OPTIMIZING SUSPENDED SOLIDS REMOVAL DURING CHEMICAL TREATMENT OF HUMIC AND LOW TURBIDITY WATER: PURIFICATION OF PEAT EXTRACTION RUNOFF

Kelechukwu Uche
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ENVIRONMENTAL ENGINEERING
Master’s Thesis

June 2018
Over the years, methods have been developed for the treatment of peat extraction runoff water such as treatment wetlands, sedimentation ponds and chemical treatment. In Finland, authorities consider chemical treatment one of the best available technologies for purifying peat extraction runoff. However, significant variation in purification efficiency has been observed in different sites, especially during periods of low suspended solid concentration in the inflowing runoff water.

The main objective of this thesis was to evaluate practical solutions for the optimisation of processes i.e. coagulation and flocculation, in order to improve the efficiency and reliability of the chemical treatment of the typically humic and low turbidity waters discharging from peat extraction sites. The aim was to investigate chemicals (including novel and hybrid products) and measures which had the potential to improve the removal of suspended solids while also identifying suitable alternatives that maintained the pH of the treated water inside acceptable levels (pH > 5). Coagulants tested were ferric sulphate, aluminium sulphate, polyaluminium chloride (conc. 45-50%), polyaluminium chloride (conc. 30-40%), polyaluminium chloride (recovered from industrial process), trinac-based biopolymer, in-house blend of ferric sulphate and polyDADMAC, in-house blend of aluminium sulphate and polyDADMAC and commercially available blend of polyDADMAC and aluminium chloride.

Jar test methodology was employed and water samples from two different locations were treated in laboratory scale experiments. Research methodology was elaborated to i) identify the optimum dosage of tested coagulants for the treatment of the different water samples, ii) investigate the influence of process parameters (pH, mixing, and sediment addition) on load removal efficiency and iii) evaluate the settling properties of flocs formed by different coagulants. Purification efficiency was evaluated based on the percentage removal of suspended solids (SS), dissolved organic carbon (DOC), total nitrogen (tot-N), total phosphorus (tot-P), phosphate phosphorus (PO4-P) and ammonium (NH4-N) from the water samples being purified.

In general, all coagulants and blends tested achieved high purification efficiencies in the treatment of both water samples. Removal efficiencies achieved were for water sample 1: 50-80% DOC, 30-60% tot-N, 78-100% tot-P and 30-80% SS. For water sample 2: 65-80% DOC, 73-83% tot-N, 67-87% tot-P and 57-85% SS. Ferric sulphate and its blends presented higher removal of DOC (ca 78%) compared to aluminium sulphate and its blends (50-60%). Ferric sulphate performed well also in the removal of nitrogen (ca 39%) but aluminium sulphate and its blends achieved best removal rates for ammonium (ca 32%). Although there was good load removal by microners and their blends, the pH of treated water was affected with values close to 4 observed. In the other hand, pre-hydrolysed coagulants performed well achieving removal rates among the highest and without affecting the water pH.

Influence of mixing on the performance of ferric sulphate and polyaluminium chloride (conc. 45-50%) was evaluated. While mixing conditions had a significant influence on the performance of ferric sulphate, removal of turbidity and colour by polyaluminium chloride was not affected by the variations applied to mixing parameters. Regarding the settling characteristics of flocs formed, ferric sulphate presented the fastest sedimentation rate while polyaluminium chloride (conc. 45-50%) was the best performing coagulant achieving the best turbidity removal after 25 mm of sedimentation. The addition of recovered sediments from a chemical treatment facility during the purification process was conducted in an attempt to improve turbidity removal. No measurable effect was observed in the purification rates achieved when sediments were added.

In conclusion, polyaluminium chloride products (conc. 45-50%) were found to be suitable solutions to improve purification efficiency and reliability of the chemical treatment of peat extraction runoff water. Furthermore, these products do not affect the pH of the water significantly avoiding the need for pH neutralisation.
Acknowledgements

First and foremost, I want to thank God for the strength and good health bestowed upon me to finish this study and making this thesis a success and without whom nothing is possible.

I want to gratefully extend my gratitude to a number of people that with their help thesis would not be possible. I really want to say a big thank you to my supervisor D.Sc. (Tech.) Elisangela Heiderscheidt for giving me the big opportunity to participate in this project. Your tireless guidance, unending patience and assistance would never go unnoticed. I also want to appreciate the advice, support and input of D.Sc. (Tech.) Anna-Kaisa Ronkanen. I want to sincerely thank Anneli Wichmann for the kind advices and suggestions, also Vapo Oy for their financial support that made this work a reality. Special thanks to Tuomo Reinikka and Tuomo Pitkanen for their immense assistance and encouragement during the laboratory phase of this project. Without them it could not be successful.

I want to pour out my heart of thanks and unending love to my family. My mother Ngozi Uche, you are my strength and backbone. Your prayers kept me going and made this work a reality and a success. My brother and sister, Chinomnso Uche and Nancy Ijomah you guys are the best. Life couldn’t be sweeter without you.

I want to also appreciate the friendship and support of Damilola Adesanya. He has great impact to my life from day one of my studies in Finland. Also, my deepest appreciation goes to Rebecca Tampio, your presence and support is one in a million. Not forgetting the guidance, support and suggestions of Kari-Pekka Tampio. It was really helpful.

Kelechukwu Uche

June 2018
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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>ACH</td>
<td>Aluminum chlorohydrate</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminum oxide</td>
</tr>
<tr>
<td>ca</td>
<td>Cira, approximately</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetre</td>
</tr>
<tr>
<td>Cq</td>
<td>Charge quantity</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
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<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>EC</td>
<td>Electroconductivity</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>Ferric ion</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>Ferric chloride</td>
</tr>
<tr>
<td>Fe₂(SO₄)₃</td>
<td>Ferric sulphate</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>L</td>
<td>Litre</td>
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<tr>
<td>M</td>
<td>Mole</td>
</tr>
<tr>
<td>mg</td>
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<tr>
<td>mg/L</td>
<td>Milligram per litre</td>
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<td>min</td>
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<tr>
<td>mL</td>
<td>Millilitre</td>
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<td>Millimetre</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>NH₄</td>
<td>Ammonium</td>
</tr>
<tr>
<td>NTU</td>
<td>Nephelometric Turbidity Unity</td>
</tr>
<tr>
<td>P</td>
<td>Phosphorous</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PAC</td>
<td>Polyaluminium chloride</td>
</tr>
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</tr>
<tr>
<td>PO$_4$</td>
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</tr>
<tr>
<td>polyDADMAC</td>
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</tr>
<tr>
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<td>Phosphate phosphorous</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
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<tr>
<td>rpm</td>
<td>revolution per minute</td>
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<tr>
<td>s</td>
<td>seconds</td>
</tr>
<tr>
<td>SS</td>
<td>Suspended Solids</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>tot-N</td>
<td>Total nitrogen</td>
</tr>
<tr>
<td>tot-P</td>
<td>Total phosphorous</td>
</tr>
<tr>
<td>µg/L</td>
<td>microgram per litre</td>
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1 INTRODUCTION

The safety and quality of water are fundamental to the well-being and development of human in the society. If we inevitably need to promote health and reduce poverty, providing access to safe water is one of the most effective tools to achieve our objectives. Human and industrial activities can produce load sources (point source and nonpoint source) which can be discharged into water bodies and cause a rapid deterioration of the water quality and can have a negative impact to the environment and its ecosystem. Point source load can include municipal waste and industrial wastewater while nonpoint source occurs when rainfall, snowmelt and irrigation water transport pollutants into water bodies. (Wu & Chen, 2013)

In Finland, peat is an important resource because it is used in over 100 power plants, in electricity and heating production. Over 1 million homes are heated by peat and wood in Finland (Vapo, 2011). Similar to peat, wood can be utilised but owing to the technical and economic reasons, peat cannot be replaced fully with wood or other renewable or recyclable fuels. Use of peat in Finland has also reduced the dependence of energy production on imported fuels. (World Energy Council, 2013)

However, activities associated with peat extraction such as peatland drainage can have major ecological and biogeochemical impacts on aquatic environments (Tolckinen et al., 2014). Drainage of peatlands can increase the rate at which suspended solids and nutrients are transported to downstream waters (Klove, 1997) and it can increase eutrophication and reduce biodiversity (Selim et al., 1994). Impacts to water resources is considered one of the key issues affecting the future of the entire Finnish peat industry due to the increasingly strict environmental regulations being proposed (Kuokkanen et al., 2015).

Numerous treatment methods have been developed for the purification of peat extraction runoff water over the past years. During this period, improvement have been made but owned to load concentration and volumetric discharge variations, the purification levels achieved by these treatment methods do not attain to the requirements set by the Finnish legislation (Silven et al., 2010). As a result, further developments to purification methods of peat extraction runoff water are needed to improve retention of pollutant substances and to protect the recipient water resources. To meet regulations requirements, new ideas
are needed, since the effectiveness of conventional water treatment methods is often limited.

The main objective of this study was to evaluate practical solutions to improve the efficiency and reliability of the chemical treatment method for peat extraction runoff. Peat extraction runoff water is humic and often presents low turbidity. The goal was to optimize the coagulation and flocculation processes for suspended solids removal while maintaining the pH of the treated water at values above 5. In order to fulfill the objectives of the project the first step was to identify possible (practical, cost effective, etc.) solutions which should be tested against the coagulant (ferric sulphate) and conditions now applied in peat extraction sites. The selection of solutions to be evaluated was done based on previous studies, other literature, and on consultations with company representatives. (Heiderscheidt et al., 2013; Heiderscheidt et al., 2016b; Heiderscheidt, 2016a)

The tested solutions are as follow:

- Metal salt coagulants
- Pre-hydrolysed metal salt coagulants
- Commercial blend of metal salt and organic polymers
- In-house blend of metal salts (ferric sulphate and aluminum sulphate) and organic polymers (synthetic and organic)
- Addition of sediments recovered from treatment facilities in peat extraction sites and increase the initial pH of the water using an alkaline agent was also investigated.

