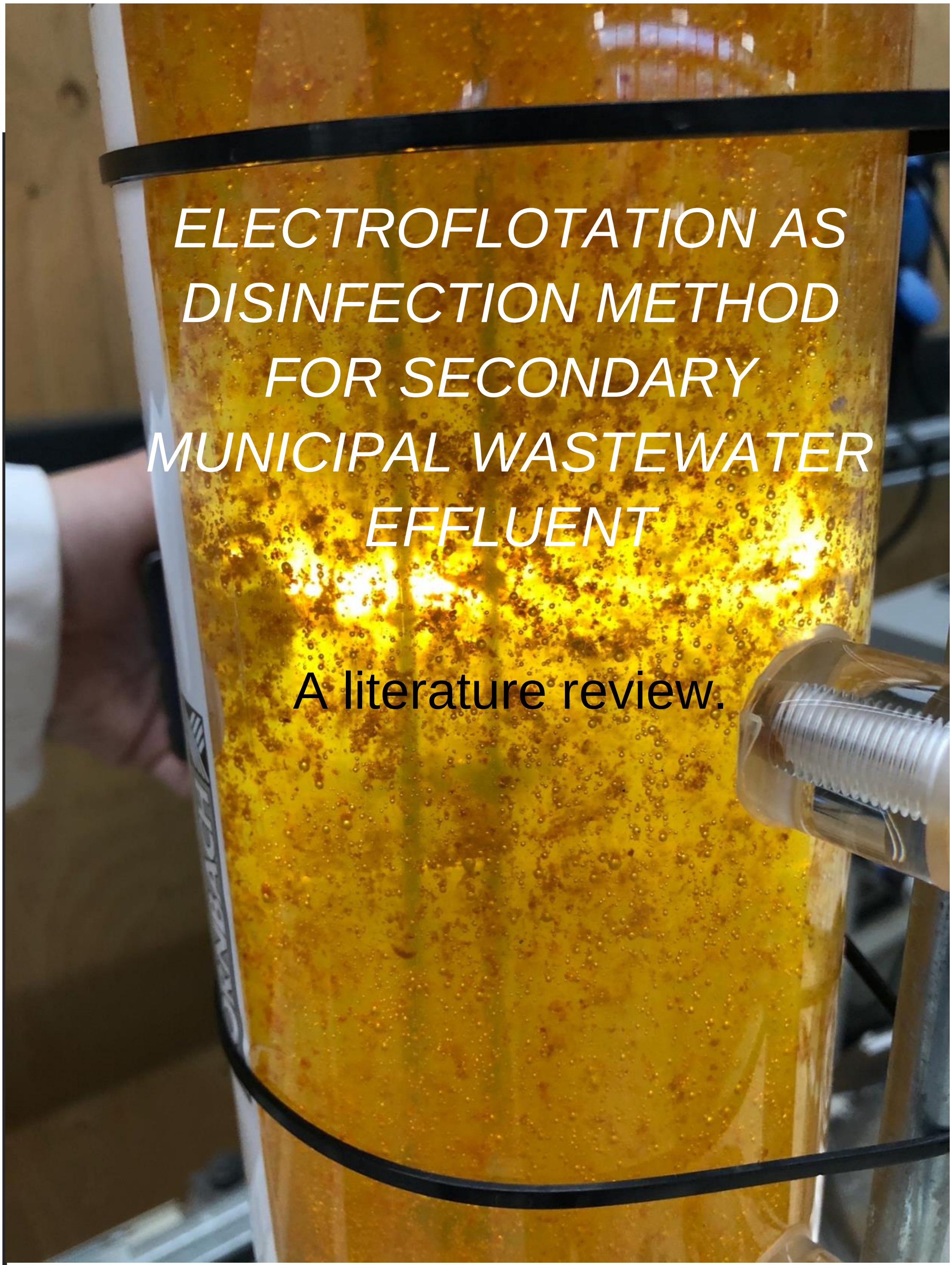

ELECTROFLOTATION AS DISINFECTION METHOD FOR SECONDARY MUNICIPAL WASTEWATER EFFLUENT

A literature review.

Additional thesis MSc Civil Engineering TU Delft
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Electroflotation as disinfection method for secondary municipal wastewater effluent. A literature review

by

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Abstract

Due to increasing water consumption and stress on natural water resources, enhanced treatment of wastewater and reuse of water are becoming more important. Treated municipal wastewater has potential to be used for irrigation purposes, but pathogens are a major concern to protect environmental and human health. Therefore, an advanced treatment step is required to reduce the levels of microorganisms, nutrients and suspended solids.

This literature review focusses on electroflotation (EF) as disinfection method of secondary municipal wastewater treatment. EF is a combination of electrocoagulation (EC) and dissolved air flotation (DAF). In EC treatment, a sacrificial metallic anode releases metal ions (usually iron or aluminium) into the solution while hydroxyl ions and hydrogen gas are produced at the cathode. Coagulants are created in situ by the hydrolysis of these metal ions to hydroxides that can destabilize pollutants. DAF is an adsorptive bubble separation process where generated gas bubbles (of 10-100 µm) separate the impurities by flotation.

This paper outlines the processes involved in EF technology and its applications in (waste)water treatment. Therefore, the processes of EC and DAF are discussed first. Influencing parameters such as electrode material, pH, retention time, charge dosage, charge dosage rate, bubble formation and size are discussed, as well as pollutant removal mechanisms. The main mechanisms responsible are charge neutralization, adsorption, sweep coagulation, microbial destruction by the electric field and deactivation by free radicals.

The conclusion is drawn that the hybrid EF technique, which has been implemented in different water treatment processes, promises to increase removal efficiencies compared to single EC and DAF treatment, but the full potential of EF as a tertiary treatment step for secondary municipal wastewater effluent is yet to be fully realized. The process needs to be empirically optimized, a challenging task due to the involvement of complex chemical and physical processes.

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Symbols and abbreviations

Al-EC	Aluminium electrocoagulation
CD	Charge dosage
CDR	Charge dosage rate
C. perfringens	*Clostridium perfringens*
COD	Chemical oxygen demand
DAF	Dissolved air flotation
DBP	Disinfection by-product
EC	Electrocoagulation
ECF	Electrocoagulation-flotation
E. coli	*Escherichia coli*
EF	Electroflotation
EU	European Union
Fe-EC	Iron electrocoagulation
N	Nitrogen
NO_3-N	Nitrate-nitrogen
NOM	Natural organic matter
NTU	Nephelometric Turbidity Unit
P	Phosphorous
SS	Suspended solids
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TSS	Total suspended solids
USEPA	United Stated Environmental Protection Agency
WHO	World Health Organization
WWTP	Wastewater treatment plant

1. Introduction

1.1 Background

One of today’s biggest challenges is to provide clean drinking water to a majority of the people around the world, especially to those living in developing countries (Mollah et al., 2001). Worldwide the fresh water demand increases due to the expansion of the population and economic development (Sharma & Chopra 2017). Water for irrigation and food production are the main responsible for the pressures on fresh water resources, with agriculture accounting for over 70 per cent of global fresh water withdrawals and up to 90 per cent in some fast-growing economies (Voulvoulis, 2018). The discrepancy between water supply and water demand is increasing drastically: a 40 percent shortfall in global water supply is estimated by 2030, if no changes are made in water management (Voulvoulis, 2018).

Unfortunately, water resources are irregularly distributed in space and time and climate changes such as prolonged droughts increase the stress on water resources even further (Voulvoulis, 2018). Additionally, the discharge of polluted wastewater globally causes a negative environmental impact (Garcia-Segura et al., 2017). Rivers, lakes and other water bodies are contaminated by industrial effluents and due to other human activities (Mollah et al., 2001). High-quality treatment of wastewater is therefore demanded and recovering (waste)water becomes inevitable. By reclaiming wastewater, the pressure on current resources can be relieved and the dependency on finding new sources reduced (Elimelech, 2006; Garcia-Segura et al., 2017).

Recycled water is seen as a viable non-conventional source, with research demonstrating that wastewater can be treated to a level where it is safe to drink (Fielding et al., 2019). Additional advantages include lower energy consumption than with options like seawater desalination, avoiding the impact of new supply developments such as dams and reducing the amount of pollutants discharged to the environment (Miller, 2006). Successful cases of implementation are found in Singapore, the United States and Namibia (Elimelech, 2006; Fielding et al., 2019). However, public acceptance is still a critical barrier in the introduction of recycled water, especially for potable use.

To handle the increase in water demand, treated municipal wastewater is offered to farmers for agricultural irrigation (Kim et al., 2014). Despite the fact that treated wastewater contains useful nutrients for crop growth, it can form a threat to human health as it harbours pathogenic microorganisms such as helminths, bacteria, protozoa and viruses. An appropriate disinfection method therefore has to be applied in order to meet the water quality criteria for safe reuse. Chlorine is a widely applied strong and cheap disinfectant but causes the formation of disinfection by-products (DBPs), which can be carcinogenic to humans when they are exposed to high concentrations of these DBPs. In contrast to chlorination, disinfection technologies such as UV radiation and membrane filtration do not to produce DBPs (Garcia-Segura et al., 2017), but they are expensive (Ghernaout et al., 2011).

Electrocoagulation (EC) is a promising alternative disinfection method. In the EC process, coagulants are introduced electrochemically and remove suspended and colloidal material, metals and pollutants like pesticides and microorganisms (Garcia-Segura et al., 2017). It has been successfully employed in both groundwater treatment and wastewater treatment (Amrose et al., 2013; Ghernaout et al., 2019). However, EC is mainly applied to treat heavily polluted industrial wastewater, such as textile, paper, food and refinery wastewater (Moussa et al., 2017). EC is considered as an environmentally friendly option because minimal sludge is produced, no additive chemicals are required (coagulants are produced in situ) and in addition, it is low-cost (Moussa et al., 2017). EC hence has the potential to extensively eliminate the disadvantages of the classic disinfection techniques (Mollah et al., 2001).

1.2 Problem description

Reuse of water reduces stress on the fresh water sources that are becoming scarcer. However, using treated secondary effluent from a municipal wastewater treatment plant comes with a risk for human health and requires effective treatment. EC is a promising disinfection method for tertiary treatment, but is still in development. Although a previous study with EC treatment of secondary municipal wastewater effluent showed high removal efficiencies of enteric pathogen indicators, the supernatant still contained minute insoluble hydroxide particles which failed to settle even after prolonged periods of gravitational sedimentation (12h) (Harif et al., 2012; Trikannad, 2019). The dispersed particles were also not lifted by the formed hydrogen gas at the cathode, suggesting that the produced bubbles during the EC process were insufficient or incapable due to their size to cause flotation.

Due to the large number of residual small particles, flotation might be a more effective separation technique than sedimentation. The process has its origin in the mineral/ore processing industry but is currently also integrated into designs of drinking and wastewater treatment plants (Edzwalds, 1995). Flotation is sometimes described in terms of material being removed or separated (mineral, precipitate or colloid flotation) or in terms of bubble formation by vacuum or pressurized methods. In this research, the theory of pressurized dissolved air flotation (DAF) is used, where pressurized aeration is applied followed by pressure release.

In electroflotation (EF), EC is combined with DAF. The flocs formed during the coagulation/flocculation process will be lifted by the added air bubbles. The smaller the bubbles are, the higher the flotation efficiency due to the larger specific surface areas for the particles to attach (Comninellis & Chen, 2010). By putting wastewater in a pressure vessel and increasing the pressure, air dissolves into the water to values above the level of supersaturation at normal pressure. When the water is released from the pressure chamber to the EF vessel – which is at atmospheric pressure –, the excess air is released, forming microbubbles. The combined process has one significance advantage compared to the two separated techniques: a much shorter retention time (Comninellis & Chen, 2010).

1.3 Aim of the study

The main aim of this literature review is to present an overview of research studies to electroflotation technology to remove different pollutants from wastewater. It is meant as a pre-study for the application of EF as disinfection method for secondary municipal wastewater effluent. As the technology of electroflotation both involves electrocoagulation and dissolved air flotation, the theory and implementation of both processes in water and wastewater treatment will be discussed. The effect of several operational parameters that influence the efficiency of EF – such as electrode material, pH, retention time, charge dosage, charge dosage rate, bubble formation and size – will be reviewed in this study. The removal of microorganisms like bacteria, protozoa and viruses is evaluated, as well as the reduction of wastewater quality parameters such as phosphorous, total nitrogen, chemical oxygen demand, total suspended solids, turbidity and colour.

