosphate ions were deducted to affect the analysis of organic matter.

The electric conductivity of the water was notably higher than in previous tests which indicates higher number of dissolved solids. This makes direct comparison for previous tests difficult as the water matrix clearly changed during testing phase.

Table 11. 250A and pH control with phosphorus acid. “<” refers to a lower limit for analysis telling that the concentration of that pollutant is less than what the value dictates

Element	Unit	0 min	60 min	120 min
COD	mgO2/l	64	84	87
Mercury, Hg,	µg/l	0.11	<0,10	<0,10
Silver, Ag	mg/l	<0,013	<0,013	<0,013
Aluminium, Al	mg/l	6.1	1.2	1
Arsenic, As	mg/l	<0,013	<0,013	<0,013
Barium, Ba	mg/l	0.13	<0,013	<0,013
Cadmium, Cd	mg/l	<0,0013	<0,0013	<0,0013

Cobalt, Co	mg/l	0.015	0.0025	<0,0013
Chromium, Cr	mg/l	0.03	<0,0063	<0,0063
Copper, Cu	mg/l	0.21	0.022	<0,0063
Iron, Fe	mg/l	4.3	0.37	0.021
Potassium, K	mg/l	150	150	150
Lithium, Li	mg/l	0.26	0.26	0.25
Magnesium, Mg	mg/l	7.1	5.2	3
Manganese, Mn	mg/l	0.26	0.044	0.011
Molybdenum, Mo	mg/l	0.79	0.77	0.71
Sodium, Na	mg/l	940	940	940
Nickel, Ni	mg/l	0.057	0.022	0.01
Phosphorus, P	mg/l	0.4	1.5	0.4
Lead, Pb	mg/l	0.021	<0,013	<0,013
Sulfur, S	mg/l	420	390	370
Antimony, Sb	mg/l	0.018	<0,013	<0,013
Tin, Sn	mg/l	<0,013	<0,013	<0,013
Vanadium, V	mg/l	<0,013	<0,013	<0,013
Zinc, Zn	mg/l	0.34	0.096	0.024
Fluoride, F-	mg/l	<1,0	<1,0	<1,0
Chloride, Cl-	mg/l	956	951	931
Bromide, Br-	mg/l	4.8	5	4.9
Sulfate, SO ²⁻ ₄	mg/l	1250	1180	1090
NH ₄ -N	mg/l	2.4	2.3	2.3
pH, 25°C		7.4	7.5	8.1
Conductivity, 25°C	μS/cm	5 390	5 230	5 130
TOC	mg/l	18.1	19.8	20.1

7.2 Graphite anode and aluminium cathode

Changing the polarity changed the process more into a direction of electrooxidation or electrochlorination rather than electrocoagulation. The idea of experiments was to remove chlorides with oxidation to chlorine and sulfates with cathodic dissolution of aluminium, a theory that was proven correct by Picard et al. (1999). However, based on the theory, it is still uncertain whether the aluminium hydroxyls generated at the cathode work efficiently enough to remove ions from the wastewater.

The first test was done at 300A and the starting voltage was 9,0 V. Voltage decreased slightly during the experiment to value of 8,5 V after 120min. Results are in table 12. Water was aerated as in previous tests to remove all detected H₂S.

Table 12. Graphite anode with aluminium cathode using current of 300A

Time, min	pH	Conductivity, $\mu\text{S}/\text{cm}$	Temp, $^{\circ}\text{C}$	Sulfate, mg/l	Chloride, mg/l	Reduction sulfate, %	Reduction Chloride, %
0	7,9	2750	10,7	767	402		
30	5,3	2600	14,3	808	398	-5	1
60	5,6	2450	15,0	805	347	-5	14
90	6,2	2400	17,7	636	314	17	22
120	6,3	2350	19,2	626	294	18	27

Notable decrease of pH was observed, and around 20% reduction of sulfates between 60min and 120 min. Reduction of chlorides was around 30%. In normal operating conditions in electrolysis with same inert electrode materials, pH tends to stay the same as H⁺ produced at the anode neutralizes the OH⁻ produced at cathode. (Ciblak et al. 2013). Decreasing pH might be explained by more abundant formation of H⁺ instead of OH⁻, or then hydroxyl radicals were part of other reactions leading to lower pH. Chlorine gas was observed small amount

(~10 ppm) in the surrounding air which suggest that chloride was oxidised to chlorine which then hydrolysis forming HOCl / OCl, and due to turbulence, minor release to air as chlorine gas happened. Next test was done by lowering the current to 250A and observing the results, which can be seen from table 13.

Table 13. Graphite anode with aluminium cathode using current of 250A

Time, min	pH	Conductivity $\mu\text{S}/\text{cm}$	Temp., $^{\circ}\text{C}$	Sulfate mg/l	Chloride mg/l	Reduction sulfate., %	Reduction Chloride., %
0	8.1	2750	11	712	393		
30	4.6	2800	15	714	431	0	-10
60	4.6	2800	17	890	412	-25	-5

Lowering the current resulted only for increase of concentrations of both, sulfates and chlorides. Also, the decrease of pH was more drastic. Experiment was ended after 60 min due to poor results. Tests were continued with maximum current and the effect of pre-aeration was investigated by conducting consecutive tests with and without aeration. RedOx was measured to gain better picture of the changes in the water. Results are presented in tables 14 and 15.

