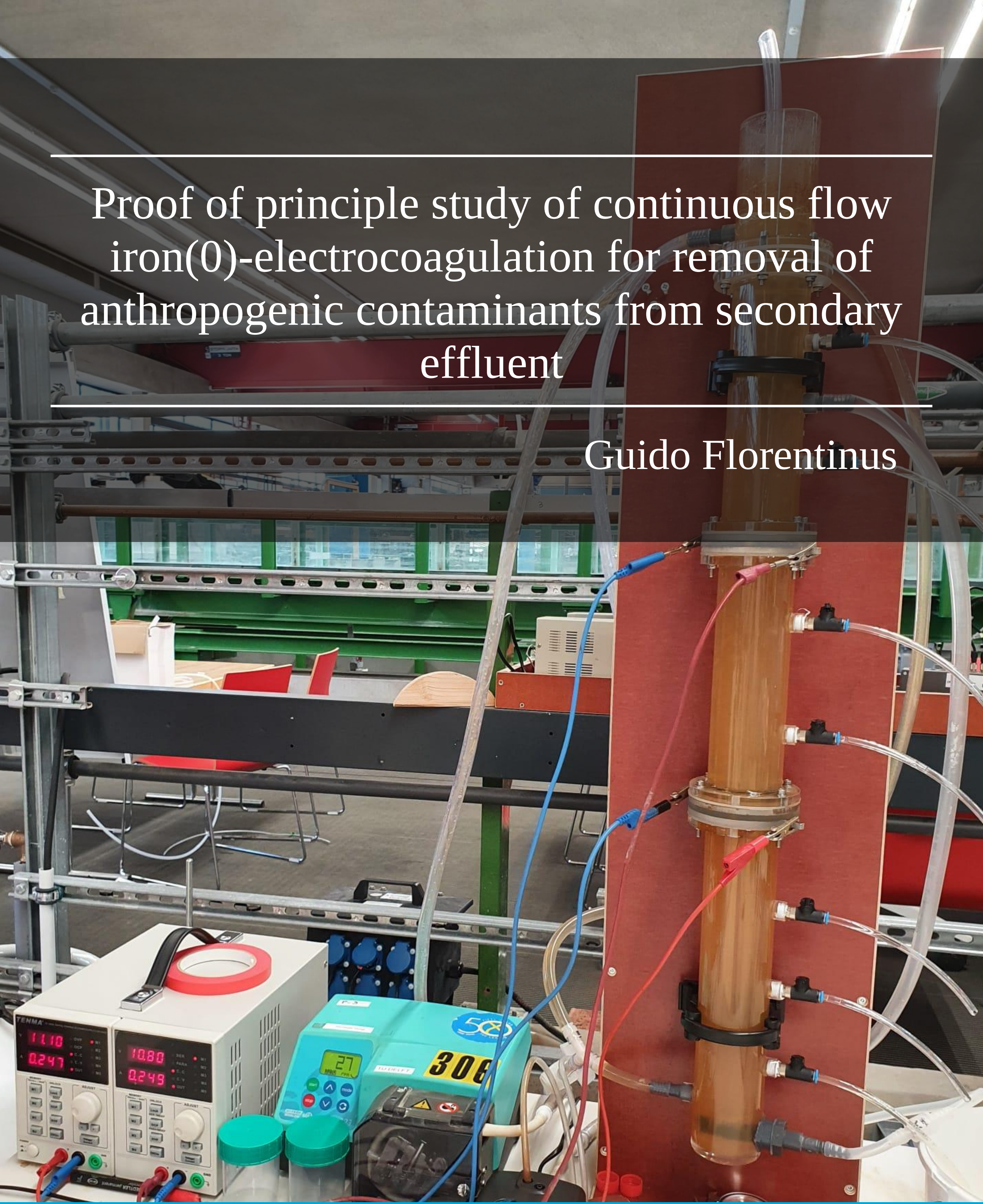
Proof of principle study of continuous flow iron(0)-electrocoagulation for removal of anthropogenic contaminants from secondary effluent

Guido Florentinus



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by

Guido Florentinus
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Thesis committee

Chair:	Dr. Ir. D. van Halem
Daily supervisor:	Ir. B. Bicudo
External supervisor:	Ir. J. Schakel
External supervisor:	Dr. Ir. R. Lindeboom

Preface and acknowledgements

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G. Florentinus
Utrecht, August 2022

Summary

With the rapid population growth and industrialization, water bodies are being infiltrated by a rising number of contaminants like metals, pharmaceuticals, pesticides and detergents (Reddy and Lee, 2012), which requires the need for novel treatment technologies. Electrocoagulation (EC) is a water treatment technology, similar to chemical coagulation, where the coagulant is dosed electrochemically from a pure metal electrode. With Fe-EC, dissolved Fe^{2+} is released at the anode and at the cathode, hydrogen gas is produced. The performance of Fe-EC in a full water column using a continuous flow setup has had little to no attention yet. The aim of this proof of principle study is to determine the feasibility and the practical potential of Fe-EC during a continuous flow implementation and gives insight to the general performance of the system in terms of water quality improvement.

Experiments were conducted in a continuous flow Fe-EC unit with a volume of 1.6 L. Inflow and outflow of the system were located close to the top and the bottom respectively, providing a descending flow. Two pairs of electrodes were used, evenly distributed along the length of the unit, and at the bottom an air diffuser was used to provide aeration. Operational configuration of the unit was needed as no prior experiments had been performed with this unit and the exact behavior of the electrodes, flow and aeration within the continuous flow system were unknown. Furthermore, experiments were conducted to evaluate the removal efficiency of Fe-EC on nutrients, organic micropollutants (OMPs), microbes and (heavy) metals at an operating pH of 8 and 7.

The operational parameters were set to deliver an Fe dosage of 50 mg/L, flow rate of 7.5 L/h, and a current density of 15 mA/cm^2. It was found that the system was able to achieve high removal of phosphorus up to 99% during all experiment sets. Highest removal of *E. coli* and coliphages was found when operating at a pH of 7, reaching 1.56 and 0.65 log removal respectively. The effect of ROS on the inactivation of microbes can be an important factor in the observed removal difference between pH 8 and pH 7. Removal of OMPs was found to vary greatly among the compounds and measurements. More stable results were found when using increased OMP concentrations, reaching removals varying from 7% to 25% at a pH of 8, and slightly lower removals from 1% to 15% at a pH of 7. Here, diclofenac reached removals of 25% and 6% respectively for pH 8 and 7. No correlation was found between the observed removal and the acid dissociation constant (pKa) or the η–octanol–water partition ratio (K_{ow}) of measured OMPs. Lastly, various heavy metals show affinity for removal during Fe-EC, such as arsenic, copper, zinc, manganese, chromium and vanadium. Using increased influent concentrations of the heavy metals resulted in removals varying from 55% to over 90%, with arsenic, zinc, chromium and vanadium all reaching removals above 85%. Comparing removal results from operating at pH 8 to 7, a slight change was observed with better removals at pH 7.

The system has shown to have high removal potential on secondary effluent, even when contaminant concentrations reach high levels. Nevertheless, uncertainties and were found for the practical implementation of Fe-EC, and design and operational parameters first have to be optimized in order to fully utilize the potential that Fe-EC has.

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1. Introduction

1.1 Background

Water plays a vital role in daily lives all around the world, either through recreational use, for sanitation, to drink, or to grow food. All this water has become less and less available throughout the past decades as fresh water sources are being overused, depleted, and contaminated. According to the WHO (2022), over 2 billion people live in water-stressed countries and as reported by the United Nations (2022), 2.4 billion people lack access to basic sanitation services. The demand for water is so high that water supply and natural recharge is trailing behind. Water scarcity is such a challenging problem that already in 1967 Raymond Nace wrote an article called "*Are we running out of water?*". Furthermore, a study by Vörösmarty et al. (2010) states that in 2000 almost 80% of all people lived in areas that experienced the threat of water scarcity. Nowadays, water stress is an often spoken about global issue, and the reason for multiple global water goals, such as the UN's Sustainable Development Goals to ensure availability and sustainable management of water and sanitation for all (United Nations, 2022). With the rapid population growth and industrialization, water bodies are still being infiltrated by a rising number of contaminants like metals, pharmaceuticals, pesticides and detergents (Reddy and Lee, 2012). Over the years, more advanced water treatment technologies, such as reverse osmosis and advanced oxidation processes have been increasingly applied to mitigate these pollutants. However, these new treatment options are expensive and more complex to operate, making them difficult to use in developing countries, where money for new water treatment technology or to maintain current ones is scarce (Treacy, 2019).

1.2 Electrochemical water treatment

Electrochemical water treatment is a method using applied electrical current for the physical-chemical conversion of contaminants and is used within both the wastewater and drinking water treatment (Chen, 2004; Martinez-Huitle and Brillas, 2008; Al-Hanif and Bagastyo, 2021; Sillanpää and Shestakova, 2017). Some fundamental electrochemical treatment techniques are electrodialysis, electroflotation and electrocoagulation.

1.2.1 Electrocoagulation

Electrocoagulation (EC) is a somewhat unconventional water treatment method, which in most aspects is identical to chemical coagulation. Both methods make use of the formation of solids which play an integral role in the removal of contaminants via an adsorption process. However, the difference between the two methods is that in EC, the metallic coagulant is dosed electrochemically from a pure metal electrode, instead of coming from a metallic salt, and thereby cut the production of sludge production in half (Barrera-Díaz et al., 2018). The most common coagulants used in both chemical and electrocoagulation treatment are iron and aluminum, because of price and availability of both metals (both as a salt or as a purified metal), and the high positive charge of their cations (Al^{3+}, $Fe^{2+/3+}$). In this study, only Fe-electrodes were used. Figure 1 displays the mechanisms of the electrocoagulation process, which can be divided in three different stages: 1 – oxidation of the anode and formation of the coagulants, 2 – destabilization of charged particles, and lastly, 3 – floc formation. At the anode, electrochemical dissolution of the Fe-electrode takes place, releasing dissolved Fe^{2+} (**Eq. 1**). At the cathode, the reduction of water and protons takes place, and depending on the pH, resulting in the production of hydrogen gas, as given in **Eq. 2** and **Eq. 3**.

$$Fe\ (S) \rightarrow Fe^{2+} + 2e^{-} \qquad E^0 = 0.44\ V \qquad \textbf{Eq. 1}$$

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad \text{at pH} < 7 \qquad \textbf{Eq. 2}$$

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \qquad \text{at pH} \geq 7 \qquad \textbf{Eq. 3}$$

Furthermore, when in solution, the dissolved Fe^{2+} cations are oxidized or react with hydroxide to hydrolyze and form the solid $Fe(OH)_3$ flocs (**Eq. 4** – **Eq. 7**). These positively charged particles act as coagulant and electrostatically attract negatively charged contaminants, destabilizing them, allowing agglomeration and causing precipitation or flotation of the formed flocs (Sillanpää & Shestakova, 2017; Mollah et al., 2001).

$$Fe^{2+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + e^{-} \qquad \textbf{Eq. 4}$$

$$Fe^{2+}{}_{(aq)} + 2OH^{-} \rightarrow Fe(OH)_{2(s)} \qquad \textbf{Eq. 5}$$

$$4Fe^{2+}{}_{(aq)} + O_{2(aq)} + 10H_2O \rightarrow 4Fe(OH)_{3(s)} + 8H^{+} \qquad \textbf{Eq. 6}$$

$$4Fe(OH)_{2(s)} + O_{2(aq)} + 2H_2O \rightarrow 4Fe(OH)_{3(s)} \qquad \textbf{Eq. 7}$$

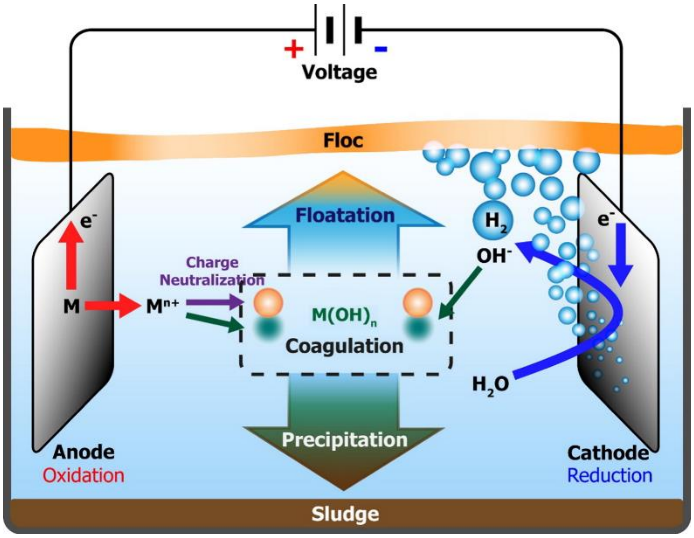

***Figure 1** - Mechanisms of electrocoagulation in a batch environment (An et al., 2017)*

The effectiveness of the EC treatment is influenced by various operational parameters, such as distance between electrodes and current density, but also by the ionic composition of the water that define the electric conductivity and pH. Current density is a measure of the applied current per area of sacrificial electrode ($^{A}/_{cm^2}$) and its effects during EC have been widely studied (Ghernaout and

Elboughdiri, 2020; Nasrullah et al., 2012; Irdemez et al., 2006; Bayar et al., 2011; Kumar et al., 2004). Current density can be controlled directly by adjusting the applied current and determines both the amount of coagulant dosed and the hydrogen produced over a period of time, and is an important parameter in the Faradaic efficiency (see section 1.2.3). It has been found that an increasing current density improves the removal (rate) of contaminants in the EC process (Nasrullah et al., 2014; Kumar et al., 2004). In addition, a higher charge dosage has been reported as an influential parameter improving the contaminant removal during EC (Bicudo et al., 2021; Roy et al., 2021). Charge dosage is defined as electric charge over volume ($^{C}/_{L}$), and may be a more significant indicator in a batch environment with a set volume and dosage time.