Based on previous studies (Heiderscheidt et al., 2013) the mixing applied can have a significant effect on purification results. According to (Heiderscheidt et al., 2016b) for humic and low SS water, mixing applied during flocculation has a more significant impact on the obtained results. Therefore, a decision was made to evaluate the effect of mixing time and intensity applied during flocculation process for the most promising solutions identified during the study.
2 PEAT EXTRACTION

Peat is an accumulation of partially decayed plant biomass in fens, bogs, salt marshes and some swamps in various parts of the world (Rezanezhad et al., 2016). Charman (2002) simply defined peat primarily as a composition of organic matter and water. During the coalification process, peat is majorly considered to be the first developing phase in the process, whereby there is a gradual increase in the carbon content of fossil organic material and an associated reduction in oxygen (Kutz, 2015). Peat is also known to be treated as a sub-category within the brown coal category also known as lignite and it is defined as a soft combustible sedimentary deposit of vegetal origin which can be cut easily and has a colour of light to dark brown, has a high-water content of about 90% in its raw state, carbon content of about 60 – 70% and ash content of 6 – 12%. It shares many similarities with coal which can be used to generate electricity and can be applied in industrial, residential and other sectors. (Höök, 2012)

Peatlands can be identified as a landscape, with unique vegetation (open treeless scenery or more forested type as pine mires), that have a naturally accumulated peat layer at the surface. A land is right to be called a peatland if the thickness of the peat layer is at least 20 cm if drained, and 30 cm if undrained. When the thickness of peat deposit and total peat volumes are known, it is still difficult to measure the energy reserve it contains because the energy content of in-situ peat is subject to its moisture and ash content. (World Energy Council, 2013)

Peatlands are important part of the biosphere because they interact with fundamental life-support processes which involves biogeochemical cycling, food chain support, hydrological dynamics and water quality and it provides habitats for many characteristic and highly adapted plant and animal species (International Peat Society, 2018). Global peatlands are a valuable but can be a vulnerable resource which represent a significant carbon and energy reservoir and play major roles in water and biogeochemical cycles (Rezanezhad et al., 2016). Most areas of peatlands have been degraded in many countries around the world, but it is estimated that about 80% of the global peatlands are still in their natural state (Trinnaman et al., 2004).

The peatland vegetation and the degree of decomposition of the plant remains is a major factor that defines the hydraulic properties of peat. Microorganisms that generate energy
from utilizing soil organic compounds are responsible for the decomposition of these plant remains. The decomposition grade and visual appearance of peat varies with the depth, age, plant community and most importantly the drainage regime. The decomposition grade can be evaluated by the use of the 10 classes of humification of the von Post scale where H1 is the least and H10 is the most decomposed peat (van Post, 1922). The von Post method of classification is mostly based on visual inspection (Fig. 1) of extracted soil solution and plant remains and could be more useful in the field.

Figure 1. Influence of decomposition to visual appearance and microstructure (Vapo, 2011).

Further research has evaluated more characterization methods that can be used to describe the degree of decomposition and it is based on size fractions, density, and fibre content (Boelter, 1969; Malterer et al., 1992) while isotopic and spectroscopic methods are used to assess the soil organic matter decomposition and associated changes in its molecular composition, functionality and reactivity (Cao et al., 2014; Drexel et al., 2002; Grover & Baldock, 2013). Relative states of peat soil decomposition can also be assessed by its carbon/nitrogen ratios (Bridgham et al., 1998; Kuhry & Vitt, 1996).

The ecology and the biogeochemistry of peat soils are completely connected to the movement through and storage of water and reactive solutes which depends highly on the chemical properties of the soil water (Hill & Siegel, 1991), microbiological and chemical
processes (Todorova et al., 2005) and the physical properties of the porous matrix (Ours et al., 1997; Paivänen, 1973).

Peat extraction can be highly sensitive to climate conditions such as extreme rainfall, and this can cause the rate of production to differ from one year to another. However, when trends are reviewed across periods of several years or full decades, the impact of changes in peat policy can be clearly seen in production volumes. In the 1980s and 1990s, rate of peat production improved. This was because of the efforts to encourage domestic energy production. But in recent years the trend has been reversed as a response to the climate impact of peat combustion and water pollution problems related to peat extraction. (Finnish Environmental Institute, 2018)

There are different stages involved in peat production (Fig. 2). It all begins with draining of the peatland, milling, harrowing, ridging, loading of dried peat, stockpiling and finally to the market. (Vapo, 2011).

Figure 2. Stages in peat production (Vapo, 2011)
2.1 Peat extraction in Finland

In Finland, there are large peatland areas (approximately 9.3 million hectares in total) and they are commonly used for forestry and agriculture (approximately 5 million hectares), swamp conservation (approximately 1.13 million hectares), and peat production (approximately 0.08 million hectares) (Fig. 3). Besides the above-mentioned uses, approximately one third (approximately 3 million hectares) of Finland’s bogs are still found in their natural state. Extracted peat is mostly used as an energy source and as environmental and horticultural peat. Peat covers 7% of energy supply and 20% of district heat in Finland. In energy supply, peat is used to supplement imported energy, which forms 70% of Finland’s energy supply. (Geological Survey of Finland, 2018)

![Figure 3. Uses of peatland in Finland (Vapo, 2011)](image)

Peat is mined openly in Finland and the ditch network (Fig. 4) is similar in appearance to that used in agriculture. The drainage network is made up of bed ditches that are 20 meters apart and the collector ditches mainly transports drainage water to a settling basin. The bed ditch pipe barrier located after the settling pond in the bed ditch serves as a blockage of the ditch pipe that connects the bed to the collector ditch. (Klove, 1998)
2.2 Impacts of peat extraction to water resources and runoff water quality

Peat extraction and forestry have been listed as one of the main stressors affecting the quality of the headwaters in Finland. Peatlands have the ability to store a substantial amount of water, which is also involved within the hydrological cycle. Runoff derived from peatlands and the water fluxes within the peatland can be dependent on a lot of factors. These factors can be the layering of peat, peat hydraulic properties, subsurface properties, and location of drainage area in the catchment. (Klöve et al., 2017; Marttila & Klöve, 2010) Peatland drainage increases the decomposition of organic matter due to increased soil oxygen (Bridgham et al., 1991; Crawford & Williams, 1983), soil temperature (Aust & Lea, 1991; Trettin et al., 1996), and substrate availability (Trettin et al., 1996), and its effect on water quality can be incredible, as the drainage has the ability to influence small headwater streams and lakes which are sensitive to nutrient and suspended solids load (Krug, 1993; Marttila & Klöve, 2010). The leaching of organic matter and nutrients, especially phosphorous (P) and nitrogen (N) causes the effluent water colour, pH, and metal concentration to change and deteriorate (Kauppila et al., 2016) and the most harmful pollutant can be suspended solids which settles to the stream beds resulting to deterioration in salmon reproduction and affects benthic communities (Heikkinen & Laine, 2000; Laine, 2001). Generally, it is being noted that the amount of phosphorus present in peat extraction runoff water is at same level with peatlands drained for forestry, whereas nitrogen leaching is significantly higher in peat extraction runoff water than forestry sites (Klöve, 2001b).
2.3 Water treatment methods in peat extraction

Point and non-point sources are responsible for the contamination of our water bodies. It's noted that activities from industries, agriculture, and household are the main water pollution sources. (Gupta et al., 2012; Holden et al., 2004) Most commonly existing harmful substances found in our natural waters are suspended solids, heavy metals, nutrients and oxygen demanding substances and they exist either in solvated, colloidal or in suspended form (Gupta et al., 2012). As mentioned above (sec. 2.2), runoff water derived from peat extraction activities contains suspended solids, nutrients, and dissolved organic substances, and to prevent water quality deterioration in the receiving water bodies, efficient treatment of the runoff waters from peat extraction sites is a necessity.

It is difficult to make a prediction on the contamination load produced by the activities of peat extraction but is highly dependent on various factors which are; moisture content of the peat in the catchment area, peat type and degree of humidification (Svalnabäck, 2007), hydraulic conductivity, drainage density, and location of the drainage area in the catchment (Holden et al., 2004). It is important to state that different peat extraction sites require a different treatment method particularly designed to suit the requirements of the peat production process, site hydrology and geology, receiving water body sensitivity and especially the current legislation of the area (Heiderscheidt, 2016c).

Over the past years, there has been an increased attention to combat water pollution in Finland specially to reduce the suspended solids and nutrient loads to water bodies, but poor chemical and ecological status still occurs in a number of surface water bodies. The Finnish regulatory authorities have intensified the regulatory pressure to further reduce nutrient concentrations in wastewaters however, with the present pollution control measures in place, the standards have not been met, and the load reduction levels achieved fell short of what was expected by the environmental authorities. (Karjalainen et al., 2016; Kløve, 2001) Conventional methods usually used in treatment of peat extraction runoff water include sedimentation ponds (Marttula & Kløve, 2010), wetlands (Ronkanen & Kløve, 2009) and chemical treatment (Heiderscheidt et al., 2013), etc.

- Sedimentation ponds: This is typically a dug pond around the peat extraction area where runoff water is discharged. It maintains a permanent pool of
wastewater and significantly improves water quality by settling of suspended solids and other pollutants that are sediment-bound. (Marttila & Kløve, 2010)

- **Treatment wetlands**: In peat extraction, treatment wetlands are called overland flow areas and are usually constructed and established on undisturbed peatlands (Postila et al., 2014). They are primarily designed to treat runoff wastewater based on sedimentation, physical filtration, geochemical process and biological process (aerobic and anaerobic) (Kadlec & Wallace, 2009). In Finland, treatment wetlands are commonly utilised because they are efficient for treating different types of wastewater. Peat-based wetlands are known to be used for treatment of peat extraction runoff water. (Ronkanen & Kløve, 2009)

- **Chemical treatment**: This is basically the addition of chemicals in order to precipitate SS and other dissolved substances present in the water (Gregory & Duan, 2001; Pernitsky & Edzwald, 2006). The process of chemical treatment consists of three interconnected processes: coagulation, flocculation and sedimentation. The aim of chemical treatment is to coagulate and agglomerate the fine particles or colloids that cannot be removed by sedimentation alone (Koohestanian et al., 2008). Finnish authorities consider chemical treatment to be one of the best available technologies for purifying peat extraction runoff water. However, it faces the major challenge of the high costs involved in procurement of the chemical and maintenance of the treatment process, it has been restricted to large peat production sites situated in the proximity of sensitive water bodies (Kløve, 1997).
3 PHYSICAL CHEMICAL PURIFICATION PROCESS

The successful removal of particles from the water being treated is an excellent indicator of the efficiency of a water/wastewater treatment facility (Jiao et al., 2017). Aggregation of the particles in wastewater is achieved in two steps. First step (coagulation), a process whereby a coagulant (trivalent metal ions or polymerized species) is added to the wastewater and primary particles are formed as a result of rapid mixing. Second step (floculation), a process where collision and agglomeration take place between primary particles, primary particles and floc, and floc and other floc. It is noted that the early stage of agglomeration starts during rapid mixing however, coagulation and floculation are completely different processes. During slow mixing, collisions occur, and this is as a result of transport mechanism of turbulent diffusion during the slow mixing. (Gregory & Duan, 2001)

3.1 Coagulation

A notable technique found to remove particulates in wastewater is coagulation because of its simplicity and efficiency when compared to sorption processes (Jiang & Wang, 2009). It was traditionally designed to reduce turbidity, particles and colour during water treatment (Volk et al., 2000). Coagulation is an important unit process for water treatment which destabilizes colloidal impurities causing smaller particles to become larger by Brownian motion (Gregory & Duan, 2001) and absorb dissolved organic materials onto aggregates that can be removed by sedimentation and filtration (Jiang & Lloyd, 2002). Proper selection of coagulants and optimisation of the process parameters can go a long way to increase the treatment efficiency. In order to achieve this, a good understanding of mechanisms involved in coagulation is paramount. Though it is difficult to identify the exact coagulation mechanism occurring, the physical-chemical characteristics of the water, coagulant type and dosage, characteristics of particles in water, and process parameters can all be factors that influence the reactions taking place during coagulation process. (Jiang & Wang, 2009; Omoike & Vanloon, 1999)
Coagulation mechanism

Coagulation being a well-established process in water treatment which removes suspended particles and dissolved substances. The mechanisms involved are normally described using particle removal for simplicity and are: charge neutralisation (destabilisation), sweeping and bridging (Li et al., 2006). An extensive review was done by (Heiderschmidt, 2011) on the mechanisms involved in coagulation and a summary is presented here.