Table 14. Experiment with pre-aeration with current of 300A

Aeration							
Time, min	pH,	Conductivity, $\mu\text{S}/\text{cm}$	Temp, $^{\circ}\text{C}$	Sulfate, mg/l	Chloride, mg/l	Reduction sulfate, %	Reduction Chloride, %
0	6,7	3350	13	725	600		
30	3,7	3670	13	800	565	- 10	6
60	3,2	3680	12	>1000	566	-	6
120	3,6	-	28	>1000	510	-	15

Table 15. Experiment without aeration with current of 300A

Without aeration							
Time, min	pH, initial	Conductivity, $\mu\text{S}/\text{cm}$	Temp, $^{\circ}\text{C}$	Sulfate mg/l	Chloride mg/l	Reduction sulfate, %	Reduction Chloride, %
0	7	3180	12	750	464		
30	5,0	3030	23	868	446	-15.7	4
60	4,7	2870	24	>1000	435	-	6
120	4,5	2640	26	883	386	-17.7	17

The tests were done in consecutive days, so the water matrix was nearly identical during both times. RedOx increased more rapidly with pre-aerated water as can be seen from figure 13. Also, the increase of sulfates in both tests were more drastic than previously.

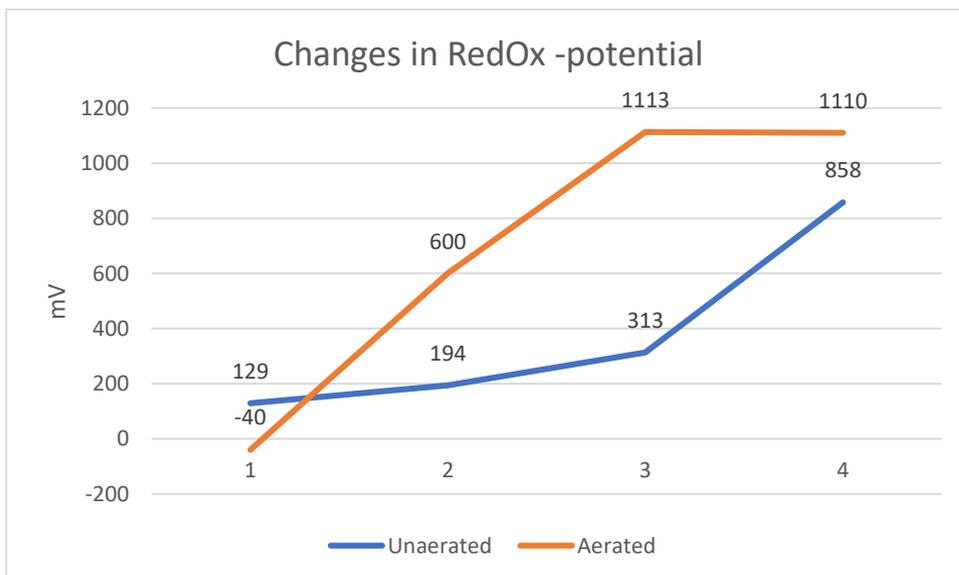


Figure 13. Changes in RedOx -potential of pre aerated and un-aerated waters

Muruganathan et al (2003) explained how titanium anode material resulted for increasing sulfate concentrations as the sulfides and sulfur in the water were oxidised to sulfates. The sharp increase in RedOx would support this theory as well as other studies that explain how sulfide ions can be oxidised, not only to sulfates, but to other products like elemental sulfur, polysulfide and thiosulfates as well. (Kharafi et al 2010)

However, it can be also seen from the results that the amount of sulfates is increasing as the number of experiments increases. During first tests, sulfates are decreasing, even though slightly, and as the experiments are repeated the increase of additional sulfate raises. The second theory is the formation and removal of sulfur layer on electrodes. The deposited sulfur can oxidise from the electrode surface as the experiments are prolonged. Kharafi et al (2010) observed white thin layer on the surface of the platinum electrode implying the deposition of sulfur products which then oxidised partially to soluble sulfates when the treatment was continued. As the experiments were done after each other while changing the polarity in every test, the deposition of salts on the electrode surface, that was explained by Vepsäläinen (2012, 37), might have occurred. When the polarity was changed, the cathode became anode and vice versa which then released the deposited salts back to the water leading to a higher concentration.

7.2.1 Controlling the pH before treatment

Because the pH decreased to a level where aluminium is in soluble form, the control of pH was introduced. The effect of initial pH was tested by increasing it with Ca(OH) before the treatment. Table 16 shows the result for that experiment.

Table 16. Results after increasing the pH before treatment

Time, min	pH, initial	Conductivity, $\mu\text{S}/\text{cm}$	Temp, $^{\circ}\text{C}$	Sulfate, mg/l	Reduction sulfate, %	Chloride, mg/l	Reduction Chloride, %
0	9,2	3020	14	732	-	440	-
30	8,8	2980	17	-	-	-	-

60	7,4	2940	22	784	-7	405	8
120	6,3	2780	26	765	-5	358	19

The higher initial pH seemed to hinder the increase of sulfates. The Redox value increased from 84 mV to 248 mV, which was notably less than without addition of Ca(OH) before the treatment. Lower RedOx leading to a smaller increase of sulfate would support the first theory about additional sulfate being from oxidation of other sulfuric species. This is also consistent with other papers around the topic. Also, as figure 3 shows, chlorine ionizes to HOCl and OCl⁻ based on the pH of the solution. At acidic pH, the HOCl is more dominant and as it is stronger oxidant, the more acidic water could result for higher RedOx and thus for increase of sulfates as sulfides are oxidized.

7.2.2 Controlling the pH after treatment

Experiments were continued by altering the pH of water in one and two hour samples by using Ca(OH). Results of the tests can be seen in table 17.