Compared to other water purification technologies, EC shows excellent removal efficacy for a wide range of contaminant in the water and has great potential for addressing limitations that traditional coagulation has (Mollah et al., 2001). Electrocoagulation offers many advantages such as its simple design, easy operation, low maintenance and does not rely on chemical dosing, minimalizing change in conductivity, secondary pollution and sludge production (Harif et al., 2012; Mollah et al., 2004).

1.2.2 Reactive Oxygen Species (ROS)

When electrochemically dosed, Fe is released as Fe^{2+}, further oxidizing itself to Fe^{3+} under the presence of oxygen. This oxidation process of Fe^{2+} (absent in Al), triggers a series of intermediate reactions which produce reactive oxygen species (ROS), such as superoxide radical ($^*O_2^-$), hydrogen peroxide (H_2O_2) or hydroxyl radical ($^*OH$). ROS are partially reduced oxygen-containing molecules that have one or more unpaired electrons, are highly reactive and are found to have very strong disinfection properties as they attack bacteria and viruses, can degrade a wide range of organic (micro) pollutants, and can potentially oxidize other hazardous substances like heavy metals (Kabdaşlı et al., 2010; Dixon and Stockwell, 2014). This seems similar to the Fenton-type process in which Fe^{2+} is used as catalyst and H_2O_2 as oxidant (Wang et al., 2016; Kabdaşlı et al., 2010). The complexity of these reactions makes it that the exact processes and roles during the disinfection steps are not fully understood. Wu et al. (2014) report various redox mechanisms related to ROS, which result in the reaction equations as given below.

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + {}^*O_2^- \qquad \textbf{Eq. 8}$$

$$Fe^{2+} + {}^*O_2^- \rightarrow Fe^{3+} + H_2O_2 \qquad \textbf{Eq. 9}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^*OH + OH^- \qquad \text{at pH} < 6 \qquad \textbf{Eq. 10}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{4+} + 2OH^- \qquad \text{at pH} \geq 6 \qquad \textbf{Eq. 11}$$

1.2.3 Faradaic efficiency

In electrochemistry, the theoretical dosage of the anode can be calculated using Faraday’s Law, as given in **Eq. 12**. The calculations are based on the electrode dimensions and the applied current. To understand the actual behavior of the electrodes in electrochemistry, the faradaic efficiency is used. This is an indicator of the performance of the electrodes, where the measured Fe dosage is expressed as a percentage of the theoretical Fe dosage calculated by Faraday's Law (Müller et al., 2019; Sillanpää and Shestakova, 2017). This means that a 100% faradaic efficiency represents a perfect electrode performance. It has been found that the faradaic efficiency is being influenced by multiple factors including electrode potential and ionic composition of the solution (Van Genuchten et al., 2017). In addition, Müller et al. (2018) show that the faradaic efficiency decreases with repeated operation, resulting in a lower Fe dosage than calculated.

$$w = \frac{I * t * M}{z * F * V} \qquad \textbf{Eq. 12}$$

where,
w = quantity of electrode dissolving [g L^{-1}]
I = electric current [A]
t = time [s]
M = molecular weight of electrode (Fe = 55.85) [g mol^{-1}]
z = number of electrons involved in the oxidation/reduction reaction (Fe(II) = 2)
F = Faraday's constant = 96,485 [C mol^{-1}]
V = Volume [m^3]

1.2.4 From batch to continuous flow

When talking about experimental procedures, a common way to conduct experiments is a batch experiment. A batch environment can be defined as a static system, where a set volume of water is used to conduct the experiment. Chemicals are (electrochemically) dosed in this system and stirred for the duration of the experiment. Concentrations are monitored during a certain time and a change can be observed during this period. Batch experiments are a fast way to study chemical reactions and behavior, but do not always represent the true natural conditions.

A continuous flow experiment is set in an open environment where there is an in- and outflow within the system. Examples of commonly used continuous flow systems are plug flow or column. Chemicals have to be dosed continuously and concentrations can fluctuate in the system due to disturbances and variations of the water flow (turbulence). The hydraulic retention time (HRT) is an important factor in a continuous experiment as it determines contact time.

***Table 1** – Biggest differences between batch and continuous experiments.*

Batch	Continuous
Set volume (closed environment)	Constantly flow (in- and outflow)
Fixed water quality	Variable water quality
Known concentrations/dosage	Average dosing/fluctuation in concentration
Mixing by mechanical means and aeration	Mixing by aeration

1.3 Characteristics of pollutants

1.3.1 Turbidity

Turbidity is a characteristic of a solution and can be defined as the measurement of the amount of light that is scattered by a solution due to suspended particles present and is a quick indicator on the amount of suspended matter in the solution. High turbidity blocks passage of light and diminishes transparency. Usually this is the result of suspended soil particles, such as sand, clay or silt, and suspended organic matter, found in natural ground- and surface waters. Waters with high turbidity both block and absorb more sunlight, resulting in the reduction of photosynthesis processes and an increase of temperature respectively, negatively affecting the aquatic life of living organisms (Hussain et al., 2016). Furthermore, solids in water provide cover, surface and nutrients for microbes to grow, resulting in a correlation between turbidity and microbe concentrations. In a water treatment plant, turbidity is usually removed at an early stage as solids increase treatment loads and cause higher operational demand. Removal of solids is often done by combinations of coagulation/flocculation, sedimentation, and filtration. The removal of turbidity is an easy first step that can significantly reduce microbial concentrations and stress on water treatment systems. On its own, turbidity is not a satisfactory indicator for the level of safety of water. A misconception may be that clear water, without solids, is safe to drink and free from any contaminants, but this cannot be assumed directly, as many contaminants can dissolve or are invisible to the naked eye. Further treatment is therefore always necessary.

1.3.2 Conductivity and pH

Similar to turbidity, conductivity and pH are characteristics that can be used to describe a solution and are determined by the composition of the solution. Conductivity is the measure of its ability to conduct electric current and is an indicator of the amount of dissolved solids, or minerals, that are present in the solution. Salts dissociate in water into anions and cations, which are negatively and positively charged respectively, and act as conductors, thus increasing the conductivity. Conductivity can therefore indicate the amount of dissolved salts present in a solution, which, for consumption, can be undesirable in high quantities. According to Lenntech (2022), ultra pure water (de-ionized) has a conductivity of 0.05 µS/cm, drinking water between 50 and 500 µS/cm and seawater can reach up to 50000 µS/cm. For electrochemical treatment purposes, conductivity is a wanted characteristic as it decreases electric resistance and increases efficiency through conducting electric current. The higher the conductivity of a solution, the more easy electric current will pass through the solution, increasing efficiency.

With solutions, pH is also a characteristic related to the chemicals dissolved in them. The term pH stands for ‘potential of hydrogen’ and relates to the acid-base balance, expressed on a scale from 0 to 14. This scale is logarithmic and expresses the concentration of hydrogen ions in the solution. The formula for pH is given in **Eq. 13**. The middle of the scale, 7, indicates a neutral solution, acids have a pH below 7 and bases above 7.

$$pH = -\log[H^+] \qquad \textbf{Eq. 13}$$

where,
$[H^+]$ = concentration of hydrogen ions

1.3.3 Nutrients

Human intake of nutrients is essential to health and lasting nutrient deficiency can cause several health problems. Nutrients are natural compounds and occur naturally in water bodies as a result of weathering, infiltration and ocean upwelling. However, anthropogenic sources such as agriculture, wastewater treatment discharges and urban runoff are the cause of highly increased concentrations found in the past decades (Bricker et al., 2008). The most commonly mentioned and studied nutrients are phosphorus and nitrogen, which are linked to eutrophication, a process in which a water body becomes more biologically active resulting in algae bloom (MECCS, 2021). Algae bloom is not always bad, but harmful algae bloom, caused by the bloom of phytoplankton, has several negative impacts on waters. It can grow too dense and block incoming sunlight, produce toxins, and use up available dissolved oxygen, which all result in unsafe water, loss of aquatic vegetation and increased treatment loads. Other nutrients are sulphur, sodium, potassium, calcium and magnesium. Their presence in the environment is of lower concern, although Qadir et al. (2018) reports that soil salinization due to these growing concentrations is a major cause of soil degradation. Conventional removal of nutrients is done by biological processes like nitrification-denitrification, or with phosphorus it is possible to dose a chemical to stimulate precipitation as a salt (Abeysiriwardana-Arachchige et al., 2020). The removal of nutrients from waters is a highly studied topic, with increasing interest in nutrient reuse and recycling as they become more limited and valuable.

1.3.4 Organic micropollutants (OMP)

Organic micropollutants are compounds classified as emerging contaminants and comprise of both industrially made as naturally formed compounds. Emerging organic micropollutants can be categorized in different classes: pharmaceuticals (including biocides), personal care products (PCP), pesticides, endocrine disruptor compounds (EDC) and, per- and polyfluoroalkyl substances (PFAS) (Bacci and Campo, 2022; Gruchlik et al., 2018). These micropollutants are of growing concern as the number of different micropollutants in the aquatic environment is found to keep rising over the past years (Eregowda and Mohapatra, 2020). Furthermore, studies have shown that most micropollutants can pass current conventional water treatment technologies, causing accumulation in surface waters (Fent et al., 2006; Zietzschmann et al., 2014).

In the treatment of micropollutants, two main removal processes occur: adsorption to suspended (organic) matter and biodegradation (Fent et al., 2006; Oulton et al., 2010; Nam et al., 2013). The adsorption process of micropollutants on coagulants has been understudied, as it is found that more effective removal occurs during biological treatment via biodegradation, making this process more cost effective (Oulton et al., 2010; Grandclément et al., 2017). However, due to rising concentrations, environmental and health concerns are growing, and new studies focus on the removal of micropollutants via adsorption on activated carbon or advanced oxidation techniques (Jian et al. 2013; Nam et al., 2014; Zietzschmann et al., 2014). In addition, Carballa et al. (2005) focused on the removal during primary treatment and showed that removal with sorption is based on the physical properties of the contaminants, where the adsorption process relies on both the hydrophobic and electrostatic characteristics of the contaminant in relation to the suspended (organic) matter.

A well-discussed characteristic of OMPs is their pK_a. In general, the pK_a is the acid dissociation constant and is an indicator of the state of dissociation of a chemical. The lower the pK_a value, the easier it can donate its protons and dissociates into its ions, where strong acids have a pK_a of less than zero. The pK_a is related to the pH, as the pK_a helps predicts the behavior of a molecule at a specific pH. The higher the pH is above the pK_a, the bigger the ratio of ions will be, as shown in **Eq. 14** below.

$$pH = pk_a + \log \frac{[A^-]}{[HA]} \qquad \textbf{Eq. 14}$$

where,
$[A^-]$ = concentration of the conjugate base of the chemical
$[HA]$ = concentration of the chemical

In addition to the pK_a, an important characteristic is the K_{ow}, or η–octanol–water partition ratio. It defines whether a chemical is more soluble in fat, in this case octanol, (lipophilic) or in water (hydrophilic). The ratio is defined as the chemical concentration in an octanol-rich phase over the chemical concentration in a water-rich phase and is usually translated to a log scale. The K_{ow} is used in environmental risk assessments as an indicator of biological persistence and therefore toxicity (Hodges et al., 2019), where hydrophobic compounds have a high K_{ow} or positive Log K_{ow} value and are found to accumulate in the fatty tissue of organisms, and in addition, compounds with a ratio of higher than 5 are classified to bioaccumulate (Oulton et al., 2010; SSC, 2018). Lipophilic chemicals are more likely to adsorb to suspended matter, as they are more repelled by water, while chemicals with a higher affinity to dissolve in water (negative log K_{ow}) are expected to be removed primarily through biodegradation (Fent et al., 2006). **Table 2** gives an overview of the characteristics of relevant OMPs.

