TAMPERE POLYTECHNIC
Environmental Engineering

FINAL THESIS

Pekka Heinonen and Sannimaria Pisto-Lopez

OPTIMIZATION OF CHEMICAL WATER TREATMENT PROCESS FOR KÄMMENNIEMI, POLSO AND KAUPPI WATER TREATMENT PLANTS

Supervisor Senior Lecturer Eeva-Liisa Viskari
Commissioned by Tampereen Vesi, Production Chemist Terttu Mäkinen
Tampere 2007

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Final thesis	69 pages, 8 appendixes
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ABSTRACT

This work has been conducted for Tampere Water between February and April 2007. The purpose of the work was to find out is it possible to decrease the dosage of the coagulant used in chemical water treatment at Kämmenniemi, Polso and Kauppi water treatment plants. Subject of the thesis is to optimize the usage of the coagulant at previously mentioned water treatment plants. These water treatment plants collect raw water from Lake Näsijärvi. The experiments were done at Rusko water treatment plant laboratory at Tampere.

Experiments were done with Kemwater Flocculator 2000 device as jar test method. After the coagulation and flocculation process the water was analyzed for residue aluminium, total organic carbon (TOC), turbidity, UV-absorbance and Molecular weight distribution with HPSEC (high performance size exclusion chromatography) the results were compared to those obtained from raw water. First the optimum pH value was determined for each water treatment plant following by the optimization of dosage of coagulant. The present dosage of coagulant is 65g/m^3 at Kämmenniemi and 55g/m^3 at Polso and Kauppi. Optimal coagulant dosage is 50g/m^3 at each plant. However the pH values vary at according to the plant. The dosage of 50g/m^3 is optimal at each plant when pH value is 6 at Kämmenniemi, 6,5 at Polso and 5,7 at Kauppi respectively. In this work also the effect of temperature and effect of the mixing velocity on coagulation and flocculation were studied.

Tampere Water can utilize the results of this study to reduce the coagulant dosage at the water treatment plants in question in order to reduce the amount of aluminium in drinking water. The state of Lake Näsijärvi is constantly changing due to natural causes. Because of this, similar researches must be done also in the future. This work can be used as a base for upcoming researches.

TAMPEREEN AMMATTIKORKEAKOULU
Environmental Engineering

Pekka Heinonen ja Sannimaria Pisto-Lopez	Kemiallisen vedenpuhdistusprosessin optimointi Kämmenniemen, Polson ja Kaupin vedenpuhdistamoilla
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TIIVISTELMÄ

Tämä työ on tehty Tampereen Vedelle Helmikuun ja Maaliskuun välisenä aikana, vuonna 2007. Työn tarkoituksena on selvittää onko saostuskemikaalin annostuksen pienentäminen mahdollista kemiallisessa vedenpuhdistuksessa Kämmenniemen, Polson ja Kaupin vedenpuhdistuslaitoksilla. Työn aiheena on saostuskemikaalin käytön optimointi edellä mainituilla veden puhdistus laitoksilla. Nämä vedenpuhdistamot ottavat raakavettä Näsijärvestä. Kokeet tehtiin Ruskon vedenpuhdistamon laboratoriossa Tampereella.

Kokeet tehtiin Kemwater:in Flokkulator 2000 laitteella, astiakoe menetelmällä. Saostusprosessin jälkeen vedestä määritettiin jäännösalumiinin määrä, kokonaisorgaanisen hiilen määrä, sameus, UV-absorbanssi ja HPSEC eli molekyylikokojakauman muutos. Tuloksia verrattiin raakavedestä saatuihin tuloksiin. Ensimmäiseksi määritettiin optimaalinen pH arvo kullekin vedenpuhdistuslaitokselle ja sen jälkeen saostuskemikaalin optimaalinen annostus. Tämän hetkinen saostuskemikaalin syöttömäärä on Kämmenniemessä 65 g/m^3 ja Polsossa ja Kaupissa 55g/m^3. Jokaisen laitoksen optimaalinen syöttömäärä on 50g/m^3. pH arvot sen sijaan vaihtelevat laitoskohtaisesti. 50g/m^3 annostus on optimaalinen jokaisella laitoksella, kun pH arvo on Kämmenniemessä 6, Polsossa 6,5 ja Kaupissa vastaavasti 5,7. Työssä tutkittiin myös lämpötilan ja prosessissa tapahtuvan sekoitusnopeuden vaikutusta saostuksen toimivuuteen.