Table 17. pH control after the treatment using graphite as anode and current of 300A

Time, min	pH, initial	pH, adjusted*	Conductivity, μ S/cm	Temp, °C	Sulfate, mg/l	Chloride, mg/l	Reduction Chloride, %
0	6,7		3350	13	725	600	
30	3,7		3670	13	-	565	6
60	3,2	8,4	3680	12	>1000	566	6
120	3,6	7,5	3680	28	>1000	510	15

Even though the pH was near neutral, the concentration of sulfates increased significantly. Chloride reduction was 15% after two hours. In order to see whether the increasing amount sulfates was due to accumulation of sulfur on electrode surface or from oxidation reaction,

another test with new electrode plates with maximum power was conducted. Results are presented in table 18.

Table 18. Results with new electrodes with pH control and current of 300A

Time, min	pH, initial	pH, adjusted*	Conductivity, $\mu\text{S}/\text{cm}$	Temp, $^{\circ}\text{C}$	Sulfate, mg/l	Chloride, mg/l	Reduction Chloride., %
0	8,2		6340	-	1700	1016	
60	4,7	8,0	5960	-	1700	937	8
120	4,0	8,0	5730	-	1700	901	11

This time, the water composition had changed to more concentrated due to weather changes making direct comparison difficult. However, concentration of sulfates stayed at 1700 mg/l while chlorides were removed by 11% after two hours. Redox increased from initial – 86 mV to 712 mV during two-hour of treatment. As the RedOx was high and the sulfates stayed at 1700 mg/l, the new electrode plates seemed to stop the increase of sulfate indicating that the theory about deposition on electrodes was right.

7.2.3 Result of graphite anode and aluminium cathode

Full analysis of graphite as anode was conducted so that pH was only observed but not controlled. Results are in table 19.

Table 19. Full analysis of graphite anode. “<” refers to a lower limit for analysis telling that the concentration of that pollutant is less than what the value dictates

Element	Unit	0 min	60 min	120 min
COD	mgO ₂ /l	74	38	<15
Mercury, Hg,	$\mu\text{g}/\text{l}$	<0,10	<0,10	<0,10
Silver, Ag	mg/l	<0,013	<0,013	<0,013
Aluminium, Al	mg/l	7.3	7.3	34
Arsenic, As	mg/l	0.014	<0,013	<0,013

Barium, Ba	mg/l	0.19	0.076	0.073
Cadmium, Cd	mg/l	0.0015	<0,0013	<0,0013
Cobalt, Co	mg/l	0.02	0.0067	0.005
Chromium, Cr	mg/l	0.034	0.015	0.015
Copper, Cu	mg/l	0.3	0.081	0.062
Iron, Fe	mg/l	7.3	0.45	0.42
Potassium, K	mg/l	160	160	150
Lithium, Li	mg/l	0.28	0.26	0.24
Magnesium, Mg	mg/l	7.7	5.5	4.2
Manganese, Mn	mg/l	0.31	0.1	0.074
Molybdenum, Mo	mg/l	0.82	0.69	0.41
Sodium, Na	mg/l	940	940	920
Nickel, Ni	mg/l	0.062	0.049	0.048
Phosphorus, P	mg/l	0.61	0.079	<0,063
Lead, Pb	mg/l	0.034	<0,013	<0,013
Sulfur, S	mg/l	440	440	440
Antimony, Sb	mg/l	0.019	0.016	0.016
Tin, Sn	mg/l	<0,013	<0,013	<0,013
Vanadium, V	mg/l	<0,013	<0,013	<0,013
Zinc, Zn	mg/l	0.65	0.25	0.45
Fluoride, F ⁻	mg/l	<1,0	<1,0	<1,0
Chloride, Cl ⁻	mg/l	1060	964	925
Bromide, Br ⁻	mg/l	5	<2,0	<2,0
Sulfate, SO ₄ ²⁻	mg/l	1390	1300	1360
Ammoniacal nitrogen, NH ₄ -N	mg/l	2.8	1.7	<0,50
pH, 25°C		7.4	5.4	4.4
Conductivity, 25°C	µS/cm	5 580	5 470	5 200
TOC	mg/l	21.8	21	22.4

As suspected, the reduction in COD was at least 80% due to chlorination. Residual aluminium increased 365% which shows that as the pH decreased, the aluminium was in soluble form thus not precipitating. However, it proved the theory about aluminium cathode dissolution. Reduction of chlorides was also fairly small which was unexpected, but still in contrast with previous tests. It is, also, noteworthy to consider the increase in electric conductivity in influent water compared to earlier tests which means that the composition of water had changed into more concentrated. Ammoniacal nitrogen showed good reductions also compared to aluminium anode tests. The level of sulfates stayed nearly unchanged which was probably due to new electrodes.

The reduction of bromide was, also, better with graphite anode. This was due to oxidation as bromide forms bromine as equation 26 shows.



Oxidation potential of bromide is 0.27 V lower than with chloride which suggests that it is more easily oxidized than chloride. Study by Sum et al (2013) investigated the bromide oxidation with water containing high shares of chlorides. They noticed that with low cell currents only bromide was oxidized, and formation of chlorine was non existing. Results in table 18 indicates that the cell voltage and current should be increased for chloride oxidation, as for now, only bromide was removed.

Final test was conducted by running the EC in continuous mode and having a pH control in flocculation basin with Ca(OH) and flowrate of 250 l/h which corresponds to a 2 hour residence time. Results are presented in appendix 4 and they show comparable results with previous test. Removal of some metals was slightly better when the pH was raised. Also, the residual aluminium was lower which shows that the pH should be in correct level. Still, reduction of chlorides was poor, and sulfates increased from initial 911 mg/l to 1080 mg/l. While the sulfates increased, the total sulfur increased in the same ration. This would support the idea of deposition/dissolution of sulfates from electrode surface rather than by oxidation

of sulfuric species to sulfates. The second experience showed, also, increase of chromium and nickel which cannot be explained otherwise than by release of earlier deposited material.

