



Humic acid removal by chemical coagulation, electrocoagulation and ultrafiltration

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<p>Abstract:</p> <p>This thesis work aimed to establish experimental procedures and compare different methods for removing humic acid (HA) from water. Three methods were investigated: chemical coagulation (CC), electrocoagulation (EC) and ultrafiltration (UF). The topic was approached by reviewing the relevant literature and performing experiments. The literature review reported here provides an overview of current experimental methods, defines HA and describes the analytical methods used to quantify HA. For the practical part of this work, experiments were held to establish CC, EC and UF procedures aiming for the highest removal rates of moderately concentrated synthetic HA. The effects of working solution pH, coagulation and flocculation times, chemical coagulant dosage and current applied on HA removal rates were investigated. HA removal values exceeding 95% were reached by EC and by CC techniques under optimum conditions and after floc removal by gravitational or centrifuge settling. UF did not achieve similarly high removal efficiencies of floc: the flocs seemed to break under pressure, which let some of them pass through the membrane and reform afterwards. An attempt was made to quantify the sizes of coagulated flocs with a microscope in order to estimate their strength. Accurate estimation of floc dimensions, however, was not possible from captured images due to the destructive sampling technique and difficulties in defining individual floc boundaries. The concentrations of HA in all samples were measured by UV-Vis spectrophotometry.</p>	
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ABBREVIATIONS

AC	alternating current	MF	membrane filtration
CC	chemical coagulation	NF	nanofiltration
DBP	disinfection by-product	NOM	natural organic matter
DC	direct current	PAC	polyaluminum chloride
EC	electrocoagulation	RF	reversible fouling
HA	humic acid	RO	reverse osmosis
HMM	high molecular mass	TF	total fouling
HS	humic substance	TOC	total organic carbon
IF	irreversible fouling	UF	ultrafiltration
LMM	low molecular mass	UV-Vis	ultraviolet-visible

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1 INTRODUCTION

Water is indisputably of great significance for human beings. Clean drinking water is essential to life and peoples' survival. If the water they consume is not clean it impacts negatively on them and may cause various diseases or even result in fatality. Municipal drinking water must meet many different quality standards and has to go through a sequence of purification methods. Surface waters cannot be used without pretreatment because of the high concentration of humic substances (HSs) that might be harmful for human health. This thesis studied chemical coagulation, electrocoagulation and membrane filtration and compared their performances in removing HSs from water. The main aim was to determine whether electrocoagulation and/or membrane filtration could be as efficacious as the established, industry-standard chemical coagulation but with lower chemical loading.

This document is divided into five chapters. The significance of the study, its main objectives and the approach are presented in the first chapter. Chapter 2 is a review of the current literature and contains all the necessary information related to the topic to help the reader further understand the experiments. Chapter 3 describes all the experiments that have been conducted, while the results are discussed and the investigated techniques of HSs removal are compared in chapter 4. The conclusions and recommendations in the final chapter include a brief description of the problem and the findings, answers to the questions raised and some suggestions for further studies based on this work.

1.1 Background

The presence of natural organic matter (NOM) in drinking water causes many problems in the water treatment processes, as it acts upon potable water quality by causing aesthetic concerns such as yellowish or brown colour, annoying taste and odour (Metsämuuronen, Sillanpää et al. 2014). Moreover, organic matter is responsible for corrosion and has a tendency to increase bacterial growth and biofilm formation in drinking water distribution systems, which essentially clogs water filtration systems in water purification facilities (Matilainen, Vepsäläinen et al. 2010). It is the presence of HSs, which are one of the fractions of NOM, in water that introduces a yellowish to brown color. Even though HSs

themselves are not toxic, they have been associated with the formation of strongly toxic disinfection by-products (DBPs), such as trihalomethanes and haloacetic acids, during the chlorination stage in drinking water treatment (Wang, Gao et al. 2009). The formation of DBPs, of which some exhibit mutagenic properties and are known human carcinogens, is directly proportional to the concentration of HSs in water. DBPs lead to dizziness, headaches, as well as problems associated with the central nervous system after short-term exposure. Thus, for example, the high concentration of humic acid (HA) in an artesian well water, along with arsenicosis, in southwestern Taiwan is the potential cause for the endemic blackfoot disease (Sudoh, Islam et al. 2015, Xiaoying 2000). HSs also tend to complex with various pollutants, such as toxic metals and hydrophobic organic matters, which causes contamination of ground and surface waters (Sudoh, Islam et al. 2015).

Not only drinking water, but also peat harvesting runoff water requires pre-treatment. The exposure of peat layers and the drainage of the peatland area are the reasons for an increase in the leaching of pollutant substances into water bodies located downstream. The leaching of pollutants, such as HSs and other NOM, has a negative impact to the local aquatic ecosystem, causing eutrophication and siltation of the receiving water bodies. Along with the fact that HSs can easily react with chlorine and form carcinogenic and hazardous disinfection by-products (e.g. trihalomethanes), this makes the removal of HSs an important part of water treatment processes.

Innovative, cheap and effective methods of purifying contaminated water are needed. HSs can be removed by a whole range of treatment processes, and their selection depends on the nature of the raw water, the space available to construct the plant, and, often, a consideration of operational costs. There may well not be a single correct process of HSs removal for particular water, but a number of possible options.

Chemical coagulation and flocculation are the most commonly used methods for the removal of HSs from raw waters and wastewaters. The most commonly used coagulants are aluminum and iron salts. They form hydrolysis products in the water; metal cations and hydroxides destabilize pollutants by reducing repulsion forces between the colloids

and by entrapping particles in the sludge. Electrocoagulation has been suggested as an alternative method for removing HSs. It has a fundamentally similar destabilization mechanism as chemical coagulation. But in this technology, metal cations are released into water through dissolving metal electrodes. The third technique, membrane filtration, is based on removing particles larger than the pore size of the membrane.

1.2 Objectives of the study

Here are the main objectives fulfilling the aim of this thesis:

- To establish a method of determining HA concentration in water in Arcada.
- To evaluate the treatability of synthetically prepared humic acid solution by chemical coagulation (CC), electrocoagulation (EC) and ultrafiltration (UF).
- To study and optimize the parameters affecting CC, EC and UF in order to achieve the highest HA removal rate.
- To investigate whether electrocoagulation (EC) can be used as a pretreatment for membrane filtration.

1.3 Approach

The topic was approached by reviewing currently existing articles explaining the importance of HSs' removal. To get an understanding of water treatment methods and establish own procedures, also experimental articles were reviewed, paying attention mostly to experiment descriptions.

Natural NOM contains a rich collection of various organic compounds, both particulate and dissolved. Particulate organic matter can be easily separated, e.g. by filter paper, whilst dissolved organic matter needs another treatment method. As HA accounts for more than half of dissolved organic matter, it was chosen as the starting material for simulated HSs in surface waters in order to simplify the determination of water content. The experimental parts of this study consisted of performing purification of water by means of CC, EC and UF. To start with, methods for preparing HA solutions and determining HA concentrations in water were established. After that, the effect of

coagulant dosage, pH of the solution, and treatment time were investigated for coagulation experiments. Additionally for EC, optimum conditions for current density and electric charge added per volume were tested. Microscopy was applied to determine the floc size. Also, membrane filtration was used to separate flocs from solutions.

2 LITERATURE REVIEW

2.1 Natural organic matter characterization

2.1.1 General

All surface waters contain natural NOM, which is defined as a complex composition of organic compounds coming from the chemical and biological degradation of plant and animal residues (Metsämuuronen, Sillanpää et al. 2014). Basically, NOM is a complex mixture of different organic materials, such as bacteria, viruses, humic and fulvic acids, polysaccharides and proteins (Vepsäläinen 2012). Its presence in drinking water causes many problems in water treatment processes, thus, making it extremely important to remove. NOM primarily consists of components with different properties and molecular sizes ranging from small molecules to macromolecules and large particles. It can be divided to particulate organic matter that can be retained by filter paper and dissolved organic matter easily passing through the filter. A great difference in NOM molecular sizes makes it problematic to completely remove from water by any single method and especially as seasonal variation has a great impact on its concentration and quality (Metsämuuronen, Sillanpää et al. 2014, Matilainen, Vepsäläinen et al. 2010, Ashery, Radwan et al. 2010).

The mixture of organic compounds of NOM can be divided into hydrophilic and hydrophobic fractions. The hydrophilic fractions of NOM are composed primarily of aliphatic carbon and nitrogenous compounds, such as carboxylic acids, carbohydrates and proteins. Hydrophobic NOM primarily consist of humic and fulvic substances and is rich in aromatic carbon, phenolic structures and conjugated double bonds. These fractions and the chemical groups they comprise are presented in Table 1 (Matilainen 2007).

FRACTION		CHEMICAL GROUP
Hydrophobic fraction	Acids	Strong acids: Humic and fulvic acids, HMM alkyl monocarboxylic and dicarboxylic acids, aromatic acids
		Weak acids: Phenols, tannins
	Bases	Proteins, aromatic amines, HMM alkyl amines
	Neutrals	Hydrocarbons, aldehydes, hmm methyl ketones and alkyl alcohols, ethers, furans, pyrrole
Hydrophilic fraction	Acids	Hydroxy acids, sugars, sulfonics, LMM alkyl monocarboxylic and dicarboxylic acids
	Bases	Amino acids, purines, pyridines, LMM alkyl amines
	Neutrals	Polysaccharides, LMM alkyl alcohols, aldehydes and ketones

Table 1. NOM fractions and chemical groups (Matilainen 2007).

2.1.2 Humic substances

NOM is mainly composed of humic substances (HSs). HSs generally account for over half of dissolved organic matter (Metsämuuronen, Sillanpää et al. 2014, Matilainen, Vepsäläinen et al. 2010). The main constituents of HSs are aromatic and aliphatic structures, carboxylic, phenolic-OH, amino and quinone groups.

HSs can be divided into three main fractions: humin which is completely insoluble, HA which is soluble at high pH but insoluble under acid conditions and fulvic acid (FA) which is soluble at any pH (Lowe, Hossain 2008, Rodrigues, Brito et al. 2008).

HAs are suspected to be a result of condensation polymerization reactions, amino acid sugar interactions and the microbiological degradation of surrounding vegetation and animal decay (Schafer 2001). They enter surface waters through rainwater run-off from the surrounding land (Lowe, Hossain 2008). HAs have molecular weights ranging from 2 kDa up to over 500 kDa, making them difficult to analyze (Stevenson 1994).

Although HSs have been widely studied, there is not enough information about their precise structure, hence, no single structural formula suffices for them (Lu, Hanna et al. 2000). They are thought to be complex molecules with amino sugars, amino acids, peptides and aliphatic compounds linked with aromatic groups. A hypothetical model illustrating a typical molecular structure of HA, which is one of the fractions of HSs, is shown in Fig. 1. It contains free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units and COOH groups randomly placed on aromatic rings.

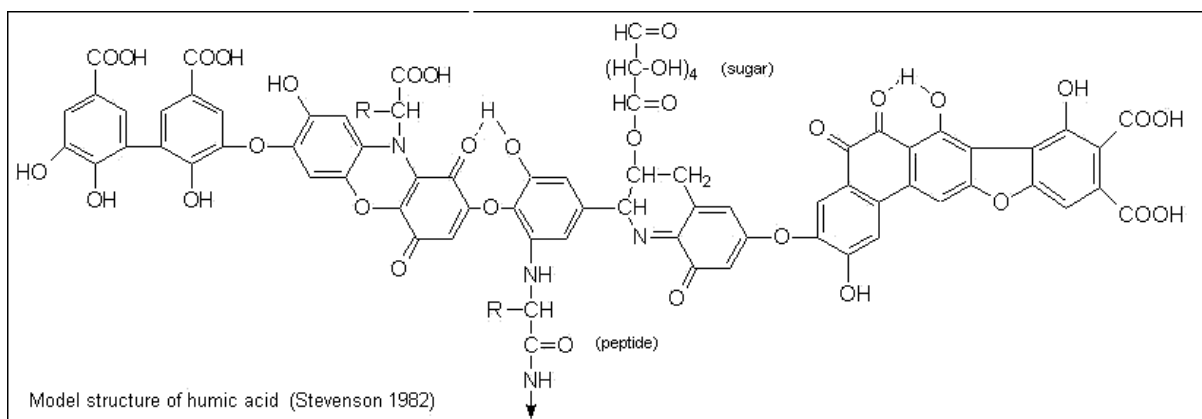


Figure 1. Model structure representative of a humic acids (Stevenson 1994).