- **Charge neutralisation (destabilisation):** When metal salts are added to wastewater to form soluble hydrolysed cations and metal hydroxide flocs which is highly dependent on the pH, then charge neutralisation is said to take place (Bolto, 1995). This mechanism takes place between colloids and one or more of the metal ion complexes and occurs at pH less than 6 (though pH at which metal ion complexes can be effective can be extended to pH approximately equal to 7) (Hendricks, 2006). Further studies also prove that charge neutralisation is dominant when pH is lower than 6.5 (Jiao et al., 2017b), and when low coagulant dosage is used (Snodgrass et al., 1984). The surface charge on the flocs after coagulation has taken place is dependent on the dosage of metal salt used, but the net charge of the optimum dosage range is normally close to zero whereby the number of positive and negative charges being almost equal (Bolto, 1995).

- **Sweep mechanism:** This gives a considerably better removal of particles than when particles are destabilized by just charge neutralisation, its reason partly being that there’s an improved aggregation rate as a result of the increased solids concentration. When metal salts are added to water at the required dosage needed to cause precipitation of amorphous metal hydroxide, colloidal particles are enmeshed in these particles (Li et al., 2006). Hydroxide precipitates have an open structure which enables even a small mass to be able to give a large effective volume concentration, hence there’s a high chance of capturing other particles. (Duan & Gregory, 2003) Also, when the pH is high, large polymeric hydrolysis products concentration increase improving the absorption and co-precipitation of particles easier. This makes it possible for sweep coagulation to be dominant up to pH values of 8.0 (Jiao et al., 2017). When the coagulant dosage is increased in the sweep region, it gives a gradual larger volume of sediment (Gregory & Dupon,
2001) but when the operational dosage is exceeded, there is little or no further improvement in the removal of particles (Duan & Gregory, 2003).

- Bridging mechanism: A smaller floc that is formed by coagulation can be built up to bigger agglomerates by introducing a polymer which forms a larger particle and accelerate sedimentation (Bolto, 1995). When some segments of a polymer chain absorb on more than one particle and links the particles together, then we can say bridging has occurred (Li et al., 2006), and this mechanism is favoured by the usage of long-chain polymers which do not have a high level of charge (Bolto, 1995). The flocs formed by bridging coagulation are much stronger than the flocs formed when particles are destabilized by simple salts (Bolto, 1995), hence, the flocs formed by polymeric flocculants are more resistant to breakage (Ray & Hogg, 1987).

### 3.2 Flocculation

Aggregation of suspended particles in water and wastewater can be achieved successfully in two steps namely coagulation and flocculation. Coagulation has been elaborated in previous section while flocculation is collision and subsequent agglomeration between; i) primary particles, ii) primary particles and floc, iii) floc and other floc. (Watanabe, 2017)

There are two stages involved in flocculation process: first is perikinetic flocculation which arises as a result of thermal agitation (Brownian motion) and is naturally a random process. This stage of flocculation starts immediately after destabilisation and is complete within seconds. Its occurrence is short mostly because there’s a limiting floc size beyond which Brownian motion can have little or no effect on.

The second stage is orthokinetic flocculation which arises from induced velocity gradients in the liquid (Bratby, 2006). These velocity gradients can be generated by setting the liquid in motion by usage of wide range of mixers such as hydraulic mixers and mechanical mixers (Vigneswaran & Visvanathan, 1997).
3.3 Sedimentation

Sedimentation can be defined as the removal of solid particles from a suspension which happens by settling under gravity. Settled particles are called sediments and when they are concentrated and compacted at the bottom of a sedimentation tank, it becomes sludge. These particles are difficult to describe by theoretical analysis because they are not regular in shape, density or size. Therefore, theory of ideal systems is considered a useful guide in interpreting the observed behaviour in complex cases. We can categorise these observed behaviours into four groups which are called settling regimes. (AWWA, 1990)

The term “settling” is generally used to describe particles falling through a liquid under the force of gravity. These settling regimes are:

Type 1: Settling of discrete particles in low concentration neglecting the flocculation and other inter-particles effect.

Type 2: Settling of particles in low concentration with effect of flocculation

Type 3: Zone/Hindered settling is developed where the concentration of particles causes interparticle effects to the extent where the rate of sedimentation is proportional to the particle concentration. Different settling velocities are observed at different zones of different concentration.

Type 4: Compression settling which develops under the layers of zone settling which is developed as a result of the force exerted by the weight of the particles which results to sedimentation by compaction/compression.

There are factors that can affect sedimentation efficiency and quality of supernatant water. These are the size and shape of the tank, surface loading, flow arrangement (inflow and outflow), water and particulate quality. (AWWA, 1990 pp. 372)
3.4 Purification chemicals

3.4.1 Metal coagulants

The most commonly used metal salt coagulants can be categorised mainly into two groups, they are those based on aluminum and those based on iron. This is mostly not because of their effectiveness as coagulants, but for their relatively low cost and their ready availability. They have an enhanced absorption property which arises mainly from their ability to form multi-charged polynuclear complexes in solutions (Bratby 2006). Aluminum and iron-based coagulants are effective in the removal of a wide range of impurities present in wastewater which includes colloidal particles and dissolved organic substances. Their behavioural characteristics can be classified into two mechanisms: charge neutralisation and incorporation of impurities in an amorphous precipitate of metal hydroxide. These mechanisms depend especially on pH and dosage of coagulant (Gregory & Duan 2001) The aluminum coagulants include aluminum sulphate, aluminum chloride, sodium aluminate, aluminum chlorohydrate while the iron coagulants include ferric sulphate, ferrous sulphate, ferric chloride, ferric chloride sulphate.

Aluminum sulphate being the most widely used coagulant has been applied in water and wastewater treatment for several centuries, its manufacture from the digestion of bauxite ores with sulfuric acid. During the process, evaporation of water results in the dry product having an approximate formula of $\text{Al}_2\text{(SO}_4\text{)}_3\cdot 14\text{H}_2\text{O}$ with Al content ranging from 7.4 to 9.5% (usually close to 9% as Al) by mass. Basically, the strength and purity of alum are expressed in terms of equivalent alumina (aluminum oxide, $\text{Al}_2\text{O}_3$); 9% Al is equivalent to 17% $\text{Al}_2\text{O}_3$. An extensive review and study concludes that charge neutralisation and sweep flocculation are involved when aluminum sulphate is used as coagulant for water treatment (Umar et al. 2016) and it easily hydrolyses to form insoluble precipitates that helps in the removal of tiny particles which is naturally impossible to be filtered or are too small to settle via gravity in a reasonable time period (USALO, 2018). Gruchlik et al. (2017) evaluated that alum addition to wastewater sludge and biosolids produced from different treatment processes reduced peak odour concentration by 60%. When sulfuric acid is added to alum acidified aluminum sulphate is formed and the blend has a ratio of 26.5 to 43.5% alum and 3 to 14% sulphuric acid. The coagulant is supplied majorly in liquid form and has a varying pH from 1.7 to 2.3. (Bratby 2006) Acid alum can be utilised in many industries such as in the municipal and industrial water treatment
plants to remove turbidity, colour, SS and oil (emulsion breaking) (USALO, 2018). It can be used also in the paper-making industry for pitch control (Bratby 2006). In water and wastewater treatment facilities where TOC (total organic carbon) removal is important, it is recommended to use acid alum as coagulant. When compared to the standard alum, water treated with acid alum produces a denser and settleable floc and reduces the residual soluble aluminum in the treated water. (USALO, 2018) In cases whereby an acid is needed to be dosed to bring the primary coagulant pH down to optimal range, usage of acid alum as a single coagulant will be useful and avoid the usage of dual solution (Bratby, 2006).

Iron-based coagulants are also widely used metal salt coagulants such e.g., ferric sulphate which is available in solid and liquid form. Its liquid form is known to be composed of 40 – 42% Fe2(SO)4 and 11.5% Fe3+ by mass. There’s also lower purity liquid grades available with a composition of 30% Fe2(SO)4 by mass. Ferric sulphate can be utilised over a wide range of pH (4.0 – 11.0) and is suitable especially for colour removal. (Bratby, 2006) Ferric chloride also is used and has a good performance on removal of turbidity and it is more effective in removal of organic carbon when compared to aluminum-based coagulants (Shi et al., 2004), achieving the same removal with a much lower dosage (Adin et al., 1998). It is available commercially in liquid (most commonly used), crystal, or anhydrous forms. Its advised to handle FeCl3 in a similar way for hydrochloric acid because of its corrosive nature. Its liquid form is known to be composed of 40 – 43% FeCl3 by mass. (Bratby, 2006)

3.4.2 Pre-hydrolysed metal coagulants

When metal coagulants are added to water, the metal ions rapidly hydrolyze but in an uncontrolled manner which forms a series of metal hydrolysis species (Bratby, 2006). Traditionally, as well as we have Al and Fe based coagulants, there are now many products available commercially that contains pre-hydrolysed forms of the metal coagulants (Gregory & Duan, 2001) and some of the available products can be categorized into Al-based and Fe-based products.