***Table 2** – Characteristics and physical properties of relevant OMPs. Source: PubChem (2022), unless stated otherwise.*

Element	**Molecular formula**	**Molecular weight**	**Charge at pH 7**	**Log K_{ow}**	**pK_a**	**General use**
1HBenzotriazole	$C_6H_5N_3$	119.12	0	1.44	8.37	Corrosion inhibitor
4,5-methyl-benzotriazole	$C_7H_7N_3$	133.15	0	1.71[a]	8.7[a]	
Carbamazepine	$C_{15}H_{12}N_2O$	236.27	0	2.77	15.96	Anticonvulsant (Anti-epileptic)
Gabapentin	$C_9H_{17}NO_2$	171.24	+/– [d]	-1.1	3.7	
Diclofenac	$C_{14}H_{11}Cl_2NO_2$	296.1	–	4.51	4.2	Anti-inflammatory
Ketoprofen	$C_{16}H_{14}O_3$	254.28		3.12	4	
Caffeine	$C_8H_{10}N_4O_2$	194.19		-0.07	14	
Theophylline	$C_7H_8N_4O_2$	180.16		-0.02	8.81	
Metoprolol	$C_{15}H_{25}NO_3$	267.36	+	1.88	9.7	Beta blocker
Propranolol	$C_{16}H_{21}NO_2$	259.34	+	3.48	9.45	
Sotalol	$C_{12}H_{20}N_2O_3S$	282.37	+	0.24	9.76	
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	253.28	–	0.89	5.7	Antibiotic
Trimethoprim	$C_{14}H_{18}N_4O_3$	290.32	+	0.91	7.12	
Clarithromycin	$C_{38}H_{69}NO_{13}$	748.0	–	3.16	8.99	
Sulfadimethoxine	$C_{12}H_{14}N_4O_4S$	310.33	–	1.63	6.91[c]	
Hydrochlorothiazide	$C_7H_8ClN_3O_4S_2$	297.7	0	-0.07	7.9	Antihypertensive Agent
Metformin	$C_4H_{11}N_5$	129.16		-2.6	12.4	Antidiabetic
Acetaminophen	$C_8H_9NO_2$	151.16		0.46	9.38	Pain reliever

a – Dummer, 2014

b – Scheytt et al., 2005

c – DrugBank, 2022

d – Henning et al., 2018

1.3.5 Microbes

Microbes is a group name for microorganisms that can only be seen through a microscope. The most common types of microbes are viruses, bacteria, protozoa, archaea and fungi. When a microbe is able to cause a disease, it is called a pathogen. Pathogen removal is a critical part in the production of drinking water, as the microbial safety of drinking waters has always been an important quality parameter. Diseases like cholera and typhoid fever are examples of waterborne diseases that have caused various outbreaks in the past. These microbial pathogens have been significantly reduced with increasing treatment technologies, resulting in a steep decrease of casualties. However, microbial pathogens are still the cause of many common illnesses, such as diarrhea, and are estimated to cause over hundreds of thousands of deaths per year, the biggest part being amongst children (Ramírez-Castillo et al., 2015). Viruses are commonly found to be between 0.05 and 0.1 µm and bacteria between 1 and 5 µm. Reduction of pathogen concentrations occurs via two pathways: removal or inactivation. Removal can be achieved via adsorption or (bio)filtration and inactivation is done by (advanced) oxidation, heat or UV techniques (Bennett, 2008). It has been found that Fe-electrocoagulation makes use of both removal pathways, with coagulation and flocculation as removal method, while ROS are the cause for inactivation (Bicudo, 2021; Ghernaout and Elboughdiri, 2019). The concentration of bacteria and viruses is commonly given in CFU (colony forming units) and PFU (plague forming units) per unit of volume respectively and concentrations are found to range between the order of 10^4 to 10^5/mL in raw wastewaters, decreasing to the range of 0 to 100/mL in discharged secondary effluent (Raboni, 2016; Bicudo, 2021). Due to the high importance of thoroughly indicating total removal efficiencies, the removal of pathogens is typically expressed as log reduction, or log-removal. Important microbial contaminant indicators are *Escherichia coli* (*E. coli*) and (somatic) coliphages, respectively used as indicators for bacteria and viruses.

1.3.6 Metals and metalloids

Water pollution due to heavy metals is one of the most serious environmental issues to date. The term heavy metals is commonly used to indicate a group of trace metals and metalloids with an atomic density greater than 4 g/cm^3, and includes arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, and zinc (Wolowiec et al., 2019; Zamora-Ledezma et al., 2021). Heavy metals end up in water bodies through both natural and anthropogenic pathways, such as rock weathering, runoff, fertilizers, mining and sewage discharge (Kumar et al., 2020; Mohammed et al., 2011). A study by Zhou et al. (2020) collected data from over 4 decades across five continents of heavy metal concentrations in rivers and lakes and found that the concentrations have risen steeply, and in some cases far above the drinking water standards as given by WHO and USEPA. Due to insufficient environmental management in many countries in Africa and Asia, heavy metal pollution is a big problem. Heavy metals cannot be biodegraded and persist indefinitely, causing build-up. Most of the heavy metals are found to be toxic to all forms of life, even in the smallest concentrations (Duruibe et al., 2007; Mohammed et al., 2011). For humans, long-term exposure to elevated levels of these heavy metals can cause many health issues ranging from mild symptoms, such as headaches, abdominal pains and vomiting, to severe diseases, such as skin diseases, cancer and kidney failure (Rusyniak et al., 2010; Mohammed et al., 2011).

1.4 Research approach

As stated, EC is still an unconventional water treatment technology with an existing knowledge gap surrounding the detailed mechanisms of the processes that help to optimize the continuous flow performance (Harif et al., 2012). This includes the exact coagulation/flocculation mechanisms, the production of ROS and disinfection possibilities. Most current knowledge on EC is based on research done in a batch environment (Holt et al., 2002; Harif et al., 2012; Dubrawski and Mohseni, 2013). At TU Delft, research on Fe-EC for disinfection, arsenic removal and OMP degradation has been conducted, yet primarily in batch experiments as well. Studies at TU Delft by Kraaijveld (2021) and Roy et al. (2021) used a continuous flow environment, however in their case, a filter bed was present in the column, thus not focusing solely on an EC system. The performance of Fe-EC in a full water column using a continuous flow set-up has had little to no attention yet. The basic, and fundamental, principle of Fe-EC has been observed and the concept of Fe-EC can be formulated to a certain extent. With other words, the technology readiness level (TRL) is found to be on the lower level, as depicted in **Figure 2**. To gain a better understanding of the viability and optimization of the continuous flow process for water reclamation purposes, a proof of principle is conducted. The aim of this proof of principle study is to determine the feasibility and the practical potential of Fe-EC during a continuous flow implementation and will give insight to the general performance of the system in terms of water quality improvement. This includes improvements in turbidity, and the reduction of nutrients, OMPs and heavy metals/metalloids. Furthermore, the disinfection of bacteria and virus indicators will be determined. In addition to these main goals, additional focus will lay on increased contaminant concentrations and variations of pH. This will help with a more specific approach and a better understanding of the removal processes occurring in Fe-EC.

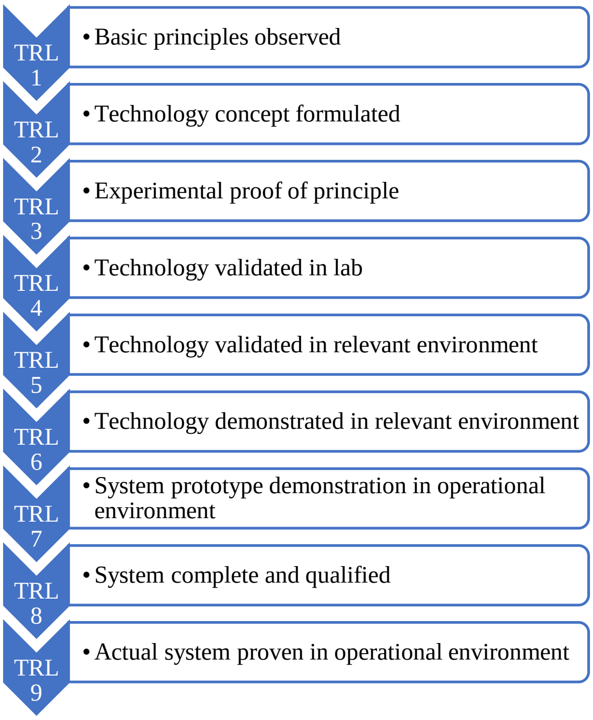

Figure 2 *- Technology Readiness Levels (TRL)*

2. Methodology

2.1 Experimental setup

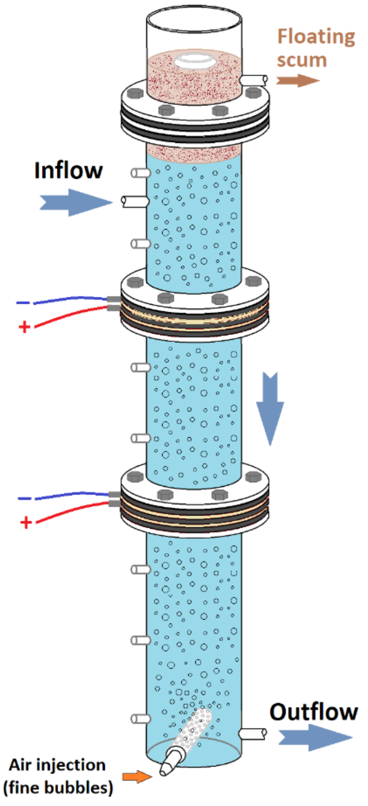

***Figure 3** – Schematic design of the continuous flow Fe-EC unit.*

To conduct all experiments, a unit was constructed as schematically shown in **Figure 3**. The unit is comprised of an acrylic tube with an effective length of approximately 83 cm and an inner diameter of 5 cm, thus giving a volume of 1.6 L. Along the length of the unit, two pairs of electrodes are located with a distance of approximately 20 cm from each other. Above the first pair of electrodes, the water inflow is located, 20 cm from the top of the unit. Near the bottom of the unit, an air diffuser is used to continuously pump air into the system, creating tiny air bubbles. The water outflow is located at the bottom of the unit, promoting a descending plug flow. The descending water flow and rising bubbles create a counter current in the unit. In the top part of the unit, an inverted funnel is located to collect and accumulate any floating particles, where they can be removed from the system. Along the length of the unit at distances of approximately 10 cm, several sampling points are added.

The electrodes have a circular shape to fit the tube and their inner part is constructed in a bar pattern to allow for minimal disturbance of the water flow, while maintaining sufficient electrode area. **Figure 4** shows the electrode used. The total effective area of a single electrode is 12 cm^2. The electrodes are made from ARMCO Pure Iron Grade 4 and their composition can be found in **Table 3**, according to the manufacturer. Each electrode pair is separated by a rubber ring with a thickness of 5 mm. After each experiment, the electrodes were rinsed with demi water, polished with sandpaper, rinsed with demi water again and lastly dried with paper towel, before placing them back in the unit.

Inside the unit, the water gains Fe^{2+}, as it passes through the electrodes, which will be oxidized to Fe^{3+} by the presence of the air bubbles during the downwards motion, in addition releasing reactive oxygen species (ROS) continuously.

***Table 3** – Chemical composition of the used electrodes* (AKSteel, 2022)

Element	Maximum %
Carbon (C)	0.010
Manganese (Mn)	0.06
Phosporus (P)	0.005
Sulphur (S)	0.003
Nitrogen (N)	0.005
Copper (Cu)	0.03
Cobalt (Co)	0.005
Tin (Sn)	0.005

***Figure 4** – Electrode design*

During every experiment, the influent was kept in a bucket and continuously stirred with a magnetic stirrer to prevent any settling of particles. From this bucket, the water was directed to the Fe-EC unit with the help of a peristaltic pump. Furthermore, a DC power unit was used to provide the electrodes with electric current and an air pump provided aeration in the unit. **Figure 5** shows the schematic overview of the laboratory setup.