As can be seen in Fig. 1, the composition of HSs, for instance HAs, is very complex. Moreover, it depends much on the area making it difficult to reliably identify and find any method for the characterization and quantification of humus content; for example, the results are absolutely different in sea waters and in degraded sediments. Table 2 illustrates the amount of HSs as a percentage of NOM depending on the place where the samples were taken.

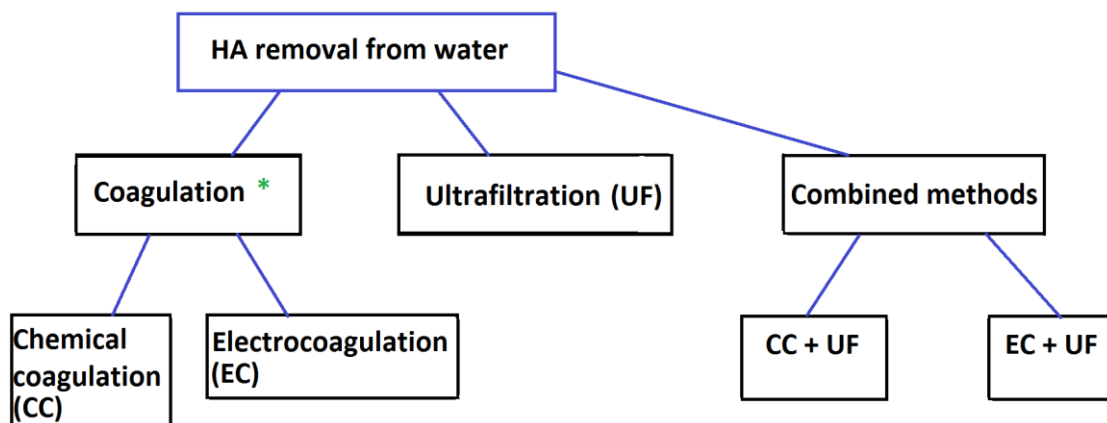
Place	Mass % of NOM
Sea waters	10-30
Rivers and streams	40-70
Lakes	~50
Degraded sediments	60-70
Highly degraded sediments	90

Table 2. Comparison of humus content in waters of Australia (Lu, Hanna et al. 2000).

2.2 Methods of HSs removal

The concentration of NOM varies from 0.1 mg L⁻¹ in groundwater to 200 mg L⁻¹ in some tropical or polluted rivers and rivers draining through swamps and wetlands (Rodrigues, Brito et al. 2008). The amount, character and properties of NOM, and HSs in particular, differ considerably in waters of different origins and depend on the biogeochemical cycles of the surrounding environments. The range of HSs components may vary also at the same location seasonally, due to, for example, floods and droughts that are the main impacts of climate change on water availability and quality (Matilainen, Vepsäläinen et al. 2010).

The great difference in HSs molecular sizes and seasonal variation impact on their concentration is one of the main problems in finding any single method to completely remove them from water. Particulate organic matter can be retained by a 0.45 µm pore-sized filter while dissolved organic matter simply passes through the filter and has to be removed in a different way (Metsämuuronen, Sillanpää et al. 2014). Fig. 2 depicts dissolved HA removal methods considered in this work.



* followed by flotation, sedimentation or filtration

Figure 2. Methods of HSS removal from water reviewed in this thesis.

The most common and economically feasible treatment processes for the removal of NOM are considered to be coagulation and flocculation followed by sedimentation/flotation and/or filtration. These processes will now be described in more detail below.

2.2.1 Theory of coagulation

Coagulation is a water treatment process where the repulsive potential of electrical double layers of colloids reduces in such a way that micro-particles can be produced. These micro-particles collide with each other and form larger structures (flocs) in the flocculation process. The floc then either floats to the top or settles to the bottom of the liquid and can be easily filtered afterwards. The aim of coagulation is to produce particles of a size that can be removed by settlement, flotation or filtration (Binnie, Kimber 2013).

Since large organic molecules carrying a negative charge, HSS are removable by coagulation and subsequent floc separation (Ulu, Barışçı et al. 2014). Example coagulation and flocculation results in HA removal from water are presented in Fig.3.



Figure 3. Chemical coagulation applied to HA synthetic water in this study. Left to right: a) 50 mg/L humic acid initial solution, b) after coagulation (PAC used as chemical coagulant) and flocculation, c) after floc removed by filtration.

Destabilization mechanisms of colloids

Colloids are microscopic particles said to be stable in water meaning that they cannot be removed within a reasonable period of time by sedimentation. Stability (or destability) of colloids in water is the result of their surface charge, in particular a balance between the repulsive electrostatic force and attractive, London-van der Waals force. The repulsive force is caused by the overlapping of the electrical double layers. The force of repulsion is an exponential function of the distance between the particles. The force of attraction, caused by the permanent or induced dipoles, decreases as an inverse power of the distance between the particles (Binnie, Kimber 2013).

For small separation distances between particles, the attractive energy G_A is inversely proportional to the sixth power of the distance between the particles h . The electrostatic energy of repulsion decays exponentially with increase of h and approaches zero at large h . The graph in the Fig. 4 shows a relationship between the attractive energy G_A , the repulsion energy G_{el} and the distance between the particles h (Vepsäläinen 2012). The total energy of interaction between to particles G_T is a simple summation of the attractive and repulsive energies, which is shown by the curve with two minima in Fig. 4.

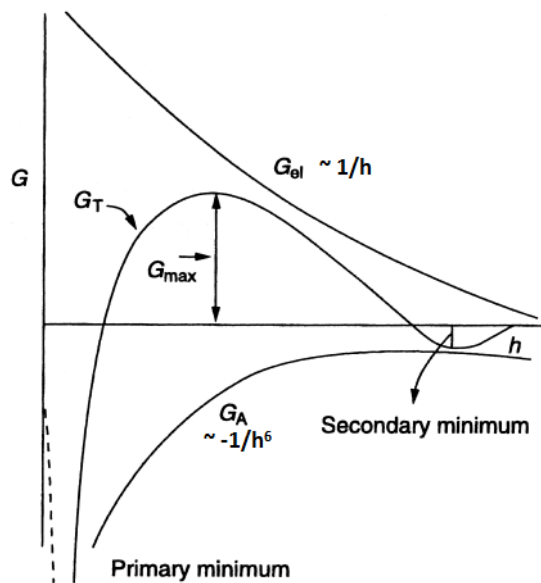


Figure 4. Energy-distance curve for electrostatically stabilized systems. Adapted from (Tadros 2007).

Particles reside after coagulation at the primary minimum. The secondary minimum is at a longer distance and this is the energy minimum of flocculation. The aim of coagulation is to overcome the energy barrier between the primary and secondary potential minima.

The destabilization mechanisms through which colloids are removed by coagulation include a combination of double layer compression, charge neutralization, entrapment and particle bridging (Matilainen, Vepsäläinen et al. 2010, Vepsäläinen 2012, Binnie, Kimber 2013). Surface charge of the colloid is dependent on the ionization of the functional groups, such as $-OH$, $-COOH$, and $-NH_2$, present in the surface, and consequently it depends on the pH of the solution as well (Vepsäläinen 2012). The prevailing destabilization mechanism is thence also controlled by the pH of the solution. Double layer compression dominates at low pH, in contrast to adsorption and bridging dominating at higher pH (Särkkä, Vepsäläinen et al. 2015).

1) Double layer compression involves the addition of an electrolyte to water to increase the concentrations of ions. This has the effect of decreasing the thickness of the electrical double layer that surrounds each colloidal particle. This allows particles to move closer to each other, meaning attractive forces have more chance of overcoming the electrical forces that keep them apart. This mechanism is rarely employed in water treatment since it requires very high salt concentrations. (Binnie, Kimber 2013) Fig.5 illustrates how a

coagulant neutralizes an electrostatic sphere of charge that surrounds small particles and keeps them separated. As coagulation proceeds, the electrical double layer gets compressed and allows the particles to come closer together and form agglomerates.

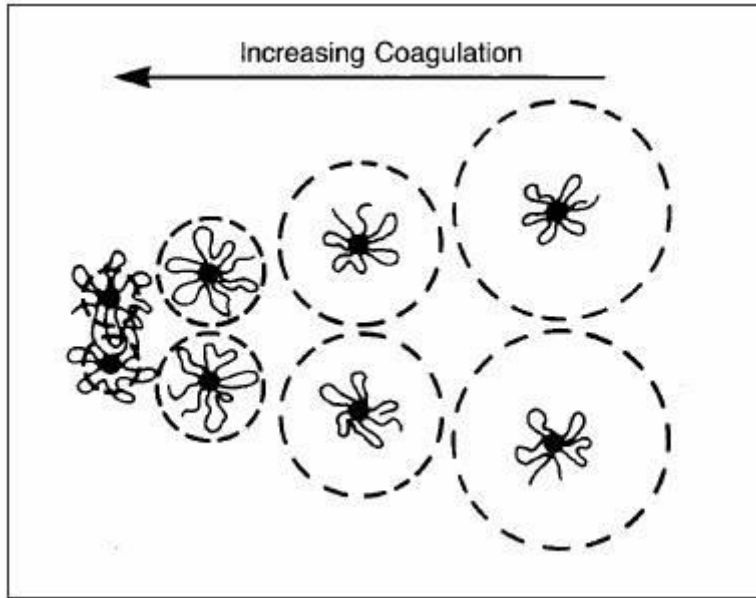


Figure 5. Schematic representation of double layer compression destabilization mechanism (Gallagher 1990).

2) Charge neutralization. Adding ions with a charge opposite to that on the colloidal particles can lead to adsorption of the ions on the colloidal material and reduction of surface charge. This reduces the electrical forces keeping particles apart and allows easier agglomeration. However, overdosing of coagulant can lead to charge reversal and re-suspension of the colloidal material, leading to poorer filtered water quality (Binnie, Kimber 2013). Fig. 6 shows an example of how charge neutralization mechanism works. Initially, particles are separated because of their negative surface charge. After addition of positive ions, aluminum ions in this case, the charge on the surface of the particles is neutralized and no longer keeps them apart.

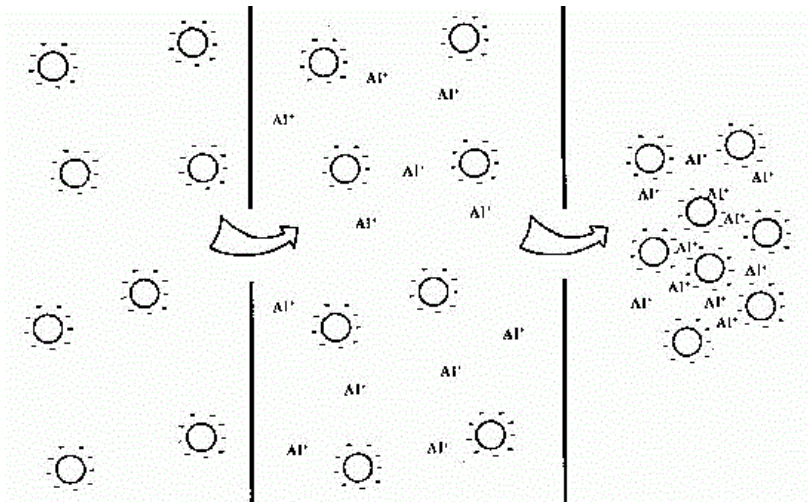


Figure 6. Schematic representation of charge neutralization destabilization mechanism (Tramfloc).

3) Entrapment in a precipitate (also called sweep floc coagulation). When aluminum or iron salts are added to water at the correct pH value, they will precipitate as hydroxide flocs. If colloids are present, then the hydroxide will tend to precipitate using colloid particles as nuclei, forming floc around colloid particles. Once the hydroxide floc has formed it may physically entrap other colloidal particles, particularly during subsequent flocculation (Binnie, Kimber 2013). The mechanism is represented in Fig. 7, where the white “clouds” are hydroxide flocs and the black spheres represent colloidal particles.