Alum (aluminum sulphate) being the most commonly used coagulant has a number of disadvantages mostly being that when it reacts in water to produce aluminum hydroxide species, it also forms a by-product (sulphuric acid) which reacts with the alkalinity in the
raw water to produce carbon dioxide, hence causing the pH to be reduced (Gebbie, 2001). It has also been studied and evaluated that high dose of aluminum can cause problems to human health for example it can increase the risk of Alzheimer’s disease, thus it is important to minimize the residual amount of aluminum in treated drinking water and water used in food industry (Tomperi et al., 2013). Over the last decades, some alternative aluminum-based coagulants have been developed which have a general formula \(\text{Al}_n\text{(OH)}_{m}\text{Cl}_{(3n-m)}\) with a polymeric structure high solubility in water. The length of the polymerized chain, molecular weight and number of ionic charges are determined by the degree of polymerization (Gebbie, 2001). Polymerized aluminum coagulants consist of different species such as \(\text{Al}_3\text{(OH)}_2^{4+}\), \(\text{Al}_3\text{(OH)}_4^{5+}\), \(\text{Al}_8\text{(OH)}_{20}^{4+}\), \(\text{AlO}_4[\text{Al(OH)}_2]_{12}^{7+}\), \(\text{Al}_{13}\text{O}_4\text{(OH)}_{24}(\text{H}_2\text{O})_{12}^{7+}\) (Bratby, 2006). The presence and distribution of these species during the preparation of aluminum chlorohydrate, polyaluminum chloride, polyaluminum sulphate chloride, polyaluminum silicate chloride is highly dependent on the type of coagulant, the total aluminum concentration, the quantity of sodium hydroxide or sodium bicarbonate added during preparation, the rate of addition of sodium hydroxide, the intensity of mixing, and the degree of aging (Fan et al. 2003). These coagulants can be produced with different substitutions which can be beneficial for treatment of certain waters. Examples of such substitutes can be found in some products that have 1 to 3% sulphate substituting for chloride, which becomes polyaluminum chloro-sulphates (PACS). Some other substitutes can be phosphate and silicate. (Bratby, 2006)

One important property of pre-hydrolysed polyaluminum coagulants is their high basicity (ratio of hydroxyl to aluminum ions) and as a result of this, it lowers the alkalinity consumption and has little or no effect on pH of raw water (Umar et al. 2016; Bratby, 2006). Relative basicity is an important parameter that describes the composition of polymerized inorganic coagulants. It is simply the molar ratio of negative to positive charges of the compound (Bratby, 2006).

Polyaluminum chloride (PAC) has received a lot of attention over the last decades because of its higher efficiency and relatively low costs when compared to traditional coagulants (Buffel et al., 1985) and has been widely utilised for water treatment in Europe, Japan, and North America (Sinha et al., 2004). The \(\text{Al}_{13}\) present in \(\text{Al}_{13}\text{O}_4\text{(OH)}_{24}(\text{H}_2\text{O})_{12}^{7-}\) is the active specie that is responsible for its coagulation or precipitation properties and is the optimum content in PAC (Lu et al. 1999; Hu et al., 2005). Most produced PAC products are in liquid form but spray granular powder products are also available with
relative basicity ranging from 30 to 80%, its aluminum content range is from 5 to 12% and its specific gravities of liquid products varies from 1.2 to 1.4 at 20°C (Bratby, 2006). Previous studies have shown that there is more rapid flocculation and stronger flocs which settle faster when PAC is utilised compared to alum at same dosages (Gregory & Duan 2001). Yuheng et al. (2011) compared the use of alum and PAC in the treatment of algae contaminated water and it was discovered that alum needed higher dosage rates compared to PAC to achieve purification. Higher performance of PAC compared to alum in the treatment of landfill leachate was also observed, although alum was better for COD removal (Ghafari et al., 2010).

Aluminum chlorohydrate (ACH) is a modern coagulant that has a high aluminum content (Lin et al., 2017) with approximately 13% Al compared to 4% Al content of alum (Bratby, 2006) and was demonstrated by Ho et al. (2015) to have a great ability to eliminate silica species from Reverse Osmosis (RO) brine. When compared to other aluminum based inorganic coagulants, ACH has shown high removal efficiency of DOC from wastewater (Younge et al., 2016) specially wastewater with higher pH values (Sadmourmohamadi & Gorczyca 2015). ACH is a high-density PAC and was first developed in the United Kingdom in the early 50s solely as a sludge conditioner. In recent years, it has been utilised as a sludge conditioner and also as a primary coagulant. Its chemical formula is Al₃(OH)₅Cl and has a relative basicity of about 83%. (Bratby, 2006)

Pre-hydrolysed metal coagulant handling: Generally, when alum or ferric coagulants react with any polymerised coagulants, precipitates are formed. It is advised to rigorously clean tanks, lines and pumps before switching between coagulants. And in a case of combined usage, they should be fed from different lines and not mixed in line before the point of application. Storage is paramount and it is dependent on the product and the storage condition. (Bratby, 2006)

3.4.3 Organic polymers

Polymers are water-soluble and macromolecular compounds that can destabilize and improve flocculation of particles present in water and wastewater. Molecules in polymers are series of repeating chemical units that are held together by a covalent bond whereby
a polymer whose repeating units are of the same molecular structure is called homopolymer and one with different molecular structure is known as copolymer. Polymers can be classified into two categories namely natural and synthetic polymers. (Bratby, 2006)

Natural polymers: Natural polymers have long been used as flocculants and examples of such products are: polysaccharide (which is mainly starch and its components), gums, cellulose, konjac, glucomannan, glycogen, tannins, chitosan, sodium alginate and seeds from moringa oleifera tree, etc. (Bratby, 2006; Ghimici & Nichifor, 2018) Natural polymers are not toxic to humans and environmentally biodegradable, but their utilisation is limited to the fact that their properties cannot be modified to significantly enhance their performance.

Synthetic polymers: The use of synthetic polymers is more prevalent because of the ability of production processes to control and change these products properties such as the type and number of charged units molecular weight to enhance their performance. Synthetic polymer has been mostly used as flocculants (Bratby, 2006). Because they have electrical ionizable sites, they are called polyelectrolytes (Richter, 2009; Libanius, 2008) and according to that synthetic polymers are broadly divided into three groups; cationic, anionic and non-ionic polymers. Cationic polymers have positive charge; anionic polymers have negative charge while non-ionic polymer have no charge at all. Polymers that possess a charge (positive or negative) are called an ampholytic or polyelectrolytes while a polymer with no ionisable functional groups are known as non-ionic polymers. Most used non-ionic polymer is polyacrylamide. Cationic polymers are said to be derived by introduction of a quaternary ammonium group to the polymer backbone. Most commonly used cationic polymer is polydiallyldimethyl ammonium chloride (polyDADMAC). The anionic polymers comprise mainly of two types in terms of most used. One type contains the carboxyl functional group (polyacrylic acid) and the second type contains the sulfonic acid groups (polystyrene sulfonic acid). (Brostow et al., 2009)

The use of polymers extensively as primary coagulants or flocculant aids can be attributed to their distinct characteristics such as higher charger densities and molecular weights which implies better aggregation properties (Tzoupanos & Zouboulis, 2011). They are convenient to use and do not affect the pH (Bratby, 2006).
Hybrid polymers: Recently, hybrid polymers have emerged as new products potentially capable to treat water and wastewater because of their ability to perform better when compared to the conventional inorganic coagulants and it is cost efficient when compared to the organic flocculants (Wang et al., 2006). Hybrid polymers are developed/prepared by the addition of an effective component into an original material to enhance the aggregating power (Tzoupanos & Zouboulis, 2011). As a result of the synergetic effect produced by hybrid coagulants, it is right to say that they have superior performance than an individual coagulant (Yang et al., 2004).

When compared to an individual coagulant, a combined functional component into one solution is a suitable alternative for treatment of water and wastewater since the process can be carried out with addition of one chemical in one tank instead of construction of two operational units for dosing of two separate chemicals. Operational time is reduced as a result of applying hybrid coagulants in a single operation (Lee et al., 2010).

3.5 Factors influencing chemical purification

There are a number factors that influence chemical treatment of water and wastewater among them are water pH, water temperature, mixing applied when chemical is added and afterwards, coagulant type and coagulant dosage. Some of these factors will be further described in the subsequent sections.

3.5.1 Effect of pH

In natural water samples, pH has an effect on the surface charge of the colloids and the dissolved matter. So, pH is considered an important factor to be taken under consideration in destabilisation with metal salt coagulants, because it plays an important role in the coagulation process specially in regard to charge neutralisation mechanism. (Mahdavi et al., 2017) It has been observed that the primary charges of the particles present in the water are directly proportional to the pH of the solution and the pH of the solution will affect the dissolution and chemistry of the coagulant added (Jiang & Wang, 2009; Perntsisky & Edzwald, 2006; Saukkoriipi & Laasonen, 2008; Volk et al., 2000) and the mechanism of coagulation (Demirata et al., 2002; Gregory & Duan, 2001). When water has lower pH value (slightly acidic), the particles and molecules present in the water are mostly negatively charged and when metal salts coagulant are added, they cause the pH
to decrease further due to the consumption of alkalinity during the coagulant hydration. At low pH, hydrolysis species of the metal salts added will be of a more positive nature. (Bratby, 2006)

3.5.2 Effect of temperature

Studies has shown that hydrolysing metal coagulants lose effectiveness at low temperatures (Bratby, 2006; Duan & Gregory, 2003; Heiderscheidt, 2011; Heiderscheidt et al., 2013) and this effect may be due to a number of factors.

Particles transportation processes are affected through the influence temperature has on the viscosity of the water (Duan & Gregory, 2003). The higher the water temperature, the lower the water viscosity which will cause a free movement of particles and higher coagulant solubility. Lower temperature increases water viscosity hence colloidal particles are less mobile and the rate of particle recovery is reduced (Bratby, 2006; Yu et al., 2007).

As described in previous sections, its known that orthokinetic collision rate supersedes the perikinetic rate due to the Brownian diffusion for particles whose size is greater than approximately 1μm. In the orthokinetic coagulation, particle collision is brought about by fluid shear and as viscosity increases as a result of decrease in temperature, it has a detrimental effect on mixing conditions which might lead to inhomogeneous distribution of the coagulant added resulting in poor coagulation. (Duan & Gregory, 2003) Furthermore, research has shown that under low temperature, iron-based coagulants perform better compared to aluminum-based coagulants in the removal of turbidity and colour. This is mostly because of the fast rate of precipitation and formation of larger flocs under low temperature with iron-based coagulants. Also, pre-hydrolysed coagulants are more effective than conventional coagulants at low temperature. (Duan & Gregory, 2003)

3.5.3 Effect of mixing

The mixing applied during the coagulation and flocculation stages of chemical treatment can have a major effect on the purification efficiency achieved. It is important to have a rapid mixing (coagulation) when coagulant is added to water because it spreads the added coagulant fast and uniformly through the mass of the water and primary flocs are formed (Lin & Lee, 2007). Soon after the rapid mixing, the slow mixing (flocculation) is introduced and its intended to help primary flocs formed during rapid mixing to agglomerate
and form larger flocs. The features of the primary flocs formed during the rapid mixing stage influences the flocculation process (Bratby, 2006).
4 RESEARCH METHODS AND MATERIALS

A research plan was elaborated based on the jar test methodology to evaluate the effectiveness of the selected solutions. Parameters used during the experiments were selected based on real conditions in peat extraction sites treatment facilities in Finland. When applicable, commercial quality products were acquired, and real peat extraction runoff water was used.

4.1 Water collection and storage

Three water samples for this study were collected from two different peat extraction sites under the management of Vapo Oy. About 450-L of water was collected from the ditch network of Verkaneva peat extraction site, a site close to Vilanti, Finland in June 2017. The water was pumped into 12 new plastic 35-L gallons. This water sample is referred to as sample 1 throughout the thesis. The second sample was collected from the ditch network of Kurisuo, a site in Suonenjoki, Finland in September 2017. The sample was collected by the extraction company in four 35-L plastic gallons and delivered to university laboratory facilities. This water sample is referred to as sample 2 throughout the thesis. Another sample was collected from Verkaneva site (as sample 1) in November 2017 and is referred to as sample 3 throughout the thesis. Prior to collection of sample 3, twelve 35-L gallons used were acid washed to eliminate any source of contamination. Although sample 1 and 3 were collected from the same site, the quality of the water varied significantly between the samples.