2. Pollutants in municipal wastewater

2.1 Microorganisms

Wastewater contains many different types of pathogens that present a major health risk (Chahal et al., 2016). Human pathogens include bacteria, viruses, protozoans and helminths (parasitic worms). The biggest source of enteric pathogens is fecal matter, which is a major component of domestic sewage. When quantifying microorganisms, it is not practical, expensive and sometimes even impossible to detect all known pathogens. For that reason, indicator organisms are used as a surrogate for the presence of fecal contamination. A good indicator is present abundantly in the wastewater, not pathogenic, easy to culture, does not regrow and shows similar behaviour as the pathogen (Chahal et al., 2016). With culture-based methods, colonies are counted in case of bacteria and protozoans (colony-forming unit) and plaques when it concerns viruses (plague-forming unit) (WHO, 2018). In this section, the main enteric pathogens present in wastewater are discussed together with the illnesses they can cause and the commonly used indicators.

2.1.1 Bacteria

Bacteria are small sized single celled organisms of typically 0.2-2 µm (WHO, 2018). They are the most diverse group of human pathogens in wastewater. Many types colonize the intestine and are excreted in feces. While many bacteria are beneficial, some are pathogenic. Enteric bacterial pathogens such as *Salmonella* spp., *Campylobacter jejuni*, *Escherichia* spp., *Shigella* spp., *Yersinia* spp., and *Vibrio cholerae* typically cause gastrointestinal infections such as diarrhea, dysentery, and gastroenteritis (Chahal et al., 2016). *E. coli* is commonly used as indicator for other enteric bacteria. It is a Gram negative, rod-shaped bacterium that lives in the gut of warm-blooded animals, including human. It is safe, easy and low-cost to culture *E. coli* and it does not regrow in wastewater, making it an ideal indicator for examining the efficiency of a wastewater treatment process in terms of disinfection. Due to the increased production of antibiotics, nowadays also antibiotic-resistant bacteria are present in wastewater. Although they form an increasing global threat to human health, they fall outside the scope of this study.

2.1.2 Protozoa

Protozoa are relatively large, single-celled microorganisms (typically 3-20 µm) that cannot replicate outside a suitable host cell (WHO, 2018). Common protozoan parasites in wastewater are *Cryptosporidium parvum*, *Cryptosporidium hominis*, and *Giardia duodenalis*, which can cause diarrhea, nausea and abdominal pain after intestinal infection of the human host (Chahal et al., 2016). Infection of *Cryptosporidium* can be fatal to human with a weak immune system. *Giardia* can lead to malabsorption and weight loss. *Cryptosporidium* is transmitted in the form of a non-reproductive and dormant oocyst. *Giardia* is also spread by a dormant cyst. Both protozoa are excreted in feces and are highly infective. They show resistance to chlorine (*Cryptosporidium* in particular) (Chahal et al., 2016). This combined with their persistence in the environment due to their robust (oo)cysts (WHO, 2018), makes them problematic organisms. The spore-forming bacterium *Clostridium perfringens*, which is present abundantly in sewage, has been considered as a conservative indicator for pathogenic protozoa. The formed spores are associated with the occurrence of *Cryptosporidium* oocysts and *Giardia* cysts in wastewater (Chahal et al., 2016).

2.1.3 Viruses

Viruses are simple infectious microorganisms, consisting only of genetic material (DNA or RNA) encased in a protein coat or capsid (WHO, 2018). They are small – in the range of 20-100 nm – and require a host cell to reproduce. Viruses are another group of waterborne human pathogens that are often poorly removed by the secondary treatment processes (Chahal et al., 2016). The main enteric viruses in wastewater are hepatitis A, norovirus, rotavirus, adenoviruses, astroviruses, and the various enteroviruses that mainly multiply in the host’s intestine but in some cases also infect other tissues. Consequently, viruses can cause a wide range of diseases such as gastroenteritis, meningitis, hepatitis, and myocarditis. An emerging virus as severe acute respiratory syndrome (SARS) coronavirus can also be shed in feces and found in wastewater (Chahal et al., 2016). Bacterial phages such as somatic coliphage and F-specific coliphage can serve as indicators for pathogenic viruses. They show similar resistance to disinfection treatment as most of the enteric viruses are abundant in wastewater. F-specific coliphages are RNA viruses that infect coliform bacteria. Somatic coliphages are DNA phages that infect *E. coli*.

2.2 Wastewater parameters

2.2.1 Phosphorous (P)

Phosphorous has proven to be difficult to mitigate in wastewater treatment plants. Currently, many conventional biological WWTPs still allow a residual phosphorous concentration in the effluent which exceeds the wastewater discharge guideline as less than 30% removal is reached (Nguyen et al., 2016). Sometimes coagulants (mainly based on iron or aluminium) are added to the process to meet discharge standards, which is an expensive measure (Nguygen et al., 2016). Phosphorous is an important nutrient that stimulates nuisance growth of algae. It can lead to eutrophication when excessive amounts are discharged to water bodies (Ghernaout et al., 2011). The formation of algae blooms can present human or environmental health hazards (Chahal et al., 2016) As P is also nutriment for microorganisms, efficient removal is required when reclaiming wastewater. In water analysis, usually the orthophosphate (PO_{43-}) content is measured in mg/L using a photospectrometer. Total phosphorous concentration is expressed in in mg P/L. Typical values in raw sewage are 4-10 mg P/L (Tchobanoglous et al., 2003; Ødegaard, 2001). Secondary municipal effluent typically contains 1-2 mg P/L.

2.2.2 Total nitrogen (TN)

Total nitrogen is the sum of nitrite (NO_{2-}), nitrate (NO_{3-}) and total Kjeldahl nitrogen (TKN), which consists of ammonia (NH_3) and organic nitrogen. TN is expressed in mg N/L. The excessive application of agricultural fertilizers has been known to cause penetration of large quantities of nitrates into ground and surface waters (Emamjomeh & Sivakumar 2009b). The natural occurring nitrate concentration in surface water is usually ~4 mg NO_3-N/L and can reach levels twice as high as a result of agricultural runoff or contamination with human/animal wastes (WHO, 2017). Concentrations of nitrate in groundwater have increased drastically, for example up to 340 mg NO_3-N/L in an agricultural area in India (WHO, 2017). The maximum acceptable level of nitrate in drinking water is 10 mg NO_3-N/L (WHO, 2017). Nitrates are serious environmental pollutants as they are toxic to aquatic species (Zhu et al., 2008). Removal of ammonia from wastewater has therefore become a worldwide concern. Biological treatment reduces nitrogen, but even treated sewage can still contain high concentrations of nitrate that end up in water bodies when they are discharged. Like phosphate, nitrogen is nutriment for algae and can contribute to eutrophication. TN can be identified with photospectrometry. Typical values in raw sewage are 40-50 mg N/L. Secondary effluent after biological treatment typically has a value of ~10-15 mg N/L (Sharma & Chopra, 2017).

2.2.3 Chemical oxygen demand (COD)

Organic load is an important wastewater parameter as it relates to oxygen consumption. Through measuring the oxygen demand, an impression is obtained of the content of organic compounds. This can be done by means of chemical oxidation: the wastewater sample is heated in strong sulphuric acid containing potassium dichromate, and the oxidized carbon is determined by the amount of dichromate used up in the reaction (Davies, 2005). The result is expressed in units of oxygen (mg O_2/L), rather than carbon, and the procedure is referred to as the Chemical Oxygen Demand (COD). The COD value is important for receiving waters because it indicates oxygen depletion potential. Raw municipal sewage typically has a COD concentration of 250-800 mg O_2/L (Pouet & Grasmick, 1995; Tchobanoglous et al., 2003; Shammas et al., 2010). The concentration after secondary treatment typically is ~50 mg O_2/L.

2.2.4 Total suspended solids (TSS)

Particulate matter can be organic or inorganic and can have different sizes, shapes and densities. Particles in wastewater are either dissolved (<0.001 µm), colloidal (0.001-1 µm), supracolloidal (1-100 µm), or settleable (>100 µm) (Chahal et al., 2016). During secondary treatment, fine particulates, colloidal particles and larger molecules become entangled to form flocs (often together with attached microorganisms) that are removed during secondary clarification (Davies, 2005). The remaining suspended solids are in the size range of 1-10 µm. Suspended solids are important for effluent discharge since they can have adverse environmental impacts, as high turbidity levels ‘have been associated with increased densities of bacteria, *Cryptosporidium* oocysts, and *Giardia* cysts’ (Chahal et al., 2016). TSS is the dry weight of suspended solids expressed in milligram per liter of water. It can be determined by filtering a water sample by a pre-weighted filter of 0.45 µm pore size, and weighing it again after drying it at 105°C for 24 hours (to be sure the weight doesn’t decrease anymore). A typical value of TSS in raw sewage is 350-500 mg/L (Pouet & Grasmick, 1995; Wang et al., 2010). After secondary treatment, ~10 mg/L remains.

2.2.5 Turbidity and colour

Turbidity is an important indicator of water quality. It is an optical parameter that refers to the clarity or cloudiness of water. In wastewater, turbidity provides a measure of the remaining suspended solids or particulates in the treated effluent, which can consist of clay, grit, organic or inorganic matter and algae or other microorganisms (Chahal et al., 2016). Elevated turbidity values are associated with the availability of a support medium to transport attached pathogens and with increased disinfection demand. The scattered amount of light that is not absorbed by the water is measured with a nephelometer and is expressed in Nephelometric Turbidity Units (NTUs). Raw sewage can have a turbidity of about 250-350 NTU (Pouet & Grasmick, 1995; Wang et al., 2010). Secondary wastewater effluent typically has concentrations of particles in the range of 1-10 NTU (Chahal et al., 2016). Small particles that do not settle contribute to apparent color. To assess true colour, the sample should be filtered with a 0.45 µm filter.

2.3 Requirements for water reuse

In locations where the available supply of fresh water has become inadequate to meet the water needs, once-used municipal water must be viewed as a resource for reuse rather than as a waste to be disposed (Tchobanoglus et al., 2003). Though not received positively in every part of the world, the concept of reuse is becoming accepted more widely. In the arid states of Florida and California in the USA for example, dual water systems exist where treated wastewater effluent is used for landscape watering and other non-potable uses. The minimum quality requirements for water reuse in agricultural irritation are discussed in this section.

In Europe, there are currently no guidelines on EU level on water reuse. The Joint Research Centre (JRC) of the European Commission published a report on minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge in 2017. This document was meant as an input to the design of a ‘Legal Instrument on Water Reuse in Europe’ (Alcalde-Sanz & Gawlik, 2017). The water quality criteria for agricultural irrigation are subdivided into different categories, where Class A covers ‘all food crops, including root crops consumed raw and where the edible portion is in direct contact with reclaimed water’ – the most stringent water quality class. The *E. coli* concentration is recommended ≤10 cfu/100 mL, while the guidelines on water reuse for unrestricted irrigation (for example of lettuce or onions) provided by the World Health Organization (WHO) are less stringent: ≤1000 cfu/100 mL (WHO, 2006). For irrigation of crops likely to be eaten uncooked, non-detectable to 200 cfu/100 mL are allowed by the United States Environmental Protection Agency (USEPA) (O'Connor et al., 2008). The European JRC recommends a TSS concentration of ≤10 mg/L and turbidity level of ≤5 NTU (Alcalde-Sanz & Gawlik, 2017). Based on the European Directive 91/271/EEC on urban treated wastewater effluent disposal, emission limits of 15 mg N/L and 1-2 mg P/L are prescribed.

When municipal sewage is treated to be used for agricultural irrigation, the performance targets of the treatment train are ≥5 log reduction for indicator organisms *E. coli* and *C. perfringens* and ≥6 log reduction for somatic coliphages, according to the European JRC (Alcalde-Sanz & Gawlik, 2017).

3. Electrocoagulation (EC)

3.1 Principle of EC

3.1.1 Theory of EC

In the electrocoagulation process, contaminants in an aqueous medium are destabilized by the introduction of an electric current into that medium. In its simplest form, an electrocoagulation reactor can consist of an electrolytic cell with one anode and one cathode (Mollah et al., 2001). When connected to an external power source, the anode material will corrode due to oxidation while the cathode will be subjective to reduction. The ‘sacrificial’ anode releases metal ions and the cathode generates hydroxyl ions and hydrogen gas. Commonly, the conductive metal plates are made of iron (Fe) or aluminium (Al). Electrocoagulation is the electrochemical production of destabilizing agents such as Fe or Al that brings about neutralization of electric charge for removing pollutants (Emamjomeh & Sivakumar, 2009a). The produced iron and aluminium cations have the same effect as the addition of Fe and Al based coagulants in conventional water treatment systems. The main advantage of EC is that the coagulants are created in situ, and thus no chemical dosing is required, resulting in less sludge generation (Moussa et al., 2017). In contrast to chemical coagulants, which are introduced as salts such as aluminium sulphate or iron chloride, no other ions that increase conductivity are added during EC. This is an important advantage when the treated water is destined for irrigation. When the in situ produced coagulants form flocs together with the targeted pollutants, they can be either removed by precipitation or by flotation (Mollah et al., 2001). A schematic diagram of an electrocoagulation cell is shown in Figure 1.