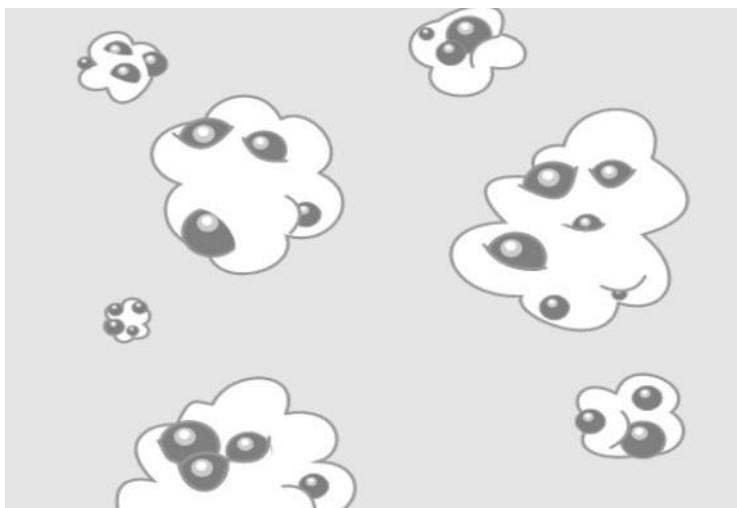


Figure 7. Schematic representation of entrapment in a precipitate destabilization mechanism (Kumar 2013).

4) Inter-particle bridging. Large organic particles with multiple electrical charges are believed to form bridges between particles. Polymerized metal coagulants can adsorb on multiple particles, thus increasing molecular weight and making bridging occur. This mechanism is susceptible to restabilization when excess coagulant is added as well. It occurs when the surfaces of the particles are completely covered by the polymer and no further bridging can occur. {{12 Binnie,Christopher 2013}} The process of inter-particle bridging is depicted in Fig. 8, where the circles stand for the particles and the squiggly lines are high molecular weight polymers that span between the particles forming “bridges”. The picture does not take into consideration the electrostatic charge spheres and the system is assumed to be well neutralized.

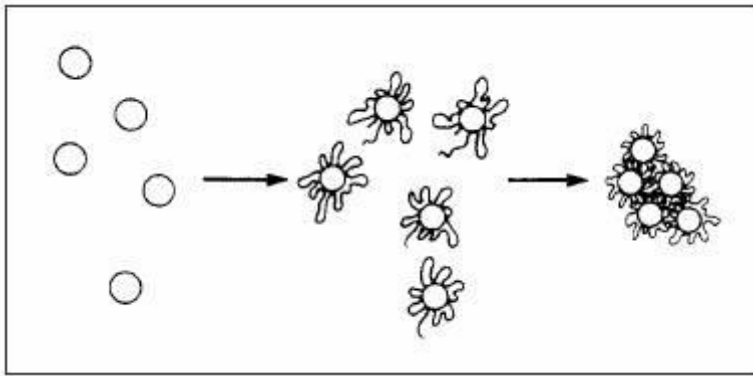


Figure 8. Schematic representation of polymer bridging destabilization mechanism (Gallagher 1990).

2.2.2 Flocculation

Coagulation brings a change in the nature of small particles, rendering them unstable, whilst flocculation is the process of transferring coagulated colloids into contact with each other via gentle mixing and the consequent formation of irregularly shaped, loosely connected aggregates, known as flocs (Xu, Gao et al. 2010, Jarvis, Jefferson et al. 2005). Currently, the floc formation process is understood as follows: initially, right after addition of coagulants, the dispersed monomeric particles quickly aggregate to small primary flocs; as the coagulation continues, the primary flocs size increase to a large size, which join together to form larger flocs; during flocs aggregation, the larger floc structure changes continually as internal bonds are destroyed under shear forces and re-form at more favorable points with greater attractive force and lower repulsive force; when the balance between the rate of breakage and the rate of aggregation for a given shear

condition is reached, flocs formation process is considered to be complete and the size of flocs reaches a steady plateau (Wang, Gao et al. 2009, Yao, Nan et al. 2015). After the flocs are formed, they are removed from water via filtration or clarification.

A better understanding of floc properties could improve the performance of water purification processes. The properties of flocs formed during the flocculation stage, such as size, structure and strength, greatly affect the efficiency of separation and purification operation. Flocs are highly porous fractal-like aggregates composed of many primary particles. Fractal dimensions characterize floc structure, for instance the space-filling capacity of an object. In addition to structure, floc strength is another important parameter to be considered. Considering the time and energy cost in developing flocs, it should be ensured that flocs avoid being broken into smaller particles under stresses to which they are exposed, as smaller particles generally have lower removal efficiencies (Wang, Gao et al. 2009).

Flocs break up if stresses acting on them exceed the floc strength. The breakage of flocs may occur due to two different mechanisms: **1) large-scale fragmentation** where a floc cleaves into two or more smaller flocs, and **2) surface erosion** where single primary particles are eroded off the floc surface. Fragmentation is thought to occur from tensile stress acting normally across the whole floc, whilst erosion is due to the shearing stress acting tangentially to the floc surface. The two mechanisms of floc breakage are simplified in Fig. 9 (Jarvis, Jefferson et al. 2005, Yuan, Farnood 2010).

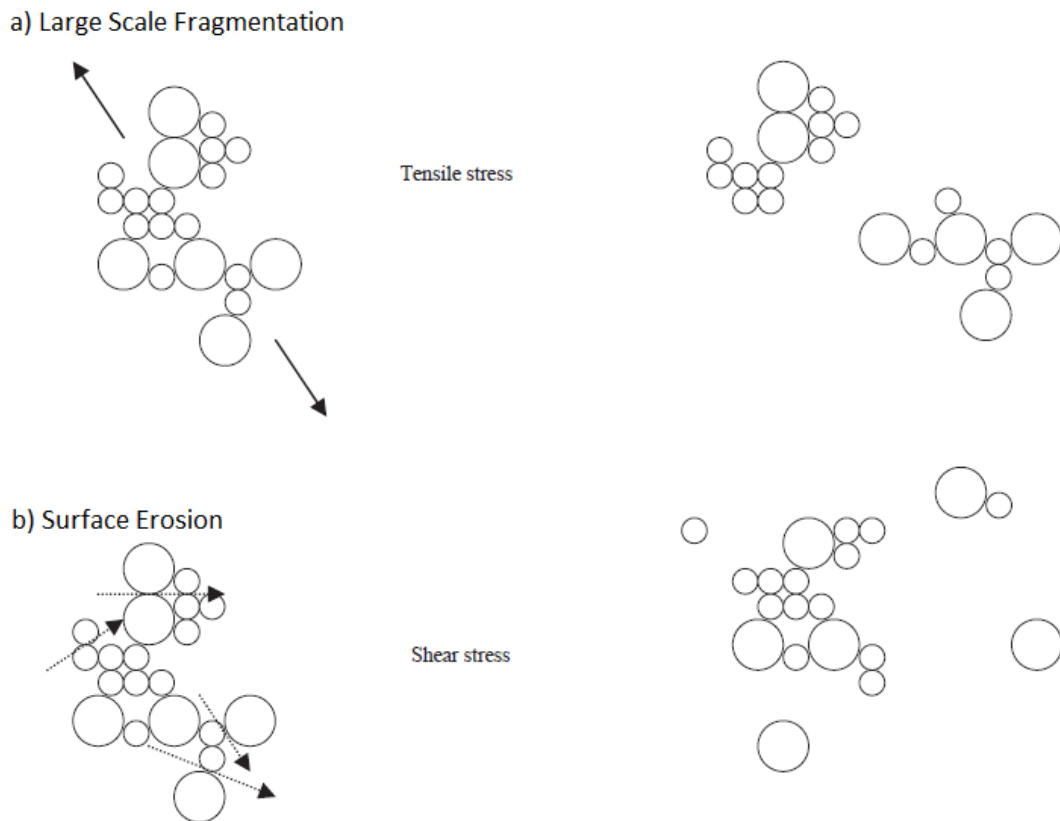


Figure 9. Two proposed mechanisms for the breakage of flocs under different shear conditions (Jarvis, Jefferson et al. 2005).

The development of a satisfactory technique to experimentally quantify floc strength has proven to be difficult (Wang, Gao et al. 2009, Jarvis, Jefferson et al. 2005). This is due to the inherent complexity, fragility and variation in floc size, shape and composition. The rate of floc formation is considered to be a balance between breakage and aggregation with flocs eventually reaching a steady-state size for a given shear rate (Jarvis, Jefferson et al. 2005). Hence, the steady-state floc size for a particular shear rate (or flocculation index) is considered to be a good indicator of floc strength. This is oversimplified since similar size flocs exhibit a large spectrum of shapes and structures and therefore respond differently under similar shear stress levels (Yuan, Farnood 2010). Furthermore, it is unclear whether the maximum or the average floc size should be measured. Despite that, most of the existing techniques estimating floc strength are based on measuring floc size at different applied shear levels, such as light scattering and transmission, microscopy, photography, and video and image analysis. It is important to ensure that the technique used to measure floc size is as non-destructive as possible and does not damage the aggregates due to their highly fragile structure. Moreover, due to the highly porous and

irregular structure of aggregates, no particle size method can be considered ideal. Such a method can be utilized for approximate measurements of floc strength, though.

A procedure of floc formation, breakage, and re-formation can roughly indicate the floc strength. In practice this is achieved by a suspension being slowly stirred for few minutes after coagulation, followed by intentionally increasing stirring rate to cause floc breakage, and after the breakage period, the slow stir is reintroduced to re-form flocs. According to previous studies, the process is numerically described by a “breakage factor” and a “recovery factor” (Yukselen, Gregory 2004).

$$\text{breakage factor} = \frac{d_2}{d_1} * 100\% \quad [1]$$

$$\text{recovery factor} = \frac{d_1 - d_2}{d_3 - d_2} * 100\% \quad [2]$$

where d_1 , d_2 and d_3 are the sizes of flocs in steady phase before breakage, after the breakage period and after the re-growth to another steady phase, respectively.

The breakage factor defines the ability of floc to resist rupture by a certain stirring velocity, whilst the recovery factor defines how sensitive the aggregating capacity of the ruptured flocs are after the breakage (Wang, Gao et al. 2009). As can be seen from the above equations [1] and [2], the larger values of breakage factors indicate that the flocs are stronger than those with lower factors, and the flocs with larger recovery factors show better re-growth after breakage. Repeating breakage/reformation cycle gives an increasing breakage factor and a decreasing recovery factor.

In addition to performing breakage/reformation procedures, the strength of a floc can be monitored by subjecting it to rising levels of stress and monitoring the number of broken flocs. By increasing the level of stress, a growing number of flocs would break up. The number of surviving flocs represents the amount of flocs that are “stronger” than the stress exerted on them. However, it might be difficult to calculate the number of broken flocs due to their particle size distribution. Initially flocs have a polydisperse size distribution schematically shown by the curve 1 in Fig. 9. Under the stress applied, weaker flocs break to give birth to a large number of smaller particles, resulting in a bimodal size distribution similar to the curve 2 in Fig. 10 (Yuan, Farnood 2010). In order to calculate the number of broken flocs based on the change in the particle size distribution, the effect of birth on

the floc count should be minimized or eliminated by monitoring the change in the total number of flocs that are larger than a threshold size.

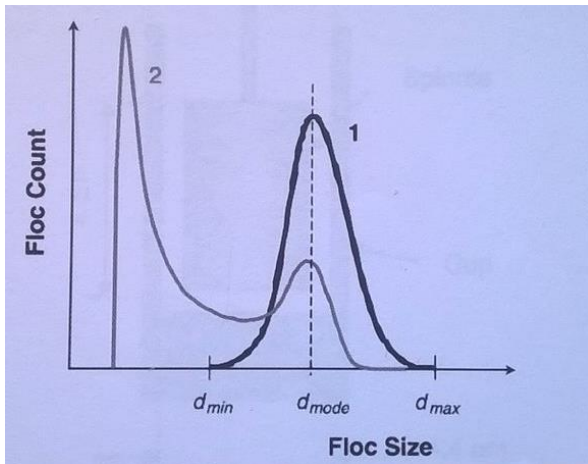


Figure 10. Schematic diagram showing the size distribution of flocs before (curve 1) and after (curve 2) exposure to shear stress (Yuan, Farnood 2010).

Microscopy is also one of the methods used for monitoring the change in floc size. It relies upon taking flocs from the containing vessel and their observation under the microscope. The applicability of microscopy to quantification of floc strength is researched in this work.

Flocs of large size and loose structure contribute the most to alleviating membrane fouling (Feng, Zhao et al. 2015), whereas, per contra, general trends show that smaller flocs tend to have greater strength than larger flocs (Jarvis, Jefferson et al. 2005). The reason for the latter may be that shear stresses break big flocs at their weakest points, which results in smaller and stronger pieces. Considering floc density, the flocs with higher density are preferable owing to their better settleability in the subsequent sedimentation process. On the other hand, in the coagulation-membrane process, flocs with lower density may form the higher porosity cake layer on a membrane surface, which is much easier to remove by backwashing processes (Yao, Nan et al. 2015). Hence, it is obscure whether target flocs are of larger or smaller size or density and it vastly depends on the water treatment method applied.