All water samples were stored in a cold room (±4°C) and prior to usage, gallons were shaken vigorously to eliminate any possibility of water quality changes during storage due to the sedimentation of particulate matter or sticking of substances to the plastic surface.

4.2 Water quality characteristics

Water quality characteristics of raw water samples (1 – 3) as well as treated samples were initially evaluated at the in-house laboratory using five different parameters (colour, turb-
bidity, pH, charge quantity and electric conductivity, EC). Raw water samples and selected treated samples (treated with optimum dosages of coagulant agents) were also submitted to suspended solids (SS) analysis at the in-house laboratory and were sent to a certified laboratory for further analysis (standards methods used are given in table A, appendix). Analysis carried out by certified laboratory: dissolved organic carbon (DOC), total nitrogen (tot-N), total phosphorous (tot-P), phosphate phosphorous (PO₄-P), ammonium (NH₄), aluminum (Al) and iron (Fe).

Water samples 1 and 3 had pH of 4.5 which was outside the scope of the project. Although some preliminary experiments were run at the natural pH of the water samples (Figs. 1 and 2 in appendix), a decision was made to increase the pH of the water to 6.5 using calcium hydroxide (Ca(OH)₂). To eliminate possible errors that could arise because of variation in water quality during storage samples were analysed at different stages during the testing period. The water quality characteristics of untreated or raw water samples are presented in Table 1.

Table 1. Water quality characteristics of runoff water samples (average ± difference in the maximum and minimum values of experimental replicates)

<table>
<thead>
<tr>
<th>Water quality parameter</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.45 ± 0.15</td>
<td>6.4 ± 0.17</td>
<td>6.83 ± 0.02</td>
</tr>
<tr>
<td>EC (µS/cm)</td>
<td>49 ± 2</td>
<td>67 ± 1.5</td>
<td>91.2 ± 1</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>13.5 ± 1.5</td>
<td>13 ± 0.5</td>
<td>7.53 ± 0.25</td>
</tr>
<tr>
<td>Colour (mg PtCO/L)</td>
<td>900</td>
<td>400</td>
<td>1250</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>18.5 ± 2.5</td>
<td>2.8 ± 0.25</td>
<td>6.75 ± 0.75</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>48.4 ± 0.4</td>
<td>36.9 ± 0.1</td>
<td>95.5 ± 0.5</td>
</tr>
<tr>
<td>tot-N (µg/L)</td>
<td>5400 ± 400</td>
<td>1400 ± 0.15</td>
<td>6450 ± 50</td>
</tr>
<tr>
<td>tot-P (mg/L)</td>
<td>0.4 ± 0.04</td>
<td>0.06 ± 0.001</td>
<td>0.155 ± 0.005</td>
</tr>
<tr>
<td>PO₄ (mg/L)</td>
<td>0.705 ± 0.035</td>
<td>0.093 ± 0.15</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>PO₄-P (mg/L)</td>
<td>0.23 ± 0.011</td>
<td>0.03 ± 0.05</td>
<td>0.065 ± 0.03</td>
</tr>
<tr>
<td>NH₄ (µg/L)</td>
<td>2550 ± 250</td>
<td>81 ± 0.1</td>
<td>3600 ± 300</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>3.675 ± 0.185</td>
<td>3.39 ± 0.1</td>
<td>3.42 ± 0.14</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>0.315 ± 0.015</td>
<td>0.44 ± 0.1</td>
<td>0.635 ± 0.005</td>
</tr>
</tbody>
</table>

4.3 Characteristics of products tested

The coagulants tested were five commercial coagulants manufactured by Kemira Oyj, Kenwater, the normally used metal salt coagulant ferric chloride (FS), aluminum chloride (AS), two pre-hydrolysed coagulants (PAC1 and PAC2), one synthetic organic polymer
with a high cationic charge (polyDADMAC), tannin-based biopolymer (BIOPOL), commercially available blend of aluminum chloride and polydiallyldimethylammonium chloride and an industrially recovered polyaluminum chloride. Acronyms in parenthesis are used throughout the thesis for identification of each chemical. The chemical composition and major characteristics of the tested products can be seen in Table 2.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Solution concentration</th>
<th>Density (g/mL)</th>
<th>Manufacturer/supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric sulphate (FS)</td>
<td>40 – 50 %</td>
<td>1.5 – 1.6</td>
<td>Kemira Oyj, Kemwater</td>
</tr>
<tr>
<td>Aluminum sulphate (AS)</td>
<td>20 – 30 %</td>
<td>1.3 – 1.34</td>
<td>Kemira Oyj, Kemwater</td>
</tr>
<tr>
<td>Polyaluminum chloride (PAC1)</td>
<td>45 – 50 %</td>
<td>1.3 – 1.4</td>
<td>Kemira Oyj, Kemwater</td>
</tr>
<tr>
<td>Polyaluminum chloride (PAC2)</td>
<td>30 – 40 %</td>
<td>1.36 – 1.42</td>
<td>Kemira Oyj, Kemwater</td>
</tr>
<tr>
<td>Polydiallyldimethylammonium chloride (polyDADMAC)</td>
<td>19 – 25 %</td>
<td>1.03 – 1.05</td>
<td>Kemira Oyj, Kemwater</td>
</tr>
<tr>
<td>Tannin based Bio-polymer (BIOPOL)</td>
<td>25 %</td>
<td>1.1713</td>
<td>Haarla Oy. Tampere Finland</td>
</tr>
<tr>
<td>Aluminum chloride + Polydiallyldimethylammonium chloride (Commercial blend)</td>
<td>10 – 50 % AlCl₃ &lt; 25% poly-DADMAC</td>
<td>1.25 – 1.35</td>
<td>SNF Oy. Helsinki, Finland</td>
</tr>
<tr>
<td>Polyaluminum chloride (recovered from industrial process, PACrec)</td>
<td>5-16%</td>
<td></td>
<td>Kierto Ympäristöpalvelut</td>
</tr>
</tbody>
</table>

4.3.1 Preparation and handling of coagulants

Stock solutions of 10 mg/L of coagulants were prepared in a 250-mL flat bottom flask. They were diluted using equation (1) and the density of each coagulant was taken into consideration. New stock solutions were prepared after each day of use.

\[ C_1 V_1 = C_2 V_2 \]  \hspace{1cm} (1)
where;

\[ C_1 = \text{initial concentration (density of the coagulant, mg/L)} \]

\[ C_2 = \text{final concentration (concentration of the stock solution, mg/L)} \]

\[ V_1 = \text{initial volume (volume of the coagulant needed for the dilution, L)} \]

\[ V_2 = \text{final volume (volume of the diluted stock solution, L)} \]

**4.3.2 Blending of novel coagulants**

In an attempt to improve the purification of the water tested while maintaining the objectives of the project, metal salt coagulants and organic polymers (synthetic and natural) were blended to form hybrid products. The methodology used for the blending was structural hybridization which is known to be a combination of materials based on the rule of mixing at a macroscopic level. In other words, inorganic coagulants were mixed with organic coagulants by physical blending at room temperature and thus no new chemical specie was created. (Lee et al., 2012).

Polydiallyldimethylammonium chloride (polyDADMAC) was selected as the organic synthetic polymer to be blended with the inorganic metal salts. The selection was based on its wide availability and good solubility in water. The product used possessed relatively high molecular weight and cationic charge. Ferric sulphate and aluminum sulphate (FS and AS) were the metal salts used for the blends based on their low cost and availability. A tannin-based natural organic polymer was tested. Its selection was based on commercial availability in Finland. Among the available products the one presenting the highest molecular weight and cationic charge was selected (BIOPOL). Blends of FS – polyDADMAC, AS – polyDADMAC, and FS – BIOPOL were formed at two different mass ratios. A magnetic mixer was used to physically blend the coagulants at 500 rpm for 20 minutes. At the end of mixing, precipitate formation was not observed for blends of FS – polyDADMAC and AS – polyDADMAC but precipitates could be seen in blends of FS – BIOPOL.
Blends of inorganic-organic hybrid coagulants were formed based on the mass ratio of polymer/metal (Fe or Al) contained in the inorganic coagulants. Blended products contained 30% or 50% of polyDADMAC compared to the mass of Fe or Al added and 30% and 50% biopolymer compared to the mass of Fe added. With respect to the density of coagulants, the volume corresponding to the needed weight (mass) of respective products were mixed thoroughly in a cylindrical beaker. Dosage of hybrid products were reported based solely on the amount of metal salt being added and were determined based on the mass of metal salt coagulant used to make the blend and the final volume of the solution (see example calculation below).

Example of calculations performed for the production of the blended products. Quantities of the products to be added for the production of 30% mass ratio of polyDADMAC blend with ferric sulphate was determined as follow:

- Total mass of blended product = 10 g
- Ferric sulphate solution (42%) = 8 g FS contains 3.4 g of Fe$_2$(SO$_4$)$_3$ which contains 0.94 g of Fe
- polyDADMAC solution (20%) = 2 g contains 0.4 g of polyDADMAC
- Volume of individual solution was calculated from their densities.
  - density of ferric sulphate = 1.54 g/mL
  - volume of ferric sulphate needed = $\frac{8 \text{ g}}{1.54 \text{ g/mL}} = 5.2 \text{ mL}$
  - density of polyDADMAC = 1.055 g/mL
  - volume of polyDADMAC needed = $\frac{2 \text{ g}}{1.055 \text{ g/mL}} = 1.9 \text{ mL}$
- Total volume of blend = 5.2 mL + 1.9 mL = 7.1 mL
- Density of blend with respect to ferric sulphate = $\frac{8 \text{ g}}{7.1 \text{ mL}} = 1.13 \text{ g/mL}$

4.4 Jar test experiments

The apparatus used for the jar test experiments consisted of five jars paddle stirrer equipment produced by Kemira Kemwater named Flocculator 2000 (Fig. 5). The dimensions of the individual jars and stirrers is presented in Table 3. The speed of rotation and the mixing time of each individual stirrer can be controlled individually which allowed each
individual jar to be programmed with the desired mixing intensity and retention time. Jar test experiments were used to simulate the coagulation, flocculation and sedimentation process to evaluate the chemical treatment purification efficiency under laboratory conditions. The experimental work was conducted in four main phases:

- Phase 1: Optimum dosage and purification efficiency achieved in the purification of water sample 1. Coagulants used in this phase were FS, AS, PAC1, PAC2, blends of FS and organic polymer (polyDADMAC), blends of FS and tannin-based biopolymer (BIOPOL).
- Phase 2: Optimum dosage and purification efficiency achieved in the purification of sample 2 using the best three solutions identified in phase 1. Coagulants used in this phase were FS, PAC1 and PAC2.
- Phase 3: Evaluating the settling characteristics. Coagulants used in this phase were FS, AS, PAC1, PAC2, blends of FS and organic polymer (polyDADMAC), blends of FS and tannin-based biopolymer (BIOPOL).
- Phase 4: Evaluating the effects of pH on purification efficiency. Coagulant used in this phase is FS.
- Phase 5: Evaluating the effects of mixing on purification efficiency. Coagulant used in this phase were FS and PAC1.
- Phase 6: Dosage range achieved in the purification of sample 1 using recovered polyaluminum chloride coagulant (result presented in Table 2, appendix).
- Phase 7: Evaluating the effects of sediment addition on purification efficiency. Coagulant used was FS.