Tampereen Vesi voi hyödyntää tämän tutkimuksen tuloksia ja niiden avulla syöttömääriä voidaan laskea tutkimuksen kohteina olleilla laitoksilla, jotta juomaveteen laskettavan alumiinin määrää vähenisi. Näsijärven tilassa tapahtuu koko ajan luonnollista muutosta. Tämän vuoksi vastaavia tutkimuksia joudutaan suorittamaan myös tulevaisuudessa. Tätä työtä voidaan käyttää vertailu pohjana tuleville tutkimuksille.

Foreword

This study has been made for Tampere Water and for final thesis work of degree program of environmental engineering at Tampere Polytechnic with guidance of Eeva-Liisa Viskari and Terttu Mäkinen.

We would like to thank Terttu Mäkinen, Sinikka Vilenius, Marja Leena Mattila, Seija Penttilä, Veli-Ville Vihersalo, Anu Matilainen and Eeva-Liisa Viskari for giving us this opportunity and advising us to make it possible. We would also like to thank the personnel at Rusko water treatment plant for their exemplary help during the work

Tampere June 2007

Sannimaria Pisto-Lopez Pekka Heinonen

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1. List of abbreviations

DOC	Dissolved organic carbon
HPLC	High performance liquid chromatofigurey
HPSEC	High performance size exclusion chromatofigurey
IC	Inorganic carbon
IR	Infrared
NOM	Natural organic matter
NTU	Nephelometric turbidity unit
POC	Particulate organic matter
PSS	Polystyrene sulphonate
TC	Total carbon
TOC	Total organic carbon
UVA-254	Ultraviolet absorbance at wavelength of 254 nm

2. Introduction

It is vital for human being to have clean drinking water. This is why municipal drinking water in Finland must meet many different quality standards and has to go trough a sequence of purification where coagulation and flocculation processes do have an important role. Surface water without treatment can’t be used as municipal drinking water because it has high concentration of natural organic matter (NOM) which can be harmful for human health and can form intolerable reactions or biological growth in distribution systems.

In coagulation and flocculation the mass removed from purified water is larger than in any other part of water purification. Suspended particles are removed by attachment to form larger aggregates. Hydrolyzing metal salts are commonly used, because of their rapid hydrolysis to form cationic species, which can be adsorbed by particles with negative charge, thus reducing the net charge. At low dosages of coagulant, charge reduction is used as a mechanism for particle destabilization. After coagulation and flocculation aggregates can be removed by sedimentation, flotation or vertical filtering.

The aim of this thesis is to establish optimal pH and coagulant dosage for three different small surface water purification plants in Tampere region, which are Polso, Kauppi and Kämmenniemi water purification plants. The tests were run in a Laboratory of Tampere Water (Tampereen Vesi) which is located in Tampere. The period when the analyses were done was between 1.2.2007-30.4.2007.

Flocculation and coagulation tests were done with jar tests. Coagulant used for water from Kämmenniemi and Polso was polyaluminium chloride (PAX 14) and for Kauppi water aluminium sulphate was used as respective to the coagulants used in the plants. It has been assumed by the staff at Tampere Water that the dosages of used coagulants could be decreased and by these tests the assumption was going to be tested.

It has been found in many studies that pH has a great effect upon the efficiency of coagulation-flocculation processes. Generally, the optimal level is pH 5-7 (in some cases optimal pH is between 5-6) but is affected by the quality of the water. The pH was optimized at that level where it gives lowest results for analysis of remaining aluminium and TOC, and as low as possible results for turbidity and UV254. From coagulated samples, TOC, UV254, HPSEC, turbidity and remaining Al was studied by different analytical methods.

The history behind the coagulation has been mainly to remove the turbidity from water but later on the removal of natural organic matter has taken more important role. The optimal pH is not necessarily the same for the TOC or turbidity removal and this is why the effect of pH must be carefully analyzed for all the waters from different areas.