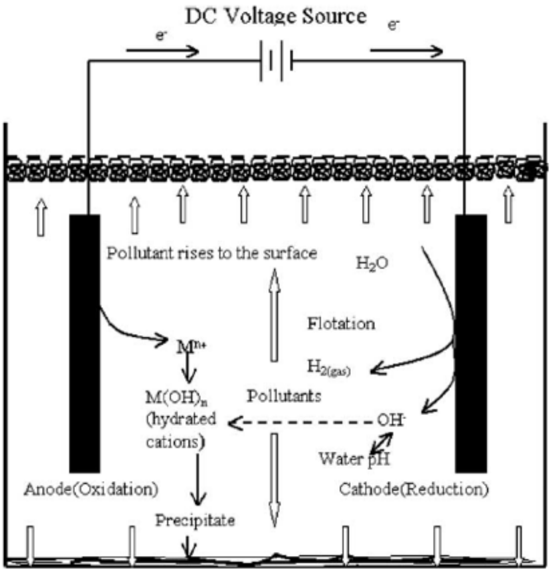


Figure 1. Representation of the electrochemical process. Source: Mollah et al., 2004

The EC process can be subdivided in three stages (Mollah et al., 2004):

1. Dissolution: release of metal ions from the anode
2. Coagulation: destabilization of the contaminants and particulate suspension
3. Flocculation: aggregation of the destabilized particles to form flocs

The stability and destabilization of contaminants and particulate suspension can be explained as follows. Microscopic particles that are typically in the range of 1 nm to 2 µm are referred to as colloids (Moussa et al., 2017). Their stability in water is attributed to the fact that they carry a similar, usually negative, charge, so they repel each other and stay suspended. When counter charged particles are attracted to the surface of the colloids, an electric double layer is formed (illustrated in Figure 2).

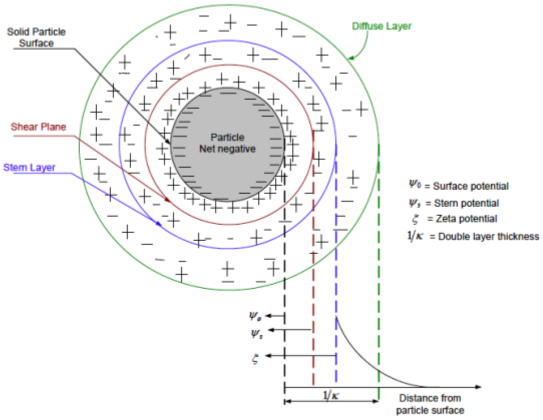


Figure 2. The electrical double layer. Source: Moussa et al., 2017

The electric double layer consists of an inner region (the stern layer), where oppositely charged ions are strongly bounded to the surface of the colloidal particles, and an outer layer (the diffuse layer), where ions can move around freely. The maximum potential occurs at the negatively charged surface and decreases across the stern layer due to the presence of positively charged ions, resulting in what is defined as the zeta potential. The higher the zeta potential, the higher the repulsion of the charged particle and hence the more stable the colloid. If the zeta potential is more positive than +30 mV or more negative than -30 mV, the particle is considered stable (Moussa et al., 2017).

If the amount of metal ions in the solution increases – for example by the addition of Fe^{3+} or Al^{3+}–, they diffuse to the surface of the colloid, causing a reduction in the thickness of the electrical double layer. As a result, the zeta potential reduces (the repulsive forces decline) and the colloid becomes unstable. Next to this compression of the double layer, other destabilization mechanisms such as adsorption or entrapment can occur at the same time (Mollah et al., 2004). In case of entrapment, a sludge blanket is created by the formed flocs that entraps colloidal particles which are still present in the solution. Adsorption shows similarities with entrapment, but the pollutant is adsorbed onto the surface of the coagulant rather than being physically dragged by the coagulant (Garcia-Segura et al., 2017). The different removal mechanisms are illustrated in Figure 3.

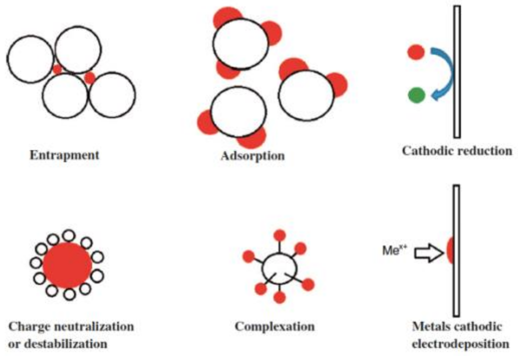


Figure 3. Main removal mechanisms during EC. Source: Garcia-Segura et al., 2017

3.1.2 Reactions at the electrodes

When an iron anode is used in EC, Fe^{2+} dissolves in the water due to oxidation of iron at the anode as shown in reaction (1). At the same time, hydroxyl ion (OH^-) and hydrogen gas (H_2) are produced at the cathode from the reduction of water (reaction (2)). The formation of ferrous hydroxide, $Fe(OH)_2$, is shown in reaction (3). Reaction (4) gives the overall reaction from the sequence of reactions (1)-(3).

Oxidation at the anode: $Fe\ (s) \rightarrow Fe^{2+} + 2\ e^-$ (1)
Reduction at the cathode: $2\ H_2O + 2\ e^- \rightarrow 2\ OH^- + H_2\ (g)$ (2)
Formation ferrous hydroxide: $Fe^{2+} + 2\ OH^- \rightarrow Fe(OH)_2\ (s)$ (3)
Overall reaction: $Fe^{2+} + 2\ H_2O \rightarrow Fe(OH)_2\ (s) + H_2\ (g)$ (4)
Source: Garcia-Segura et al. (2017)

The production of OH^- from reaction (2) causes an increase in pH, leading to the formation of different iron hydroxide complexes in the solution. In the presence of O_2, Fe^{2+} easily oxidizes to $Fe(OH)_3$, letting ferric hydroxide become the dominant coagulant as shown in reaction (5). The Fe^{3+} species could also be directly generated from the anode depending on the voltage applied by direct charge transfer (Garcia-Segura et al., 2017). However, the electrochemical dissolution mechanism of iron anodes reported in literature is not consistent and often lack experimental proof of the actual species formed during EC (Lakshmanan et al., 2009; Moussa et al., 2017).

If anode potential is sufficiently high, secondary reactions may occur, such as direct oxidation of organic compounds and of chloride ions present in wastewater (Kobya et al., 2003). Meanwhile, the cathode may be chemically attacked by OH^- ions generated during hydrogen evolution at high pH values (Kobya et al., 2003). In case of high anode potential, water can be oxidized to hydronium cathode (H_3O^+) and O_2. Also, Cl^- ions can oxidize to Cl_2, which is a strong oxidant that contributes to the oxidation of dissolved organic compounds (Hakizimana et al., 2017). Chlorine gas can react with water to form ClOH that also plays the role of oxidizer.

The protons formed by reaction (5) can be neutralized by hydroxyl ions from reaction (2), or be directly reduced at the cathode by means of reaction (6).

$$4\ Fe^{2+} + 10\ H_2O + O_2\ (g) \rightarrow 4\ Fe(OH)_3\ (s) + 8\ H^+ \qquad (5)$$

$$2\ H^+ + 2\ e^- \rightarrow H_2\ (g) \qquad (6)$$

Source: Garcia-Segura et al. (2017)

The predominance-zone diagram for Fe^{2+} (upper graph in Figure 4) shows that insoluble $Fe(OH)_2$ precipitates at pH > 5.5 and remains in equilibrium with Fe^{2+} up to pH 9.5 or with the monomeric species $Fe(OH)^+$ from pH 9.5 to 11.4 and $Fe(OH)_3^-$ from 11.8 to 14.0.

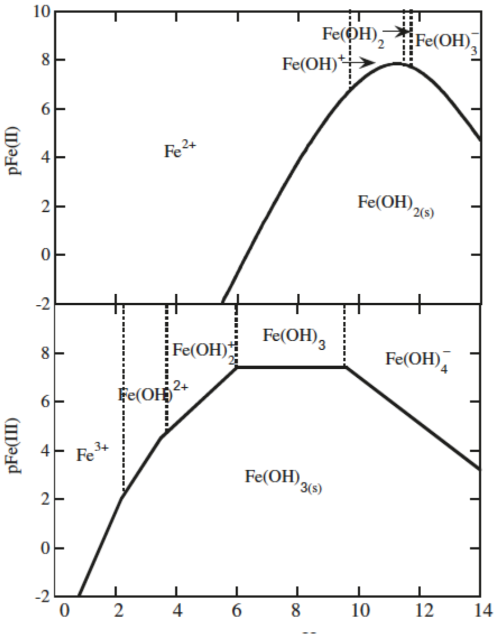


Figure 4. Predominance-zone diagrams for Fe^{2+} (top) and Fe^{3+} (bottom) in aqueous solution in function of pH. Source: Garcia-Segura et al., 2017

From the predominance-zone diagram for Fe^{3+} (bottom graph in Figure 4) can be deducted that that $Fe(OH)_3$ coagulates at pH > 1.0. The insoluble species stays in equilibrium with different soluble species as a function of the pH range (Garcia-Segura et al., 2017). $Fe(OH)_3$ is in equilibrium with Fe^{3+} up to pH 2.0, with $Fe(OH)^{2+}$ between 2.0 and 3.8, with $Fe(OH)_2^+$ from 3.8 to 6.2 and with $Fe(OH)_4^-$ from 9.6 to 14.0. $Fe(OH)_3$ is the unique species present in the pH range of 6.2-9.6. This is considered as the preferred coagulant which is the main agent responsible for the removal of pollutants by mechanisms such as charge neutralization, destabilization and adsorption.

Theoretically, the electrolytic oxidation of iron could result in ferrous or ferric generation at the anode (Lakshmanan et al., 2009). However, Lakshmanan et al. (2009) found that regardless of initial pH, current (in the range of 0.05-0.8 A) or rod purity, 80-95% of iron was present as Fe^{2+} under N_2-purged condition after two minutes of electrochemical treatment, confirming that this is the primary species formed during electrolysis. The oxidation of Fe^{2+} to Fe^{3+} strongly depends on pH and the dissolved oxygen concentration (Hakizimana et al., 2017). Lakshmanan et al. (2009) showed that with chemical coagulation approximately 80% Fe^{2+} was oxidized within 10 min at pH 7.5, while at pH 6.5 it took about 5 hours for the same oxidation to occur (at DO of 8-9 mg/L). These results are consistent with literature reporting on the kinetics of the oxidation of ferrous iron near neutral pH as shown in the equation below, where k is the rate constant ($M^{-2}atm^{-1}min^{-1}$), P_{O_2} the partial pressure of oxygen (atm) and the brackets represent molar concentration (M/L) (Davison & Seed, 1983; Lakshmanan et al., 2009). Davison & Seed (1983) suggested a ‘universal’ rate constant of ~$2*10^{13}$ $M^{-2}atm^{-1}min^{-1}$ for natural fresh waters in the pH range 6.5-7.4.

$$\frac{d[Fe^{2+}]}{dt} = -k[Fe^{2+}]P_{O_2}[OH^-]^2$$

In acidic solutions, Fe^{2+} ions oxidize very slowly to Fe^{3+} in contact with oxygen, while in neutral or alkaline waters, Fe^{2+} immediately complexes with OH^- to form $Fe(OH)_2$. In the presence of O_2, this ferrous hydroxide is quickly oxidized to ferric hydroxide, or $Fe(OH)_3$ (Hakizimana et al., 2017). The iron hydroxides have a strong affinity to suspended solids and can coagulate and form bigger flocs. Different precipitates are formed that can be separated from the liquid in different ways. Larger, heavier flocs with settle after some time and can be removed from the bottom of the system. Smaller flocs that are much lighter will not settle and remain floating in the solution. They can be lifted by the produced hydrogen bubbles at the cathode and afterwards be scraped of the surface. Due to the involvement of gasses, the EC process is often associated with electroflotation. In chapter 5 this technique is discussed.