In order to achieve the best removal results, optimum conditions should be set up accordingly. Coagulation conditions, such as coagulant type and dose, mixing mode, etc.,

have a great impact on the characteristics of flocs. Effective coagulation conditions generally produce larger particles, and thus reduced membrane fouling by reducing adsorption in membrane pores, increasing cake porosity and transport of contaminant away from the membrane surface. If floc of greater strength is required, coagulation needs to be optimized for a suitable compromise between floc strength and size. Electrocoagulation, for example, is capable of generating a range of flocs and their growth rates and structural properties are highly dependent on the operating conditions. For instance, larger flocs are observed at initial pH 4 rather than the initial pH 5 and 6 (Ulu, Barışçı et al. 2014).

2.2.3 Chemical coagulation

Chemical coagulation is achieved by addition of inorganic coagulants, such as aluminum or iron salts. The characteristics of the water to be treated (e.g. alkalinity, pH, and NOM content) play a major role in the choice of a proper coagulant. The most common coagulants used in water and wastewater treatment are aluminum salts. They are effective in treating a wide range of water types and have relatively low cost. On the basis of conventional aluminum salts, such as $AlCl_3$ and alum, prehydrolyzed aluminum coagulants have been developed rapidly and researched recently, and nowadays they are widely applied to water treatment (Feng, Wang et al. 2015). Polyaluminum chloride (PAC) has been made by partially neutralizing $AlCl_3$ to different basicity ratios, and it has replaced a large part of other traditional coagulants in recent years (Matilainen, Vepsäläinen et al. 2010). PAC is superior to traditional aluminum salt coagulants in higher organic matter removal efficiency (Feng, Wang et al. 2015). The prehydrolyzed polymer coagulants have been reported to have other advantages over conventional coagulants as well, including lower dose requirement, less temperature and pH dependence, and less sludge production. Moreover, the amount of residual aluminum in treated water is greatly reduced compared with the use of conventional aluminum salts; aluminum in drinking water is thought to pose a risk towards Alzheimer's disease (Matilainen, Vepsäläinen et al. 2010, Sudoh, Islam et al. 2015). Furthermore, they perform faster floc formation and they are effective even at low temperatures, which explains their popularity in Nordic countries (Binnie, Kimber 2013).

The effectiveness of coagulation on HSs removal depends on several factors, including coagulant type and dosage, mixing conditions (too high water velocity may cause floc breakdown), pH, HSs properties (such as size, functionality, charge and hydrophobicity), as well as the presence of divalent cations and concentrations of destabilizing anions (bicarbonate, chloride and sulfate).

HSs have been noted to carry high levels of negative charge due to presence of ionized groups such as carboxylic and phenolic groups, and fractions with higher charge are observed to be more amenable to removal (Matilainen, Vepsäläinen et al. 2010). Thus, the nature of HSs has a significant effect on the coagulant dose. For water with HMM HSs the optimal coagulant dose is expected to be lower.

Mixing in coagulation processes is typically divided into two stages. At the point of coagulation, rapid stirring is required to properly mix a coagulant with solution and promote particle collisions. After this stage, water goes into slow mixing stage providing particles opportunities for contact and further particle size growth. However, it should be taken into consideration that too high water velocity may cause floc breakdown (Vepsäläinen 2012).

Coagulation pH controls the precipitation of metal hydroxides and also the charges on the intermediate products arising from dosing of metal salts. It is, therefore, most important in ensuring effective and economic coagulation. The usual aim is to coagulate at the pH value where the solubility of ferric or aluminum hydroxide is at a minimum. The pH value can theoretically be derived from solubility calculations for particular water at a given temperature. However, this is impractical in practice. Empirical results of (Ashery, Radwan et al. 2010) for NOM removal are the best at a pH range from 5 to 6, as at pH > 6 the removal of NOM was poor and needed higher dosage of coagulant.

2.2.4 Electrocoagulation

Kuokkanen (2013) defined electrocoagulation as an electrochemical treatment process of applying an electrical charge to water that changes the particle surface charge, making suspended matter form flocs. Electrocoagulation (EC) is innovative, inexpensive and effective in purifying waters, and an alternative method to chemical coagulation. It combines the functions and advantages of conventional coagulation and electrochemistry in water and wastewater treatment. It is based on dissolution of the so-called “sacrificial anode” producing metal ions which act as coagulant agents by destabilizing contaminants in an aqueous solution. Electrocoagulation uses soluble anodes made of coagulating, cheap, non-toxic and readily-available metals such as iron or aluminum with electrolytic dissolution to Fe^{2+} or Al^{3+} ions, which are further hydrolyzed to polymeric hydroxides. Coagulation occurs when these metal cations combine with the negative particles carried toward the anode by electrophoretic motion with various destabilization mechanisms and simultaneously occurring beneficial side-reactions, such as pH-change and hydrogen bubble formation. Destabilization is achieved mainly by means of two mechanisms: 1) charge neutralization of negatively charged colloids by cationic hydrolysis products; and 2) “sweep flocculation”, or entrapment in a precipitate, where impurities are trapped and removed in the amorphous hydroxide precipitate produced (Kuokkanen, Kuokkanen et al. 2013),(Matilainen, Vepsäläinen et al. 2010).

At its simplest, an EC reactor is made up of an anode and a cathode made of metal plates, both submerged in the aqueous solution being treated. Fig. 11 depicts a scheme of the simplest EC set-up (Kuokkanen, Kuokkanen et al. 2013). When a potential is applied from an external power source, the anode undergoes oxidation, while the cathode is subjected to reduction. The applied potential causes two separate reactions as summarized in Fig. 12:

- The anode generates metal ions ($\text{Fe}^{2+}/\text{Al}^{3+}$) which almost immediately hydrolyzed to excellent coagulant agents, such as polymeric iron or aluminum hydroxide. The consumable anodes continuously produce polymeric hydroxides in the vicinity of the anode. Metal cations combine with the negative particles carried toward the anode by electrophoretic motion, causing coagulation.

- A parallel reaction electrolyzes water, producing small bubbles of oxygen at the anode and hydrogen at the cathode. These bubbles float the flocculated pollutants to the surface through natural buoyancy.

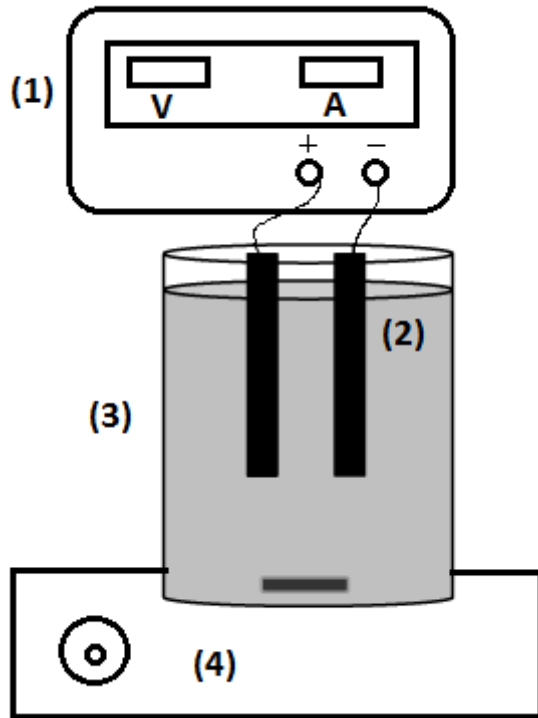


Figure 11. Set-up for electrocoagulation system: 1) DC power source, 2) electrode pair, 3) treated solution with a magnetic bar-stirrer on the bottom of the beaker, 4) magnetic stirrer.

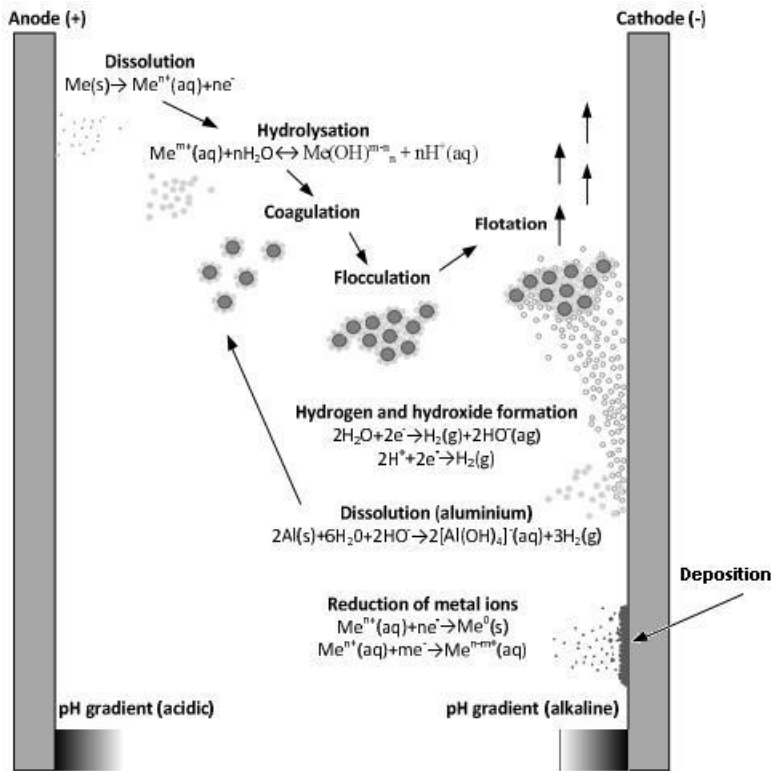


Figure 12. Schematic representation of the typical reactions occurring during EC treatment (Vepsäläinen 2012).

The amount of metal dissolved is dependent on the electricity passed through the electrolytic solution (Mollah, Morkovsky et al. 2004). The relationship is based on Faraday's law:

$$m(\text{metal}) = \frac{I * t(s) * M}{z * F} \quad [3]$$

where $m(\text{metal})$ is the mass of the metal dissolved (g), I is the applied current (A), $t(s)$ is the treatment time (s), M is the molar mass of the electrode material ($M(\text{Al}) = 26,982$ g/mol), z is the valency of ions of the electrode material ($z(\text{Al}) = 3$), and F is Faraday's constant (96485 C/mol) (Vepsäläinen 2012, Kuokkanen, Kuokkanen et al. 2013). The experimental values of anode metal dissolution are a little higher than the theoretically expected value due to pitting corrosion, especially in the presence of chlorine ions (Chen 2004).

Treatment parameters

The efficiency of EC to remove NOM and particles depends on several factors, including the electrode materials used, applied current density, treatment time, and solution chemistry, such as initial pH and the chemical composition of the aqueous solution being removed (Kuokkanen, Kuokkanen et al. 2013). To optimize NOM removal, EC characteristics are adjusted for specific contaminants.

The material of the electrodes is usually either iron or aluminum. In general, aluminum seems to be preferable compared to iron considering the efficiency of the treatment and no coloration of water. However, iron electrodes are cheaper and can significantly decrease the cost of treatment (Kuokkanen, Kuokkanen et al. 2013).

The pH of the solution has to be neutral or slightly alkaline in order to achieve a reasonable reaction rate and prevent formation of a gel layer on the electrode surface. Oxygen has to be present as well. Vepsäläinen et al. (2012) found that the highest NOM removal is achieved at a low pH of 4.3. Another research group indicated that the maximum removal efficiency is achieved at pH 6, which might be because that at close to their isoelectric point HA molecules become more hydrophobic and insoluble (Feng, Zhao et al. 2015).

Current density and treatment time affect the rate of electrochemical reactions taking place on the electrode surface. According to Faraday's law (Eq. 3), coagulant dose produced by electrolysis is directly proportional to the electric charge added per volume. Thus, at higher current density, a larger amount of anode dissolves and so the removal of pollutant increases. Vepsäläinen et al. (2012) reported that optimum HA removal is achieved at a current density of 0.48 mA/cm^2 , whilst Ulu et al. (2014) suggested using 1.2 mA/cm^2 to achieve the best short-term performance.

Passivation of electrodes

Electrocoagulation is based on metal electrodes being dissolved electrochemically to induce the coagulation of the contaminants in water. This obviates the need for liquid coagulant addition required by the chemical coagulation method. On the other hand, it is well known that during the aluminum dissolution reaction [4], the electrode is rapidly

covered by a passive layer of aluminum oxide [5] and hydroxide [6] leading to current densities decaying rapidly to essentially zero. The presence of NOM, for instance HA, only exacerbates the problem (Mechelhoff, Kelsall et al. 2013).