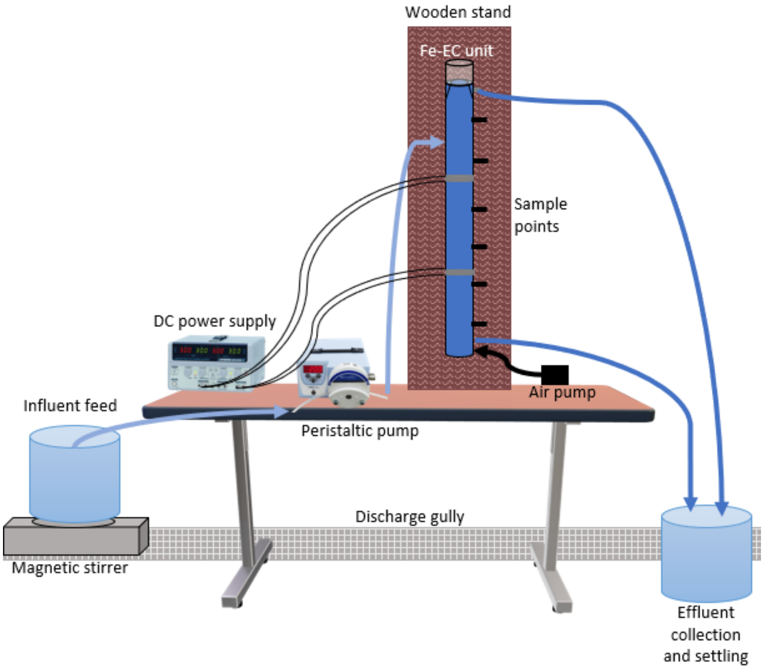

***Figure 5** – Schematic design of the laboratory setup and the equipment.*

2.2 Research phases

The research had been divided into separate research phases. Within each phase, the focus of study was on a certain set of operational parameters or contaminants, to better comprehend the influence that each aspect has on the system. In addition, the phases were added to provide structure and clarity to the research.

2.2.1 Configuration of the unit (troubleshooting)

Before the start of the experiments, the unit first had to be configured, tested and adjusted accordingly, in order to reach a system viable for the removal of contaminants. This was needed as no prior experiments had been performed with this unit and the exact behavior of the electrodes, flow and aeration within the continuous flow system were unknown. The design of the column, as described in section 2.1, was determined and set beforehand, thus altering the dimensions of the unit was not part of this phase. During the configuration, water from the Schie canal was used as influent for the unit, which was readily available via a pipeline.

The objective of this phase was to better understand the working of the unit and to configure the EC system so that removal of contaminants was determined to be viable. It was decided that this process would be complete when the system reached total removal of (dosed) iron, a faradaic efficiency of above 99%, and a notable reduction of turbidity to below 1 NTU. In order to achieve this, the electrode composition and design were tested and adjusted, and variable parameters such as electric current, flow rate, flow direction, and aeration were set. The sampling points along the unit were used to obtain samples at various heights and to determine the local performance and composition. All (operational) parameters set during this phase remained unchanged during the next phases.

To determine the theoretical iron dosage, and the faradaic efficiency from the electrodes, Faraday's Law was used. However, as the unit provides a continuous flow environment in contrary to a batch environment, Faraday's Law, as given in **Eq. 12**, had to be adjusted accordingly into **Eq. 15**. In this new equation, the flowrate within the system was introduced as a variable.

$$w = \frac{I * M * 3600}{z * F * Q}$$ **Eq. 15**

where,
w = quantity of electrode/iron dissolved [g L^{-1}]
I = electric current [A]
M = molecular weight of electrode (Fe = 55.85) [g mol^{-1}]
z = number of electrons involved in the oxidation/reduction reaction (Fe(II) = 2)
F = Faraday's constant = 96,485 [C mol^{-1}]
Q = flowrate [L/h]

2.2.2 General operational performance

After all the operational parameters had been determined, the general operational performance of the Fe-EC unit could be studied during continuous flow on an influent feed of secondary effluent. The secondary effluent was collected from WWTP Harnaschpolder, located in Den Hoorn, and stored in the fridge between experiments at a temperature of around 5 ºC. In this phase, only contaminants already present in the collected secondary effluent were used to determine the performance, as no additional contaminants were dosed to the influent feed. This phase was used to gain insight to the general and possible performance of the system, and to determine what contaminants show, or do not show, affinity for removal by the EC treatment. In addition, to obtain an idea of the removal capacity of the formed flocs, additional effluent samples were continuously stirred for 24 hours, making sure an equilibrium was reached, before analysis. Results obtained in this phase were used as a reference for validation and comparison of the next phases.

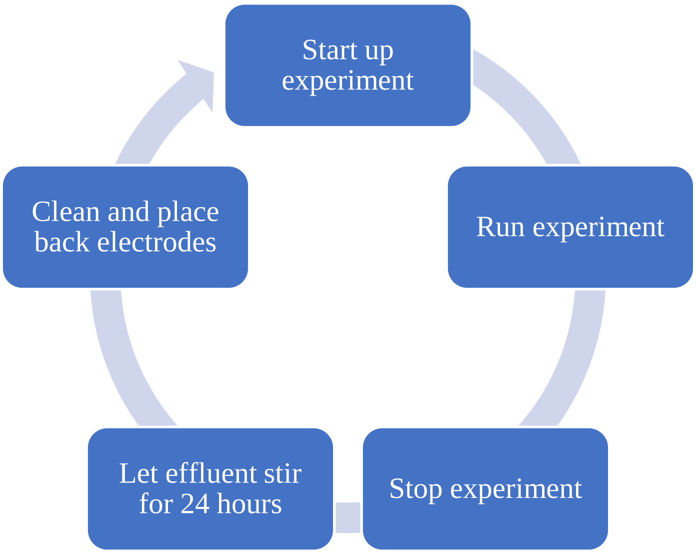

Figure 6 *- Stepwise experimental procedure of the general operational performance experiments.*

2.2.3 Determination of the influence of pH and ROS

In this next phase, experiments were conducted to determine the influence of increased contaminant concentrations, and that of pH and ROS. For this, some changes were made to the characteristics and composition of the influent feed, while operational parameters stayed unchanged. The removal capacity of the flocs, by determination of contaminant concentrations in the effluent after 24 hours of continuously mixing, was not included in this phase. In total, this phase consisted of two sets of experiments to determine a more in-depth potential of the Fe-EC unit. This was done by further studying the removal of selected contaminants and in addition, by determining the influence that pH and ROS have on this removal. Contaminants were selected based on the results obtained in the previous phase, where the observed removal of a contaminant determined possible affinity with EC. It was decided to further investigate the removal of six OMPs, five metals, one nutrient and two microbes (shown in **Table 4**), with increased influent concentrations. For this purpose, a stock solution containing high concentrations of these OMPs, metals and nutrient was prepared beforehand and stored in the fridge between experiments. The full composition of this stock solution can be found in Appendix A. To achieve the desired increase of contaminant concentrations in the influent, 10 mL of stock solution was spiked per liter of influent, aiming for theoretical concentrations of 50 µg/L, 80 µg/L and 4 mg/L for OMPs, metals and the nutrient respectively. The concentrations were chosen as they were deemed high enough to be able to see relevant removal, and in addition, using these concentrations it was expected that effluent concentrations would stay above the lower measurement limits of the analytical equipment. Due to the potentially dangerous nature of microbes, nonpathogenic strains of *E. coli* (WR1) and somatic coliphage (FX174) were spiked separately in the influent at the start of every experiment, aiming for an initial concentration of 10^3 to 10^4 forming units/mL. The first set of experiments was conducted at a pH of 8, which is comparable to that of the secondary effluent used in the previous phase. The second set of experiments was lowered to a pH of 7, to determine the effect that pH and ROS have. **Table 5** shows the mentioned differences between the sets of experiments.

Table 4 *- Selected contaminants and their theoretical spiked concentration*

Nutrient (4 mg/L)	**Microbes** (10^3–10^4 FU/mL)
Phosphorus	Somatic coliphage FX174 *E. coli WR1*
OMPs (50 µg/L)	**Metals** (80 µg/L)
Caffeine	Arsenic as As(V)
Metformin	Copper
Gabapentin	Zinc
Trimethoprim	Chromium
Sulfamethoxazole	Vanadium
Carbamazepine	

Table 5 *- Experimental settings for the different experiment sets*

	pH	**Increased contaminant concentrations**
Reference	8	No
Set 1	8	Yes
Set 2	7	Yes

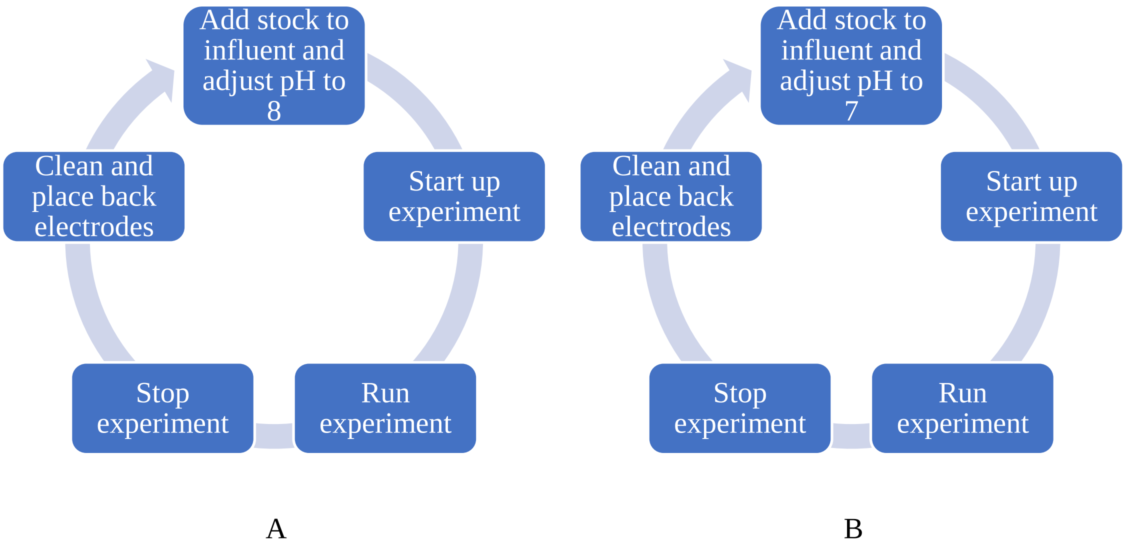

Figure 7 *- Stepwise experimental procedure of the pH experiments, with a pH of 8 (A) or a pH of 7 (B).*

2.3 Sampling and analysis

Each experiment was run for 90 minutes, where the first half was used to reach a steady-state system and ensure total breakthrough of contaminants, which was determined during the configuration of the unit and will be discussed in section 3.1. All samples were taken directly from the influent or effluent feed during different moments in time after the start up was completed. Two main kinds of samples were collected: filtered and unfiltered. Filtered samples were directly filtered over an 0.20 micron filter after collection to remove the solid flocs and to stop the flocculation process. These samples were then immediately prepared for the analytical instruments according to their method. Unfiltered samples were collected to determine the faradaic efficiency, to continue to mix for 24 hours, or to let settle and determine microbe concentrations from the supernatant, as filtered samples are unfit for microbial quantification. Filtered samples were all analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Liquid Chromatography Mass Spectrometry (LC-MS) and Ion Chromatography (IC) to determine concentrations. To prepare samples for the ICP-MS and ICP-OES, nitric acid (NO_3) reaching 1% v/v was added to the samples. Metals and common compounds can be detected with the ICP-MS and ICP-OES, OMPs with the LC-MS and ions with the IC. The ICP-MS, ICP-OES and the LC-MS were operated by trained lab technicians. The detection limit of the ICP-MS, ICP-OES and the LC-MS can be found in Appendix B for every measured compound (based on a pure water matrix). In order to determine the faradaic efficiency, the total iron was measured using Spectroquant® Iron Cell Test (1-50mgFe/L) and read in Spectroquant® NOVA60 (Merck, Germany) photometer. Determination of bacteria and viruses was performed with a culture method. For bacteria, membrane filtration assays were used and incubation for 24h at 37 °C in Chromocult® coliform agar, and for viruses, the method followed ISO 10705-2_2000.