7.3 Summary of aluminium and graphite electrode pair

During the aluminium and graphite electrode tests, the water matrix changed from water containing low concentration of elements into water with high concentrations of elements. The tests were done so that polarity was changed between the trials to prevent electrode passivation. Removal of sulfates with aluminium anode was proven to be more efficient with lower pH reaching around 50% of removal, which is compatible with other researches around the topic. Aluminium showed, also, good efficiency in other pollutants as long as the pH was controlled so that it stayed under 10. For controlling the pH, HCl was proven to be superior choice when compared to citric acid or phosphorus acid. Pre-aeration of water did not show any effect for the removal of compounds, but it was still used for removing H₂S and other volatile compounds before treatment.

When graphite was used as anode, the oxidation reactions removed COD, ammoniacal nitrogen and bromide efficiently. Some of the measured metals were also removed successfully, whereas, sulfates increased in most of the tests. The pH of the water decreased rapidly to acidic, which resulted for soluble aluminium species. Raising the pH showed slightly better removals of certain metals. In addition, residual aluminium was noticeably less than without correction of pH. The increase of sulfate concentration seemed to originate from deposition and dissolution of sulfur species on the electrodes from the previous experiments. This was supported by the installation of new electrodes which stopped the rise of sulfates. However, the reduction was still non-existent. Also, the increase of chromium and nickel during the process cannot be explained otherwise than deposition to electrode surface. RedOx potential of the water increased during the process which oxidized organic matter efficiently. Even though, the reason for small increase of TOC while COD decreased was not proven, but it might have been due to excess use of polymers for better coagulation performance which affected the analysis.

Polarity changes during treatment were tried with different intervals, but it was proven to be not effective, and reduction of pollutants was non-existing. Still, the difference between anode materials and removed species of pollutants would support the idea of combined electrocoagulation and electrooxidation processes in two separate electrolysis units. The possible deposition and dissolution of elements on the electrode surface would, also, make the periodical polarity change a difficult matter.

8 PERFORMANCE OF ALUMINIUM AND IRON ELECTRODES

8.1 Iron anode and aluminium cathode

During the tests, pH was first monitored, but not controlled. The idea was to reach at least equal results with previous tests without the need for pH correction as it makes the process more complex and, as observed, the addition of unsuitable acids affects the efficiency of treatment. Experiments were done with maximum current in order to have comparable results. Table 20 shows the outcome of the first experiment. Voltage stayed around 5,0 – 5,3 throughout the experiments which was a result of high conductivity of water.

Table 20. Result for iron anode and aluminium cathode using maximum current

Time, min	pH,	Conductivity, $\mu\text{S}/\text{cm}$	Temp, $^{\circ}\text{C}$	Sulfate, mg/l	Chloride, mg/l	Reduction sulfate, %	Reduction Chloride, %	Redox, mV
0	7,5	6770	17	1746	1084			-32
60	6,9	6370	21	1520	1140	13	-5	-300
120	6,9	5880	22	1374	1095	21	-1	-450

During the experiment, pH decreased slightly but remained near neutral which is unlike in other studies that observed the rise of pH to around 9-10 when using iron electrodes. The decline of pH can thus be explained to originate from the use of aluminium as cathode. (Hakizimana 2016). Still, the reduction of sulfates was slightly lower than with aluminium and graphite combination. Resulting precipitant was green which indicated that it was a mix of different ferrous and ferric hydroxides. (Garcia-Carrillo 2019). The presence of $\text{Fe}(\text{OH})_2$ was, also, supported by the negative redox value in all samples. Fe^{2+} is known as less effi-

cient coagulant as Fe^{3+} due to higher solubility, therefore not achieving efficient colloid destabilization, and due to lower positive charge. It is known that Fe^{2+} is sometimes oxidised automatically to Fe^{3+} during electrocoagulation if the pH is alkaline and RedOx positive or the anode potential is high enough. (Vepsäläinen 2012, 34; Hansen, 2006).

Next step was to oxidise the water and mix the sample again as suggested by Hakizimana et al (2016) to see if the oxidation could be done afterwards for maximizing formation of $\text{Fe}(\text{OH})_3$ in the flocculation phase, and whether it would affect the efficiency. Oxidation was done with pressurised air and the resulting Fe^{3+} formed iron hydroxyls which was observed by reddish-brown precipitant seen in appendix 5, which indicated that, at least, most of the iron was in preferred trivalent form.

Table 21 shows the new results for the aerated sample. The outcome is only slightly better, and tests should be repeated several times in order to have reliable data before making further conclusions. The pH after 120 minutes was the same as in earlier test but since the initial value was higher, there was more noticeable drop.

Table 21. Result for iron anode and aluminium cathode experiment after aeration of sample

Time, min	pH	Conductivity, $\mu\text{S}/\text{cm}$	Temp, $^{\circ}\text{C}$	Sulfate, mg/l	Chloride mg/l	Reduction sulfate, %	Reduction Chloride, %	Redox, mV
0	8,5	6450	14	1648	1110			85
60	7,2	6050	17	1544	1170	6	-5	-515
120	7,2	5690	19	1144	1004	31	10	-345

Results were not taken to full analysis as the removal of chlorides was bad. The decreasing electric conductivity and visually good precipitation implied that reduction of other ions was rather successful.

8.2 Aluminium anode and Iron cathode

For the next experiment aluminium was set as anode and iron as cathode. Results are in table 22. Again, current of 300A was used and other parameters kept the same.