In principle, dissolution can occur only through defects in the passive film at high electrode potentials or by lowering the pH near the electrode to values smaller than 7 (Mechelhoff, Kelsall et al. 2013).

In order to reduce the cathode passivation and to extend the lifetime of the electrodes, instead of using direct current (DC) technology the cathode and anode can be switched periodically (Mechelhoff, Kelsall et al. 2013, Vasudevan, Lakshmi et al. 2011, Cerqueira, Souza et al. 2014). This leads to the idea of adopting alternating current (AC) in electrocoagulation process. The cyclic energization between the anode-cathode in an alternating current (AC) system is assumed to stimulate the manual reversion of polarity (Vasudevan, Lakshmi et al. 2011).

2.2.5 Comparison of chemical coagulation and electrocoagulation

Electrocoagulation and chemical coagulation seem to have similar destabilization mechanisms and nearly the same efficiency in terms of removing pollutants from water under the same conditions with minor influencing factors, such as reduction on the cathode surface and anions added with a chemical coagulant (Vepsäläinen 2012, Särkkä, Vepsäläinen et al. 2015). Several research groups have shown that very high HA removal efficiencies can be achieved with both electrocoagulation and conventional chemical coagulation. For example, according to Zhang 2015, chemical coagulation is able to remove up to 98.5% of HA from water under optimum conditions. At the same time, Vepsäläinen 2012 reports over 90% HA removal by electrocoagulation.

Electrocoagulation can be called “a green technology” because it requires very little or even no chemical additions. According to Mohammad (2004), the advantages from using electrochemical techniques include versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness. Other benefits of electrocoagulation over conventional coagulation include not only economic aspects, such as low maintenance, energy, and treatment costs, but also lower volume and better quality of sludge produced (Matilainen, Vepsäläinen et al. 2010, Kuokkanen, Kuokkanen et al. 2013). Compared with the conventional coagulation techniques, EC removes small colloidal particles more efficiently due to the greater probability of small charged particles being coagulated and destabilized by an electric field that forces them into motion (Mollah, Morkovsky et al. 2004). The floc formed by electrocoagulation is almost similar to the one formed by chemical coagulation, but the former contains less bound water and has a tendency to be much larger, more stable, and acid-resistant. Thus, it is separated faster by subsequent filtration (Chen, Deng 2012).

The disadvantages of EC technology include the passivation of electrodes and precipitation layers on the electrode surfaces, the dissolution of the electrodes and the low conductivity of the surface waters (Mollah, Schennach et al. 2001). High voltages can be avoided by reducing the distance between the electrodes. As the electrode material dissolves, electrodes need to be replaced regularly.

Comparisons of operating costs of electrocoagulation and chemical coagulation have been made in a few articles. Cost calculations include the cost of chemicals, electrodes and energy and they do not typically include investment costs and therefore, operating costs are roughly estimated. For example, it is difficult to obtain reasonable information on the price of chemical coagulants, since some bulk chemicals coagulants, such as ferric chloride and aluminum sulphate, are cheap, whereas new prehydrolysed metal coagulants are more expensive. Obviously, the price of chemicals depends on the amount required, and major consumers pay less for their chemicals than smaller users. However, all the research groups agree that electrocoagulation is 2-5 times cheaper than conventional chemical coagulation (Bayramoglu, Eyvaz et al. 2007, Espinoza-Quiñones, Fornari et al. 2009, Meunier, Drogui et al. 2009).

2.2.6 Membrane filtration

Membrane technology is becoming increasingly important in water treatment. It can be applied not only as a stand-alone process but also as a technique fulfilling and enhancing other treatment processes, e.g. coagulation and flocculation, to purify drinking water. A membrane is a selective physical barrier removing all particles larger than its smallest pore size, whilst the smaller compounds may be rejected by charge repulsion if they contain negatively charged groups and the membrane is negatively charged. Hence, the removal of particles increases with decreasing membrane pore size and with increasing charge density on the membrane surface and in the pores. These conditions are favorable at higher pHs and at low ionic strengths (Metsämuuronen, Sillanpää et al. 2014).

The pressure driven membrane mechanisms include reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF), which are classified according to pore size dimensions of the membrane and type of constituents rejected, as listed in Table 3.

Membrane type	Pore size (µm)	Types of rejected materials
Microfiltration	0,1	Particles, algae, bacteria, protozoa
Ultrafiltration	0,01	Colloids, viruses
Nanofiltration	0,001	Dissolved organics, divalent ions (Mg ²⁺ , Ca ²⁺)
Reverse Osmosis	Non-porous	Monovalent species (Na ⁺ , Cl ⁻)

Table 3. Pore size and rejected material for membrane types

Nanofiltration covers the area with effective pore size of 1-10 nm, ultrafiltration is from 10 to 100 nm, and microfiltration covers 100-10000 nm (Moeller 2012). Dissolved HA easily passes through MF and UF membranes. Hence, when applied for HA removal, they both require pretreatment.

The flow rate of water through these membranes is described by the Hagen-Poiseuille equation (Moeller 2012):

$$\Delta p = \frac{128\eta l Q}{\pi d^4} \quad (7)$$

where Δp is the pressure drop (N m^{-2}); l is the pore length (m); Q is the volumetric flow rate (m^3s^{-1}); d is the diameter of the pore (m); and η is the dynamic viscosity of the fluid (N s m^{-2}). The flux per unit area then becomes

$$J = \frac{Qn}{A} = \frac{N\pi d^4 \Delta p}{128\eta l} \quad (8)$$

where n is the total number of pores and N is the pore density defined as a number of pores per unit area of the membrane (n/A).

It is clearly seen from the Eq. 8 that the pore diameter critically affects the water flux. For instance, increasing pore diameter by a factor of 10 (at equivalent porosity) leads to a 100-fold increase in water flux. So, the size of the pores should be carefully determined.

One of the major problems associated with membrane techniques is their high operational cost because of HA's tendency to severely foul the membrane (Feng, Wang et al. 2015). Fouling is defined as the deposition of retained particles, macromolecules, colloids, etc. on the membrane surface or inside the pores on the pore wall (Lowe, Hossain 2008). Fouling results in a decrease of membrane flux, either temporarily or permanently. Fouling poses a serious threat to the application and popularization of the membrane filtration technology (Bai, Liang et al. 2015). Being a very complex phenomenon, fouling depends on composition of feed solution (concentration of components, pH), membrane properties (hydrophobicity, roughness, pore size, pore size distribution, porosity) and operating conditions (temperature, trans-membrane pressure and cross-flow velocity). If particles are smaller than membrane pores, they can enter and stick to them. If particles are nearly of the same size as membrane pores, they can cause pore blocking (Metsämuuronen, Sillanpää et al. 2014). In general, NOM is recognized as a major foulant that blocks the membrane pores and reduces membrane flux (Chen, Luo et al. 2015).

The operation of membranes usually involves periodic cleaning procedures to remove foulant. These can be back-flushing (pure water applied to the permeate side of the membrane with reversal of pressure) and/or chemical cleaning (chlorinated water solutions, detergents, and/or disinfectants) (Moeller 2012). If the pollutant on a membrane surface can be removed by hydraulic backwash process, this pollutant is classified as reversible fouling (RF), while contaminant remaining on the surface of a membrane is classified as irreversible fouling (IF). Both kinds of fouling together are total fouling (TF)

(Yao, Nan et al. 2015). Irreversible fouling is more problematic and necessitates chemical cleaning (Chang, Qu et al. 2015). However, in the case of drinking water treatment, chemical cleaning cannot be applied as drinking water should contain as few chemicals as possible.

Pretreatment with coagulation is an effective method to prevent these adverse effects, and a combination of coagulation and membrane filtration also reduces the amount of coagulant needed (Feng, Wang et al. 2015). Moreover, as it has been mentioned earlier, HA cannot be removed only with UF or MF without any pretreatment, and as decreasing the pore size increases the processing time, NF cannot be realistically applied either.

2.2.7 Combination of membrane filtration and coagulation

UF alone is ineffective in the removal of HA and in preventing the bacterial re-growth potential in drinking water distribution systems (Metsämuuronen, Sillanpää et al. 2014). In addition, the accumulation of colloids on the surface or inside the pores of UF membranes leads to a severe increase in energy demand during filtration and higher operational costs (Chen, Deng 2012). In order to reduce membrane fouling and improve water quality, coagulation has been adopted as a pretreatment process for membrane filtration (Judd, Hillis 2001).

Integration of coagulation to membrane filtration can prevent these negative effects, thus enhancing the NOM removal and improving product water. The combination of these two techniques might give a hybrid process with a better performance in removing processes than either of them in separate use. It can increase HAs rejection, reduce membrane fouling and decrease transmembrane pressure (Chen, Deng 2012).

These two unit operations can be combined with or without settling as presented in Fig. 13. The first way is to use a coagulation tank divided into rapid mixing and slow mixing/flocculation parts, and settling to remove flocs from water. Then water without flocs is conveyed to membrane filtration. Another way is to convey water directly from

flocculation to the membrane unit without removal of flocks. The most recent is in-line coagulation where coagulant is added to water immediately prior to the membrane process. Advantages of the last method include reduced water treatment time and less coagulant required, since descending flocks are not needed as flocks will be removed by membrane filtration (Metsämuuronen, Sillanpää et al. 2014).

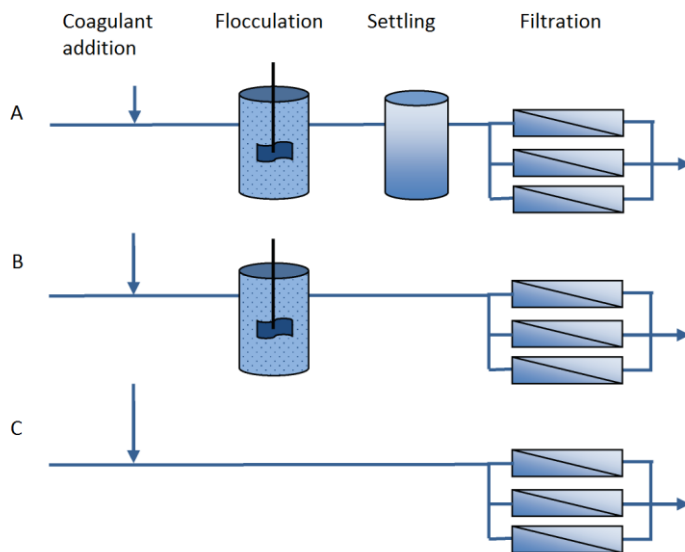


Figure 13. Coagulation – membrane filtration systems: a) conventional, b) direct filtration, c) in-line coagulation (Metsämuuronen, Sillanpää et al. 2014).

Coagulation will improve membrane performance when the size of flocks is larger than membrane pores so that they are unable to enter into the pores. Hence, the optimal flock size depends mostly on the membrane pore size.

2.3 NOM analysis methods

Humic waters are yellow-brown and a rough correlation exists between the darkness of water and its humic content. Thus, one of the easiest ways to estimate humic content in natural waters is measuring the colour of water. The visual method of comparing colours is not precise and cannot be used in science (Hautala, Peuravuori et al. 2000). Hence, total organic carbon (TOC) and absorbance of ultraviolet light with a wavelength of 254 nm

(UV₂₅₄) measured by spectrophotometry have been introduced instead (Rodrigues, Brito et al. 2008, Lawrence 1980).

Spectrometry is based on the capacity of HSs to absorb UV light at 254 nm, which increases with their content of aromatic rings, the ratio between aromatic and aliphatic carbon, the total carbon content in the water, and the molecular weights of the HSs (Vogel, Geßner et al. 1999). According to the Beer-Lambert law the UV light absorbance of any substances at a specific wavelength is proportional to their concentration. Thus, given two absorption values at the same wavelength of the water before and after the treatment, one can determine the efficiency of the treatment method in HSs removal by looking at the ratio of these two values.

One more method of monitoring approximately the amount of NOM in surface waters is by measuring the TOC content. It quantifies organic carbon independently of molecular configuration; thus, the chemical reaction between constituents of the solution, namely molecular aggregation, has less influence on the accuracy of results than the same results obtained by spectrophotometry. However, spectrophotometry requires less expensive equipment and is easier to maintain and operate, as the only sample pretreatment is filtration and the sample analysis takes approximately one minute for each sample.