3.2 Applications of EC in water treatment

3.2.1 Industrial wastewater

Electrocoagulation is a widely applied technique in the treatment of industrial wastewater effluents of for example refineries, the textile and paper mill industry and the food industry. EC has the potential of treating oily water, where the electric current contributes to the electrocoalescence of oil droplets (Moussa et al., 2017). Electrocoalescence effectively deals with tight emulsion where droplets are very small, as often encountered in the oil and gas industry. When fine oil droplets in water or vice versa merge and form bigger droplets, they are easier to separate. In the textile industry, EC successfully removes dyes from textile waste streams and heavy metals such as chromium from tanning baths effluents (Butler et al., 2011). Kobya et al. (2003) demonstrated that high strength waste water – effluent with a high chemical oxygen demand (COD) and a strong dark colour – could be treated well with EC. COD and turbidity removal efficiencies showed that iron was superior to aluminium as sacrificial electrode material. In acidic medium (pH < 6), COD and turbidity removal efficiencies of aluminium are higher than those of iron, with 61-65% COD removal and 98% turbidity removal. These removals drop dramatically when pH > 6. For iron, with an initial pH of 3-7, 47-77% COD removal and 75-98% turbidity removal is reached. For the same turbidity or COD removal efficiencies, iron requires a current density of 80-100 A/m_2, while aluminium requires 150 A/m_2 for 10 minutes of treatment. The energy consumption was calculated to be 0.65 kWh per kg COD removed for iron between pH 5 and 9, about half the amount consumed with aluminium electrodes (Kobya et al., 2003).

EC is also applied to treat olive mill, distillery and slaughterhouse wastewaters. According to Valero et al. (2011), EC is a suitable technology for the treatment of wastewater generated in the almond industry, where large streams with high levels of organic matter and suspended solids have to be treated in a short period of time (Valero et al., 2011). Wastewaters from agricultural industries are characterized by high CODs due to their high concentration of organics. This applies to the dairy industry as well, that produces a huge amount of waste streams (Tchamango et al., 2009). In order to recycle or discharge these streams, the high COD levels have to be reduced. Electrocoagulation of dairy effluents have been carried out with steel and aluminium electrodes by Şengil & Özacar (2006) and Tchamango et al. (2009) respectively, where iron showed to be more efficient. With iron electrodes, 98% COD removal was reached (Şengil & Özacar, 2006), while only a 61% COD reduction was reached with aluminium, which was almost identical to the removal with chemical treatment using aluminium sulphate (Tchamango et al., 2009).

3.2.2 Surface and groundwater

A conventional drinking water treatment plant that uses surface water as water source usually consists of coagulation with a metal salt coagulant such as alum or ferric chloride, followed by sedimentation and granular filtration to remove suspended solids (SS), which cause turbidity (Ghernaout et al., 2011). As a final step disinfection is applied – often in the form of chlorination – to inactivate pathogens. In this regard, electrocoagulation is a promising alternative treatment technology as it both reduces SS and microorganisms without the addition of chemicals. Ghernaout et al. (2008) researched EC treatment as bacteria disinfection method of surface waters. They showed that the survivability of *E. coli* declined with increasing current intensity and treatment time. For the more, bacteria cells were effectively disinfected (96% removal for Fe-EC; 99.7% removal for Al-EC) were reached within 35 minutes. Zu et al. (2005) investigated virus removal by iron EC of synthetic surface water. It proved to be an excellent pretreatment for virus removal by microfiltration, outperforming chemical coagulation as pretreatment step. However, a discrepancy between synthetic and natural waters was observed by Tanneru & Chellam (2012). They demonstrated that conventional chemical coagulation outperformed electrocoagulation pretreatment for virus control of natural waters due to the presence of natural organic matter (NOM) in surface waters, which inhibits virus removal by pairing with ferrous iron.

Abuzaid et al. (2002) investigated the application of iron EC to turbid groundwater in the Eastern Province of Saudi Arabia. Bentonite causes turbidity due to its stability in water. The clay particles remain in suspension and therefore they cannot be removed by traditional sedimentation. The EC process showed excellent turbidity removal efficiencies. Amrose et al. (2013) studied the removal of arsenic from contaminated groundwater in Bangladesh and Cambodia. With iron EC, they were able to reduce concentrations of up to 3000 µg As/L to below the maximum level recommended by the WHO of 10 µg As/L at a various range of current density (0.02-100 mA/cm$_2$) and charge dosage rates (0.06-18 C/L/min). Arsenic(V) species adsorb on the surfaces of hydrous ferric oxides (HFOs), which aggregate to form flocs that can be separated from the water. A batch reactor trial in Amirabad Village showed that the technique is effective in realistic conditions. The high performance and low consumable cost suggest that EC could provide clean water in rural areas at a locally affordable price ($0.22 per m$_3$).

3.2.5 Municipal wastewater

After secondary biological treatment in a typical municipal wastewater treatment plant (WWTP), the quality of the effluent often meets the standards required for the discharge into a receiving water body (Rodrigo et al., 2010). In some cases, additional disinfection may be required. Chlorination is currently the major method of disinfection in wastewater treatment (Ghernaout et al., 2011). If the effluent is going to be reused, its quality should also be further improved. In several studies, electrocoagulation has been investigated as an alternative treatment method for traditional wastewater treatment processes or as a tertiary treatment method.

Bukhari (2008) applied iron EC on raw municipal sewage and efficiently removed TSS and turbidity. EC with aluminium electrodes was studies as a tertiary treatment step by Rodrigo et al. (2010). It was considered as a robust treatment that can help to reduce the organic load with low applied currents. Sharma & Chopra (2017) researched the influence of operational parameters of Al-EC on the removal of nitrate and sulphate from biologically treated municipal wastewater. Fe-EC was used by Al-Shannag et al. (2013) to enhance the removal of nutrients and COD. Nguyen et al. (2016) evaluated the removal of phosphorous from South-Korean municipal wastewater effluent by iron EC. With their optimized system they could meet the stringent discharge standards of less than 0.2 mg P/L. EC was therefore found an appropriate technology that could be designed in the form of compact modules, capable of treating large volumes of wastewater.

EC treatment of wastewater specifically for reuse in irrigation and plantation in Pakistan was investigated by Saleem et al. (2011). They treated raw wastewater in order to bring up the quality to international wastewater reuse standards of the WHO and several countries (the USA, China, Saudi Arabia, Pakistan and Jordan). It was found that the studied parameters were within allowable limits for landscape irrigation and plantation after treatment. The COD content was 84 +/- 3 mg O_2/L. Furthermore, the treated water contained 21.4 +/- 0.2 mg NH_4-N/L, 2.7 +/- 0.1 mg NO_3-N/L and had a total phosphate concentration of 15.7 +/- 0.5 mg/L. Microbiologically the treated water was safe, as the total coliforms were below the detection limit. With a conductivity of 650 +/- 10 µS/cm, the salt content was also within reasonable limits (Saleem et al., 2011). Though EC is considered as a cost-effective technology, a reasonable amount of electricity is required, which can be a limiting factor for remote communities that are not connected to the power grid. To overcome this problem, an increasing amount of studies are being done to solar powered EC, for example by Sharma et al. (2011) for remote Australian communities and by Nawarkar & Salkar (2019) in India.

4. Dissolved air flotation (DAF)

4.1 Principle of DAF

Flotation nomenclature can be confusing; it is used to describe the removal/separation of material, but it can also refer to the method of bubble formation such as electroflotation, dispersed air flotation or dissolved air flotation (Edzwald, 1995). The focus in this section is pressurized dissolved air flotation, simply referred to as DAF. This technique is used mainly to remove suspended and colloidal solids from (waste)water by decreasing their apparent density (Wang et al., 2005).

DAF is an adsorptive bubble separation process that makes use of the selective adsorption of impurities at the gas/liquid or gas/solid interfaces of rising bubbles (Wang et al., 2005). In DAF, air is used as gas but there are also other dissolved gas flotation techniques that make use of nitrogen, carbon dioxide and ozone (Wang et al., 2005). In general, grease, grit, solids, colloidal substances and dissolved solutes can be removed all in one (Wang et al., 2005). The main advantage compared to traditional sedimentation for removing impurities is that DAF requires less contact time and a much smaller tank. This benefit is depicted in Figure 5 below.

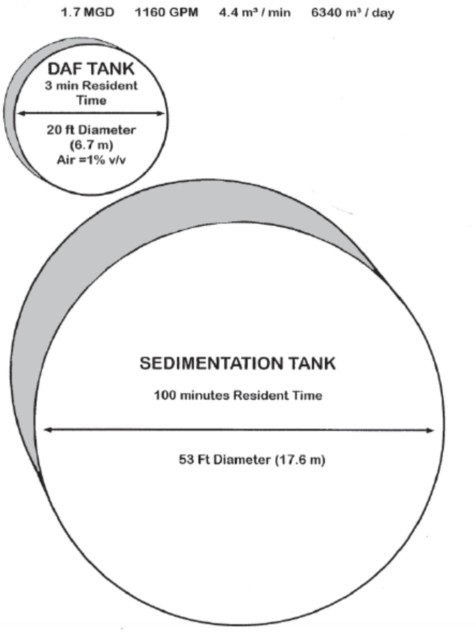


Figure 5. Size comparison among a DAF tank and a traditional clarifier. Adapted from Wang et al. (2005).

The DAF system consists of four major components: air supply, pressurizing pump, retention tank (i.e. pressure vessel) and flotation chamber (Wang et al., 2005). At atmospheric pressure the air solubility decreases with increasing temperature of the water. At 20°C, the air solubility is 20.1 mL/L, whereas at 30°C it has reduced to 17.9 mL/L (Wang et al., 2005). According to Henry's law, the solubility of a gas in water increases with increasing pressure. A common DAF configuration is illustrated in Figure 6.

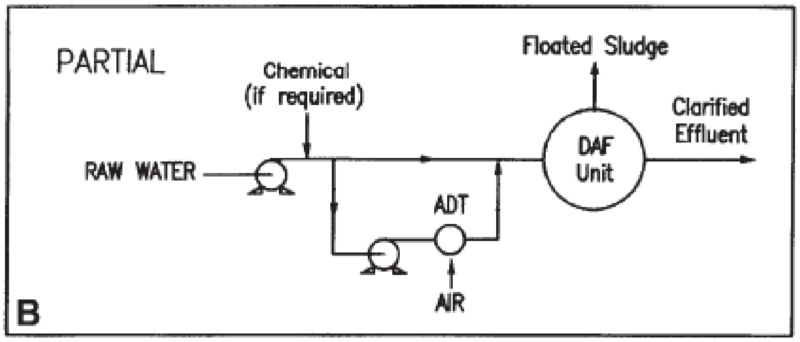


Figure 6. Partial flow pressurization. Adapted from Wang et al. (2005).

With a pressurizing pump, (a part of) the feed stream can be saturated at several times the atmospheric pressure. This happens in the retention tank. The water is held there for about 0.5-3 min to provide sufficient time for air dissolution into the stream to be treated (Wang et al., 2005). Normally 5-15% of the amount of the water to be treated is supersaturated (Kiuru, 2001). Subsequently, this stream is released to the flotation chamber, which is at atmospheric pressure. The large pressure drop right after the pressure-reducing valve results in the release of microscopic air bubbles (Wang et al., 2005). The small air bubbles are in the range of 10-100 µm (Kiuru, 2001; Wang et al., 2005) with an estimated average of 40 µm (Edzwald, 1995). The process of bubble formation consists of two stages: nucleation and growth. The large pressure difference across the valve leads to the spontaneous production of bubble nuclei in the supersaturated water, according to the thermodynamic principle of minimizing the free energy change. When the air is assumed as an ideal gas, the diameter of the nucleus can be calculated with following formula:

$$d_{bubble} = \frac{4 * \sigma}{\Delta P}$$

with σ being the surface tension (N/m) and ΔP the pressure change (N/m2) (Edzwald, 1995). Applying higher pressures generates smaller bubbles, but this effect diminishes above a certain pressure. An increasement of the pressure above 5 bar has limited effect on bubble size (Edzwald, 1995). To obtain small bubbles, pressure differences of 4-6 bar are generally recommended (Edzwald, 1995; Kiuru, 2001). When this pressure difference is applied to ~5-15% of the total stream to be treated, suspended solids are removed effectively up to a concentration of 400-500 mg/L (Kiuru, 2001).

As the bubbles rise to the surface, a decrease in hydrostatic pressure takes place, enabling bubble growth. However, this has a negligible effect on the small bubbles formed during the DAF process (Edzwald, 1995). The velocity at which the bubbles rise to the surface depends on their size. Bubbles of <100 µm are found to rise as rigid spheres under laminar flow conditions and obey Stokes' law (Edzwald, 1995). Larger bubbles occur as ellipsoids (1-10 mm) or spherical caps (>10 mm), which have larger upwards velocities (Edzwald, 1995). The vertical rising rate of air bubbles ranges from about 15 to 60 cm/min. The bubbles attach to suspended or colloidal particles in the water. The formed agglomerations have – due to the entrained air – a lower net density than water molecules, allowing them to rise to the surface. The floated particles form a layer at the surface which can be removed by specially designed scrapers or other skimming devices (Wang et al., 2005).