Table 22. Results of aluminium anode and iron cathode using current of 300A

Time, min	pH, initial	pH, adjusted	Conductivity $\mu\text{S}/\text{cm}$	Temp, $^{\circ}\text{C}$	Sulfate mg/l	Chloride mg/l	Reduction sulfate, %	Reduction Chloride, %	Redox, mV
0	8,5		6720	14,1	1774	1068			-32
60	10,2	7,8	6750	18,4	1402	1068	21	0	-112
120	10,2	8,3	6700	21,4	1156	1042	35	2	-250

pH increased to above 10 as in tests using aluminium anode and graphite cathode, so the correction was done with HCl, as it was previously observed that the performance became poor when pH raised over 10. Chloride concentration was measured before addition of the acid from both samples. From 120 min sample, sulfate concentration was also measured before pH correction at pH value of 10,2 with a result of 1420 mg/l, so the previous observations about the negative effect of highly alkaline conditions leading to $\text{Al}(\text{OH})_4^-$ and bad efficiency were confirmed again as the concentration was 1156 mg/l at pH of 8,3 as seen in table 22. The aluminium anode seemed to be more effective during first hour of treatment than iron anode. However, due to the rapid rise of pH and poor performance in reduction of chlorides, the aluminium and iron combination was deemed inferior compared to aluminium and graphite combination.

8.3 Summary of aluminium and iron electrode pair

Aluminium and iron combination worked in similar fashion compared to aluminium and graphite for removing sulfates and chlorides. During both treatments, RedOx value decreased to negative, which was also the case with aluminium anode when graphite was used as cathode.

When iron was anode, the pH decreased slightly. However, the pH stayed near neutral throughout the experiment and inside suitable range for insoluble iron hydroxyl formation, which removed the need for additional pH adjustment. The resulting precipitant was aerated for better Fe^{3+} formation, however, the result did not show major difference compared to unaerated samples. Aluminium anode required lowering the pH afterwards. This resulted for the same results as with aluminium and graphite pair. Only difference was slightly worse reduction of sulfates and non-existent reduction of chlorides.

The decreasing electric conductivity with iron anode suggested good removal of other elements. Nonetheless, the experiments were not continued, or analysed further, as theory and practical tests did not support the removal of chlorides. Results also indicate that graphite is needed for chloride removal as even the aluminium anode / iron cathode pair resulted for zero reductions.

9 PERFORMANCE OF IRON AND GRAPHITE ELECTRODES

9.1 Graphite anode and iron cathode

Graphite anode with iron cathode showed poor efficiency in both, sulfate and chloride removal as seen from table 23. The working mechanisms was in a similar fashion than with graphite anode and aluminium cathode as the RedOx increased while pH decreased. Changes were smaller as the RedOx increased only to a value of 165 mV while decrease of pH was to 6,2. Sulfate levels stayed the same, while chlorides were removed with 20% efficiency after 120 minutes. As there was no visible precipitant, the chemical reactions concerned mostly oxidation and/or ionization of species. The cathodic dissolution seemed to, also, concern only aluminium as the almost neutral pH would support insoluble iron species which were not observed. As the first experiment showed bad results and the literature reviews around the topic did not support effective removals with such a combination, the polarity was changed to iron anode and graphite cathode.

Table 23. Results for graphite anode

Time, min	pH, initial	Conductivity, $\mu\text{S}/\text{cm}$	Temp, $^{\circ}\text{C}$	Sulfate, mg/l	Chloride mg/l	Reduction sulfate, %	Reduction Chloride, %	Redox, mV
0	7,9	4130	24	1174	559			-90
60	6,9	4070	27	1256	552	-7	1	90
120	6,2	3930	31	1256	447	-7	20	165

9.2 Iron anode and graphite cathode

Iron anode and graphite cathode combination was taken to laboratory analysis so that comparable results with aluminium / graphite pair could be achieved. The result show rapid increase of pH to around 9 which is still in the range of insoluble iron species and thus pH was left unadjusted. Still, reduction of sulfates, and chlorides was poor, even tough, rest of the metals were treated with high efficiency and treatment produced insoluble hydroxide precipitant. The reduction of COD was around 40%, as well as, TOC. Relatively high initial aluminium concentration was probably from earlier tests as it was impossible to ensure 100% removal of residuals from previous tests. Still, the reduction of aluminium was good with at least 98% of removal. The produced precipitant was in a form of green rust and was not aerated afterwards. Some residual iron was observed in 60min and 120 min samples, which could have been extracted with an aeration.

Table 24. Full analysis of iron anode and graphite cathode. “<” refers to a lower limit for analysis telling that the concentration of that pollutant is less than what the value dictates

Element	Unit	0 min	60 min	120 min
COD	mgO ₂ /l	150	120	86
Mercury, Hg	µg/l	0.14	<0,10	<0,10
Silver, Ag	mg/l	<0,013	<0,013	<0,013
Aluminium, Al	mg/l	10	<0,5	<0,13
Arsenic, As	mg/l	0.033	<0,013	<0,013
Barium, Ba	mg/l	0.2	0.037	0.037
Cadmium, Cd	mg/l	<0,0013	<0,0013	<0,0013
Cobalt, Co	mg/l	0.025	<0,0063	<0,0013
Chromium, Cr	mg/l	0.04	<0,0063	<0,0063
Copper, Cu	mg/l	0.25	<0,0063	<0,0063
Iron, Fe	mg/l	10	2.9	3.6
Potassium, K	mg/l	140	150	140
Lithium, Li	mg/l	0.35	0.34	0.34
Magnesium, Mg	mg/l	15	6.6	0.81