Since seasonal changes have great effect on Finnish surface waters, also effect of temperature, which varies trough the seasons, was studied by following the same methods as usual apart from conducting the jar test in 7^{o}C in a cold room for the optimal pH and dosage found in the previous analyses. Additionally, because the jar test was used, where samples with coagulant and adjusted pH are agitated with different velocities, the effect of agitation was tested with few tests with different agitation velocity (rpm) and let settle.

3. Lake Näsijärvi

Näsijärvi is 16. largest lake in Finland and the largest lake in Tampere region. It has a surface area of 25680 hectares and it is divided into three major areas, Vankavesi, Koljonselkä and Näsinselkä. (6)

Water treatment plants used it this work are utilizing water from Lake Näsijärvi and are found in the figure 3.1.

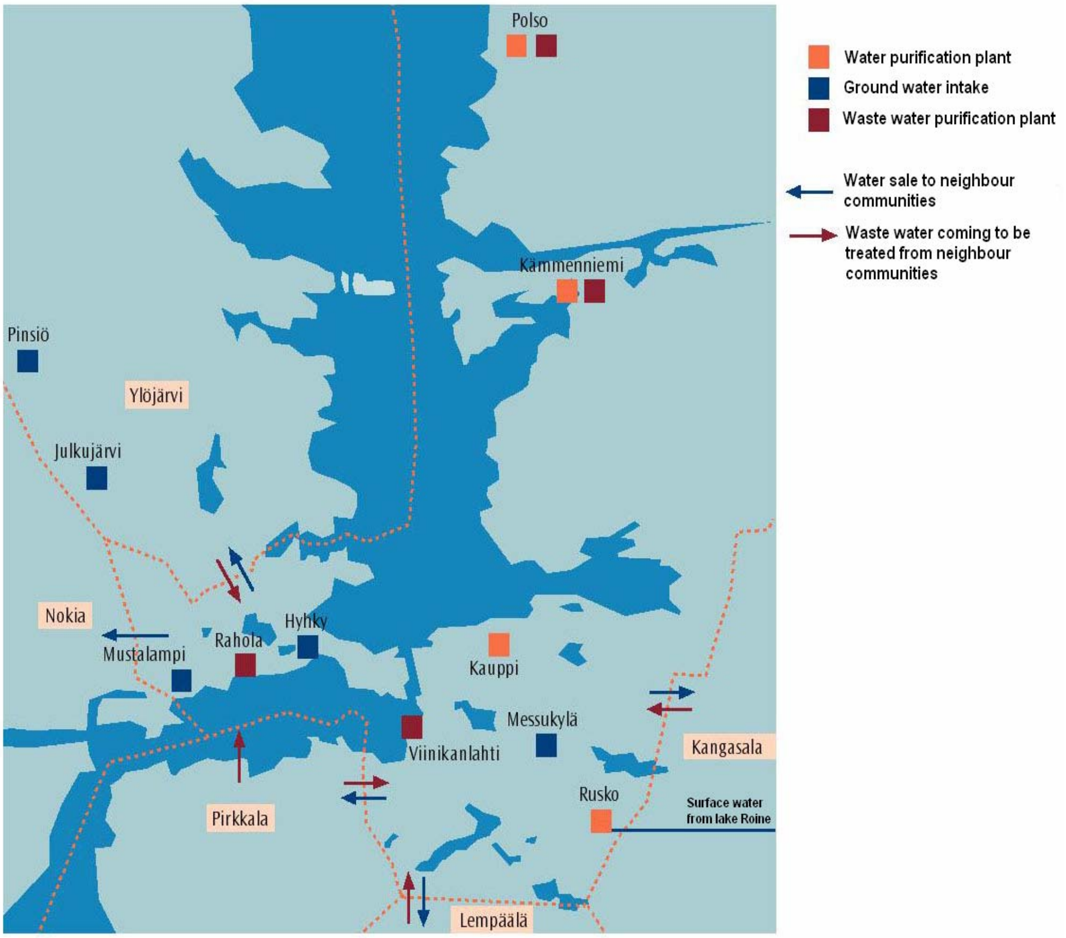

Figure 3.1. Water facilities in Lake Näsijärvi surroundings (source: Tampere Water)