The effectiveness of the DAF process depends on the attachment of the air bubbles to the particles. The attraction between the bubbles and particles is primarily a result of the surface charge of the particle and the bubble-size distribution (Wang et al., 2005). Two important mechanisms describing the bubble-particle interaction are (Edzwald, 1995):

1. Entrapment of formed bubbles in large floc structures
2. Particle collision and adhesion with formed bubbles

The first mechanism is important when larger flocs have already formed, in case a coagulant is dosed for example. The second mechanism – illustrated in the figure below – is assumed to be the most important (Edzwald, 1995). The contact angle between the air bubble and the particle must be large enough (Figure 7a) such that the adhesion of water to the solid is larger than its cohesion to water (Edzwald, 1995). In other words: a large contact angle results in a hydrophobic surface that is forced upwards. Figure 7b shows the size range and scale of bubbles and particles.

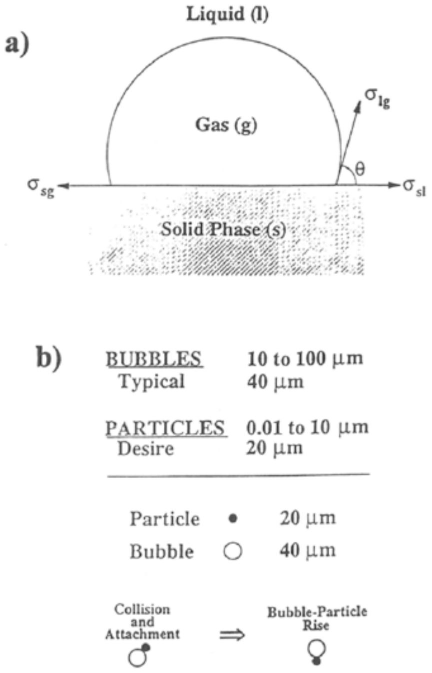


Figure 7. (a) Contact angle for the attachment of a gas bubble to a solid; (b) Scale of the bubble-particle interaction. Source: Edzwald, 1995

The size of the particles is an important factor affecting the process. It has been presented that the attachment of smaller colloidal particles depends on charge neutralization by the bubbles that carry a negative charge (Edzwald, 1995). Minutely small particles cannot be floated at all. In general, floatability increases with increasing particle size (Wang et al., 2005). Various (chemical) coagulants can help to increase the particle size by flocculation (Wang et al., 2005). Surfactants such as detergents are added to decrease the surface tension, enabling the pollutant to float (Wang et al., 2005; Ghernaout et al., 2011). Surfactants are however costly (Ghernaout et al., 2011). In chapter 5 a combination of DAF with EC, where coagulants that stimulate flocculation are created in situ, is discussed.

4.2 Applications of DAF in water treatment

4.2.1 Industrial (waste)water

In the early twentieth century, DAF was recognized as an effective separation method for mineral ores (Edzwald, 1995). Ever since, it has been applied in many other industrial processes, including treatment of paper mill and refinery wastewaters, waste sludge thickening and recycled paper de-inking (Edzwald, 1995; Wang et al., 2005). The sharp increase of plastic wastes has put great pressure on the environment. In the past decade, DAF was stated to be an effective separation method for a wide range of plastic from waste streams for recycling purposes (Wang et al., 2015).

In the mining field, DAF offers advantages over traditional separation techniques as the microbubbles produced in DAF enhance the capture of ultrafine particles (<5 µm) ore particles (Rodrigues & Rubio, 2007). Other flotation devices usually generate coarser bubbles of 600-2500 µm that do not capture the very fine particles such as small, light particles, metal-ion hydroxide flocs and bacteria, leading to considerable losses (Rodrigues & Rubio 2007). The study of Santana et al. (2012) showed that with applying bubbles of less than 100 µm, the extraction of fine apatite – a phosphate containing ore – reached a recovery of over 60%, which is considered as economically attractive. Simultaneously, a P_2O_5 content in the concentrate of >30% is required. With DAF treatment, a mean value of 29% was reached, compared to 24% with a conventional flotation column (Santana et al., 2012).

DAF is also used in food processing wastewater treatment plants as separation technique. The large streams of meat industry wastewater with high levels of organic matter require adequate treatment, as they are coloured dark brown and have a strong smell (De Sena et al., 2009). De Sena et al. (2009) demonstrated that initial COD concentrations of 2800-3000 mg O_2/L and turbidity levels of 1000-1200 NTU could be reduced by 80.3% and 88.4% respectively by DAF treatment only – with addition of an optimal dosage of ferric sulphate. These removal efficiencies were raised to 97.6% and 96.2% respectively when combined with extensive advanced oxidation, resulting in levels of organic load acceptable to discharge (De Sena et al., 2009).

4.2.2 Surface water

DAF was first used for drinking water clarification in the 1960s in Scandinavia and South Africa (Edzwald, 1995). In 1965, a DAF application for potable water treatment was installed in Windhoek, Namibia for the flotation of algae containing water (Schofield, 2001). Currently, DAF is used widely around the world (Edzwald, 2010). For surface water treatment it is an emerging technology as an increased removal of protozoa cysts such as *Cryptosporidium* and *Giardia* is reached (Edzwald, 1995). Experimental studies have shown that DAF alone is capable of removing oocysts up to 2.5 log, and even a 5-log removal is achieved in combination with filtration (Schofield, 2001). Where traditional clarification can reach a water turbidity of 1 NTU, most DAF clarifiers attain 0.5 NTU (Schofield, 2001; Edzwald, 2007). The high solids removal in DAF also shows to have a high disinfection capacity. In a pilot study for the Frankley Water Treatment Works in Birmingham, Schofield et al. (1991) could not detect coliforms in 87% of the samples fed with water containing coliforms and *E. coli* in the range of hundreds cfu/ml.

4.2.3 Municipal wastewater

In the past decades, DAF has become the most commonly used flotation process in municipal wastewater treatment (Wang et al., 2005). In particular, DAF is gradually replacing conventional sedimentation processes for clarification. New sequencing batch reactors (SBR), involving the use of DAF instead of sedimentation, have been developed for example (Wang et al., 2005).

In Kiuru (1990), the performance of flotation combined with filtration as tertiary treatment is evaluated in a traditional activated sludge plant in Finland. The WWTP in Savonlinna is responsible for treating a combined flow of municipal sewage and process wastewater from a fiberboard mill, requiring an extremely high removal of suspended solids (Kiuru, 1990). Values of <0.3 mg P/L, <1 mg NH_4-N and <5 mg SS/L were continuously achieved. Koivunen & Heinonen-Tanski (2008) studied DAF as tertiary treatment of municipal wastewater on a pilot-scale. They achieved 90–99% reduction in the numbers of enteric microbes (total coliforms, enterococci and F-RNA coliphages). The average reductions of total phosphorus and COD demand were 55–81% and 28–39% respectively (Koivunen & Heinonen-Tanski, 2008). The produced float (sludge) layer that is produced during the DAF process can contain up to 5% solids (Edzwald, 2010), which is attractive as it makes dewatering cheaper.

5. Electroflotation (EF)

5.1 Principle of EF

5.1.1 Theory of EF

Electroflotation is inextricably linked to electrocoagulation. The terms are often combined and considered as the electrocoagulation/flotation (ECF) process. This alternative technique to remove pollutants from (waste)water involves the application of an electric current to sacrificial electrodes inside a reactor where the current generates a coagulating agent and gas bubbles (Emamjomeh & Sivakumar, 2009a). The released metal ions coagulate with pollutants in the water are can be removed by sedimentation or flotation. The different interactions in the ECF process are depicted in Figure 8.

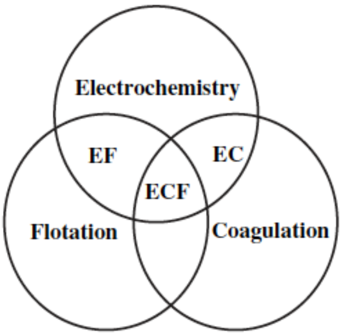
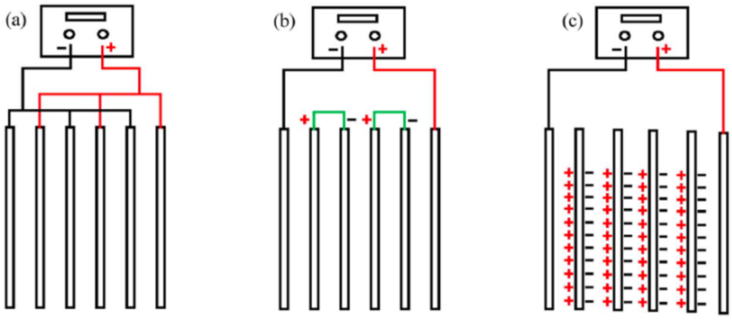


Figure 8. Interactions during the ECF process. Source: Emamjomeh & Sivakumar (2009a)

The basis of the electrocoagulation/flotation process consists of three mechanisms:

1. Electrode oxidation
2. Gas bubble generation
3. Sedimentation and flotation of the formed flocs

The release of coagulants by means of oxidation of the metal anode occurs in the same way as described in part 3.2.1 of the chapter Electrocoagulation. The reactions that cause gas bubble generation are described in more detail in the section below. Both electrocoagulation and electroflotation are based on the theory of electrochemical cells, known as electrolytic cells. These cells are commonly configurated with monopolar electrodes connected in parallel or series, or with bipolar electrodes connected in series, as shown in Figure 9. The electrode arrangement does not only affect removal efficiency but also energy consumption and costs (Garcia-Segura et al., 2017). In monopolar arrangement, each electrode serves as a cathode or anode depending on its electrical polarity in the electrochemical cell. When the monopolar electrodes are arranged in parallel, all anodes are connected to each other as well as all cathodes. In monopolar in series connection, each pair of anode-cathode is connected but they are not connected to the outer electrodes. Bipolar electrodes have an anodic and a cathodic side, depending on the charge of the opposite electrode. They are always connected in serial mode. In parallel arrangement, the electric current is divided between all the electrodes in relation to the resistance of the individual cells (Mollah et al., 2001). Higher potential differences are required when a serial arrangement is used, but the same current is distributed between all electrodes. In terms of energy efficiency, parallel arrangements show to be advantageous (Garcia-Segura et al., 2017).



Monopolar electrodes
in parallel connection
(MP-P)

Monopolar electrodes
in series connection
(MP-S)

Bipolar electrodes
in series connection
(BP-S)

Figure 9. Different electrode arrangements. Source: Garcia-Segura et al. (2017)

Electrolytic flotation is also suggested as a more appropriate term for electroflotation as electrolysis of the aqueous medium is used to generate bubbles (Kyzas & Matis, 2016). A stressed advantage of EF is that the electrodes can be arranged in such a way that they cover the whole surface area of the flotation tank, achieving uniform mixing between the wastewater and the gas bubbles. A large amount of very fine bubbles is produced with minimum turbulence, which results in effective clarification. The generated bubbles are very pure: since they are created from water and no handling of the gasses occurs before they are used, the gas remains uncontaminated (Wang et al., 2010). The rate of generation is controlled by the current: the more current applied, the more gas produced. EF is simple in operation and easy to manufacture (Wang et al., 2010). The process is safe in operation as well, as only low voltage (5-20 V) is used (Kyzas & Matis, 2016).

5.1.2 Reactions at the electrodes

The gas that enables flotation in EF consists of hydrogen and oxygen produced by the electrolysis of water. At the anode, oxygen is produced due to the oxidation of water as shown in reaction (7). At the cathode, water is reduced and thus hydrogen gas is formed as shown in reaction (8). Reaction (9) gives the overall reaction from aforementioned reactions.

Oxidation at the anode: $2\,H_2O \rightarrow 4\,H^+ + O_2\,(g) + 4\,e^-$ (7)
Reduction at the cathode: $4\,H_2O + 4\,e^- \rightarrow 4\,OH^- + 2\,H_2\,(g)$ (8)
Overall reaction: $2\,H_2O \rightarrow O_2\,(g) + 2\,H_2\,(g)$ (9)

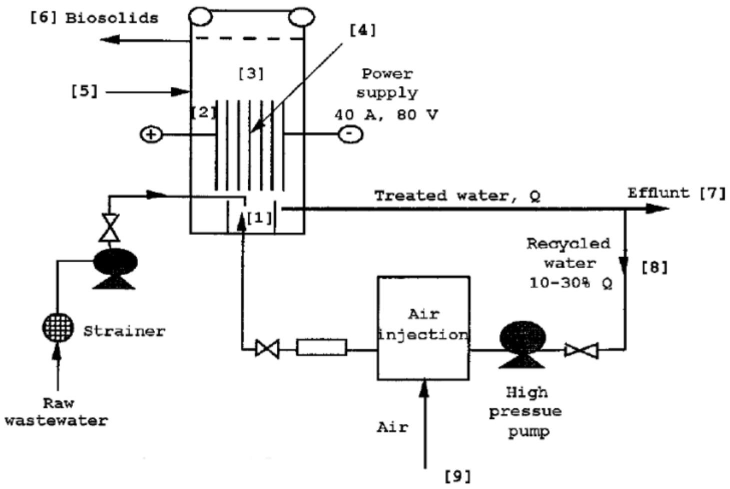
Source: Wang et al. (2010)

It can be seen that for each 4 electrons of current passed between the electrodes, one mole of O_2 and two moles of H_2 are produced. This means that 0.174 mL of gas, measured at standard temperature and pressure, is formed by each coulomb of current (Wang et al., 2010). The relative quantities of gases produced are a function of current density and the conductivity (salinity) of the solution (Kyzas & Matis, 2016). Dispersed gas bubbles formed from electrolysis are extremely fine and uniform (Emamjomeh & Sivakumar, 2009a). Their size is in the order of 100 µm (Wang et al., 2010). Chen et al. (2000) even report typical bubble sizes in EF of 20-70 µm, smaller than those produced in conventional flotation. The rising swarm of small bubbles produces a blanket effect that carries SS and oil globules to the surface. A floating sludge layer is formed that can be mechanically removed.