3. Results

3.1 Configuration

Configuration of the Fe-EC unit started with basic flowthrough tests to get a sense of the visible behavior, like flow profile, size of the air bubbles, and floc formation. At this very beginning, the electrodes that were used had a grid pattern, as shown in **Figure 8**, and it was seen that the gap size was too small, causing disturbance to both the flow profile, and the air bubbles. Air bubbles would get stuck beneath and between the electrodes blocking passage and reducing effective electrode area. The trapped air bubbles collide together forming air pockets and growing in size until they would burst due to water pressure from above, causing disruptions in the flow and spikes in voltage. A new design of the electrodes was made as a bar grid (**Figure 4**), including larger gaps without reducing the total

Figure 8 - *First iteration of the electrode design*

electrode area. It was found that this bar design did not notably obstruct the passage of air bubbles, or cause spikes in voltage.

To configure the operational settings, literature was used to determine starting values. According to Sillanpää, M. and Shestakova, M. (2017), current density using EC should be in the range of 1 – 50 mA/cm^2 , and in addition, Kobya and Demirbas (2015), van Genuchten et al. (2017), and Nariyan et al. (2017), state that the current density for optimal contaminant removal should be (below) 20 mA/cm^2. Furthermore, Bicudo et al. (2021) determined that an Fe dosage of 50 mg/L was ample enough for sufficient bacterial removal. Given these two factors, electric current and flow rate were determined using Faraday's Law (**Eq. 15**) by filling in 50 mg/L as desired Fe dosage:

$$0.05 = \frac{I * 55.85 * 3600}{2 * 96485 * Q} \qquad \textbf{Eq. 15}$$

With the current density being linked to the electric current, the above could be rewritten through:

$$CD = \frac{I}{A} \;\Rightarrow\; I = CD * A \qquad \textbf{Eq. 16}$$

Implementing these together gave the correlation between the current density (in mA/cm^2) and flow rate (in L/h) with a ratio of 1:2 respectively.

$$CD \left[{}^{mA}/_{cm^2}\right] = \frac{0.05 * 2 * 96485 * Q}{55.85 * 3600 * 24e^{-3}} = 1.999 * Q = 2Q \qquad \textbf{Eq. 17}$$

***Table 6** – Correlation between flow rate, current density and electric current, at an Fe dosage of 50 mg/L.*

Flow rate [L/h]	6	6.5	7	7.5	8	8.5	9	9.5	10
Current density [mA/cm^2]	12	13	14	15	16	17	18	19	20
Electric current [mA]	288	312	336	360	384	408	432	456	480

It was decided to operate the system with a flow rate of 7.5 L/h, which gave a current density of 15 mA/cm^2 and an applied current of 360 mA in total, meaning 180 mA to each electrode pair. The voltage that was needed to supply this varied between 7 and 7.5 V. All the operational parameters can be seen in **Table 7** below.

***Table 7** - Operational parameter values*

Parameter	Value	Unit
Flow rate	7.5	L/h
Hydraulic retention time	13	minutes
Current per pair	180	mA
Total current	360	mA
Total voltage	7 – 7.5	V
Theoretical Fe dosing	50	mg/L
Current Density	15	mA/cm^2

With a flow rate of 7.5 L/h, the flow velocity in the unit was 3.8 m/h and the average hydraulic retention time was 13 minutes. To obtain information about the actual retention times in the system, a breakthrough experiment was performed using Schie canal water as influent, dosed with 1 g/L NaCl to create a high conductivity. The results of this experiment are given in **Figure 9**. It can be seen that the first four minutes show no breakthrough yet, after which the breakthrough gradually increases. From this experiment it was found that the system reaches steady state after about 30 to 35 minutes.

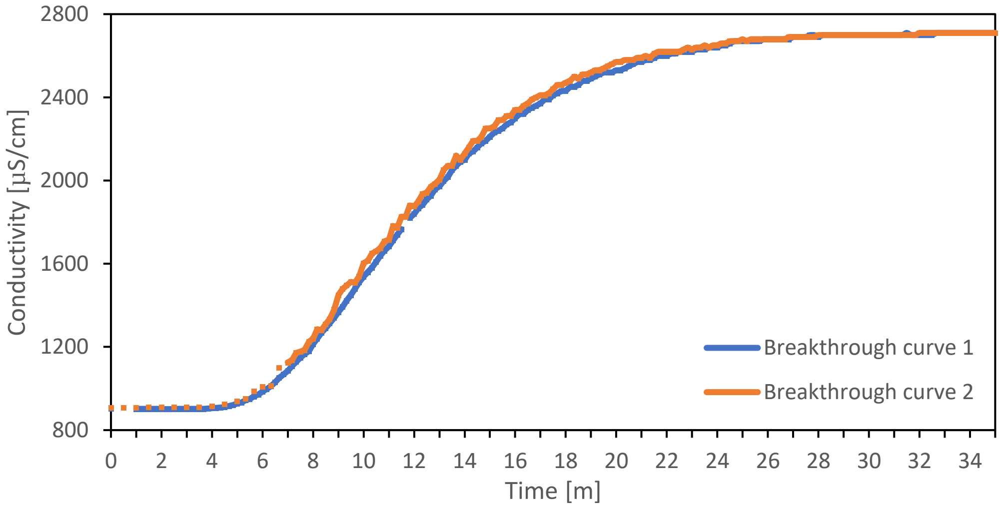

Figure 9 *- Breakthrough curves of the Fe-EC unit using Schie canal water with 1 g/L NaCl as influent.*

With the operational parameters set, the system was tested for some general water quality parameters. **Table 8** shows the results of these runs and the general measurements show little to no change in pH and electrical conductivity (EC). On the other hand, a steep decrease in turbidity was found, reaching under 1 NTU. Furthermore, Fe shows a decrease to under 70 µg/L in the initial effluent and under 40 µg/L after 24 extra hours of stirring. Considering an additional 50 mg/L is dosed in the unit from the electrodes, it can be said that all iron is removed. This decrease also validates the oxidation of almost all Fe^{2+} to Fe^{3+}-precipitates, which function as the coagulant in the Fe-EC and leave the system as flocs. In addition, it was found that the total Fe concentration within the unit was 49.7 mg/L, reaching a faradaic efficiency of 99.4%. With these results, the configuration of the system had been reached.

Table 8 *- General measurement values, determined during system configuration.*

Parameter	Unit	Influent	Effluent	Effluent (24h)
pH	-	8.06	8.35	8.17
Conductivity	µS/cm	1125	1099	1091
Turbidity	NTU	4.15	0.698	0.684
Iron (Fe)	µg/L	137.4	67.7	39.4

3.2 Nutrients

Removal of nutrients is an important aspect of water treatment and as stated before, removal of phosphorus and nitrogen is highly desired due to their concerning presence in the environment. **Table 9** shows the concentrations of ten nutrients that had been analyzed. It was found that phosphorus had almost been removed fully, reaching concentrations of 0.04 mg/L. Even though removal of phosphate shows great promise, removal of nitrogen (as nitrite, nitrate and ammonium) was observed to be neglectable in both the initial effluent as the 24-hour effluent. This same result was found for all other nutrients, unable to reach removal of over 10%, showing no affinity for nutrient removal by EC.

Table 9 *- Nutrient concentrations in the influent (secondary effluent), the effluent, the removal percentage based on the influent and effluent, and the effluent after 24 hours of continuously stirring.*

Element	Symbol	Influent	Effluent	%Removal	Effluent (24h)
Sodium	Na	125.7	125.8	-0.08	127.4
Calcium	Ca	75.4	69.8	7.44	73.6
Magnesium	Mg	14.5	13.9	4.33	14.1
Nitrite	NO_2^-	1.1	1.0	3.35	1.2
Nitrate	NO_3^-	13.2	12.9	1.90	13.1
Ammonium	NH_4^+	1.0	1.0	-5.35	1.2
Phosphorus	P	0.57	0.04	92.2	0.05
Sulphate	SO_4^{2-}	68.4	67.8	0.95	67.0
Potassium	K	29.0	29.0	0.05	29.4

Concentrations given in mg/L.

To further test the removal of phosphorus in the Fe-EC unit, the influent concentration was increased to about 5 mg/L. It was found that phosphorus was removed close to 99%, decreasing from 4.89 mg/L and from 4.46 mg/L to the detection limit of 0.06 mg/L (using the ICP-OES) when operating with a pH of 8 and 7 respectively, proving Fe-EC to be a great treatment method for the removal of phosphorus. These results were as expected as it has already been found that EC has significant removal efficiency for phosphorus and notably less for nitrogen (Inan and Alaydın, 2013; Symonds et al., 2015).

Table 10 *- Removal of phosphorus during operation with pH 8 and pH 7.*

	Set 1 (pH 8)			Set 2 (pH 7)		
Element	**Influent**	**Effluent**	**%Removal**	**Influent**	**Effluent**	**%Removal**
Phosphorus	4.89	0.06	98.8	4.46	0.06	98.7

Concentrations given in mg/L.

3.3 OMPs

In the reference experiments, the aforementioned 18 OMPs were all analyzed as they were present in the secondary effluent. The removal results are shown in **Table 11**. First to notice is that the concentrations in the influent feed are fairly low to begin with ranging from 0.04 µg/L for sulfadimethoxine to 4.29 µg/L for hydrochlorothiazide, with the mean influent concentration of all OMPs together being 1.07 µg/L. Second to notice is the high range of removal percentage. It was observed that compounds like diclofenac (67%), sulfadimethoxine (43%) and acetaminophen (41%) reach a relatively high removal percentage, while other compound are found to show little to no removal. However, in the case of diclofenac, concentrations in the 24h effluent seem to have increased to its influent concentration again. It should be mentioned that concentrations and concentration differences are so low, that minor errors in the equipment, sample handling or measurements can have a relatively big influence. With this, it was found that relative standard deviations within the measurements range from 0.5% to 92% (Appendix C), which attest to relatively big scatter in some measurements. Although detection limits of the LC-MS are very low (Appendix B), sample volumes and internal standard volumes used are very small, leading to a larger possible error with human handling. On this note, ketoprofen and theophylline were found to significantly increase in concentration during the EC treatment, which is expected to be due to errors as Fe-EC does not create OMPs.

To differentiate the OMPs, their observed removal has been categorized in a removal rating from ‘none’ to ‘excellent’. It can be seen that the categories are distributed quite evenly, with four OMPs showing an increase (none), three are found to have poor removal, five show moderate removal, three show good removal and, again, three show excellent removal. It has to be mentioned that these categories and their matching range of %Removal were chosen based on the results and may not correspond to other literature.

Table 11 *- OMP concentrations in the influent (secondary effluent), the effluent, the removal percentage based on the influent and effluent, the effluent after 24 hours of continuously stirring, and their respective removal given as none (< 0%),poor (> 0-5%), moderate (5-15%), good (15-35%) or excellent (35% >).*

Compound	Influent	Effluent	%Removal	Effluent (24h)	Removal
1H-Benzotriazole	1.85	1.68	9.33	1.70	Moderate
4,5-methyl-benzotriazole	0.88	0.81	7.66	0.81	Moderate
Carbamazepine	0.45	0.37	18.57	0.43	Good
Gabapentin	1.92	1.84	4.01	1.78	Poor
Diclofenac	0.18	0.06	67.00	0.18	Excellent
Ketoprofen	0.11	0.21	-83.59	0.11	None
Caffeine	0.42	0.39	7.52	0.41	Moderate
Theophylline	0.99	1.23	-24.05	1.16	None
Metoprolol	2.44	2.37	2.74	2.22	Poor
Propranolol	0.19	0.15	19.45	0.18	Good
Sotalol	2.50	2.38	4.87	2.32	Poor
Sulfamethoxazole	0.29	0.30	-3.89	0.32	None

Trimethoprim	0.13	0.12	7.74	0.15	Moderate
Clarithromycin	1.55	1.36	12.54	1.60	Moderate
Sulfadimethoxine	0.04	0.03	43.37	0.04	Excellent
Hydrochlorothiazide	4.29	3.55	17.18	4.67	Good
Metformin	0.92	0.92	-0.02	0.91	None
Acetaminophen	0.15	0.09	40.72	0.06	Excellent

Concentrations given in µg/L.