4. Introduction of Tampere Water

Tampere Water is municipal water supplier and distributor owned by city of Tampere. It is also responsible for taking care of waste water collection and treatment. The amount of personnel is about 160. Tampere Water is handling water and waste water activities according to laws and regulations and developing water services in a way that Tampere keeps up with development of the society. City council and board set the economical and functional goals for Tampere Water. Activities are funded with payments collected from customers and possible profit goes to the city of Tampere (24)

The mission of Tampere Water is to take care of the pure water delivery, treatment and distribution, building and maintenance of pipelines, wastewater treatment, rain and melting water leading to sewers and some duties concerning water conservation. (24)

Environmental issues are handled according to ISO-1400 standard. Environmental permission office, Pirkanmaa regional environmental centre and Environmental monitoring of the city of Tampere are responsible for public authority surveillance. (24)

There are over 200 000 residents in city of Tampere. About 19 billion cubic meters of clean drinking water is delivered for them every year. More than half of the capacity (about 64%) is lead to household use and the share of industry is about 8%. The rest (about 5%) is pumped for sale to neighbor municipalities. Those are Pirkkala and according to needs Nokia, Lempäälä, Ylöjärvi and Kangasala. (24)

The raw water capacity of Tampere Water consists of four surface water pumping stations and five groundwater stations. The four water treatment plants working at Tampere area are handling about 30 billion cubic meters of waste water yearly. (24)

5. Kämmenniemi flotation plant

Flotation is the main treatment system used at Kämmenniemi plant. Flotation is water treatment mechanism used to purify water from rough impurities. Dispersion water is used to raise the flock that has been made with coagulant to the surface of flotation basin. Dispersion water is water that is mixed with large amount of air at 5-6 bar pressure. This gives the water a quality to rise quickly to the surface. Thus, dispersion water lifts the flock to the surface as it flows from the bottom of the pool through the water mass. The flock gathered to the surface of the pool is then flushed to sewer by raising the water level by inserting more water in to the pool from the bottom. After flotation the water is filtrated with activated carbon.

At Kämmenniemi treatment plant the amount of water purified during the year 2005 was 48120 m^3. From which 36476 m^3 was pumped to distribution network. This was 0,2% of the annual consumption at city of Tampere. (26)