3 EXPERIMENTAL

Since natural waters rich in HAs contain plenty of other organic compounds, a synthetic analog of HA containing water was used for all the experiments to simulate the natural waters and control the variables better. First experiments were held to determine a procedure of how to produce stock solutions of aqueous synthetic HA. After this had been established, the next goal was to determine the analytical method for interpreting the results of coagulation and membrane filtration. Hereafter, three methods were investigated for the removal of HA from water. The first method used was a well-established, commonly used in industry chemical coagulation. As soon as the chemical coagulation procedure was optimized, the experiments proceeded with an alternative method: electrocoagulation. When the parameters of both CC and EC were established to achieve good HA removal efficiencies, we started with membrane filtration experiments. Ultrafiltration was utilized to separate the floc from the solution. In addition to this, an attempt on quantifying flocs strength and size with microscopy was done and a few simple experiments utilizing AC for alleviating electrode passivation during EC were held.

3.1 Synthetic test water preparation

Humic acid (HA) solutions were prepared from HA granules (Sigma Aldrich, technical grade), and were used as well-defined, synthetic approximations to natural humic substances (HSs) in surface waters. The first attempts at dissolving HA included adding a certain amount of HA granules to deionized water in order to make a 100 mg/L HA solution and stirring it for 60 h or ultrasonic mixing for 1 h in the Finnsonic bath, or a combination of stirring and ultrasonic mixing.

These attempts did not fully succeed due to HAs having high molecular weights and thus cannot be fully dissolved (Matilainen, Vepsäläinen et al. 2010). Even after stirring had been prolonged for an extra 48 hours, some particles were still easily seen. To solve the problem of dissolving HA, a series of experiments was performed. To start with, HA granules were ground with pestle and mortar to make particles smaller for their easier dissolution. The literature occasionally mentions dissolving HA in solutions of various

pH achieved with HCl and NaOH. Hence, I tried to replicate such dissolutions both in acids and bases as follows: 10 mg of ground HA were put into five test tubes and five different reagents were added:

1. 5 mL H₂O
2. 5 mL 0.1 M HCl
3. 5 mL 1 M HCl
4. 5 mL 2 M HCl
5. 5 mL 2 M NaOH

Samples were treated with ultrasound in the Finnsonic bath at 43 °C for approximately 75 min. The result was that reagents of pH lower than 7 did not dissolve HA at all, while sample No. 5 (2 M NaOH as solvent) showed complete dissolution. Thus, all further concentrated HA stock solutions were prepared as follows: 10 mg of HA was dissolved in an aqueous solution of 5 mL of 2M NaOH and treated with ultrasound in an ultrasonic bath for 30 min. The solution was diluted with deionized water to 100 mL and stirred for 30 min. The concentration of HA in the stock solution was, thus, 100 mg/L, the concentration of NaOH was 0.1 M, and the pH was 11-12. The synthetic test water was prepared by diluting the right amount of HA stock solution with deionized water.

3.2 HA concentration analysis method

Concentrations of HA were determined by measuring their absorbances with a dual-beam UV-vis spectrophotometer (Jasco V-670) in 1-cm path length quartz cuvettes. Measurements were done with several concentrations of HA in the range 0–100 mg L⁻¹. The HA removal efficiency was determined from relative changes in the absorbance at UV wavelength 254 nm. Some of the samples were measured only at specific wavelengths (254 nm) but for most of the samples whole spectra were scanned from 700 to 200 nm.

To start with, the machine was calibrated with a baseline measurement without cuvettes. The absorbencies of all the solutions were recorded relative to this baseline value. A portion of the solution to be analyzed was transferred to one cuvette and a cuvette with deionized water was also prepared. The cuvettes were placed in the appropriate place in the spectrophotometer, arranged in a way that two equal beams of UV/visible light were passed, one through the test sample, one through the water. The intensities of transmitted beams were then compared over the selected wavelength range, and after that the spectrophotometer displayed the amount of light absorbed relative to the initial substance.

3.3 Chemical coagulation

Coagulation tests were performed to ascertain the optimum conditions for wet chemical HA removal, such as coagulant dosage, pH of solution and type of neutralizer, and to assess the ability of PAC to remove humic substances. A beaker with 50 mg/L HA solution was placed onto a stirring plate and the solution was mixed rapidly for 30 s. Under rapid stirring a certain quantity of PAC (PAX-XL100, Kemira Oy) was added. The rapid stirring stage was followed by a 15 min slow stirring stage to make particles gather together, i.e. to flocculate. The samples were either left to settle or were centrifuged to separate the floc from the clean water. The water samples were collected using a syringe from about 0.5 cm below the water surface, to avoid collecting the sedimented floc from the bottom and the floated floc from the top of the water. After that, the samples were analyzed by UV-vis spectrophotometry.

The very first chemical coagulation experiments were performed without adjusting the pH of the solution and did not succeed. After reviewing the relevant literature, it was clear that coagulation is highly pH dependent. The later experiments were carried out with the pH 6 recommended by (Ashery, Radwan et al. 2010) for the best performance of chemical coagulation, which also made the coagulated product safe for environmental release. Solution pH was adjusted before coagulant adding to the desired value using small amounts of either 2 M HCl or 2 M NaOH as needed. The aim of the next experiments was to figure out the ideal PAC dosage to achieve satisfactory results with the least

amount of the coagulant. Less coagulant added saves money, improves final water quality, and makes it less harmful for the environment.

It is highly important that the pH of the solution is adjusted prior to any coagulation experiments. The pH can be adjusted by a number of different chemicals. When the optimum coagulant dosage had been established, a few coagulation tests were done to compare how different chemicals used to adjust the pH affected the total coagulation efficiencies for a fixed amount of PAC used as the coagulant and the sludge volumes produced. The lower sludge the volume is, the more clean water is produced. The chemicals used were NaOH (Emsure grade, E. Merck KG), CaCO₃ (technical grade, VWR), Ca(OH)₂ (95% purity, Alfa Aesar), and Na₂CO₃ (99% purity, E. Merck KG).

3.4 Electrocoagulation

The EC cell was composed of one plane anode and one plane cathode, both made of aluminum (EN 1020413.1B, Terästarvike Oy), so that it would be possible to compare the performances of aluminum ions produced by CC and EC. The total active area of the electrodes was 30 cm². There was a 10 mm gap between electrodes, and they were connected to a digital power supply, as shown in Fig. 14. Prior to the experiments, electrodes were rinsed with ethanol first, and then with deionized water to remove any dirt from them. In each run, electrodes were submerged into the beaker containing 60 mL of HA solution (50 mg/L) which was stirred with a magnetic stirrer. Electrical currents were held constant for each run. After EC treatment, solutions were left for settling. After settling, the water samples were collected using a syringe from about 0.5 cm below the water surface to avoid collecting sedimented floc from the bottom and floated floc from the top of the water. After that, the samples were analysed by UV-vis spectrophotometry.

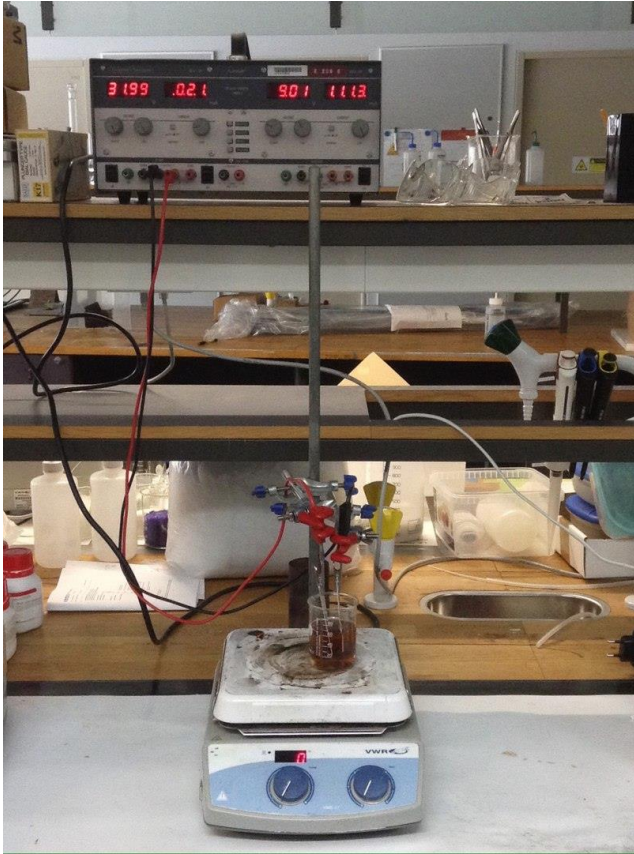


Figure 14. Electrocoagulation apparatus.

The optimum current density for HA removal by EC suggested by (Vepsäläinen 2012) was 0.48 mA/cm^2 . In order to check this statement three different current densities (0.24 , 0.48 and 0.72 mA/cm^2) were applied to see their effect on HA removal. Current densities were calculated for each current by dividing the applied current by active total surface area.

The first electrocoagulation experiments were conducted to determine the optimal operating conditions for HA removal, such as pH of the solution, and the effect of current, voltage and treatment time on the HA removal. After a series of experiments, it was noticed that the HA removal efficiency of the system decreased with time for the same current densities due to the cathode becoming covered by a passive layer of aluminum oxide with time. The anode and the cathode can be switched periodically in order to reduce the cathode passivation. Therefore, two simple experiments using alternating current (AC) to reverse the polarity of the electrodes were introduced:

1. Electrocoagulation was performed utilizing AC for HA removal from water. The results were compared to results obtained with DC under the same conditions. The current density was $0,72 \text{ mA/cm}^2$ and the current was applied for 10 min under medium speed stirring, followed by 10 min flocculation under slower stirring.
2. To investigate the general difference in passivation of electrodes in electrically conductive solutions using AC and DC, fresh aluminum electrodes were submerged into 500 mL of 10 mM HCl solution, and the voltage (AC) was applied and kept constant for 3.5 hours. The electrodes' condition and the current densities were observed at the start and at the end of the experiment.

3.5 Floc analysis

General trends show that large and loose flocs alleviate membrane fouling, and thus they are more desirable than smaller and higher density flocs. In order to achieve the desired floc properties for more efficient subsequent membrane filtration, it was necessary to learn how to analyze and quantify floc, before planning any floc properties optimization experiments. Microscopy analysis was applied to floc analysis and quantification. Previous experiments have shown that the structure of chemically and electrically coagulated flocs are very similar. To start with, the size of the floc obtained by electrocoagulation was determined by analysing images taken with an optical microscope (Zeiss Axio Scope A1), and the results used to evaluate floc strength. The active area of electrodes used for this experiment was 20 cm^2 and the current used was 15 mA, thus making the current density 0.75 mA/cm^2 . The current was applied for 15 min under rapid stirring. These conditions were based on the optimum conditions for the efficient HA removal found earlier during the previous EC experiments. For the flocculation part, a milling machine (W-HAAS TM-1HE) was used for attaining a constant stirring velocity of 50 rpm. The flocculation took 15 min, samples of the floc were taken every 1 min with a pipette in the least destructive way possible, put onto a glass slide and covered with a cover glass slip. Flocs image were captured manually with a camera using a microscope with a dark field illumination and a total magnification of 20 x. The images were analyzed by floc distinction and length calibration to determine the floc size.

3.6 Membrane filtration

The floc used for membrane filtration experiments was achieved in the same manner as described in the “Floc analysis” section above. For the membrane filtration experiments, the water containing flocs was forced through a polycarbonate track etch membrane of 100 nm pore diameter and $12 \mu\text{m}^2$ pore density (RoTrac, Oxyphen) under pressure of approximately 2.5 bar and the clean water which passed the membrane was analyzed by UV-Vis spectrophotometry.

In dead-end filtration, when the feed is passed through the membrane, the solids are trapped in the filter and the filtrated water is released at the other side. In the experiments reported here, cross-flow filtration instead was used. In cross-flow filtration, unlike dead-end filtration, the majority of the feed flow travels across the surface of the membrane, rather than into the filter, which washes the cake layer, thus increasing the operating time of the unit. Fig. 15 depicts the cross-flow filtration unit used in all membrane filtration experiments for this work.