Manganese, Mn	mg/l	0.38	0.081	0.025
Molybdenum, Mo	mg/l	0.46	0.026	0.015
Sodium, Na	mg/l	630	640	630
Nickel, Ni	mg/l	0.088	0.032	0.024
Phosphorus, P	mg/l	4.8	0.086	0.082
Lead, Pb	mg/l	0.043	<0,013	<0,013
Sulfur, S	mg/l	380	370	340
Antimony, Sb	mg/l	0.017	<0,013	<0,013
Tin, Sn	mg/l	<0,013	<0,013	<0,013
Vanadium, V	mg/l	<0,013	<0,013	<0,013
Zinc, Zn	mg/l	0.77	<0,0063	<0,0063
Fluoride, F ⁻	mg/l	<1,0	<1,0	<1,0
Chloride, Cl ⁻	mg/l	600	556	562
Bromide, Br ⁻	mg/l	3.6	3.8	3.3
Sulfate, SO ²⁻ ₄	mg/l	1140	990	977
NH ₄ -N	mg/l	5.2	4.8	4.8
pH, 25°C		7.4	9	9.3
Conductivity, 25°C	μS/cm	4 100	3 940	3 820
TOC	mg/l	48	37.9	29.1

9.3 Summary of iron and graphite electrode pair

Graphite anode showed poor performance when combined with iron anode. Even though, the pH stayed in good range for soluble iron species, no precipitation was observed and the removal of both, sulfates and chlorides, was poor. The electric conductivity of water, also, stayed unchanged which indicates poor removal of ions.

Iron anode with graphite cathode showed good performance for COD and TOC removal. pH raised to alkaline, but still stayed in sufficient range for soluble iron. The removal of wide

variety of metals was good reaching 70% - 100% reductions in most of them. As this combination removed the need for pH control, it showed high value when compared to aluminium.

10 CONCLUSION

Electrocoagulation with different electrode materials was found to be effective way of removing wide variety of constituents from the industrial landfill runoff waters in pilot scale installation. However, sufficient removal of salts was proven to be difficult and requiring long treatment times. Many small-scale laboratory studies with synthetic waters are found, which have left demand for scale up experiments and changing water quality. The water from Fortum's treatment centre was a mixture of different elements and changing quality. The work was conducted during a period lasting from early spring to end of summer. This made it possible to observe how the electrocoagulation behaved with different concentrations of elements. The main object of interest was the capability to treat high concentrations of sulfates and chlorides, while at the same time ensure proper removal of heavy metals and organic matter.

Aluminium alloy, iron and graphite electrodes were used in different variations and running parameters were changed based on the results. Experiments were started with aluminium / graphite pair as the theory showed most potential for sulfate and chloride removal with such combination. The achieved results were used as benchmark for other electrode pairs.

All the electrode materials showed different results and removals towards different species. Aluminium anode resulted for alkaline pH with either graphite or iron cathode. pH control improved the results and sulfates were removed better as the water approached acidic conditions. From three different acids, HCl showed best results as it did not form any competing ions or affected the coagulation performance otherwise. When aluminium was anode, 200A/500l - 300A/500l showed comparable results but as current was lowered to 150A/500l, the results deteriorated.

Iron anode showed similar results than aluminium when combined with graphite cathode. The rise of pH was not as sharp as with aluminium which meant that formed iron hydroxide stayed in insoluble form. The removal of COD was better than with aluminium, while metals were treated with nearly same efficiency, besides some exceptions like molybdenum which had almost total removal compared to 40% with aluminium anode. Only highest current was tested as the purpose was to compare results for previous tests and as the highest current was

used most of the times, the tests were repeated in a same fashion. When iron anode was installed with aluminium cathode, the reduction of sulfate and chloride was bad. pH declined slightly while reduction of sulfates was 20% after 2 hours and chloride levels stayed unchanged.

Graphite anode behaved totally differently compared to iron or aluminium. pH of the water decreased rapidly to acidic at which point aluminium was in soluble form. The residual aluminium at 60 min and 120 min samples proved that the aluminium cathode dissolved in the water as suspected. By increasing the pH, part of the aluminium precipitated, and the residual aluminium remained low. Still, the reduction of sulfates was bad. By using graphite anode, the process was more like electrooxidation than electrocoagulation resulting for oxidation of species. COD, bromide and ammoniacal nitrogen showed better removals than with other configurations. Graphite anode worked only with highest current thus it was used in all tests. Graphite anode with iron cathode showed bad results as sulfate was not removed at all while chlorides had 20% of removal. The pH stayed nearly same as did electric conductivity which indicated bad efficiency in removal of other pollutants as well.

The possibility to utilise polarity changes based on the water composition was deemed to be difficult as it was suspected that some species accumulated on the electrode surface and were released back to the water as the direction of current was changed. The increase of sulfates happened only when using graphite anode which could also be implication of oxidation of sulfuric species to sulfates. However, full analysis of the experiments showed that total sulfur increased in the same ratio with sulfates. This would support the idea of partial deposition of sulfur on electrode surface which were then released back to the water as the experiments were continued. Be that as it may, exact mechanism behind deposition and dissolution was not fully resolved which leaves room for further research around the topic.

Summary of all the full analysis can be found in appendices 6 and 7. Tables show the reduction percentages next to each other for easy comparison. It should be noted that the water matrix is different in all tests which can be seen from the electric conductivity. Therefore, the results should be viewed with critical mindset and understanding of different variables. Also, in some tests the influent concentration of certain species is already under the lower value of analysis thus not showing if any reduction happens.

Based on the experiments, suitability of electrocoagulation for industrial effluents can be drawn. Most of the metals were removed with good efficiency in all configurations in relatively short time, excluding alkali metals (Li, Na, K) which were not notably affected. Removal efficiencies of chlorides had big variation in experiments throughout the period which was partially due to alternating concentrations in influent. Still, it was noticed that graphite was needed for chloride removal as the aluminium / iron pair resulted for zero removal. Sulfates were removed better as the pH of the water was lowered reaching almost 50% reductions. Organic matter was removed most efficiently with iron or graphite anode. Graphite oxidized organics with direct oxidation and by indirect with a of formation of oxidizing species like chlorine, whereas, iron anode removed species by precipitation/coagulation. In conclusion, findings show that proper removal of sulfates and chlorides was uncertain and sensitive for variables like pH and concentration of other elements. This would increase the risk of major industrial investment for types of waters tested.