The formed H_2 and O_2 bubbles during the EF process tend to accumulate at the metal cathode and anode respectively (Mollah et al., 2004). This accumulation increases the electrical resistance of the cell, resulting in using more energy to achieve optimum removal efficiency. To release the bubbles from the electrode surface, the electrolyte flow has to be increased to sweep out the bubbles (Mollah et al., 2004). Introducing extra turbulence by applying DAF to the system could overcome this problem.

5.1.3 EF as coupled EC and DAF

EF or ECF process can refer to a process with one electrolytic cell (Holt et al., 2005; Belkacem et al., 2008; Ricordel et al., 2010), where gas bubbles and coagulants are formed in the same step. In some cases, an EC cell is followed by an EF cell (Chen et al., 2000; Zuo et al., 2008). However, electroflotation can also refer to the application of coupled EC and DAF (Pouet & Grasmick, 1995; Wang et al., 2010). The DAF process – where (a part of) the wastewater is pressurized, saturated with air and decompressed again, releasing fine bubbles – is in this case improved by the release of oxygen and hydrogen caused by the electrolysis of water (Pouet & Grasmick, 1995). In Figure 10, an example pilot plant is depicted where a fraction of the EC treated water is recirculated back to the separation chamber after being pressurized and saturated with air (Wang et al., 2010). The pilot is designed to treat raw municipal sewage.



[1] diffusion chamber
[2] electrocoagulation cell
[3] electrocoagulation device
[4] aluminum electrodes
[5] separation chamber (flotation cell)
[6] biosolids scraped from the top
[7] treated wastewater effluent
[8] recirculated water
[9] air saturation

Figure 10. Pilot configuration of an EC-DAF system for the treatment of raw sewage. A part of the wastewater is recirculated to the EC reactor after air injection. Source: Wang et al. (2010)

5.2 Applications of EF in water treatment

5.2.1 Industrial wastewater

A combined process of electrocoagulation and electroflotation in a continuous flow reactor was used by Chen et al. (2000) to treat wastewater from restaurants in Hong Kong with a high oil and grease content. Here, electrocoagulation destabilized and aggregated the fine particles while electroflotation was responsible for floating the flocs produced in the electrocoagulation unit. The EC cell consisted of aluminium electrodes; the EF cell had a stainless-steel cathode and the anode was coated with titanium. Oil and grease, COD and SS were significantly removed, being 99%, 88% and 98% respectively, with a retention time of less than 4.5 min (Chen et al., 2010). The power requirement was calculated to be only 0.5 kWh/m$_3$. EF can be a very interesting treatment technique for industrial effluents having a high oil or heavy metal content (Emamjomeh & Sivakumar, 2009a; Chen et al., 2010; Belkacem et al., 2008; Merzouk et al., 2009).

Metal finishing industries and wastewater from dyeing and finishing processes in the textile industry severely pollute the environment by the discharge of often untreated effluent (Belkacem et al., 2008). These disposals contain toxic species such as heavy metals (nickel, copper, zinc, lead and cadmium) whose increased concentrations in the human body may cause serious health-problems in the long run. For example, copper can cause gastric irritation, cadmium is related to severe stomach and/or lung damage and lead can cause headaches, paralysis and is carcinogenic (Marin-Galvin, 1996). Belkacem et al. (2009) studied Al-EF for the clarification of strongly polluted textile wastewater from an Algerian velvet manufacture. The results showed a high removal of COD (90.3%), SS (93.3%), turbidity (78.7%) and colour (>93%) under the optimal operating conditions of an applied voltage of 20 V, 1 cm electrode distance and a run time of 20 min. EF allowed a quick separation (<15 min) of heavy metal ions such as iron, nickel, copper, zinc, lead and cadmium, reaching removal rates of 94-99%.

5.2.2 Surface and groundwater

Water is needed in many industrial uses, but processes such as washing or cooling do not require drinking water quality. Ricordel et al. (2010) researched the efficiency of aluminium EF treatment of surface waters in order to obtain waters able to be used in cooling water towers. The results show a very good removal efficiency for phosphate (99%) and fairly good ones for total suspended solids (51% for river water and 46% for pond water) and nitrate (26% and 62% for river and pond water respectively). The higher nitrate removal for pond water was probably due to the lower initial concentration. The authors claim a 'bacteria-free solution' after 30 minutes of electrolysis for river water and a 94.5% average bacteria removal for pond water with a set current value at 0.22 A (Ricordel et al., 2010). These efficiencies only indicate that the bacteria in the treated water were not detectable by the classical cultivation method.

Jiang et al. (2002) developed an electrocoagulation-flotation process for drinking water treatment in the UK. The performance of the aluminum ECF was found to be superior to that of conventional coagulation with aluminium sulphate for treating synthetic water, with 20% more organics removal – measured as dissolved organic carbon (DOC) – for the same Al^{3+} dose. However, for a surface water sample from the River Thames, the two processes achieved a similar performance. It was evaluated that an upflow configuration performed better than a horizontal one (Jiang et al., 2002). Zuo et al. (2008) proposed a combined treatment of an EC and an EF step to remove fluoride from groundwater for the production drinking water. Long-term consumption of water containing excessive amounts of fluoride can lead to dental fluorosis and to skeletal damage (Zuo et al., 2008). According to the WHO, the concentration should be <1.5 mg/L. The authors could reduce the fluoride concentration from initially 4 mg/L to values below 1 mg/L – therewith meeting the Chinese guidelines that suggest a limit of 1 mg/L – at an EC current density of 22 A/m^2 and an average EF current density of 75 A/m^2. Aluminium electrodes were used in the EC cell; the EF cell consisted of titanium containing electrodes. The overall energy consumption of the EC-EF system was about 1.2 kWh/m^3 (Zuo et al., 2008).

5.2.3 Municipal wastewater

In France, Pouet et al. (1992) studied wastewater treatment of sea resorts with electrocoagulation-flotation. To study the effectiveness of combined ECF, the authors compared three different situations: flotation by itself, EC without flotation and EC with flotation. For turbidity, COD and SS, flotation only showed 25%, 26% and 10% removal respectively, EC without flotation 67%, 53% and 33% removal and EC with flotation 89%, 69% and 60% removal. When the ECF treated water was extensively treated with microfiltration, 99% turbidity, 77% COD and 98% SS removal was reached, obtaining an effluent of suitable quality for irrigation (Pouet et al., 1992). Pouet & Grasmick (1995) studied a coupled treatment of EC and DAF for urban wastewater. A comparison between the separated processes showed that DAF is responsible for removing the finest particles (<1 µm) of the raw sewage (30% removal both for DAF alone and EC-DAF). EC is the main responsible for removing supracolloidal particles (65% removal for EC alone, 20% removal for DAF alone and 80% removal for EC-DAF). The combined EC-DAF process removed 90% turbidity, 75% COD and 85% SS. These values are slightly lower than the removal reached with conventional chemical dosing followed by sedimentation (Pouet & Grasmick, 1995).

Holt et al. (1999) promoted EC as a cost-effective method for the treatment of polluted water in Australia, where the natural water sources are limited and reuse of wastewater is an increasing interest. In 2005, Holt et al. identified an ECF system as appropriate treatment technology for localized treatment after observing a growing need for small-scale decentralized water treatment facilities. In an ECF batch reactor with aluminium anodes and iron cathodes, the applied current was varied over the range 0.25-2.0 A (equivalent to a current density of 3.4-27 A/m$_2$). It was demonstrated that at low current density (3.4 A/m$_2$), sedimentation was the dominant SS (clay) removal mechanism (26% of the initial SS was removed from the top and 73% from the base after 4 hours of operation). At the highest current density of 27 A/m$_2$, flotation was favoured as 63% of the initial SS had been transported to the surface after only 1 hour of operation (Holt et al., 2005).

6. Operational parameters

6.1 Electrode material

In the coagulation process, in general, the electrical double layer is compressed due to the increase of counter-ions (coagulants) in the solution that migrate close to the particle's surface and reduce its repulsive forces (Garcia-Segura et al., 2017). Different metal ions have different destabilization abilities. As the charge of the added ions increases, its ability to destabilize the colloids increases as well (Moussa et al., 2017). Therefore, it is favorable to use divalent or trivalent metal ions to destabilize counter-charged colloidal particles. The higher the charge valence of the coagulant, the less dosage is required to obtain the same results (Garcia-Segura et al., 2017).

For coagulation with EC, the choice of electrode material is thus of importance for the efficiency of the system. The most commonly applied electrode materials are iron and aluminium. They are preferred due to their easy availability, high rate of dissolution and low costs (Garcia-Segura et al., 2017). Dissolution of iron anodes lead to a green colour which then turns orange and makes the water turbid. This effect is caused by the formation of Fe^{2+} ions that are oxidized to Fe^{3+} in the presence of O_2. $Fe(OH)_3$ formation and precipitation gives orange coloured water and increases its turbidity. To overcome this drawback, some prefer aluminium electrodes (Ricordel et al., 2010). The disadvantage of aluminium is, however, a higher energy consumption (Kobya et al., 2003). Two additional advantages of iron over aluminium are its non-toxicity and the lower price: about 0.5–0.8 \$/kg, while aluminum costs lie between 1.5 and 3 \$/kg (Hakizimana et al., 2017).

Inert (non-sacrificial) electrodes such as titanium have been observed to initiate coagulation of suspended solids (Moussa et al., 2004). Oxidation of organics and the removal of oil, grease, SS and COD from restaurant water were found very effective using different metal/metal oxide-coated titanium electrodes (Chen et al., 2000). However, the high cost and the large energy consumption of titanium electrodes limit their wide application. (Moussa et al., 2004)

6.2 pH

The pH of the water to be treated electrochemically affects the treatment performance as it influences the species of coagulant formed and the stability and size of the aggregated flocs (Kobya et al., 2003; Daneshvar et al. 2006; Lakshmanan et al., 2009). In general, the pH of the medium changes during the process dependent on electrode material (Kobya et al., 2003). In case aluminium is used, the final pH is higher for initial pH <8, and above initial pH 8 the final pH is lower. For iron, the final pH is always higher than the initial pH, but the difference diminishes for initial pH >8 (Kobya et al., 2003). These pH effects 'suggest that electrocoagulation exhibits some pH buffering capacity, especially in an alkaline medium' (Kobya et al., 2003). As discussed in section

3.2.1, initial pH affects removal efficiencies of COD and turbidity: initially acidic or neutral solutions show higher reductions than alkaline solutions. Independently of the initial value, pH also increases during the EC process due to the generation of OH^- ions. As removal efficiencies of initially alkaline solutions decrease, it is favorable to have a slightly acidic or around neutral pH at the start of the treatment. In the study of Daneshvar et al. (2006), the maximum colour removal efficiency was reached when the pH of the dye solutions was between 5.5 and 8.5.

6.3 Retention time

The EC study of Saleem et al. (2011) showed that the time of operation has a significant effect on pollutant removal. When the retention time was increased from 10 to 30 minutes – applying a constant current density of 24.7 mA/cm^2 –, the removal of TSS increased from 39.5% to 68.5%, COD from 49.6% to 77.2% and turbidity removal from 52.9% to 91.8%. The authors observed two stages, involving destabilization and aggregation, where the first stage is relatively short compared to the second stage. Results showed that maximum efficiency of the process was obtained at a treatment time of 30 minutes and further increase in treatment time had no significant improvement in the removal efficiency of the studied parameters (Saleem et al., 2011). A combined EC-DAF system presumably leads to equal removal efficiencies within less time due to the more abundant presence of bubbles.