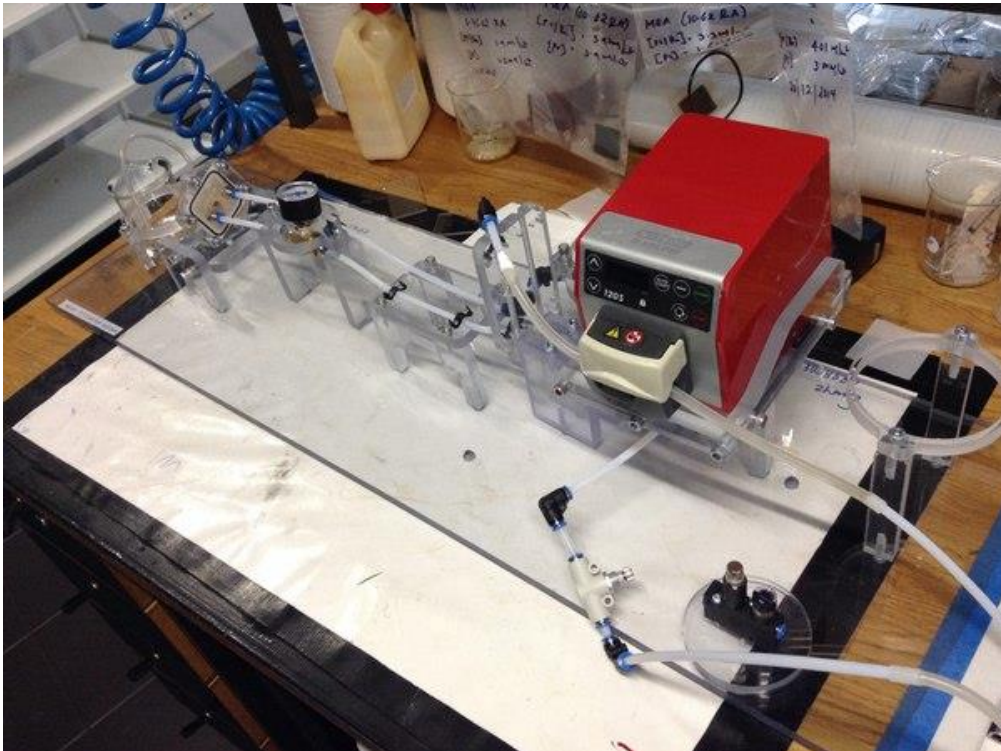


Figure 15. Membrane filtration set-up.

4 RESULTS AND DISCUSSION

4.1 Calibration of HA concentrations by UV absorbance

In order to establish the relationship between UV_{254} and the concentration of tested HA, a concentration series of HA solutions, ranging from 0 to 100 mg/L, was measured by UV-vis spectrophotometry. The concentrations were achieved by dissolving known amounts of HA in 0.1M NaOH. The empirical relationship between the UV absorbance and HA concentration is presented in Fig. 16. From the figure, it can be seen that UV_{254} is directly proportional to the concentration of HA. The possible effect of NaOH on the spectra was excluded by a comparison of NaOH and pure H_2O spectra, which showed that NaOH did not have peaks in a range of 300-0 nm.

The linear relationship indicates that UV spectrophotometry is a suitable method for quantifying the removal efficiency of HA.

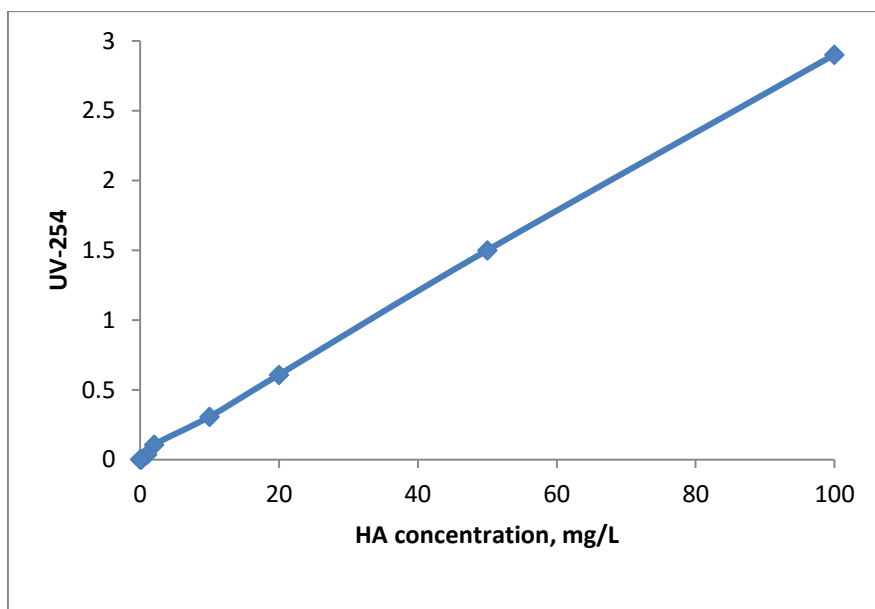


Figure 16. Absorbance of 254 nm UV light as a function of HA concentration for the HA concentration series used to calibrate the spectrophotometric method.

4.2 Chemical coagulation

The first chemical coagulation experiment consisted of adding a range of 0-50 mg PAC to 100 mL of test solution without any pH adjustment. The experiment showed that PAC does not work at any dosages in highly basic solutions. The value of the pH to be used further was determined experimentally to be 6, which correlates with the results of Feng, 2015 and Ashery, Radwan et al. 2010.

The next experiments investigated the dependence of HA removal efficiency on coagulant dose, ranging from 0 to 350 mg/L. Fig. 17 shows the variation of HA removal results as a function of the PAC dosage. The highest HA removal ratio was found to be 92.4% when 350 mg/L of PAC was used. According to Fig. 17, the efficiencies increased with dosage ranging from 0 to 175 mg/L, and then reached a plateau when dosage was higher than 175 mg/L. As the efficiencies of HA removal were greater than 90% with lowermost PAC dosage of 175 mg/L, this dosage was chosen as the optimum dosage for further experiments. The results of the centrifuged samples are significantly higher at a point of 100 mg of PAC added, because of the fact that the flocs formed were not yet large enough to settle but were already big enough to be separated with a help of centrifugation.

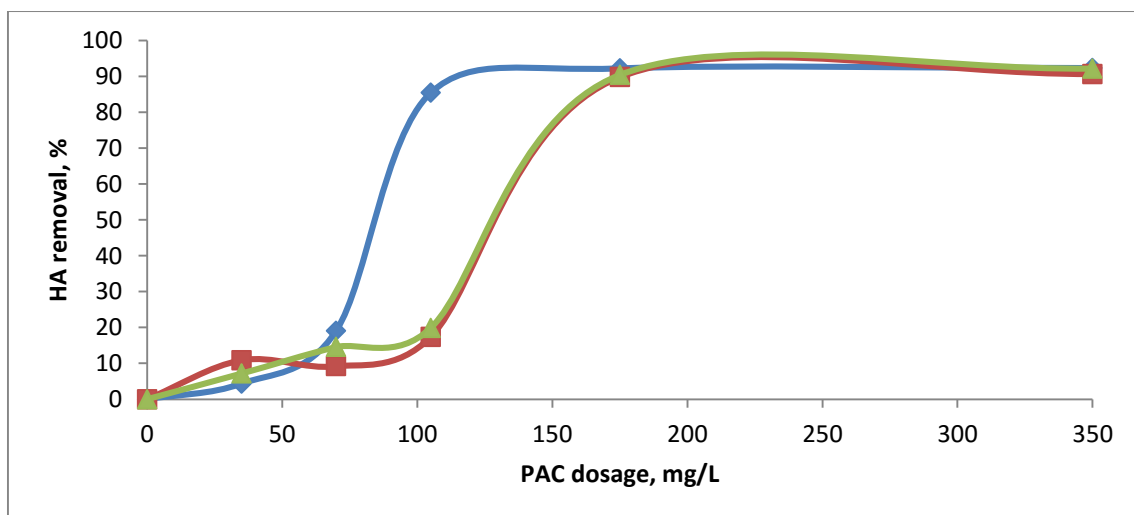


Figure 17. HA removal from water with respect to increasing coagulant dosages Blue line – centrifuged samples centrifuged for 30 min without settling, red line – samples left for settling and measured after 2 hours, green line – samples left for settling and measured after 24 hours.

The further experiments focused on comparing four different chemicals used for adjusting the pH of the solution during the process. Small dosages of neutralizers were added to solutions until their pH was around 6. The results are represented with a bar chart in Fig. 18. All the neutralizers showed good results in HA removal. Na_2CO_3 was the least effective and produced the sludge that was roughly 70% of the volume. NaOH showed the highest efficiency of all and produced less sludge. The results are presented in Fig. 19.

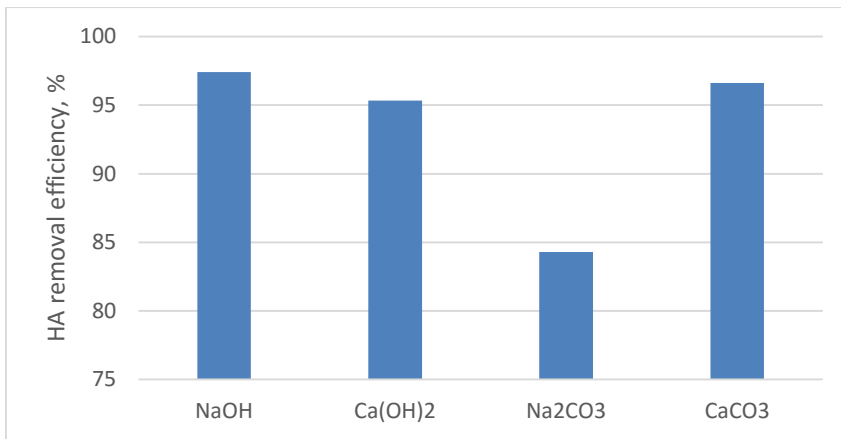


Figure 18. HA removal efficiencies depending on neutralizers used. The neutralizers were used to adjust the pH of the solution prior to addition of PAC. The dosage of PAC used was 175 mg/L for all the experiments. The flocculation stage took about 0.5 h, and after that, the samples were left for settling for an extra 1 h.



Figure 19. A comparison of different chemicals used for pH adjustment of the solution. From left to right – $\text{Ca}(\text{OH})_2$, CaCO_3 , Na_2CO_3 , NaOH . The fourth sample (with NaOH as a neutralizer) was not settled completely when the picture was taken. The volume of sludge for this sample reduced twice after an hour of full settling time.

4.3 Electrocoagulation

4.3.1 Current density and treatment time

For the first electrocoagulation experiment, the current density used was 0.48 mA/cm^2 and the pH of the initial solution was adjusted to 6 in the same manner as for chemical coagulation experiments. The test solution was 100 mg/L HA dissolved in 0.1 M NaOH. The value of a current density was chosen as a starting point in an attempt to reproduce the results of Vepsäläinen 2012 and Feng et al., 2015. It was found that with the treatment time increasing from 1 to 2 min, the HA removal increased gradually with the increase in time and reached 97.7% at 2 min. As the time further increased to 15 min, the removal rate was over 90% for all treatment times, as shown in Fig. 20. The removal rates obtained with centrifuged samples were close to the values when samples were analysed after 3 h of settling. Hence, for further electrocoagulation experiments the author provides the reader with centrifuged values only to simplify the graphs.

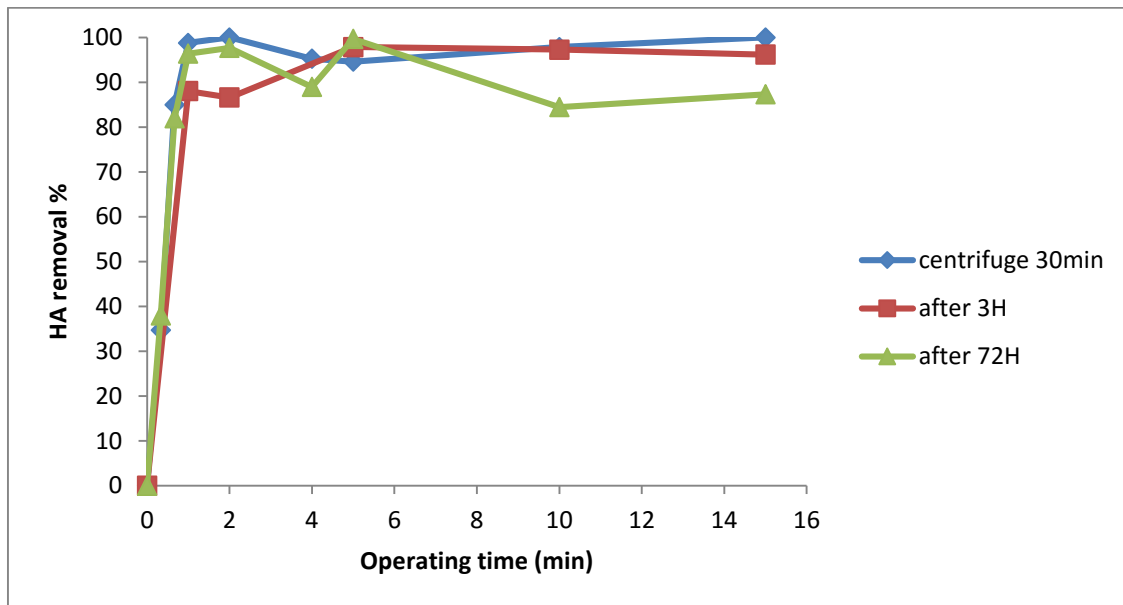


Figure 20. HA removal efficiency during the EC process at 0.48 mA/cm^2 current density (pH 6).