To better quantify and characterize the removal potential of Fe-EC, several OMP concentrations in the influent feed were increased to about 50-60 µg/L. With this higher concentration, a more accurate analysis of the removal could be conducted, as minor errors are less significant. The selected OMPs were chosen based on their (physical) characteristics in order to ensure a variation between Log K_{ow}, pKa, and observed removal in the reference. With this selection, a comparison between the behavior of OMPs was made based on their difference in characteristics. The measurement results are shown in **Table 12** for both sets of experiments. Notable are the influent concentrations that vary between the sets, clearly showing the inaccuracies of spiking the influent feed using a separate stock solution. The low solubility of the OMPs plays an important role in this, as undissolved particles create an uneven concentration distribution. The range in %removal between the different OMPs is not as big as seen in the reference, only having a maximum %removal difference of 17% between metformin (7.7%) and carbamazepine (24.6%). Set 1 shows similar removal behavior as the reference, with carbamazepine showing higher removal, followed by trimethoprim, caffeine and gabapentin with slightly lower removal, and the lowest removal found in sulfamethoxazole and metformin. Comparing operational pH values, it was found that in the first set, at a pH of 8, removal was higher than in set 2, operating at a pH of 7. In set 1, removal of four out of the six OMPs exceeds 15%, while in set 2 none of the OMPs are removed above 15%. Furthermore, removal of carbamazepine and gabapentin show a steep decrease of 18% and 15% respectively between set 1 and set 2. All results were found to be lower than what has been reported in other studies using Fe-EC, where removal efficiencies range between 40% and 90% (Ensano et al., 2017; Ensano et al., 2017; Nariyan et al., 2017). However, between these studies, operational settings vary greatly and are therefore difficult to compare.

***Table 12** – OMP removal comparison between set 1 and set 2.*

	Set 1 (pH 8)			Set 2 (pH 7)		
Compound	**Influent**	**Effluent**	**%Removal**	**Influent**	**Effluent**	**%Removal**
Carbamazepine	48.11	36.27	24.61	28.08	26.39	6.02
Sulfamethoxazole	42.45	39.18	7.69	39.11	38.64	1.19
Trimethoprim	59.59	48.58	18.48	49.64	42.26	14.87
Caffeine	58.84	48.87	16.94	50.61	43.14	14.76
Gabapentin	55.32	44.66	19.28	45.35	43.50	4.09
Metformin	61.17	56.46	7.69	52.04	47.58	8.56

Concentrations given in µg/L.

3.4 Microbes

Observed concentrations of *E. coli* and somatic coliphages are displayed in **Figure 10**, and their corresponding log removal in **Table 13**. During the reference experiments, while performing the virus screening and observing the results, it was found that concentrations were not as high as anticipated, giving results below allowable detection limit (< 30 PFU/plate). This meant that larger sample volumes were needed in order to satisfactory determine the concentration. Unfortunately, these volumes were not collected and the concentrations of somatic coliphages was not determined during the reference. All other determinations were performed and it was found that the removal of *E. coli* reached a log removal of 1.13 and 1.56, when operating with a pH of 8 and 7 respectively. This same correlation was observed in the removal of somatic coliphages, reaching a log removal of 0.20 and 0.65, again for a pH of 8 and 7 respectively. This increase in removal at a lower pH can be the result of increased inactivation due to the presence of more active ROS. Studies have shown that electrocoagulation can reach removals of *E. coli* of up to 4log and removal of somatic coliphages up to 2log (Bicudo, 2021; Ghernaout, 2008). This shows that the operational settings, or the dimensions of the unit, are not optimized for microbial removal.

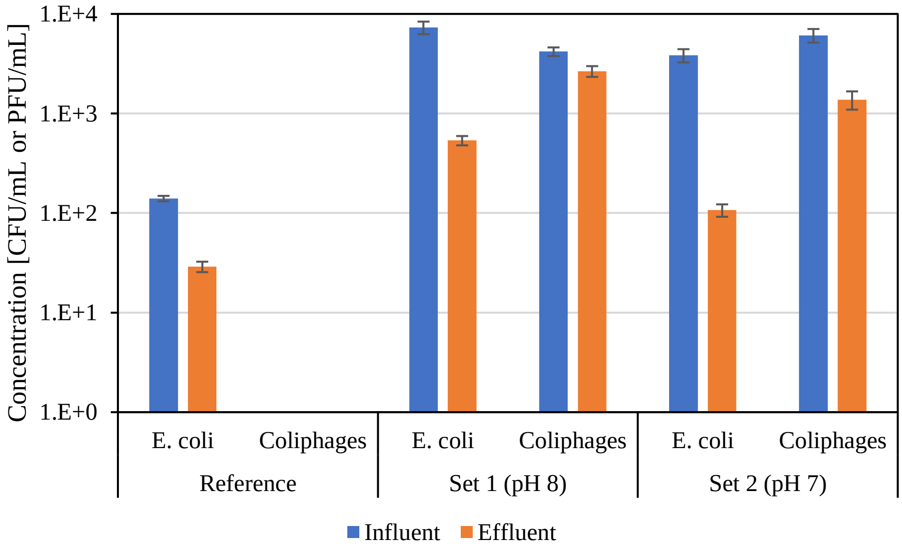

***Figure 10** – Microbial concentrations of E. coli and somatic coliphages in the influent and effluent.*

***Table 13** – Microbial log removal of E. coli and somatic coliphages.*

	Reference	Set 1 (pH 8)	Set 2 (pH 7)
Microbe	**Log removal**	**Log removal**	**Log removal**
E. Coli	0.68	1.13	1.56
Coliphages	N.D.	0.20	0.65

N.D. = not determined

3.5 Metals and metalloids

Metals and metalloids are present in secondary effluent in small amounts, which gave the opportunity to determine the possible removal efficiencies of these metals during Fe-EC. The concentration of 13 metals was determined with the ICP-MS and results are shown in **Table 14**. In addition to the concentration and removal, it is given whether or not the corresponding metal may be found in the electrode according to the manufacturer, and if so, as what maximum percentage. Besides iron, only copper, manganese and cobalt are supposed to be found as part of the electrode. It is notable that from these, only cobalt shows an increase in concentration. Looking at the influent, concentrations vary a lot ranging from 0.36 µg/L for cobalt to 133.25 µg/L for manganese. High concentration of manganese is not uncommon in water bodies as it is a highly naturally found element, also present as trace metal in the human body. Very interesting is the steep increase of nickel, from 4.40 µg/L in the influent to 7.74 µg/L in the initial effluent and even increasing to 8.66 µg/L in the 24-hour effluent. As the manufacturer claims that nickel cannot be found in the electrode, this increase is not as expected. High removal (> 30%) can be found for a few metals, including arsenic, copper, zinc, manganese and vanadium.

***Table 14** – Metal and metalloid concentrations in the influent (secondary effluent), the effluent, the removal percentage based on the influent and effluent, the effluent after 24 hours of continuously stirring, and whether or not they can be found in the electrode material, according to the manufacturer.*

Element	Symbol	Influent	Effluent	%Removal	Effluent (24h)	In electrode?
Arsenic	As	2.24	< 1	> 55.36	< 1	No
Nickel	Ni	4.40	7.74	-75.96	8.66	No
Copper	Cu	3.02	1.85	38.64	2.79	Yes [0.03%]
Zinc	Zn	10.95	4.71	56.97	2.56	No
Manganese	Mn	133.25	89.83	32.59	64.61	Yes [0.06%]
Lithium	Li	10.32	10.59	-2.57	10.75	No
Boron	B	> 100	> 100	–	> 100	No
Chromium	Cr	2.75	2.25	18.14	2.34	No
Cobalt	Co	< 1	< 1	–	< 1	Yes [0.005%]
Titanium	Ti	1.1	< 1	> 9.01	< 1	No
Vanadium	V	1.72	< 1	> 41.86	< 1	No
Molybdenum	Mo	1.97	2.72	-38.21	2.64	No
Antimony	Sb	< 1	< 1	–	< 1	No

Concentrations given in µg/L.

Based on the removal achieved during the reference experiment, five metals were added to the stock solution to reach an increased concentration of 80 µg/L. These metals are arsenic, copper, zinc, chromium and vanadium. In addition, iron is added to these results to show the residual concentration in the effluent. Iron has not been added to the stock solution and its presence comes from secondary effluent and the electrodes. The results are shown in **Table 15**. It can be seen that reaching the target influent concentrations of 80 µg/L did not work. As both sets show similar influent concentrations, (in)solubility should not be the reason, but using an incorrect amount of compound is more likely the case. Appendix A shows the composition of the stock solution and the mass added per compound. In both set 1 and set 2 it was observed that the metals reached high removal, higher than observed during the reference, making it possible that other metals measured in the reference could have reached greater removal at higher concentrations. Arsenic and chromium reached effluent concentration lower than the detection limit of the ICP-OES of 6 µg/L, and vanadium was removed with 91%. It was found that for most of these metals operating at a pH 8 or pH 7, similar removal occurs, with a slightly higher removal at pH 7. More notable was the abundance of Fe in the effluent of set 2, reaching almost 2 mg/L. This increase was validated by the turbidity of the samples of set 2, increasing from 2.73 NTU in the influent to 24.01 NTU in the effluent. This gives the notion that not all Fe^{2+} was oxidated to Fe^{3+} in the unit and oxidation continued after the samples were taken.

Table 15 *– Metal and metalloid concentrations in the influent and effluent of set 1 and set 2.*

	Set 1 (pH 8)			Set 2 (pH 7)		
Element	**Influent**	**Effluent**	**%Removal**	**Influent**	**Effluent**	**%Removal**
Iron	95.71	47.49	50.38	107.15	1927.63	-1699.04
Arsenic	39.15	< 5	> 87.23	38.41	< 5	> 86.98
Copper	50.89	22.65	55.49	50.16	15.85	68.40
Zinc	72.71	9.47	86.97	77.78	8.72	88.79
Chromium	47.72	< 5	> 89.52	49.25	< 5	> 89.85
Vanadium	> 100	8.27	> 91.73	> 100	5.94	> 94.06

Concentrations given in µg/L.

4. Discussion

4.1 Removal of OMPs

Removal of OMPs varied between the compounds, as shown in section 3.3. For example, concentrations for ketoprofen were found to have increased, which can be accredited to the margin of error that the analytical equipment has at such low concentrations. On the contrary to ketoprofen, reductions up to 67% were found for diclofenac. Micropollutants are found to vary significantly in terms of their composition, chemical behavior, toxicity, and treatment (Chavoshani et al., 2020), which can significantly influence their removal.

First to state is that the general use, as given in **Table 2**, did not show a clear correlation for removal efficiency, where OMPs with the same general use did not show similar removal efficiencies. Physical properties like Log K_{ow} and pK_a values are estimated to play an important factor in the removal process. The biggest influence was expected from the K_{ow}, which defines a pollutants solubility in fat or in water and increasing log K_{ow} values represent stronger lipophilic behavior with the preference to attach to fatty tissues, and stronger repel water. With this it was predicted that lipophilic compounds would be more likely to attach to suspended particles and therefore show more affinity to the EC treatment. To add to the K_{ow}, Fent et al. (2006) states that sorption of acidic contaminants is found to be hardly existing. This is where the pK_a value of a compound and the pH of the solution play an important role. The pK_a predicts the behavior of a compound at a certain pH. The lower the pK_a is under the pH, the more a compound will dissociate and is expected to be present in ionic form. This means that acidic compounds (lower pK_a) are expected to be found more as anions at neutral pH. This however contradicts the statement from Fent et al. (2006), as one would expect anions to show affinity for sorption to positively charged Fe-particles. It has thus been hypothesized that the removal of OMPs via a sorption process can be predicted based on their pK_a, but more so on their Log K_{ow}, where lipophilic compounds are expected to show greater removal. This hypothesis has been depicted in **Table 16**, sorting all the OMPs by descending log K_{ow} values, and also showing their removal classification as described in section 3.3. Starting at the top of the table, diclofenac did show excellent removal and has a high log K_{ow}, in combination with a low pK_a. However, looking at the rest of the table it can be seen that the hypothesis does not show in the other observed removal results. For example, ketoprofen has quite a high log K_{ow} (3.12) and low pK_a (4) just like diclofenac, but shows no removal at all. The opposite can be said for hydrochlorothiazide, showing good removal, while having a negative log K_{ow} (-0.07).