Together with the charge dosage rate, the treatment time determines the amount of coagulant produced. When applying low rates, a longer contact time is required to reach a desired coagulant concentration, ensuring the adsorption of pollutants onto formed flocs. A longer contact time however also reduces floc density, making it more difficult for the flocs to settle (Amrose et al., 2013). The introduction of more bubbles by DAF could possibly overcome this problem by letting the suspended flocs float.

6.4 Charge dosage (CD)

Charge dosage, q (C/L), is an important operational parameter expressing the total charge that passes through the solution by the current:

$$q = \frac{J * t * A}{V}$$

where A is the active surface area of the electrode (m^2), t the time of operation (s), J the current density (A/m^2) and V the wastewater volume (L) (Amrose et al., 2013). The theoretical dissociation of iron from the anode can be described using Faraday’s law:

$$m = \frac{I * t * M_w}{n * F}$$

where m is the mass of anode dissolved (g), I the current (A), M_w the molecular weight of the applied metal (g/mol), F Faraday's constant (96,485 C/mol) and n the number of electrons involved in the reaction (Moussa et al., 2017). With a charge dosage of for example 200 C/L, theoretically 58 mg Fe/L is dosed to the system.

Charge dosage determines both the dosage of coagulant and the amount of bubbles generated. It has been identified as the key operational parameter influencing which pollutant removal mechanism dominates in an electrocoagulation-flotation system (Holt et al., 2005). At low applied current density (3.4 A/m_2) with 240 min of treatment time (charge dosage of ~500 C/L), settling of the aggregated pollutant is the dominant removal mechanism. Fewer bubbles are produced at the cathode, resulting in less mixing and material uplift. Conversely, in case a higher current density (27 A/m_2) is used with 60 min of operating time (charge dosage of ~1000 C/L), flotation of the pollutant is preferred above settling due to the higher bubble density and coagulant dosage rate (Holt et al., 2005). However, applying a high current density is not the most efficient mode of operation. An optimal current density therefore needs to be found that involves a trade-off between operational costs and efficient use of the introduced coagulant, where efficiency is defined as 'the pollutant mass removed to the surface per unit of coagulant provided' (Holt et al., 2005). In the research of Holt et al. (2005), this optimal current density was determined to be 14 A/m_2 with 60 minutes of treatment time (on aluminium basis).

6.5 Charge dosage rate (CDR)

Charge dosage rate, *dq/dt* (C/L/min), expresses the amount of coagulant produced per volume per unit time:

$$\frac{dq}{dt} = \frac{I}{V} = \frac{J * A}{V}$$

CDR can be used to calculate the minimum EC operation time to achieve the desired coagulant concentration (charge dosage). In their research to arsenic removal from Bangladeshi and Cambodian groundwater, Amrose et al. (2013) found that charge dosage rate, as opposed to current density, has a significant effect on both the removal capacity – µg As removed/Coulombs – and treatment time. CDR influences the contact time between an HFO particulate and the remaining pollutant in the solution (Amrose et al., 2013). Decreasing charge dosage rate with an increasing retention time showed increasing removal capacity, resulting in a lower charge dosage. The effect of decreasing dosage rate simultaneously results in a longer treatment time (also with low charge dosages, it takes longer to reach it). The researchers found that CD could be reduced 6-fold but only with a corresponding increase of 40 times in minimum contact time (Amrose et al., 2013). To minimize energy consumption, this trade-off is an important factor in designing an economically feasible reactor.

Trikannad (2019) also observed higher pollutant removal at low charge dosage rate. High bacteria attenuation (>3.5 log removal for *E. coli*, >2 log removal for somatic coliphages and 2.7 log removal for *C. perfringens* spores) were reached at a charge dosage of 400 C/L with a low dosage rate of 7.2 C/L/min, allowing higher adsorption onto the iron flocs with longer contact time. Additionally, the variation in pollutant reduction at low and high CDR demonstrated the effect of sedimentation and flotation mechanisms. A low CDR of 7.2 C/L/min instigated low bubble density, causing sedimentation of flocs to be the dominant removal mechanism. By applying intermediate and high CDRs of 36 and 72 C/L/min – resulting in high current and voltage – the production of hydrogen gas benefited pollutant removal by flotation (Trikannad, 2019).

6.6 Bubble formation and size

Both bubble size and numbers of bubbles are of key importance for efficient pollutant removal (Chen et al., 2000; Han et al., 2002; Wang et al., 2010). Chen et al. (2000) observed that uniform tiny bubbles were not formed by the electrocoagulation process. The H_2 bubbles produces at the cathode were >100 µm. In general, it applies that the smaller the bubbles, the higher the removal efficiency due to the larger surface area. The generated bubbles also did not mix properly with the wastewater, as they tended to rise along the cathode surface (Chen et al., 2000; Mollah et al., 2004). This decreases the chance of contact between the bubbles and the particles. The production of ‘large’ bubbles in EC have been associated with the surface structure of the (aluminium) electrode, which is usually rough due to the dissolution that takes place (Chen et al., 2000). Rough electrode surfaces provide larger adhering forces to bubbles than smooth surfaces. To obtain small bubbles, it is thus very important to regularly smoothen the electrode’s surface (Chen et al., 2000). To release the bubbles from the electrodes, the electrolyte flow could be increased (Mollah et al., 2004). Another solution to improve the performance is to install the electrodes at an angle to the horizontal plane, which enhances the mixing of the bubbles with the wastewater (Chen et al., 2000). The drawback of this arrangement however is that the electrodes may be bent after usage for a certain amount of time.

When EC is followed by a separated EF step, the system can be improved. Inert electrodes such as a smooth activated titanium anode and a stainless-steel mesh cathode can be used to produce large amounts of tiny bubbles (Chen et al., 2000). Another method to increase the production of tiny bubbles is by the introduction of DAF to the system. The bubble size that is generated with DAF is generally reported to be 10-100 µm, with an average diameter of about 40 µm (Edzwald, 1995; Han et al., 2002). Pressure conditions of 2-6 bar, which are known to affect bubble size the most, are commonly applied (Han et al., 2002). Han et al. (2002) showed that the bubble size decreased as pressure increased up to a pressure of 3.5 bar. They stated that it is unnecessary and costly to maintain a pressure above this value if the goal is only to produce tiny bubbles (Han et al., 2002). A comparison of bubble formation by DAF and EF showed that the relative size was 75 µm for dissolved air systems, and 100 µm for EF systems, with density (numbers, million per cubic centimeter), of 3.2, and 1.0 respectively (Wang et al., 2010). DAF thus provides the largest number of smaller bubbles and hence has the largest surface area for particulate removal.

7. Pollutant removal

Inactivation of pollutants by charge neutralization, adsorption, entrapment or compression of the double layer has been discussed briefly in section 3.1.1. In addition, the process of electrolysis – that takes place during electrocoagulation and literally means breaking substances apart with the use of electricity – can destroy microorganisms including bacteria and algae (Ghernaout et al., 2011) and is therefore an interesting alternative disinfection method. A current intensity of >1 A is required for direct microbial inactivation (Anfruns-Estrada et al., 2017). In this section, the removal mechanisms for each of the in chapter 2 identified pollutants are discussed.

7.1 Microorganisms

7.1.1 Bacteria

Delaire et al. (2016) reported two processes that contribute to bacteria attenuation in Fe-EC. The first mechanism is physical removal caused by the adhesion of EC precipitates to bacteria cell walls, resulting in 'bacteria enmeshment' in ferric iron flocs and subsequent settling (Delaire et al., 2016). In a combined EC-DAF system, the smaller, lighter flocs are removed by flotation (Pouet & Grasmick, 1995). Secondly, inactivation by reactive species that are produced upon Fe^{2+} oxidation by O_2 takes place. Underlying fundamental aspects of these two processes remain unknown (Delaire et al., 2016). Using *E. coli* as model indicator, the first mechanism is considered the most dominant, which is driven primarily by interactions between iron precipitates and negatively charged phosphate functional groups present on the bacterial cell wall (Delaire et al., 2016).

Feng et al. (2004) considered *Legionella* disinfection as the synergistic effect of oxidation at the anode, the formation of reactive free radicals and exposure to an electric field. The pulses of the electric field make the membrane of the microorganism cell permeable, which can result in swelling and eventual rupture of the cell membrane (Feng et al., 2004). Voltages between 1 and 1.5 kV were applied. Microbial destruction by the electric field is also attributed as fundamental disinfection mechanism by Ghernaout et al. (2019). Besides, the adsorption of bacteria onto Fe/Al hydroxides is considered as a key mechanism. Strongly oxidative but short-lived intermediate radicals are attributed as possible deactivators, but this deserves more research (Ghernaout et al., 2011; Ghernaout et al., 2019). In their study from 2008, Ghernaout et al. showed that Al-EC was slightly more effective than Fe-EC for electrodisinfection. The survivability of *E. coli* declined with increasing current intensity and treatment time (Ghernaout et al., 2008). Anfruns-Estrada et al. (2017) showed that Fe-EC treatment at 200 A/m^2 allowed 3.84 log removal for *E. coli* from secondary municipal wastewater effluent.

7.1.2 Protozoa

Protozoa showed to be more resistant to Fe-EC treatment than bacteria. Anfruns-Estrada et al. (2017) reported a poor decay of 0.61 log removal of *C. perfringens* spores from secondary effluent, even after 90 minutes of electrolysis. Edzwald (2010) reported on the performance of DAF removing protozoan (oo)cysts from water. Compared to traditional sedimentation, DAF is more effective in removing *Giardia* cysts and *Cryptosporidium* oocysts. With DAF, 2-3 log removals were achieved compared to removals by sedimentation of 2 log that decreased to 1 log or less for winter water temperatures (Edzwald, 2010). Removal is also depended on type of coagulant and pH. Bustamante et al. (2001) indicated that *Cryptosporidium* oocysts, unlike inorganic colloidal materials such as metal oxides, appear to have a lower surface density of charged sites. This combined with the rapid precipitation of iron salts might be responsible for the lack of adsorption (Bustamante et al., 2001). Therefore, sweep coagulation is the more likely removal mechanism when iron is dosed. A stronger link between hydrolyzed aluminium species and the oocyst's surface was observed, causing charge neutralization (Bustamante et al., 2001).

7.1.3 Viruses

Zhu et al. (2005) studied virus removal from surface water by iron EC, using MS2 bacteriophage as virus tracer. A >4 log removal was reached when EC treatment was followed by microfiltration. The experimental data indicated that at lower iron dosages and pH (<8 mg Fe/L and pH 6.3 and 7.3), the negatively charge viruses adsorbed onto the positively charged iron hydroxide flocs. When higher iron dosages and pH were applied (>9 mg Fe/L and pH 8.3), virus removal was attributed predominantly to enmeshment by the iron flocs (Zhu et al., 2005). Somatic coliphages were undetectable after Fe-EC treatment of both primary and secondary wastewater effluent (Anfruns-Estrada et al., 2017). The presence of natural organic matter tends to hinder iron oxidation to HFO flocs and can therefore reduce coagulant precipitation and sweep flocculation (Ghernaout et al., 2011).

7.2 Wastewater parameters

7.2.1 Phosphorous

Nguyen et al. (2016) studied phosphorous removal by EC from the effluent of a municipal wastewater treatment plant in South Korea. The initial concentration of 1.73-3.2 mg TP/L was reduced to values below 0.2 mg/L within 2 to 5 min. The initial pH of 6.3-7.4 remained in the neutral range despite achieving the highest P removal (98%). It was found that an increase in conductivity, voltage or electrolysis time correlated with improved phosphorous removal (Kuokkanen et al., 2015; Nguyen et al., 2016). Phosphate can form precipitates with released Fe_{2+} or Fe_{3+} ions, as shown in the reactions 10 and 11 below.

$3\ Fe^{2+} + 2\ PO_4^{3-} \rightarrow Fe_3(PO_4)_2\ (s)$ (10)

$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4\ (s)$ (11)

Source: Nguyen et al. (2016)

TP was shown to be effectively removed at the beginning of the EC process. Next to direct adsorption of PO_4^{3-} onto dissolved Fe^{2+} or Fe^{3+} species, there is a second mechanism responsible for P removal. Phosphate can also complex with iron hydroxides, resulting in charge neutralization and possibly creating sweep flocculation. Colloidal particles then form large aggregates, therefore rapidly removing contaminants (Nguyen et al., 2016). Initial pH has a significant effect on removal efficiency. Kuokkanen et al. (2015) studied P removal by EC with hybrid (Al/Fe) electrodes from industrial wastewaters. A clear trend of rising phosphate removal efficiency with lowering initial pH was observed. Adjusting the initial pH to 5 was found to be optimal, with 94% phosphate removal (Kuokkanen et al., 2015).