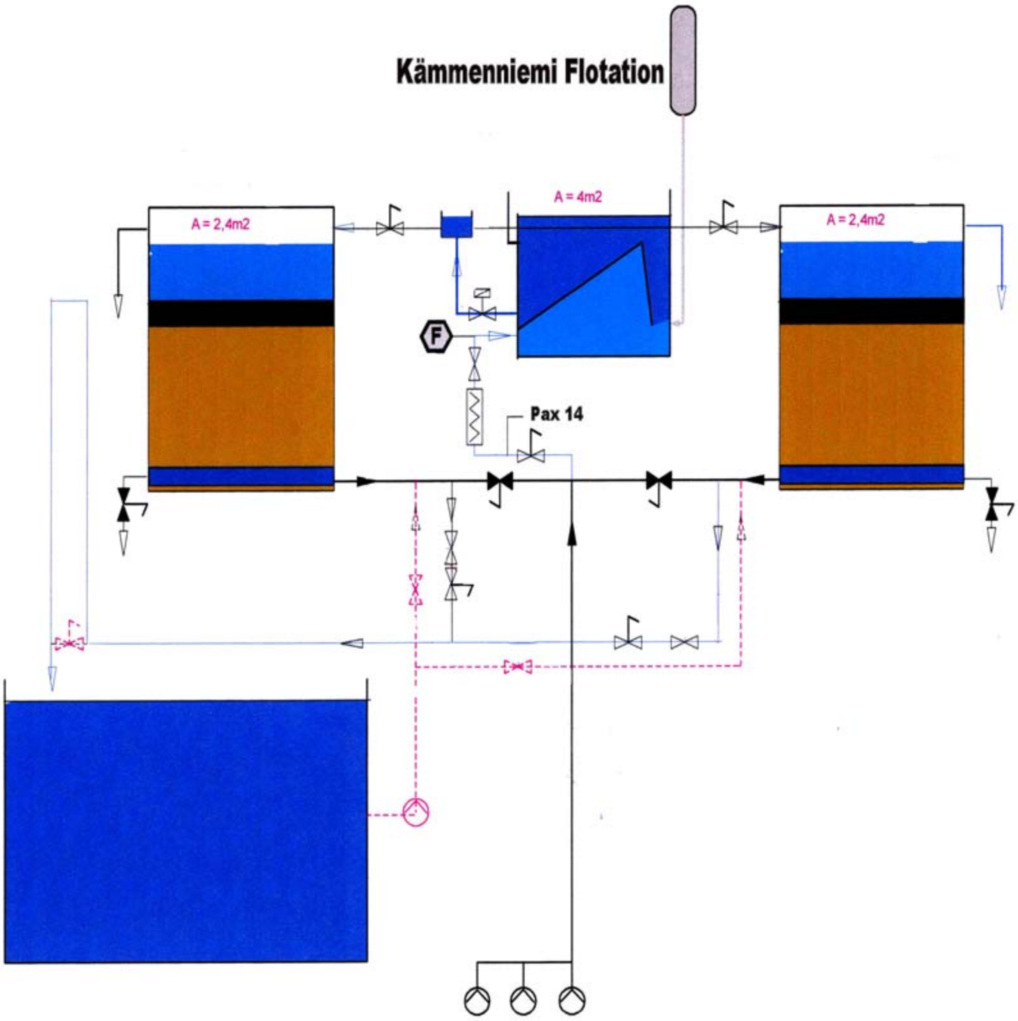

Figure 5.1. Schematic picture of Kämmenniemi flotation plant (Source: Tampere Water)

Figure 5.2. Is taken from flotation of Rusko water treatment plant, but Kämmenniemi plant utilizes the same principle in smaller scale (photo by Pekka Heinonen)

This picture is taken from flotation of Rusko water treatment plant, but Kämmenniemi plant utilizes the same principle in smaller scale.

6. Polso contact filtration plant

Polso treatment plant utilizes contact filtration to purify raw water. After the contact filtration also activated carbon filtration is used. Polso purification plant is the smallest surface water treatment plant of Tampere Water. The amount of water purified in year 2005 was 21483m^3. From which 21066 m^3 was pumped to distribution network. This was 0,11% of city of Tampere consumption on that year. (25)