Table 3. Jar test equipment dimensions

<table>
<thead>
<tr>
<th>DIMENSION</th>
<th>BEAKER</th>
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<tbody>
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</tr>
<tr>
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</tr>
<tr>
<td>Volume</td>
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<td></td>
</tr>
<tr>
<td>Length of paddle</td>
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Phase 1 – Optimum dosage and purification efficiency of sample 1

All selected coagulants were tested in this phase using the jar test procedures as stated below:

a) Pre-test: One jar was filled with 1-L of untreated water and increasing dosages of coagulant was added while visual observations were made to identify the formation of flocs. Cumulative dosage at which flocs were observed was used as the starting point for the determination of optimum dosage range of each product.

b) Based on the pre-test data, 10 increasing dosages of each product were applied to individual jars filled with one litter of untreated water (Fig. 6) at the start of mixing.

c) To determine the initial conditions of the untreated water it was analysed for turbidity, colour, pH, charge quantity and electro conductivity.

d) Constant and equal mixing conditions were applied in the five individual mixers. Fast mixing time and intensity was 30s at 300 rpm, slow mixing time and intensity was 5 min at 20 rpm. A 30 min sedimentation time was allowed where no mixing was applied.

e) After the sedimentation time had elapsed (Fig. 7), samples of the supernatant water were carefully extracted from each of the individual jars and analysed for turbidity, colour, pH, electric conductivity and charge quantity.
f) Based on the data from step e) the dosages that showed reasonable removal of turbidity and colour was reapplied (step 2 to 6 was repeated).

g) Purification efficiency was evaluated and reported as the removal of colour and turbidity with applied dosage.

h) Dose of coagulants that presented the best removal of turbidity and colour were identified as the optimum dosage while the dosage that presented about 40 to 60% removal efficiency in turbidity and colour was identified as the lowest working dosage.

i) Samples treated with optimum dosages of individual coagulants were sent to a certified laboratory for further analyses.

According to the results obtained during phase 1 of tests, it was decided that three coagulants would be tested in the second phase. **Phase 2 had similar procedure as phase 1.** With respect to that, steps a – i were repeated in the second phase.

![Figure 6. Jar test equipment with untreated water sample. (Photo by U. Kelechukwu, 2017)](image-url)
Phase 3 – Evaluating the settling characteristics

All selected coagulants were tested in this phase using the jar test procedures as stated below with water samples 1 and 2. Procedure b – d of phase 1 were conducted and followed by:

a) One jar was used for each experiment with the outside wall of the jar marked round its circumference with a line 8 cm from the bottom.
b) Optimum dosage of coagulant was applied. At the end of the slow mixing stage and during the sedimentation stage 30 ml samples of treated water were extracted at different time intervals with a volumetric pipette. The pipette was inserted in the water down to the 8 cm mark. Samples extraction times were 0, 1, 2, 3, 4, 6, 8, 11, 13, 17 and 25 minutes (sedimentation phase). Note that, about 30 seconds before the end of the slow mixing (floculation), 30ml of treated water sample was extracted and it is referred to as the zero-minute sample.
c) Samples extracted were analysed for turbidity and the 25th minute sample was also analysed for pH. Turbidity was the parameter used as an indicator of to the number of particles in the water. The goal was to monitor how the concentration of particles changed over time at a constant depth in the jar.
d) Two replications of settling test were performed for all coagulants (optimum dosage) in this phase.
Phase 4 – Evaluating the effects of pH on purification efficiency

Ferric sulphate coagulant (FS) was tested using the jar test procedures as described in phase 1. Procedure b - d of phase 1 was followed however before the start of the procedure, the pH of untreated water sample 1 was increased to 7.5 and 9 using 0.5M stock solution of sodium hydroxide (NaOH). As in previous phases, the extracted supernatant water was analyzed for turbidity, colour, pH and electro conductivity. Two replicates were performed. Samples treated with identified optimum dosages at the different pH were also sent to a certified laboratory for further analysis.

Phase 5 – Evaluating the effects of mixing on purification efficiency

Based on previous studies (Heiderscheidt et al., 2013) the mixing applied can have a significant effect on purification results especially during flocculation for humic and low SS waters (Heiderscheidt et al., 2016). Therefore, a decision was made to evaluate the effect of mixing time and intensity applied during flocculation. Mixing parameters applied in previous phases were selected to represent condition in real treatment facilities, thus short mixing time and low mixing intensity were applied. During this phase the effect of applying previously identified optimum mixing on purification results were evaluated (Heiderscheidt et al., 2016). To evaluate the effects of mixing parameters on purification efficiency, jar test experiments were performed with water sample 3 using procedures outlined in phase 1 except:

a) Individual stirrers were programmed using different slow mixing parameters according to pre-selected values.

b) Factorial design was applied to plan the experiments. Three factors (coagulant type, mixing intensity and mixing time) were varied two levels (Table 4). Fast mixing time and intensity parameters were kept constant.

c) Coagulant selected was ferric sulphate (FS) and polyaluminum chloride (PAC1) for low and high levels of coagulant type respectively. Optimum dosages were used.

d) Eight experimental runs were conducted for which two replicates were performed.

e) The treatment combinations and runs carried out are presented using capital and lower-case letter to represent the high level and low level respectively of each factor. The runs were also determined randomly to satisfy the experimental analysis procedures.
f) The sequence of parameters variation and actual values applied is shown in Table 5

Table 4. Factors and levels evaluated

<table>
<thead>
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<th>Parameter</th>
<th>Factors</th>
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<td></td>
<td>Factors</td>
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<td>Slow mixing intensity (rpm)</td>
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Table 5. Randomized order of experiment

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Phase 7 – Evaluating the effects of sediment addition on purification efficiency

In this phase, sediment collected by Vapo Oy. and delivered to university laboratory facilities. The sample consisted in sediments cleared from a sedimentation basin from a chemical treatment facility in one of Vapo Oy peat extraction sites.

a) The sediments in a slurry form and was oven dried at 60°C for 24 hours. The temperature was selected so as not to burn the residual peat present in the sediment.
The weight of the sediment was measured before and after oven drying and water content of the sediment was calculated to be between 39 – 41%.

b) To have uniform size particles, the dried sediments was crashed to smaller particles because there were large lumps present.

c) Sieve analysis was done to the sediment to determine the particle sizes present. 5% of the sediment was retained on the 2 mm meshed pan, 28.5% of the sediment was retained on the 1 mm meshed pan, 30.5% of the sediment was retained on the 0.5 mm meshed pan, 15.5% of the sediment was retained on the 0.25 mm meshed pan, 20.5% of the sediment passed through and remained on pan.

d) **Applied constant and equal mixing intensity and time to the five individual mixers.** Fast mixing time and intensity was 40s and 300 rpm, slow mixing time and intensity was 5 min and 20 rpm. Afterwards, 30 min sedimentation time was allowed where no mixing was applied.

e) Increasing dosage of the sediment was added from first jar to fifth jar at the same time of start of mixing while constant dosage of coagulant was added after 10s of fast mixing (coagulation).

f) After the sedimentation time had elapsed, samples of the supernatant water were carefully extracted from each of the individual jars and analysed for **turbidity, colour, pH, electric conductivity and charge quantity.**

g) Two replicates of the tests were performed.
5 RESULTS AND DISCUSSION

The results of laboratory experiments are presented and discussed. Observations from different phases of tests are combined when appropriate.

5.1 Optimum dosage range and purification efficiency

The results and findings of the laboratory experiments performed during phases 1 and 2 are hereby introduced. For clarity, the results are presented in two sections. The first section describes how increasing dosages of the coagulants tested affected the removal of turbidity and colour from the water samples being treated. The second section describes the purification efficiency achieved by the optimum dosages of coagulants tested regarding the removal of pollutants such as tot-N, DOC, tot-P etc.

5.1.1 Optimum dosage ranges of coagulants tested

Metal salts

Removal of colour and turbidity from water samples 1 and 2 with increasing dosages of coagulants and the resulting water pH and charge quantity are reported (Fig. 8 – 11). Overall, higher dosages of coagulants were needed for effective removal of colour and turbidity from water sample 1 (Figs. 8 and 9) when compared to water sample 2 (Figs 10 and 11).

Generally, the product AS required substantially higher dosages than the other tested products and obtained lower removal of colour and turbidity. FS performed slightly better than AS at lower dosages (Figs. 8a and 8b). The pre-hydrolysed products obtained significantly higher removals of colour and turbidity at dosages similar to FS (Figs. 8c and 8d) in the purification of both water samples. Pre-hydrolysed products, especially PAC1, did not cause a decrease in the pH of the water as observed when FS and AS were used (Fig. 8). Optimum dosage of coagulants was identified based on turbidity and colour removal. For water sample 1 optimum dosages were: 170 mg/L for FS, 500 mg/L for AS, 200 mg/L for PAC2 and 190 mg/L for PAC1. Identified optimum dosages of coagulants tested in
the purification of sample 2 were: 160 mg/L for FS, 140 mg/L for PAC2 and 180 mg/L for PAC1.

Figure 8. Removal of turbidity and resulting water pH with increasing dosages of metal salt coagulants in the purification of water sample 1.
Figure 9. Removal of colour and resulting charge quantity (Cq) with increasing dosages of coagulants in the purification of water sample 1.
Similar patterns of turbidity removal were observed for the metal salt coagulants whereby a sharp increase in turbidity occurred when coagulant dosages lower than optimum were added (Fig. 8). Turbidity values subsequently decrease with increasing dosages until the optimum range was reached. Over dosing resulted in the resurgence of turbidity in most samples, apart from samples treated with AS. Optimum dosage of coagulants presented Cq close to zero which is as a result of charge neutralisation (Figs. 9 and 11). Charge neutralisation can be emphasized as the dominant coagulation mechanism taking place in the system. Studies has identified that the coagulation mechanism dominant in the purification of humic and low turbid waters is charge neutralisation (Heiderscheidt et al. 2016; Kleimann et al. 2005; Wei et al. 2009; Kvinnesland and Odegaard, 2004). Furthermore, according to data regarding the charge quantity (Cq), charge reversal (from $-C_q$ to $+C_q$) only occurred for dosages of PAC2 (Fig. 9) higher than optimum. However, it is clear that after Cq values close to zero were reached, higher dosages of coagulants caused re-stabilization of the suspensions leading to increasing colour and turbidity values of the samples.
Figure 10. Removal of turbidity and resulting water pH with increasing dosages of metal salt coagulants in the purification of water sample 2.
Figure 11. Removal of colour and resulting charge quantity (Cq) with increasing dosages of coagulants in the purification of water sample 2.