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Appendix 1: Resulting precipitant from aluminium anode / graphite cathode experiment when using HCl as pH control chemical



Appendix 2: Result of citric acid as pH control chemical. The lack of precipitant shows how the coagulation performance is hindered with citric acid.



Appendix 3: Full analysis of phosphorus acid as pH control chemical with passivated electrodes. “<” refers to a lower limit for analysis telling that the concentration of that pollutant is less than what the value dictates.

Element	Unit	0 min	60 min	120 min
COD	mgO ₂ /l	88	170	170
Mercury, Hg	µg/l	<0.1	0.13	<0.1
Silver, Ag	mg/l	<0.013	<0.013	<0.013
Aluminium, Al	mg/l	13	2.4	2.1
Arsenic, As	mg/l	0.018	<0.013	<0.013
Barium, Ba	mg/l	0.11	<0.013	<0.013
Cadmium, Cd	mg/l	<0.0013	<0.0013	<0.0013
Cobalt, Co	mg/l	0.011	0.0014	<0.0013
Chromium, Cr	mg/l	0.023	<0.0063	<0.0063
Copper, Cu	mg/l	0.13	0.0093	<0.0063
Iron, Fe	mg/l	13	0.21	0.073
Potassium, K	mg/l	150	140	130
Lithium, Li	mg/l	0.29	0.31	0.31
Magnesium, Mg	mg/l	5.9	3.6	2.6
Manganese, Mn	mg/l	0.27	0.036	0.027
Molybdenum, Mo	mg/l	0.58	0.46	0.4
Sodium, Na	mg/l	930	920	900
Nickel, Ni	mg/l	0.03	0.017	0.011
Phosphorus, P	mg/l	0.28	15	5.2
Lead, Pb	mg/l	0.017	<0.013	<0.013
Sulfur, S	mg/l	460	430	410
Antimony, Sb	mg/l	<0.013	<0.013	<0.013
Tin, Sn	mg/l	<0.013	<0.013	<0.013
Vanadium, V	mg/l	<0.013	<0.013	<0.013

Zinc, Zn	mg/l	0.9	0.15	0.13
Fluoride, F ⁻	mg/l	<1	<1	<1
Chloride, Cl ⁻	mg/l	845	694	690
Bromide, Br ⁻	mg/l	5.1	4.3	4.2
Sulfate, SO ²⁻ ₄	mg/l	1370	1250	1220
Ammoniacal nitrogen	mg/l	3.6	3	3.1
pH, 25°C		7.4	7.1	7.2

Appendix 4: Results of graphite anode and aluminium cathode with constant flow of 250 l/h. “<” refers to a lower limit for analysis telling that the concentration of that pollutant is less than what the value dictates.

Element	Unit	Influent	Effluent	Reduction %
COD	mgO ₂ /l	66	44	33,3
Mercury, Hg	µg/l	< 0,1	< 0,1	-
Silver, Ag	mg/l	< 0,013	< 0,013	-
Aluminium, Al	mg/l	2,2	1,8	18,2
Arsenic, As	mg/l	< 0,013	< 0,013	-
Barium, Ba	mg/l	0,13	0,053	59,2
Cadmium, Cd	mg/l	< 0,0013	< 0,0013	-
Cobalt, Co	mg/l	0,012	0,0042	65,0
Chromium, Cr	mg/l	0,014	0,21	-1400
Copper, Cu	mg/l	0,15	0,0079	94,7
Iron, Fe	mg/l	2,8	0,023	99,2
Potassium, K	mg/l	100	97	3,0
Lithium, Li	mg/l	0,55	0,44	20,0
Magnesium, Mg	mg/l	9,7	6,9	28,9
Manganese, Mn	mg/l	0,28	0,16	42,3
Molybdenum, Mo	mg/l	0,46	0,22	52,2
Sodium, Na	mg/l	550	530	3,6
Nickel, Ni	mg/l	0,028	0,22	-685,7
Phosphorus, P	mg/l	0,32	0,083	74,1
Lead, Pb	mg/l	0,024	< 0,013	45,9
Sulfur, S	mg/l	300	360	-20,0
Antimony, Sb	mg/l	< 0,013	< 0,013	-
Tin, Sn	mg/l	< 0,013	< 0,013	-
Vanadium, V	mg/l	< 0,013	< 0,013	-

Zinc, Zn	mg/l	0,18	0,0098	94,6
Fluoride, F ⁻	mg/l	-	-	-
Chloride, Cl ⁻	mg/l	551	538	2,4
Bromide, Br ⁻	mg/l	3	< 2	> 33,3
Sulfate, SO ²⁻ ₄	mg/l	911	1080	-18,6
Total solids	mg/l	31	2	93,5
Ammoniacal nitrogen	mg/l	< 5	< 5	-
pH, 25°C		7,8	8,2	
Conductivity, 25°C	μS/cm	3 630	3 790	
TOC	mg/l	20,8	22,3	-7,2

Appendix 5: Samples from treatment with iron anode and aluminium cathode. Aerated sample on the left and unaerated on the right.



Appendix 6: Comparison of all full analysis of 60 minutes samples from most promising tests. Results are shown as reduction percentages where “>” refers to a reduction of at least or more than what the value dictates. “-“ indicates that the concentration in influent was already under the lower limit of analysis. The name of the experiments shows the electrode configurations, pH control chemical and current.