Table 16 *- Removal classification of OMPs during the reference experiment sorted by descending log K_{ow} values.*

Compound	Removal (own data)	Log K_{ow}	pK_a
Diclofenac	Excellent	4.51	4.2
Propranolol	Good	3.48	9.45
Clarithromycin	Moderate	3.16	8.99
Ketoprofen	None	3.12	4
Carbamazepine	Good	2.77	15.96
Metoprolol	Poor	1.88	9.7
4,5-methyl-benzotriazole	Moderate	1.71	8.7
Sulfadimethoxine	Excellent	1.63	6.91
1H-Benzotriazole	Moderate	1.44	8.37
Trimethoprim	Moderate	0.91	7.12
Sulfamethoxazole	None	0.89	5.7
Acetaminophen	Excellent	0.46	9.38
Sotalol	Poor	0.24	9.76
Theophylline	None	-0.02	8.81
Caffeine	Moderate	-0.07	14
Hydrochlorothiazide	Good	-0.07	7.9
Gabapentin	Poor	-1.1	3.7
Metformin	None	-2.6	12.4

Further analyzation of OMP removal showed that again no correlation was found between the removal and Log K_{ow} or pKa, as presented in **Table 17**. However, operational pH did affect the overall removal, as it was observed that the removal showed higher efficiencies at pH 8 than it did at pH 7. Again, this is not in line with what to expect considering the differences of pKa values, where compounds with a high pKa value, for example carbamazepine, were expected to be influenced inversely to compounds with a low pKa value, for example gabapentin. This was not the case as both carbamazepine and gabapentin showed a significant removal decrease at pH 7 compared to pH 8.

Table 17 *– Removal of selected OMPs during set 1 and set 2, sorted by descending Log K_{ow} values.*

			Set 1 (pH 8)	Set 2 (pH 7)
Compound	**Log K_{ow}**	**pKa**	**%Removal**	**%Removal**
Carbamazepine	2.77	15.96	24.61	6.02
Trimethoprim	0.91	7.12	18.48	14.87
Sulfamethoxazole	0.89	5.7	7.69	1.19
Caffeine	-0.07	14	16.94	14.76
Gabapentin	-1.1	3.7	19.28	4.09
Metformin	-2.6	12.4	7.69	8.56

Removal of OMPs with Fe-EC was influenced more by change in pH than physical characteristics of the OMPs itself. Where no correlation was found between removal and Log K_{ow} or pKa, the results showed that higher removal was achieved when operating at pH 8, rather than pH 7. All results showed big scatter and removal of OMPs with Fe-EC remains uncertain.

4.2 Adsorption of metals and metalloids

The results in section 3.5 showed that Fe-EC has the ability to remove some metals, but the removal efficiency varied greatly between metals. Their variation in properties like melting point, conductivity, density, and ionic charge can all play a role in the affinity they show for adsorption on Fe-solids.

In the reference experiments, removal of arsenic, copper, zinc, manganese and vanadium showed potential with removals above 30%. Moussa et al. (2017) reports the removal of several heavy metals, such as arsenic, zinc, nickel, copper and chromium, on electrocoagulation reactor units where it is found that removal efficiencies up to 90% can be reached for all metals. However, these results include very different EC operational parameters, such as Al electrodes, batch environment and bipolar electrode configuration. Given these literature results, high removal of metals seems to be feasible, but operational differences and optimalization might alter this process, especially between individual metals. Results of experiments using increased concentrations of selected heavy metals (arsenic, copper, zinc, chromium, and vanadium) showed very different results than found in the reference, with removals ranging from 50% to 90%. These removal efficiencies were significantly higher and came closer to results reported in Moussa et al. (2017). Higher influent concentrations were thus found to positively affect the removal process, even being able to decrease concentrations to below their drinking water standards as set by the WHO.

Comparing results from operating at different pH values, little difference in removal between pH 8 or pH 7 was observed, with removals at pH 7 showing slightly higher values. Kumar et al. (2004) also showed that removal of arsenic was not significantly affected by a change in pH in the range of 6-8. However, Al-Shannag et al. (2015) found that maximum removal efficiencies for selected heavy metals occurred between pH 8 and 9.5, and in addition, Bhagawan et al. (2014) found increasing removal efficiency when increasing the pH from 4 to 6 to 8. The exact influence of pH on the removal of heavy metals during Fe-EC remains therefore still uncertain, although it has been shown that increased heavy metal concentrations favor the overall removal greatly.

4.3 Fe-EC: a bulldozer technology

Fe-EC features various chemical and physical conversion processes, covering a wide variety of removal pathways, like adsorption, oxidation and complexation (Zaied et al., 2020). Many of these processes are still not exactly understood. Based on the results presented in section 3, observations were made about the removal of many different contaminants, both organic and inorganic, and presenting a variation of behavioral traits and removal possibilities, even without full optimization of the system. The ability of Fe-EC to tackle a wide-range of contaminants present in (waste)water makes the treatment technology an attractive option. This study focused on the global removal potential for a wide-range of contaminants during continuous flow Fe-EC, and the determination of exact removal of contaminants, or optimization of the Fe-EC system were not part of this study.

Next to the observed removal of phosphorus, OMPs, and metals, microbial assay results showed that removal of *E. coli* and coliphages occurred during Fe-EC, however it did not reach expected log removals of 3 log as found in other studies. Nevertheless, removal up to 1.5 log was found for *E. coli* during operation at pH 7. Optimization of the system is assumed to have the ability to increase this removal closer to results found in other literature. The effect of ROS on the inactivation of microbes can be an important factor in this process, which also showed in the results with an increase of 0.4 log removal at pH 7 in comparison to pH 8. More removal may be observed when focusing more on the inactivation process during Fe-EC.

Considering this wide variety of contaminant removal that Fe-EC has shown during this study, Fe-EC can be considered a promising option for the treatment of a wide range of (waste)waters. Furthermore, Fe-EC has a fairly simplistic design, and is easy to operate and maintain, giving opportunity to the application of Fe-EC in various environments.

4.4 Considerations for practical implementation

Operational parameters such as applied current, current density, aeration, flow rate, Fe dosage and pH, all show to have influence on the performance of EC. In addition, reactor design parameters such as electrode distance, electrode orientation, reactor size and flow direction influence the effectivity of the operational parameters. For the most part of this study, operational parameters remained fairly constant and design parameters did not change. During configuration, operational parameters were set based on literature and full optimization was not part of this study. The results that were found therefore reflect more to an understanding of the possible contaminant removal rather than the maximum possible removal. In order to understand the full potential and limitations of the Fe-EC unit, more parameters should be optimized and tested.

To start, improvements can be made to the design of the used unit, as it was desired to create a floating scum layer at the top of the water column. The flocs did not show any behavior towards floating and all flocs remained suspended in the effluent, settling when velocities decreased. The reason behind this still remains unclear and fell outside the scope of this study, as it has been shown that many factors, such as hydrodynamics, aeration, and electrolyte composition, play an important role in the floc forming process (Liu et al, 2021; Tegladza et al. 2021; Lee and Gagnon, 2016). Because the flocs were suspended in the effluent, an additional manual filtration step was added to remove flocs after collecting samples, which is not desired as extra removal can occur through this filtering process, such as adsorption of OMPs, increasing removal that would have otherwise not been observed. Floc characteristics were not determined, but may help in the optimalization of the unit. In addition, to replace the manual filtration, another filtration can be added as second treatment step, after the Fe-EC unit, solely to remove the flocs. Getting the flocs to float can be an important aspect, able to increase the removal, as flocs would counter the flow direction and increasing the contact time with contaminants.

In the unit, two pairs of electrodes were located and used simultaneously. The gap between the cathode and anode was 5 mm, while the electrode pairs were split along the length of the unit, approximately 20 cm from each other. This configuration was used to evenly distribute the electrodes along the unit. The exact influence of this design has not been studied, however it can be hypothesized that this resulted in a variation of contact time within the system. Firstly, the release of Fe at the lower cathode is located close to the outlet point of the flocs decreasing retention time of these Fe-solids and their possible contact time with contaminants, thus decreasing efficiency. Furthermore, it was observed that not all Fe^{2+} had oxidized during operation at a pH of 7. This is most likely the result of the lower retention time of the bottom electrode, as it is known that oxidation of Fe occurs at a slower rate at lower pH, not giving enough time to fully oxidize all released Fe. As 2 mg/L was only 4% of the total dosed Fe, it was assumed that this did not affect the removal of contaminants. It can be helpful to investigate the effect of unbalancing the applied current per electrode pair, increasing and decreasing the Fe release at the top and bottom pair respectively. Secondly, electrode positioning has been found to disturb local flow profiles and current densities, with McBeath et al. (2020) observing that current density can be distributed unevenly along the surface of the electrode, which is generally accompanied by higher velocity flow. They also found that a larger inter-electrode gap yielded in a more uniform current distribution, due to greater flow uniformity. It can be assumed that this occurred in the used Fe-EC unit as well, with increased velocities between the electrodes.

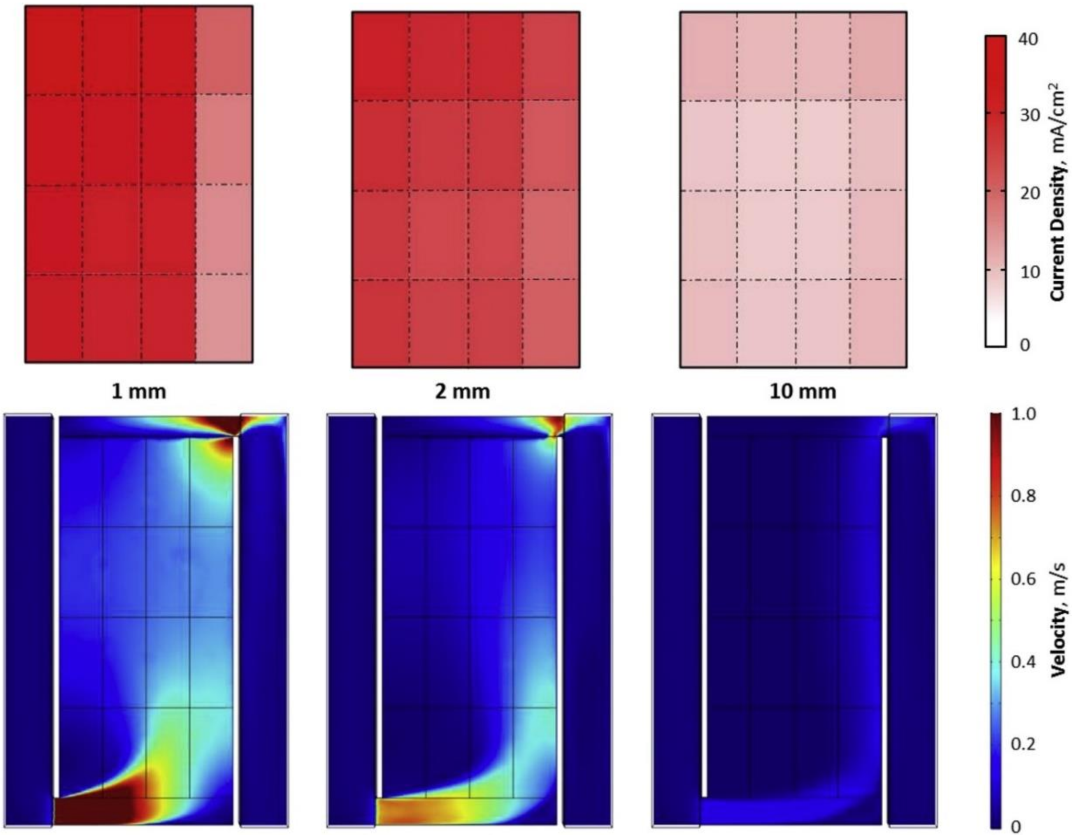

Figure 11 *– Distribution of current density along the electrode surface and flow velocities in an EC reactor for 1.35 L/min at 1, 2 and 10 mm electrode gaps. In the reactor, the inflow is at the bottom left and the outflow at the top right. (McBeath et al, 2020).*

The operational parameters as chosen in section 3.1 remained unchanged during all experiments. To be able to optimize the system, the difference in performance on varying flow rates, current densities and Fe dosages should be investigated. These parameters are depended on one another and a middle ground should be found to improve removal efficiencies. **Figure 12** shows the correlation between the flow rate and current density (CD) as determined in **Eq. 17**, and in addition, the correlation between the flow rate and hydraulic retention time (HRT), at an Fe dosage of 50 mg/L. Increasing the current density has positive effect on the removal of contaminants (Nasrullah et al., 2014; Kumar et al., 2004), however to achieve this, the flow rate has to increase, decreasing the HRT and therefore the contact time in the unit, which is expected to decrease the efficiency. This feedback loop between the parameters has to be tested in order to successfully implement Fe-EC.