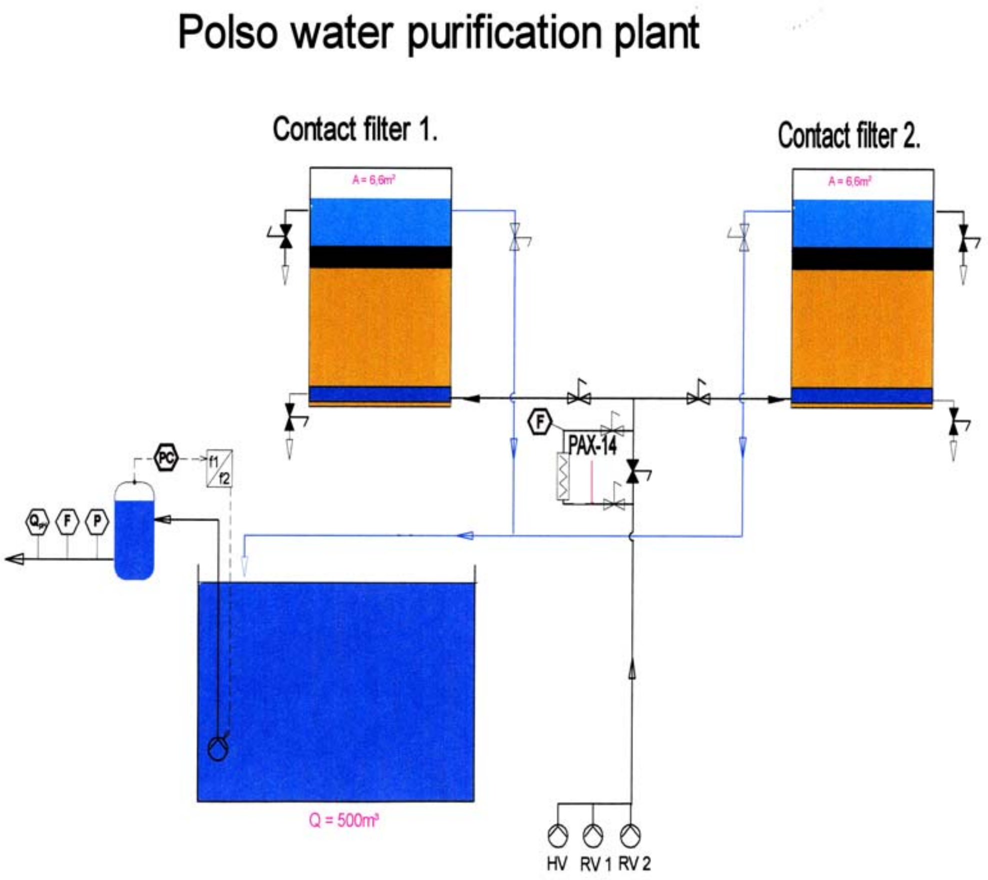

Figure 6.1. Schematic picture of Polso purification plant (source: Tampere Water)

7. Kauppi Horizontal sedimentation plant

The water treatment method used at Kauppi treatment plant is horizontal sedimentation which is followed by sand filtering. Kauppi drinking water treatment plant is used as back up plant at the moment. It has been collecting water from Lake Näsijärvi and it still does. However, since some decades ago the condition of water in Lake Näsijärvi was a lot worse than it is today, Lake Roine has become the biggest source for raw water utilized by Tampere Water. Nowadays the load of pollution from industry around Lake Näsijärvi is not so heavy anymore Näsijärvi serves as good source for raw water. Kauppi treatment plan has old technique and would need to be updated to meet today’s methods. It can be said that Kauppi water purification plant has a lot of potential and it will be interesting to see how it will be utilized in the future. However before it could be taken in everyday use, some investments must be made to modernize the system at the plant.

8. Coagulation

In coagulation, the attachment of small particles to one another and to surfaces is promoted in aquatic environment (14), thus the repulsive potential of electrical double layer of colloids is reduced to produce micro flocks, which are larger aggregates. When micro flocks collide they form aggregates which are larger structures, and are generally stated as flocks. Inorganic coagulants which normally are iron or aluminium salts are added to provoke chemical coagulation (16). This process is necessary to remove particulate matter which is too small in size to settle by gravity in sufficient time frame (13), with the color and microbiological contaminants such as bacteria, viruses and cysts. (14).

In processes of coagulation and flocculation, three main mechanisms take place where the removal of organic matter is provoked. They are listed to be colloidal destabilization, precipitation and co precipitation, where colloidal destabilization stands for coagulation. In lots of literature, the distinct difference between the terms coagulation and flocculation is seldom clearly clarified (13).

There are several reasons why the dosage and pH should be optimized for each water purification plant. For example, the amount and type of coagulant which is in use can have great effect over the conditions and amount of residues, which have a great impact on the costs of treatment and environment. Those aspects must be considered when selecting the right coagulant and its use. In enhanced coagulation, pH is adjusted at the optimal level, which will significantly reduce the necessity of high dosages of coagulant. (13)

There are certain parameters that effective coagulation is dependent on. They are the dosage and type of coagulant (15), feed concentration of coagulant (1), final pH, temperature, intensity and duration of mixing (1). The coagulant dosage is dependent on the high humic content of natural water (11) and in general is proportional to the colloidal charge in the raw water (11). Optimum pH has often stated to be 5-7 or sometimes when using aluminium salts and, for iron salts slightly lower (5-6) (11). In coagulation, the pH has great effect on inorganic coagulation species and the dissociation of the humic and fulvic acids. (11). The demand for coagulant is often decreased at lower pH values, because of the increasing protonation of organics, and more positively charged coagulation species. Consequently the coagulant dosage required becomes less due the enhanced adsorption in the ideal pH. (11). Under very low pH, precipitation may reduce, or reduce partially, following of enhanced charge neutralization and co precipitation by adsorption. (12).

Coagulation aids are sometimes used, often to adjust the pH. The most common acid used in this purpose is sulphuric acid and as a base lime is most common (12).

The impurities that require the consideration must be followed; in this water was analyzed for turbidity, UVA254 for DOC, TOC and residue aluminium after coagulation-flocculation process. The quality of water from natural sources varies due the seasons, and therefore needs testing during the changes.

In jar test method, coagulation can be referred as the rapid mixing phase of the process.