60 min	Al/Gr_HCl_3 00A	Al/Gr_ H ₃ PO ₃ _300A	Fe/Gr_30 0A	Al/Gr_ H ₃ PO ₃ _250A	Gr/Al_30 0A
COD	27,2	-93,2	20,0	-31,3	48,6
Mercury, Hg,	-	-30,0	> 28,6	> 9,1	-
Silver, Ag	-	-	-	-	-
Aluminium, Al	90,0	81,5	> 95,0	80,3	0,0
Arsenic, As	> 63,9	> 27,8	> 60,6	-	> 7,1
Barium, Ba	69,1	> 88,2	81,5	> 90,0	60,0
Cadmium, Cd	-	-	-	-	> 13,3
Cobalt, Co	> 84,5	87,3	> 74,8	83,3	66,5
Chromium, Cr	> 74,8	> 72,6	> 84,3	79,0	> 55,9
Copper, Cu	> 96,7	92,8	> 97,5	89,5	73,0
Iron, Fe	99,5	98,4	71,0	91,4	93,8
Potassium, K	-18,2	6,7	-7,1	0,0	0,0
Lithium, Li	-7,4	-6,9	2,9	0,0	7,1
Magnesium, Mg	98,1	39,0	56,0	26,8	28,6
Manganese, Mn	> 93,5	86,7	78,7	83,1	67,7
Molybdenium, Mo	41,5	20,7	94,3	2,5	15,9
Sodium, Na	-3,3	1,1	-1,6	0,0	0,0
Nickel, Ni	79,4	43,3	63,6	61,4	21,0
Phosphorus, P	> 79,0	-5257,1	98,2	-275,0	87,0
Lead, Pb	> 38,1	> 23,5	> 69,8	> 38,1	> 61,8

Sulfur, S	31,4	6,5	2,6	7,1	0,0
Antimony, Sb	-	-	> 23,5	> 27,8	15,8
Tin, Sn	-	-	-	-	-
Vanadium, V	-	-	-	-	-
Zinc, Zn	97,0	83,3	> 99,2	71,8	61,5
Fluoridi, F ⁻	-	-	-	-	-
Chloride, Cl ⁻	-32,5	17,9	7,3	0,5	9,1
Bromide, Br ⁻	30,3	15,7	-5,6	-4,2	> 60,0
Sulfate, SO ₄ ²⁻	28,6	8,8	13,2	5,6	6,5
Ammoniacal nitrogen	-9,5	16,7	7,7	4,2	39,3
pH, 25°C	7,2	7,1	9,0	7,5	5,4
Conductivity, 25°C	3880	5040	3940	5230	5470
TOC	-	-37,4	21,0	-9,4	3,7

Appendix 7: Comparison of all full analysis of 120 minutes samples from most promising tests. Results are shown as reduction percentages where “>” refers to a reduction of at least or more than what the value dictates. “-“ indicates that the concentration in influent was already under the lower limit of analysis. The name of the experiments shows the electrode configurations, pH control chemical and current.

120 min	Al/Gr_HCl_ 300A	Al/Gr_H ₃ PO ₃ _ 300A	Fe/Gr_3 00A	Al/Gr_H ₃ PO ₃ _ 250A	Gr/Al_3 00A
COD	26,3	-93,2	42,7	-35,9	> 79,7
Mercury, Hg,	-	-	> 28,6	> 9,1	-
Silver, Ag	-	-	-	-	-
Aluminium, Al	95,1	83,8	> 98,7	83,6	-365,8
Arsenic, As	> 63,9	> 27,8	> 60,6	-	> 7,1
Barium, Ba	64,5	> 88,2	81,5	> 90,0	61,6
Cadmium, Cd	-	-	-	-	> 13,3
Cobalt, Co	> 84,5	> 88,2	> 94,8	> 91,3	75,0
Chromium, Cr	> 74,8	> 72,6	> 84,3	> 79,0	55,9
Copper, Cu	> 96,7	> 95,2	> 97,5	> 97,0	79,3
Iron, Fe	98,6	99,4	64,0	99,5	94,2
Potassium, K	-9,1	13,3	0,0	0,0	6,3
Lithium, Li	0,0	-6,9	2,9	3,8	14,3
Magnesium, Mg	94,1	55,9	94,6	57,7	45,5
Manganese, Mn	85,5	90,0	93,4	95,8	76,1
Molyb- denium, Mo	73,2	31,0	96,7	10,1	50,0
Sodium, Na	-3,3	3,2	0,0	0,0	2,1
Nickel, Ni	79,7	63,3	72,7	82,5	22,6
Phosphorus, P	> 79,0	-1757,1	98,3	0,0	> 89,7
Lead, Pb	> 38,1	23,5	> 69,8	> 38,1	> 61,8
Sulfur, S	48,6	10,9	10,5	11,9	0,0

Antimony, Sb	-	-	> 23,5	> 27,8	15,8
Tin, Sn	-	-	-	-	-
Vanadium, V	-	-	-	-	-
Zinc, Zn	92,7	85,6	> 99,2	92,9	30,8
Fluoride, F ⁻	-	-	-	-	-
Chloride, Cl ⁻	-51,2	18,3	6,3	2,6	12,7
Bromide, Br ⁻	36,4	17,6	8,3	-2,1	> 60,0
Sulfate, SO ₄ ²⁻	48,9	10,9	14,3	12,8	2,2
Ammoniacal nitrogen	-2,4	13,9	7,7	4,2	> 82,1
pH, 25°C	7,2	7,2	9,3	8,1	4,4
Conductivity, 25°C	3890	4870	3820	5130	5200
TOC	-	-40,1	39,4	-11,0	-2,8