7.2.2 Nitrogen

Nitrate (NO_3^-) is a stable and highly soluble ion with low potential for precipitation or adsorption, making it a difficult pollutant to remove by conventional water treatment methods (Emamjomeh & Sivakumar, 2009b). With batch EF experiments using aluminium electrodes, Emamjomeh & Sivakumar (2009b) studied denitrification. A removal efficiency of 85% was reached with an initial pH of 8 – the lowest initial value investigated. The optimum nitrate removal was reached at a pH in the range of 9-11. Nitrate removal was 93% with an initial concentration of 100 mg/L and an electrolysis time of 40 min. It was shown that the nitrate concentration decreased with increasing current rate (Emamjomeh & Sivakumar, 2009b; Sharma & Chopra, 2017).

Nitrate removal mechanism is due to a reduction-oxidation reaction and is not caused by complexation between aluminium and nitrate ions in the solution (Emamjomeh & Sivakumar, 2009b). Nitrate is first reduced to nitrite at the cathode and can then be converted to ammonia and nitrogen gas. Although EF effectively reduced excessive nitrogen, an additional treatment step to strip the ammonia from the solution is required (Emamjomeh & Sivakumar, 2009b).

Sharma & Chopra (2017) researched nitrate removal by Al-EC from secondary municipal wastewater effluent. A maximum removal of 63% was reached under optimal operating conditions: current density 2.65 A/m^2, initial pH 7.5 and treatment time 40 min. The nitrate concentration was reduced to below the desirable limit of 50 mg NO_3^-/L (~10 mg NO_3-N/L) for drinking water by the WHO (Sharma & Chopra, 2017). However, a settling time of 60 min was required to reach this value. Applying a combined EC-DAF system could benefit the removal by flotation and speed up the process.

7.2.3 Chemical oxygen demand (COD)

COD is a measure of the amount of oxygen used in the chemical oxidation of inorganic and organic matter present in water (Moreno-Casillas et al., 2007). Though it is not a specific compound, it is an indicator of the degree of pollution. Moreno-Casillas et al. (2017) observed an extremely high variability in COD removal efficiency, varying from 0.5 to 86.4%. The efficiency depends on the ability of compounds to form flocs with the introduced coagulant; particles that react with Fe^{2+} or Fe^{3+} to form insoluble compounds are easily removed. The part of COD which is not removed consists of soluble compounds – such as glucose, lactose, phenol, isopropyl alcohol and sugar – that do not react with iron species to form insoluble flocs (Moreno-Casillas et al., 2017). pH is related to COD removal as it influences the formation and solubility of compounds (Kobya et al., 2003; Moreno-Casillas et al., 2017). With Fe-EC, a COD removal of 98% was reached around a pH of 6-7 (Şengil & Özacar, 2006).

Current density and treatment time were also related to COD removal (Kobya et al., 2003; Şengil & Özacar, 2006; Moreno-Casillas et al., 2017). When holding the pH and current density constant, COD concentration decreased as a function of elapsed time. After 60 s of treatment time, the maximum removal capacities were reached for current density values 0.6, 1.2 and 1.8 mA/cm^2 (Şengil & Özacar, 2006). For a current density of 0.3 mA/cm^2, it took longer to reach its maximum removal capacity. Removal capacity increased with increasing current density as more coagulant was produced. In all experiments the used electrodes had a total area of 333 cm^2, treating a volume of 650 mL (Şengil & Özacar, 2006).

7.2.4 Total suspended solids (TSS)

The removal of TSS was shown to be related to applied current and treatment time (Bukhari, 2008). Bukhari (2008) distinguished different removal mechanism for low and higher applied currents: 'The dominant removal mechanism of suspended/colloidal matter, when using the lower currents of 0.05 A and 0.1 A was shown to be consistent with charge neutralization coagulation mechanism. For the higher currents of 0.2 A, 0.4 A, and 0.8 A, the results suggest that the dominant removal mechanism of suspended/colloidal matter is consistent with sweep-floc coagulation mechanism as more of the soluble ferrous ions are converted to insoluble ferric ions due probably to oxidation of ferrous ions to ferric ions with chlorine produced in the electrochemical process.' The highest TSS removal efficiency of 95.4% was reached at a current of 0.8 A with 5 min of contact time (Bukhari, 2008). Each experiment was carried out with a wastewater sample of 1.2 L.

7.2.5 Turbidity and colour

In the research of Abuzaid et al. (2002), the applied electrical current was found to be inversely proportional to the turbidity of the water, as shown in Figure 11. The highest turbidity removal efficiency of 95% was achieved at a current of 1 A and 5 min of treatment. When the current was reduced to 0.5 A and the contact time was increased to 10 min, the turbidity was reduced from 4.0 to 1.6 NTU. Furthermore, similar turbidity removals were achieved at a much shorter contact time (2 min) when 1 g/L sodium chloride was added to the test water (Abuzaid et al., 2002).

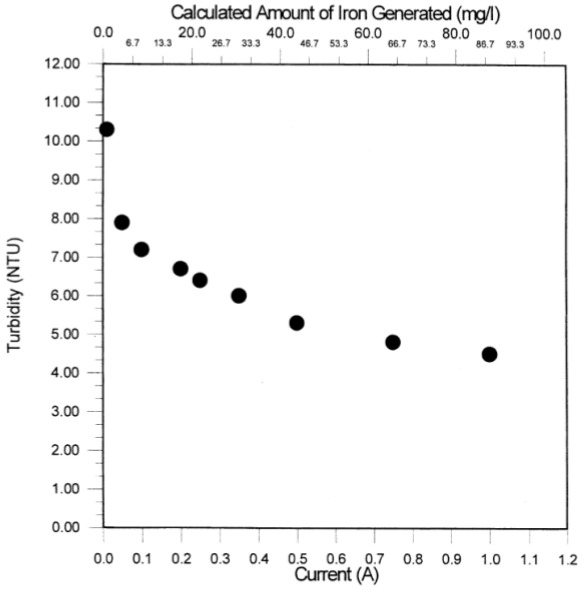


Figure 11. The effect of applied current on turbidity removal at a contact time of 5 min. Initial turbidity was 76 NTU. Source: Abuzaid et al. (2002)

With an EC-EF set-up, Aoudj et al. (2017) successfully removed organic and inorganic pollutants from semiconductor wastewater, generated during the production of silicon wafers that for example are used to manufacture solar cells. An increase of turbidity during the EC step from 30 to ~80 NTU was observed – as a result of the coagulation process –, followed by a rapid decrease to 4.35 NTU during the EF step. An increase in current density did not have an effect on their turbidity removal (Aoudj et al., 2017). Daneshvar et al. (2006) studied decolourization of dye solutions by EC. They showed that an increase in current density up to 60-80 A/m$_2$ enhanced the colour removal, using steel electrodes with an active surface area of 56 cm$_2$ and treating 250 mL of dye solution. pH and treatment time also influenced decolourization. An electrolysis time of 5 min and an initial pH in the range of 5.5-8.5 showed to be most efficient (Daneshvar et al., 2006).

According to Feng et al. (2004), the decrease of turbidity can be explained by the electric field neutralizing the surface charges of the colloid particles present in the (waste)water. This results in their agglomeration and sedimentation or flotation. Removal of turbidity also enhances the removal of microorganisms, as disinfection is hampered by high turbidity (Feng et al., 2004).

8. Discussion

The operational parameters discussed in chapter 6 are based on results of various EC, EF/ECF and DAF studies. It gives an idea of important influential operational parameters, but the overview is not completely inclusive. Parameters such as electroconductivity, electrode distance, electrode arrangement, operational modes are shortly touched upon but are not studied in detail. They however also affect the performance of electrochemical treatment (Kobya et al., 2003; Emamjomeh & Sivakumar, 2009a). For DAF, the air-to-solids ratio is an important design parameter (Wang et al., 2005), as well as the type of valves or nozzles that are implemented; they influence the gas bubbles formation and thus the overall efficiency (Schofield, 2001). These aspects deserve further attention as they also influence the electroflotation process. Furthermore, sludge production, initial pollutant concentration, reactor design and energy consumption are of importance to consider as well to determine the overall performance of the treatment system.

DAF is particularly good in capturing the finer solids (Schofield, 2001). It is however reported that floc particles <20 μm will not adhere to bubbles and removal is very poor as the particulate size approaches 1 μm. Therefore, it is essential that the colloidal solids are converted to bigger particles. Electrochemical introduction of coagulants can have a strong enhancing effect.

The advantage of DAF is that high rates can be applied, resulting in smaller flotation tanks than required for traditional sedimentation (Comninellis & Chen, 2010). Both EC and DAF are known for reduced chemical usage, where coagulants are formed in situ in the latter case, not needing additional salt dosing (Mollah et al., 2001; Moussa et al., 2017). The clarified water of the individual processes have shown consistently high microbiological quality; combining the two possibly increases microbial stability, making it suitable for water reuse for irrigation purposes.

For EC only one unit required, while combining EC and DAF asks for an additional retention chamber (pressure tank). DAF has higher service costs compared to other technologies (Schofield, 2001), so a cost-benefit analysis should be made. Both technologies are chemical and physical intensive processes. By combining the two, an even more complex process exists with many influencing operational parameters. The examples of EF as application in water treatment as discussed in section 5.2 are promising but not a lot is known about EF treatment for municipal wastewater in general or as tertiary treatment for municipal wastewater effluent in particular (except for the mentioned study of Pouet & Grasmick (1995)). To fully understand the technology, lab-scale and pilot-scale tests should be executed with synthetic and real wastewater effluent.

9. Conclusion

One of major challenges of the near future is to provide new sources of water, especially in countries where the lack of natural water resources has become a serious problem. Regeneration of urban wastewater seems a good possibility to reduce stress on water sources. By improving the quality of effluents of municipal wastewater treatment facilities, water could be provided for many different uses such as irrigation, repletion of aquifers and for industrial purposes.

Electrocoagulation (EC) technique, where coagulants are introduced electrochemically to remove suspended solids, metals and microorganisms, has shown to be effective in (industrial waste)water treatment with significant reduction of COD, TSS, turbidity and nutrients. Bacteria and viruses are also effectively removed by EC treatment, while protozoa are more resistant to EC treatment than bacteria and viruses. However, when reuse of water for irrigation is intended, stringent requirements on water quality apply. With EC treatment alone, very small suspended solids – which are carriers of microorganisms – were not sufficiently removed from secondary municipal wastewater effluent as they did not settle.

Flotation was suggested as a more effective separation technique. In the process of dissolved air flotation (DAF), air bubbles in the range of 10-100 µm are introduced that adsorb impurities. Applications in industrial processes and in some water treatment plants demonstrated the high solids removal capacity of DAF, together with a high disinfection capacity. Combination of EC and DAF could thus enhance removal of microorganisms. This so called electroflotation (EF) technique lies at the intersection of three fundamental processes: electrochemistry, coagulation and flotation. The aim of this study was to provide the theoretical background of EF and the state-of-the-art of its implementations.

There are many factors that influence the effective removal from wastewater pollutants by EF treatment, such as electrode material, pH, retention time, charge dosage, charge dosage rate, bubble formation and size. The main mechanisms responsible for pollutant removal are charge neutralization, adsorption, sweep coagulation, microbial destruction by the electric field and deactivation by free radicals. However, the mechanisms involved are yet to be clearly understood as a wide variety of opinions can be found from literature.

The hybrid EF process, which has been implemented in different water treatment processes, promises to increase removal efficiencies compared to single EC and DAF treatment, but the full potential of EF as a treatment technology for secondary municipal wastewater effluent is yet to be fully realized. The process needs to be empirically optimized, a challenging task due to the involvement of complex chemical and physical processes.

10. Recommendations

1. The opinions on which ions (Fe^{2+} or Fe^{3+}) are formed during electrochemical disinfection with iron electrodes strongly diverge. This should be studied in more detail in order to fully understand the underlying processes.

2. In the EC process, charge dosage is often seen as key parameter, which also determines the amount of gases produced. In case DAF is introduced to the system, the formation of bubbles by EC is influenced, resulting in CD as a dependent parameter. This should be considered in further research.

3. Operational parameters such as electroconductivity, electrode distance, electrode arrangement, operational modes, air-to-solids ratio, sludge production and initial pollutant concentration should be studied in more detail.

4. Both EC and DAF require electrical power for the generation of coagulants and air bubbles respectively. A thorough cost-analysis has to be made to determine if EF is a cost-effective technology.

5. Experimental laboratory and pilot scale studies should be performed to determine the removal efficiency of EF treatment.

6. It would be interesting to investigate the influence of different recycle ratios for EF, as operational costs can be lowered when only a part of the water to be treated is pressurized instead of the whole batch (less power consumption).

7. Usually pressure differences of 4-6 bar are applied to generate bubbles. However, a pressure of 3.5 bar also showed to produce tiny bubbles (Han et al. 2002). It is recommended to evaluate removal capacity at this lower pressure as it would reduce the treatment costs significantly.

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