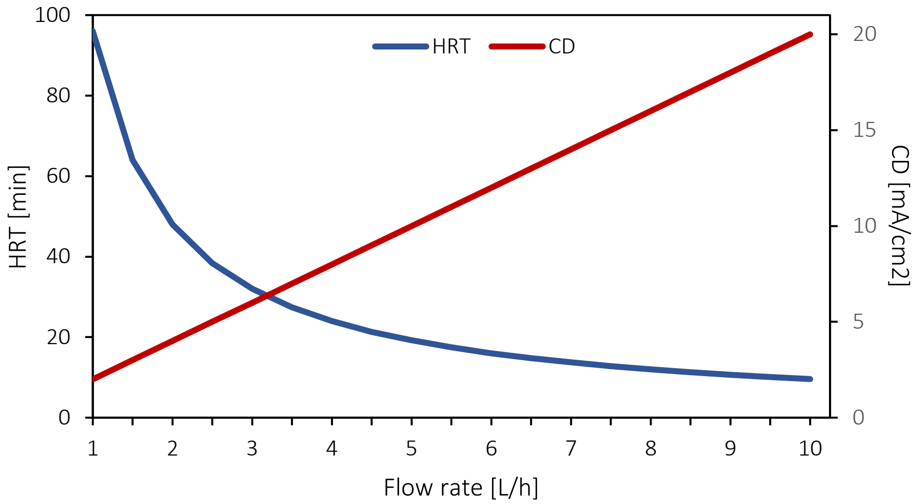

***Figure 12** – Correlation between flow rate and hydraulic retention time, and flow rate and current density.*

An undiscussed aspect in this study is the energy consumption. Energy use is an important aspect of electrochemical treatment technologies, as it can be used to determine the removal efficiency against energy consumption. Energy consumption is determined by the applied current, which can increase over time as electrodes degrade. During the use of electrodes, two main degradation processes occur (mainly of the anode): pitting due to Fe release and passivation due to adsorption or deposition of a passivating compound (Ingelsson et al., 2020; Barek, 2021). This degradation negatively affects the Fe release, and lowering the faradaic efficiency, especially in the long term (Müller et al., 2019; van Genuchten et al., 2017). In order to ensure sufficient Fe release from the anode, the applied electric current has to increase (**Eq. 15**), and therefore increasing the overall power requirements as well. The long term operational performance can be investigated by significantly increasing the amount of experiments or by operating the system for a long continuous period. At the end of this study, a faradaic efficiency of 99% was still found, showing that no noteworthy degredation of the electrodes had occurred. When comparing a new electrode with an used electrode, as in **Figure 13**, it can be seen that some degredation did occur in the form of pitting and deposits. Operating the system on a much longer term would likely result in a notable decrease of faradaic efficiency and increased power requirements.

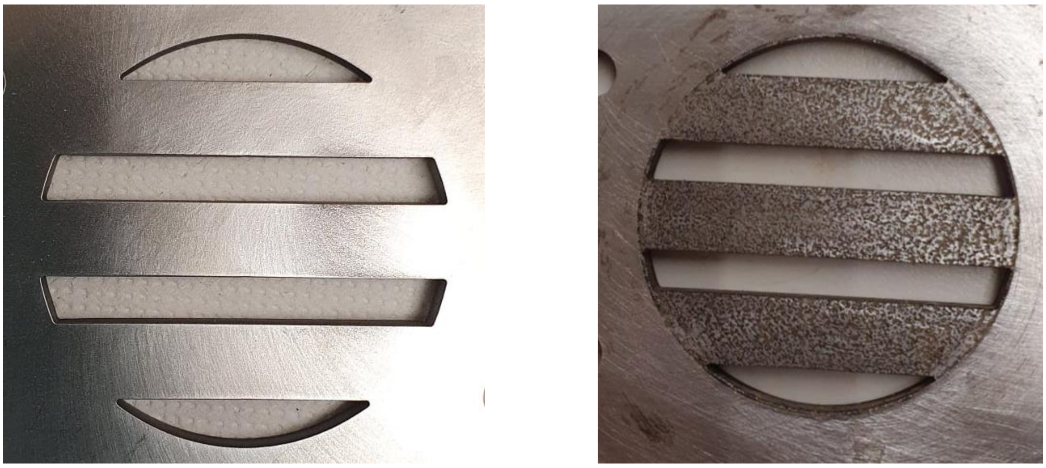

***Figure 13** – Comparison of new (left) and used (right) electrode surfaces.*

5. Conclusion and recommendations

In this study the potential removal of various contaminants during continuous flow Fe-EC on secondary effluent was investigated. The aim of this proof of principle study was to determine the feasibility and the practical potential of Fe-EC during a continuous flow implementation, and to give insight to the general performance of the system in terms of water quality improvement. In order to achieve this, the Fe-EC system was configured based on literature findings, in order to accommodate for sufficient contaminant removal. Several experiment sets were used in order to validate the removal and to obtain a better understanding of its feasibility.

Reference experiments were operated solely on secondary effluent and showed that the removal of contaminants present in the secondary effluent varied greatly. It was observed that turbidity decreased from above 4 NTU to under 1 NTU. From the nutrients, it was found that only phosphorus has high removal potential, as expected from literature. Uncertainties remained in the removal results of OMPs, as not only removal, but also increased effluent concentrations were observed, and relative standard deviations reached up to 90%. In addition, no correlation between physical characteristics of the OMPs (K_{ow} and pKa) and their removal potential was found. A few heavy metals, such as copper, zinc, manganese and vanadium were observed to be removed above 30%, arsenic above 55%, and others showed little to no change in concentration. These results of the reference experiment were used to select the contaminants that showed potential for removal, in order to further test the removal capabilities of Fe-EC.

During further experiments, with increased concentrations of the selected contaminants, removal efficiencies were again determined, and in addition the differences between operating at pH 8 and pH 7 were investigated. These experiments validated some results found during the reference, such as the high removal of phosphate, reaching above 98% removal. In addition, OMP removals showed that again no correlation was found between the removal and Log K_{ow} or pKa. Removal efficiencies also showed little correlation to the reference, however it was found that lower removals were reached at pH 7 than at pH 8. Removal of the metals still showed high removal and even improved a lot with removals ranging from 55% for copper to 90% for vanadium. For these metals, little difference was found between operation on pH 8 of pH 7. The exception for this is iron, where it was found that when operating at pH 7, not all Fe^{2+} had sufficient retention time in the system to fully oxidize, flushing out 2 mg/L (4%) of the dosed iron with the effluent. This was assumed to not affect removal of contaminants, which was partly validated by the removal that microbes showed. Both *E. coli* and coliphages were found to achieve increased removals of about 0.4 log removal at pH 7 compared to pH 8. Maximum removal or *E. coli* and coliphages reached 1.56 and 0.65 log removal respectively, which was not as high as expected from results found in literature.

The wide variety of contaminant removal that Fe-EC has shown during this study makes this technology a great promise. The system has shown to have high removal potential on secondary effluent, even when contaminant concentrations reach high levels. Nevertheless, uncertainties were found for the practical implementation of Fe-EC as design and operational parameters first have to be optimized in order to fully utilize the potential that Fe-EC has. An important next step in the optimalization of continuous flow Fe-EC is to investigate the influence and dependence of reactor design parameters, such as the location of in- and outflow (including flow direction), and electrode placement. Additionally, a better understanding of the relationship of operational parameters such as current density, flow rate and Fe dosage will greatly improve the technology's readiness level, making its practical implementation one step closer.

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Appendix

Appendix A – Stock solution composition (900 mL)

Target compound			**Actual compound**							
Name	**Target mass [mg]**	**MW [g/mol]**	**Name**	**CAS**	**MW [g/mol]**	**Purity [%]**	**Solubility [mg/L]**	**Proportion**	**Needed mass [mg]**	**Mass used [mg]**
Caffeine	4.50	194.19	Caffeine	58-08-2	194.19	100	20	1.000	4.50	4.9
Metformin	4.50	129.16	1,1-Dimethylbiguanide hydrochloride	1115-70-4	165.62	97	1000	1.282	5.95	6.1
Gabapentin	4.50	171.24	Gabapentin	60142-96-3	171.24	100	4000	1.000	4.50	4.6
Trimethoprim	4.50	290.32	Trimethoprim	738-70-5	290.32	100	400	1.000	4.50	5.1
Sulfamethoxazole	4.50	253.28	Sulfamethoxazole	723-46-6	253.28	100	38	1.000	4.50	4.8
Diclofenac	4.50	296.15	Diclofenac Sodium Salt	15307-79-6	318.13	98.5	15	1.074	4.91	4.3
Carbamazepine	4.50	236.27	Carbamazepine	298-46-4	236.27	100	18	1.000	4.50	4.7
Arsenate	7.20	138.92	Sodium Arsenate dibasic heptahydrate	10048-95-0	312.01	98	390	2.246	16.50	16.75
Copper	7.20	63.55	Copper(II) sulfate hydrate	23254-43-5	159.61	98	200	2.512	18.45	19.72
Zinc	7.20	65.38	Zinc(II) chloride	7646-85-7	136.28	98	4000	2.084	15.31	15.73
Chromium	7.20	52.00	Chromium(III) nitrate nonahydrate	7789-2-8	400.15	99	800	7.695	55.97	57.19
Vanadium	7.20	50.94	Vanadium(V) oxide	1314-62-1	181.88	98	700	3.570	26.23	25.77
Phosphorus	360	30.97	Sodium phosphate monobasic	7558-80-7	119.98	99	600	3.874	1409	1411

Appendix B – Detection limits of analytical instruments

ICP-MS

- **1 ppb – 100 ppb**
  Arsenic, Boron, Cobalt, Chromium, Copper, Lithium, Manganese, Nickel, Antimony, Titanium, Vanadium, Zinc

- **1 ppb – 5000 ppb**
  Sulphur, Phosphorus

- **1 ppb – 7500 ppb**
  Calcium, Iron, Potassium, Magnesium, Sodium

ICP-OES

- **5 ppb – 100 ppb**
  Arsenic, Chromium, Copper, Zinc, Vanadium

- **60 ppb – 5000 ppb**
  Phosphorus

LC-MS

- **0.005 ppb – 10 ppb**
  Benzotriazole, 4-5-methyl-benzothriazole, Carbamazepine, Metroprolol, Sulfamethoxazole, Propranolol, Sotatol, Trimethoprim, Clarithromycin, Metformin

- **0.01 ppb – 10 ppb**
  Diclofenac, Sulfadimethoxine, Caffeine, Theophylline, Gabapentin

- **0.05 ppb – 10 ppb**
  Ketoprofen, Acetominophen

- **0.5 ppb – 10 ppb**
  Hydrochlorothiazide

IC

- **1 ppm – 100 ppm**
  All ions

Appendix C – (Relative) Standard Deviations of OMP removal results from reference experiments

Compound	Influent	STD	RSD	Effluent	STD	RSD
1H-Benzotriazole	**1.85**	0.16	8.76	**1.68**	0.18	10.76
4,5-methyl-benzotriazole	**0.88**	0.06	7.04	**0.81**	0.09	10.89
Carbamazepine	**0.45**	0.04	8.55	**0.37**	0.04	10.68
Diclofenac	**0.18**	0.02	11.68	**0.06**	0.01	22.71
Hydrochlorothiazide	**4.29**	1.14	26.63	**3.55**	0.65	18.20
Metoprolol	**2.44**	0.25	10.36	**2.37**	0.28	11.89
Sulfamethoxazole	**0.29**	0.04	13.21	**0.30**	0.05	15.81
Propranolol	**0.19**	0.01	5.32	**0.15**	0.03	21.51
Sotalol	**2.50**	0.04	1.49	**2.38**	0.27	11.48
Trimethoprim	**0.13**	0.01	5.08	**0.12**	0.02	14.44
Clarithromycin	**1.55**	0.21	13.76	**1.36**	0.23	16.91
Ketoprofen	**0.11**	0.06	49.50	**0.21**	0.19	92.75
Caffeine	**0.42**	0.08	18.70	**0.39**	0.08	21.76
Theophylline	**0.99**	0.60	60.98	**1.23**	0.51	41.70
Gabapentin	**1.92**	0.28	14.44	**1.84**	0.27	14.54
Metformin	**0.92**	0.53	57.20	**0.92**	0.52	56.23
Acetaminophen	**0.15**	0.00	0.34	**0.09**	0.06	73.21
Sulfadimethoxine	**0.04**	0.00	5.38	**0.03**	0.00	16.65

Concentrations and STD given in µg/L.
RSD given in %.

$$STD = Standard\ deviation = \sigma = \sqrt{\frac{\sum(x_i - \mu)^2}{N}}$$

$$RSD = Relative\ standard\ deviation = \frac{\sigma}{\mu} * 100\%$$

where,
x_i = individual measurement value
µ = measurement mean
N = number of measurements