The next electrocoagulation experiments investigated the removal efficiency dependence on the current densities coupled with treatment time. Three current densities were utilized: 0.24 , 0.48 and 0.72 mA/cm^2 . The stirring was fast while the current was applied, followed

by the slow stirring for 10 min flocculation to allow the particles to form the floc. All samples were centrifuged after the flocculation stage. The HA removal efficiencies at 1 min are presented in Table 4. Over a period of 17 min, humic acid removal reached over 95% for all current densities studied.

Current density, mA/cm ²	HA removal efficiency, %
0.24	30
0.48	75.64
0.72	86.83

Table 4. HA removal efficiencies depending on the current densities applied, when the EC treatment time was 1 min.

The results were plotted as a relationship between the HA removal efficiency and the total charge applied and presented in Fig. 21.

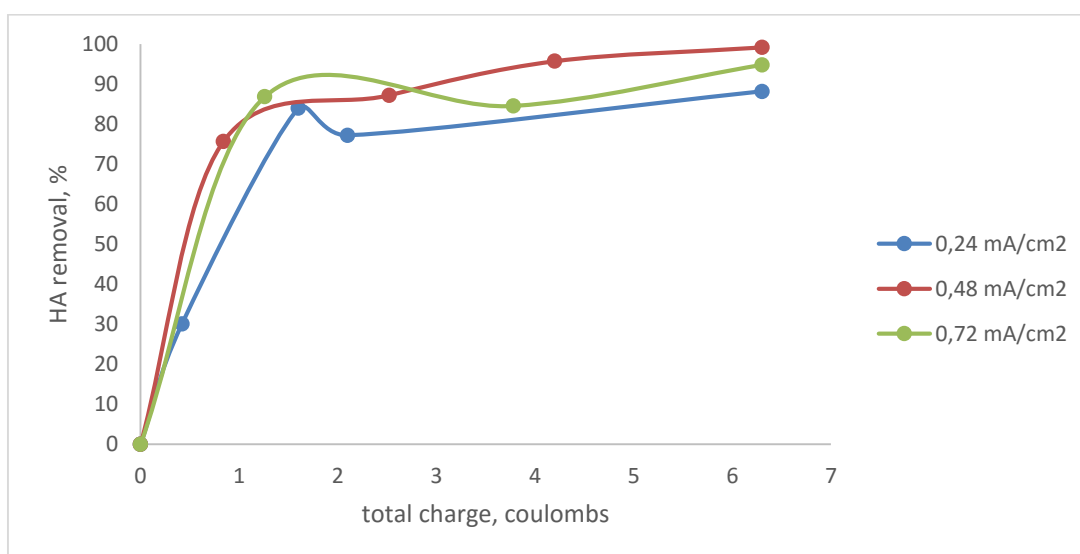


Figure 21. The relationship between HA removal rates for various charge densities as a function of the total charge applied.

The graph in Fig. 21 clearly indicates that high removal rates can be achieved with any of the current densities used. Even small current densities can be effective enough if applied for a long enough time. A higher current density, though, provides more efficient removal at a shorter time.

4.3.2 Floc

The volume of sludge produced with electrocoagulation method is approximately 2-3 times less than the one left after chemical coagulation. Visually, the electrocoagulated floc seems to be larger and contains less water, and thus, in principle, might be separated more easily by membrane filtration.

4.3.3 Alternating current

Alternating current (AC) with rectangular wave was applied to a standard HA test solution with pH adjusted to 6. The HA removal was 93.9% (after centrifuge), which is nearly the same value as the one obtained with the DC power source.

The next experiment with AC included applying current to water containing HCl and observing the electrodes' surfaces and possible current decline. The results are summarized in Table 5.

Time	Parameter	Alternating current (AC)	Direct current (DC)
0h	Voltage / V	4.0 (peak-to-peak)	2.0
	Current / mA	19.5	22
	Conductivity / mS	9.8	11
3,5h	Voltage / V	4.2 (peak-to-peak)	2.0
	Current / mA	18.0	12
	Conductivity / mS	8.6	6.0

Table 5. Comparison of conductivity characteristics of AC and DC setups.

Keeping voltage constant for both currents used, the current goes down from 22 mA to 12 mA in case of DC, while the current drop in AC setup (from 19.5 mA to 18 mA) is almost insignificant. This means that the electrodes in the AC setup do not passivate and lose their conductive properties as fast as the electrodes in the DC setup. This makes AC a good alternative for EC applications.

4.4 Microscopic analysis of electrocoagulated floc

The development of the electrocoagulated floc during the flocculation period was analyzed with a microscope. Some of the images obtained through the flocculation stage are shown in Fig. 22. The results demonstrate the flocculation phase starts with formation of small primary flocs of 2 μm in diameter (Fig. 22A), followed by their aggregation to larger flocs of different sizes, with maximum dimensions 4 μm x 7 μm (Fig. 22B-D), and, when the balance between the rate of aggregation with attractive force and the rate of breakage with repulsive force is achieved, the size of flocs reaches a steady plateau (Fig. 22E-F). The size of the largest flocs is nearly impossible to determine as it is unclear whether there are forces in between its parts.

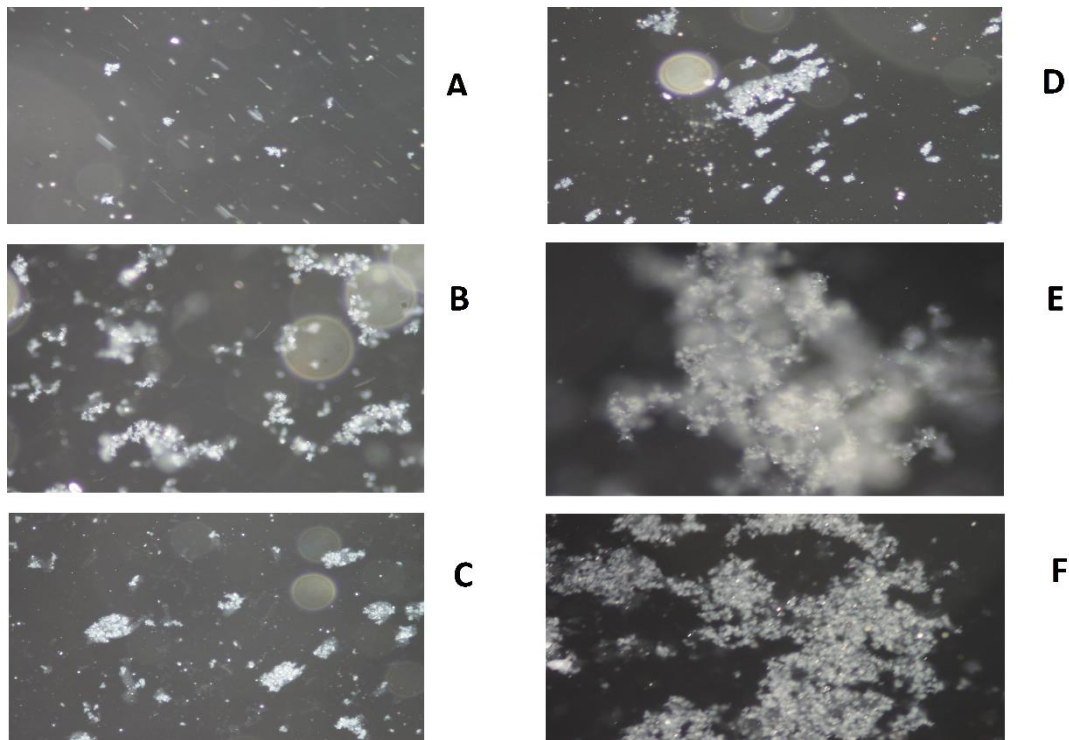


Figure 22. A – right after electrocoagulation, before the flocculation stage. Flocculation: B – 2 min, C – 6 min, D – 10 min, E – 12 min, F – 14 min.

The pictures captured with a microscope can be used to demonstrate the formation of larger aggregates from the primary tiny flocs with time during the flocculation stage.

Nevertheless, this method cannot be applied for scientific floc quantification and analysis as the floc size does not display a steady-state behaviour due to the shear stresses, and therefore, cannot be used to determine the floc strength. It should also be mentioned that the sampling procedure leads to significant floc breakage, such that the original floc size, and therefore strength, may not be measured.

4.5 Membrane filtration

The floc for membrane filtration experiments was achieved by electrocoagulation of a HA test water with 0.72 mA/cm^2 current density, 3 min treatment time, and 15 min flocculation time. The sample water was not left for settling, but was treated with membrane filtration right after. Before that, 7 mL of the sample water was centrifuged and analyzed with UV-spectroscopy to show that the electrocoagulation was efficient and removed 97.3% of HA.

It was obvious that some of the flocs broke before passing through the membrane and partially reformed after, because the final water was not transparent and some flocs were clearly seen. The water which passed through the membrane was left for settling for an hour and the clean water from the top of the beaker was analyzed by UV spectrophotometry. This combination of EC, UF and settling removed 73% of the humic acid (HA), which means some flocs were not strong enough to reform after the breakage.

5 CONCLUSIONS AND RECOMMENDATIONS

Chemical coagulation (CC) is the most commonly applied water treatment technique for the removal of HA. The experimental results show that good results can be reached under optimum conditions with PAC used as a coagulant. The highest HA removal ratio was 92.4% at a concentration of PAC exceeding 350 mg/L and pH adjusted to 6, which is very close to the value of 98.5% removal achieved by Zhang 2015. However, an optimum coagulant dosage is dependent on the solution and mixing conditions and has to be determined every time for a new setup.

Electrocoagulation (EC) is a relatively simple technique able to show even better results than CC. The highest result of 98.4% HA removal was achieved with 0.48 mA/cm² current density applied for 15 min. The efficiencies higher than 95% had been already reached after 2 min from the start of EC process. It was found that the performance of the technique is linear with the total charge per volume applied; therefore, even small current densities, when used for long enough time, are effective in HA removal. The volume of sludge produced with EC was less than the one left after CC. Due to the EC floc being larger than CC floc, the former was used for membrane filtration experiments.

Unfortunately, ultrafiltration was not effective in separating flocs from clean water. Flocs seemed to break before passing through the membrane and reform right after. In order to increase the floc strength, the flocculation process had to be investigated by microscopy. The sampling technique was highly destructive and also, due to the variation in floc size, it was impossible to quantify floc strength as a function of its size with a microscope.

Despite the fact that the results demonstrated that a sufficient HA removal efficiency can be obtained by both CC and EC processes, in the author's opinion, the EC technique has a high potential as a water treatment alternative to CC. It is a simple technology, which avoids excessive use of chemicals and so there is reduced need to neutralize them, and the floc produced by EC seems to be more stable. On the other hand, the EC method has a disadvantage of electrode passivation. The results of AC tests indicate that the problem

can be successfully solved by utilizing an AC power source. Thus, both the EC and the CC techniques are good methods for treating water containing HA. They are still empirically optimized processes that require more fundamental understanding for improved engineering design, though.

Further researches could design experiments combining CC and EC. In theory, the addition of a chemical coagulant decreases the pH of the solution, whereas EC increases it, resulting in pH stabilized to a neutral region. This could possibly reduce energy consumption but negatively affect the corrosion of the electrodes.

More experiments have to be done to compare the effects of AC and DC on EC performance. Furthermore, an effectiveness of different chemical coagulants and treatability of water containing HA flocs with a simple dead-end filtration could be investigated before proceeding with more complicated cross-flow filtration. In order to improve the efficiency of membrane filtration, floc strength has to be improved. Ultrasound treating could be applied to determine the strength of the flocs, or a non-destructive method of sampling needs to be found for microscopy.

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