In-house blend of metal salts and organic polymers

In an attempt to improve the removal of turbidity while decreasing the effect FS and AS have on the pH of treated water, blends of FS – polyDADMAC, AS – polyDADMAC, and FS – BIOPOL were created by adding the cationic polymers to the metal salts. Blend of 30% and 50% (mass) of organic polymers were added with respect to the iron content (mass) of FS and Al content of AS (please note that the ratio refers to the mass of polymer
to the mass of Fe added and not to the mass of ferric sulphate). Comparison of the removal of colour and turbidity and the resulting water pH and Cq between the blends and the metal salts alone are presented (Figs. 12 – 15). Dosages reported refer to the amount of metal salts contained in the added blends.

Optimum dosages (mg/L of the metal salts in the blend) identified for the blended products containing polyDADMAC in the purification of water sample 1 were: 1) FS: 160 mg/L 30% ratio and 120 mg/L for 50% ratio, 2) AS: 520 mg/L for 30% ratio and 500 mg/L for 50% ratio. The optimum dosage of FS for blended product containing the BIOPOL was 200 mg/L for 30% and 240 mg/L for 50% ratio.

Lower turbidity and colour values were observed at lower metal salt dosages for blends with polyDADMAC (Fig. 12 and 13) specially for the 50% mass ratio. Overall, removal of colour and turbidity were also higher at optimum dosages for blended products (Figs. 12 and 13). Because the best removal efficiencies were achieved at lower dosages of FS and AS slightly higher pH values were observed in samples treated by optimum dosages of blended products. However, the pH of treated samples still ranged close to 4 (Fig. 12). Less negative Cq values were measured for samples treated with blended products (Fig. 13) compared to the same dosages of FS, this suggests that polyDADMAC cationic characteristics also helped in the neutralisation of charges in solution.
Figure 12. Comparison of the removal of turbidity and resulting water pH with increasing dosages of metal salt coagulants and blends with polyDADMAC in the purification of water sample 1.
Figure 13. Comparison of the removal of colour and resulting charge quantity (Cq) with increasing dosages of metal salt coagulants and blends with polyDADMAC in the purification of water sample 1.
While blends of FS and polyDADMAC reduced the required dosage of the metal salt needed, blends of FS and the tannin-based biopolymer produced an opposite trend (Fig. 14 and 15). Optimum dosages of the blended product contained similar or higher dosages of FS than that required by the metal salt alone. While slightly higher removal of turbidity (Fig. 14) and colour (Fig. 15) were achieved at optimum dosages of the 50% mass ratio blend, these correspond to high coagulant dosages. Similar pH values were observed in samples treated by optimum dosages of blended products with 30% BIOPOL but slightly lower pH value was observed in samples treated by optimum dosages of blended product with 50% BIOPOL. However, the pH of treated samples still ranged close to 4 (Fig. 14).

Figure 14. Comparison of the removal of turbidity and resulting water pH with increasing dosages of FS alone and blend with BIOPOL biopolymer in the purification of water sample 1.
Figure 15. Comparison of the removal of colour and resulting charge quantity \( (C_q) \) with increasing dosages of FS blend with BIOPOL biopolymer and FS alone in the purification of water sample 1.

**Commercially available blend of metal salts and organic polymer**

In general, coagulant dosages required for the purification of water sample 3 were higher than for the other samples. The commercially available blend of polyDADMAC and aluminum chloride was tested and the removal of colour and turbidity with increasing product dosage is reported (Fig. 16). Optimum dosage identified for the blend in the purification of water sample 3 was 320 mg/L. This was the same optimum dosage as was identified for FS in the purification of the same water sample and pH was also below 5.
Figure 16. Comparison of the removal of turbidity with increasing dosages of commercially available blended coagulant (polyDADMAC + AlCl₃) and FS alone, colour and resulting water pH in the purification of water sample 3.

5.1.2 Purification efficiency at optimum dosages

Removal efficiency represents the concentration of analyzed substances (DOC, tot-N, tot-P, PO₄-P, NH₄, and SS) removed by the chemical treatment relative to their initial concentration. Removal efficiency achieved by coagulants tested in the purification of water samples 1 and 2 are reported (Figs. 17 and 18). All coagulants tested achieved fairly high removal efficiency levels in the purification of both water samples with more than 50% removal of DOC, tot-N, tot-P and PO₄-P observed. In general, removal efficiencies were higher in the purification of water sample 2. This is because there were much more impurities (organic matter, total nitrogen, total phosphorous, phosphate, ammonium and humic acid) present in water sample 1 compared to water sample 2 (Table 1).

FS and FS containing blends presented better removal of DOC (ca 78%) specially when compared to AS and AS containing blends (50 – 60%) (Fig. 17). While FS products also performed well regarding the removal of nitrogen, AS and AS containing blends achieved the best removal rates specially for NH₄ (ca 52%) which it removed about 20% more than FS products (Fig. 17). Pre-hydrolysed products performed really well, specially PAC1 which archived removal rates among the highest and did not affect the water pH (Fig. 17 and 18).
Figure 17. Average removal efficiency of DOC, tot-N, tot-P, PO_{4-P}, NH_{4}, and SS for optimum dosages of tested coagulants in the purification of water sample 1.

Figure 18. Average removal efficiency of DOC, tot-N, tot-P, PO_{4-P}, NH_{4}, and SS for optimum dosages of tested coagulants in the purification of water sample 2.
For the in-house blends, reduction in dosages of metal salts were significant! However, when looking at the amount of polymer needed and the cost of polymer, we can say that the total dosage of FS blends and AS blends are high, and it costs more than the the metal salts alone. This is because polyDADMAC costs about 4 times more than FS. 120 mg/l of FS has 42% Fe(III) = 50.4 mg. This has about 28% Fe = 14.1 mg. For the 50% ratio then about 7 mg of polyDADMAC was added. Because the polydadmac solution is sold as 20% concentration the actual dosage of product will be about 35 mg/L. So total dosage about 155-160 mg/L which is the same dosage needed for FS alone. But, 35 mg of poly-DADMAC cost 4 times more than FS so this dosage of blended product would cost as much as a FS dosage of 260 mg/L. Also considering the energy costs for blending and transportation to the site, it will be really expensive to utilise.

In general, high purification efficiencies were obtained by all coagulants with the following removal efficiencies achieved for sample 1: 50 – 80% DOC, 30 – 60% tot-N, 78 – 100% tot-P, 30 – 80% SS and water sample 2: 65 – 80% DOC, 73 – 83 % tot-N, 67 – 87 % tot-P, 57 – 85% SS. According to the International Peat Society, the obtained results conform to the load removal levels expected for chemical treatment of peat extraction runoff water (30 – 60% tot-N, 75 – 95% tot-P, 30 – 90% SS) (IPS, 2009).

Significant variations in the removal efficiencies between different water samples as well as different coagulants were observed. This is because chemical purification is affected by the water quality as well as the coagulant characteristics. There was a significant drop in water pH in samples treated with optimum dosages of ferric sulphate (pH=3.47) and aluminum sulphate (pH=4.30). This was expected as it was also noticed in the study made by Heiderscheidt et al. (2013) when aluminum and ferric based coagulants both in solid and solution forms was used to treat peat extraction runoff water. Furthermore, iron-based coagulant (FS) performed 10 – 25% better than aluminum-based coagulant (AS) in removal of organic matter and this was expected because various studies have recorded same outcome (Volks et al., 2000; Matilainen et al., 2005, 2010; Heiderscheidt et al., 2013).

The pre-hydrolysed coagulants were found to be much more effective producing good removal rates at reasonable dosages. Furthermore, they had little effects on the pH of water thus eliminating the need for pH correction. This is mostly because they are already
neutralized (pre-hydrolysis). The extent of pre-hydrolysis can be determined by the basicity of each product. (Zhao et al., 2015)

PAC1 and FS presented a better removal of DOC (88% and 83% respectively), nitrogen (both 35%) and phosphate phosphorous (97% and 94% respectively) when compared to the commercially available blend (77%, 26% and 87% for DOC, nitrogen and phosphate phosphorous respectively) (Fig. 19). Blended products are more expensive than metals salts and around the same price as pre-hydrolysed products. However, utilising the commercial blend is not a feasible alternative considering its cost and PAC1 and FS performed better than it (Fig. 19).

![Graph showing average removal efficiency of DOC, tot-N, tot-P, PO4-P, NH4, and SS for optimum dosages of commercial blend coagulant, FS and PAC1 in the purification of water sample 3.]

Figure 19. Average removal efficiency of DOC, tot-N, tot-P, PO4-P, NH4, and SS for optimum dosages of commercial blend coagulant, FS and PAC1 in the purification of water sample 3.

5.2 Settling characteristics

The ability of a coagulant to form suitable flocs that can sediment in short time and produce a clarified supernatant water is referred to as the settling characteristics of the coagulant. The settling characteristics of the formed flocs can be an important factor in evaluating the performance of each coagulant (Heiderscheidt et al., 2013). The settling characteristics of metal salts alone and of blends (optimum dosages) of organic products with
metal salts when applied to water sample 1 and 2 are presented in Figures 20 and 21 respectively. It is important to note that there was a significant increase in the initial turbidity of the samples when the coagulants were added. The metal salts (FS and AS) produced more turbidity than the pre-hydrolysed (PAC1 and PAC2) products. Reported turbidity value of 0 minute is the turbidity value measured at the end of mixing (Figs. 20 and 21). It is seen (Fig. 20a) that FS presented the fastest sedimentation rate achieving 90% removal from pre-sedimentation turbidity within 4 minutes. AS and PAC2 achieved within 4 minutes, 60% and 85% removal of pre-sedimentation turbidity respectively. This was possible because of high pre-sedimentation turbidity of the water after the coagulants were added (50 – 90 NTU) which can be linked to high particle concentration and results to higher sludge formation. As a result of that, there was a formation of relatively high dense flocs that sediment fast. Compared to other metal salts, PAC1 (pre-sedimentation turbidity of 37.5 NTU) had a slower initial sedimentation rate achieving 27% pre-sedimentation turbidity removal within 4 minutes. However, PAC1 achieved 91% and 98% removal of pre-sedimentation turbidity within 6 minutes and 8 minutes respectively. In terms of water clarification, PAC1 had an overall higher clarification of the supernatant water with final turbidity value of 0.39 NTU after 25 minutes. Also, it is important to note that high pre-sedimentation turbidity results to high sludge formation which leads to often cleaning of sedimentation tank, so it is economical and financial benefit to utilise PAC1 which produces less pre-sedimentation turbidity.

The settling characteristics of blends with FS and AS was also observed and compared to FS and AS alone (Fig. 20b – 20d). It is noted that due to high pre-sedimentation turbidity (60 – 130 NTU), there was high rapid settling experienced in all blends. All blends achieved 70% removal of pre-sedimentation turbidity within 4 minutes of sedimentation. Though there was a reduction in the sedimentation rate when organic polymer was added to FS as compared to FS alone (90% within 4 minutes), the overall final turbidity removal after 25 minutes was improved. Sedimentation rate was improved with AS blend with organic polymer when compared to AS alone (60% with 4 minutes) and overall turbidity removal after 25 minutes was improved also.

The ability of metal salts to form suitable and dense flocs in order to achieve a fast sedimentation time was also reported by Heiderscheidt et al. (2016) and this can be attributed to the formation of insoluble hydrolysis products which increases the number of particles in suspension (Amy et al., 1983; Packham, 1972). Pre-hydrolysed products are known to
have already gone through hydrolysis and therefore they will not produce as much precipitate. The amount of precipitate produced depends on the product characteristics.

Figure 20. Turbidity removal as a function of time for optimum dosages of coagulants applied to water sample 1 (dotted line represents raw water turbidity (12.8 NTU); a- metal salts, b and c comparison of FS and blends and d- comparison of AS and blends)

Settling characteristics of flocs formed by the addition of coagulants to water sample 2 exhibited similar outcome (Fig. 21), PAC2 achieved fastest sedimentation rate achieving
72% removal of pre-sedimentation turbidity with 4 minutes. FS and PAC1 achieved within 4 minutes, 58% and 12% removal of pre-sedimentation turbidity respectively. PAC1 removed 92% of pre-sedimentation turbidity within 11 minutes, rate which improved further leading it to have an overall higher clarification of the supernatant water after 25 min of sedimentation.

![Turbidity removal as a function of time for optimum dosages of tested coagulants to water sample 2](image)

**Figure 21.** Turbidity removal as a function of time for optimum dosages of tested coagulants to water sample 2

### 5.3 Influence of pH on purification efficiency

The pH of peat extraction runoff water is known to fluctuate in different sites but also during the year. Heiderscheidt et al. (2015) reported that the fluctuation range varies from as low as 4.5 to as high as 7.0. Chemical purification significantly reduces the runoff water pH with most sites discharging water with pH values close to 4. The effect of increasing the water pH to values between 6.5 and 9.0 were evaluated. Comparison between the removal of colour and turbidity from water sample 1 at different pH with increasing dosages of FS are reported (Figs. 22). Identified optimum dosages of FS in the purification of sample 1 at different pH were: 170 mg/L for pH 6.5, 220 mg/L for pH 7.5 and 280 mg/L for pH 9. Increasing the pH of raw water sample resulted on an increase in the coagulant dosage required to achieve similar removal of turbidity and colour (Fig. 22).
The effect of pH variations on purification efficiency (Fig. 23) was also evaluated. Similar removal efficiency of DOC, tot-N, tot-P and PO₄-P were achieved at all pH levels though lower dosages of coagulant was used in the purification of water samples with lower pH. Higher removal of NH₄ was achieved at lower pH levels.
Coagulation pH is one of the most important factors affecting chemical purification, it affects the way the added coagulant reacts with the water and the pollutants present in the water because it affects the chemistry of the coagulant and the molecules as particles in the water (Gregor et al. 1997; Volk et al., 2000; Cheng, 2002; Perntsky & Edzwald, 2006). As noted in the results, higher initial water pH required higher dosages of coagulant to achieve desired purification levels. This was also reported by Cheng (2002) and it is due to the fact that at high pH, functional groups (carboxylic and hydroxyl) of the humic acids present in the water deprotonate and become highly negatively charged. At high pH, the hydrolysis rate of the ferric ions are enhanced forming hydrolysis species with less positive charge. Therefore, more iron salt is required at higher pH for humic acids to be removed. Heiderscheidt et al. (2016) also recorded similar results where the dosage of coagulant increased greatly when pH of raw water was increased from 4.5 to 6.5. Overall, as concluded by Heiderscheidt et al (2016), satisfactory removal efficiency can be achieved at lower pH and with significantly lower dosages of coagulant therefore pH adjustment should be conducted at the end of the treatment process if ferric sulphate is adopted as coagulant agent.

5.4 Influence of mixing

An important parameter in coagulation-flocculation process is mixing. It is important because it is required for blending the coagulant with the water and to provided motion needed for particles to collide and agglomerate as flocs. The objective of this experimental phase was to identify the magnitude and direction of the influence of the mixing applied during the flocculation process on the coagulants performance. Although a factorial design was used in the experimental planning and execution, statistical analysis (ANOVA) of the data was not conducted. The results are presented as the removal of turbidity achieved by the coagulant under different slow mixing times and intensities applied (Fig. 24).

Variations in mixing time and intensity had a significant effect on the performance of FS with longer mixing times and more intense mixing (15 min, 50 rpm) producing the best removal of turbidity (Fig. 24). The product PAC1 showed similar removal levels in all applied mixing rates (Fig. 24). Lower mixing time and intensity represent conditions
found in real treatment facilities. It is therefore important to take the results obtained under considerations. The pre-hydrolysed product represents a better option as it does not suffer with suboptimal mixing conditions.

Figure 24. Removal of turbidity with variations in mixing time and intensity in the purification of water sample 3 by FS and PAC1.

5.5 Influence of sediment addition

Sediments (chemical treatment residual) recovered from one of the chemical treatment facility of Vapo Oy was used as aid to the process in an attempt to improve the removal of turbidity by increasing the number of suspended particles in suspension and thus increasing the availability of nucleus for floc formation. It was also hypothesized that by using iron-rich sediments, the dosage of coagulant needed could be reduced. In general, sediment addition did not affect the purification of the water sample. The methodology used to grind the sediments was not effective enough because it resulted in large particle sizes which settled quite fast and did not act as a nucleus to floc formation. Uncertainty regarding the location where the sediment sample was collected by Vapo Oy, meant that the real precedence of the sample cannot be certified. The sediment was not analysed for its composition.
It is recommended that the sediments recovered should be grinded to fine particles, so it can provide the opportunity to form nucleus with flocs in raw water sample and then potentially improve purification. Though this can be beneficial, but it might not be cost effective because of the energy needed to make this sediment in powdery form.

Table 6. Sediment addition and resulting water quality of treated samples.

<table>
<thead>
<tr>
<th>Iron dose (mg/L)</th>
<th>Sediment dose (mg)</th>
<th>Turbidity (NTU)</th>
<th>Colour (mg PtCO/L)</th>
<th>pH</th>
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<td>503.2</td>
<td>7.48</td>
<td>120</td>
<td>3.41</td>
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</table>
6 CONCLUSION AND RECOMMENDATIONS

Overall, relatively high purification efficiencies were achieved by the coagulants tested (50 – 80% DOC, 30 – 83% tot-N, 67 – 100% tot-P, 30 – 85% SS) in the treatment of the peat extraction runoff samples collected. The removal levels achieved conform with those expected from chemical treatment of peat extraction runoff water by environmental authorities. Among the metal salt and blended coagulants tested, PAC1 was the best performing coagulant agent. At the same optimum dosage as FS (170 mg/L), which is the coagulant used by the company, PAC1 achieved 55-65% higher removal of SS than FS without decreasing the pH of the treated water. It is also important to note that high pre-sedimentation turbidity results to high sludge formation which leads to increase need of cleaning of sedimentation tank, so it is economical and financial benefit to utilise PAC1 which produces less pre-sedimentation turbidity.

Among the other solutions tested in an attempt to improve SS removal while keeping the treated water pH above 5 were the increase of raw water pH and the addition of sediments recovered from sedimentation basins. The initial pH of water had an impact on the coagulant performance. Though the purification efficiencies of initial pH of 6.5, 7.5 and 9 were similar, it required more dosage of coagulant to purify water sample of higher initial pH. Furthermore, the increase in initial water pH did not result in an increase in treated water pH, with samples treated by FS presenting pH values <4. It can be concluded that lower initial pH requires lower dosage of coagulant to achieve satisfactory purification and thus the increase in water pH prior treatment is not beneficial. It is more cost effective to treat humic water at low pH and increase the pH to desirable level at the end of treatment process.

The mixing applied during the flocculation stage of the chemical treatment of peat extraction runoff water had an impact the coagulants performance especially for the FS. A comparison was made between FS (the coagulant been used by the company presently) and PAC1 (best performing coagulant in this study), while FS needed optimum mixing conditions to achieve best removal of turbidity PAC1 performance was independent mixing applied. In the now existing treatment facilities, no mixing is applied during the flocculation process apart from the slow flow of the water through the sedimentation basin. Such conditions of inadequate mixing appear not to affect the performance of the pre-
hydrolysed product PAC1 thus making it a good alternative to the now used iron-based product FS.

In general, it was evident that chemical treatment of peat extraction runoff water is highly dependent on a number of factors such as the type of coagulant and its dosage, the initial pH of the water and other physical-chemical characteristics and the mixing applied. According to the results obtained it can be concluded that the pre-hydrolysed PAC1 product is a good alternative to the company as it is not affect by the applied mixing, it is capable of improving SS removal while maintaining the water pH above the threshold of 5. Nevertheless, further investigations are recommended for testing the sediments being recovered from the sedimentation basin from now existing treatment facilities which use FS as coagulant. It has the potential of reducing the dosage of coagulant needed for treatment there by making it possible to utilize product already used and minimizing costs.
REFERENCES


Ho, J.S., Ma, Z., Qin, J., Sim, S.H. and Toh, C., 2015. Inline coagulation-ultrafiltration as the pretreatment for reverse osmosis brine treatment and recovery. Desalination, 365, pp. 242-249.


## Appendix

Table 1. Methodology of the outsourced performed analysis

<table>
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<tr>
<th>Analysis</th>
<th>Method</th>
<th>Unit</th>
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<tr>
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<td>SFS-EN ISO 11732:2005</td>
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<td>tot-P</td>
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<td>SFS-EN ISO 15681-2:2005</td>
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</tr>
<tr>
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<td></td>
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</tr>
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</tr>
<tr>
<td>Fe</td>
<td>SFS-EN ISO 11885:2009</td>
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Figure 1. Removal of turbidity and resulting water pH with increasing dosages of metal salt coagulants in the purification of water sample 1 at pH 4.5. (Note: FS1 is ferric sulphate with concentration of 30 – 32%).
Figure 2. Removal of colour with increasing dosages of metal salt coagulants in the purification of water sample 1 at pH 4.5. (Note: FS1 is ferric sulphate with concentration of 30 – 32%).
Table 2. Dosage range of recovered PAC and resulting water quality of treated samples.

<table>
<thead>
<tr>
<th>Dosage (mg/L)</th>
<th>Turbidity (NTU)</th>
<th>Colour (mg PtCO/L)</th>
<th>pH</th>
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