9. Flocculation

Flocculation is a stage that is rapidly followed by coagulation. When in coagulation the fine particles changed the electronic current to be dragged together, flocculation is a phase where the flocks begin to form from ever larger particles.

Flocculation happens in slower mixing stage. The particles are encouraged to form larger particles while the water is gently mixed. The mixing must not be too rough or the already formed flock will break up and therefore, become re-stabilized. Eventually flocks can then be removed by mechanical means of sedimentation, flotation or filtration through granular media (12), such as sand- and active carbon filter.

10. Coagulants

Polyaluminium chloride is used in flocculation at Kämmenniemi and Polso water purification plants. In Kauppi, aluminium sulphate is used. The respective coagulants were used in the analysis in this project by testing the effect of the coagulant dosage with jar test method. The results were represented as concentration of aluminium in water, mg/l.

10.1 Polyaluminium chloride PAX-14

$(Al(OH)_{1,5}(SO_4)_{0,125}\ Cl\ _{1,25})n$

Polyaluminium chloride is partly hydrolyzed aluminium chloride with small amount of sulphate added to it. It is suifigure coagulant especially if raw water is found turbid. This is because it has higher efficiency over the process in comparison to other products on the markets (1). Polyaluminium chloride used was a product of Kemwater and has commercial name of PAX-14. It is yellowish solution and has 7,2 % of aluminium (Al^{3+}). Polyaluminium chloride is not as sensitive to changes of pH in comparison to other coagulants. Also, like some polycations it contains high positive charge which gives it high efficiency when neutralizing negatively charged colloidal particles in water. (22) The rest of the characteristics are presented in the figure 10.1

Chemical and physical information	
Presence	Yellowish solution
Al $^{3+}$	7,2 ± 0,3%
Active compound (Me $^{3+}$)	2,7 ± 0,1 mol/kg
Iron (Fe $^{3+}$)	<0,02%
Chloride (Cl^-)	22 ± 2 %
pH	<1,0
OH/Al	0,7 ±
Density	1320 ± 50 kg/m^3
Viscosity	24 cP

Figure 10.1. Kemwater PAX-14 product information

10.2 Aluminium sulphate

$Al_2(SO_4)_3$ x $14H_2O$

Aluminium sulphate is probably the most common used coagulant. It has aluminium oxide concentration of about 14-18% (1)

11. Chemistry of Aluminium

When aluminium is added to solution, it will begin to form hydrated reaction products (1), which means that one or more hydrogen ions are released when electron densities are drawn in the direction of central metal atom and oxygen-hydrogen bond becomes disturbed (13). Trivalent aluminium ions are formed, and ion forms compounds with water ion. (13, 1).

There is debate between the scientists of the exact nature of hydrolyzed species (13, 1), suggestions of forming of monomeric species of aluminium is presented in the figure 11.1

Species	**Reaction**
Al^{3+}	$Al(OH)_2(s) + 3H^+ \rightarrow Al^{3+} + 3H_2O$
$AlOH^{+2}$	$Al^{3+} + H^2O \rightarrow Al(OH)^{2+} + H^+$
Al(OH)2+	Al3+ + 2H2O→Al(OH)2 + + 2H+
Al(OH)30	Al3+ + H2O→Al(OH)30 + 3H+
Al(OH)4-	Al3+ + 4H20 →Al(OH)4- +4H+

Figure 11.1 Hydrolysis reactions of Al(III)(Dentel and Gosset 1988, Stumm and Morgan 1981)(14)

Also polymers are formed and three suggestions for those have been $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and also $Al_2(OH)_2^{4+}$ is detected (12). Different varieties are dependent on the pH or the concentration of OH^- ions in solution (1). Adding of coagulant or rising pH of solution will decrease the charge in the metal ions. (14). This means that all the desirable results of these reactions take place in defined range of pH which is dependent on the nature of the water (3), and is often found to be in range of 5-7. (3).

The hydrolysis reaction for the first one can be written

$Al(H_2O)_6)^{3+} \Leftrightarrow (Al(H_2O)_5OH)^{2+} + H^+$ (1)

12. Jar tests

The method of jar testing is popular among the research made to study the efficiency of coagulants (13, 14). The samples were analysed as soon as possible after taking the samples or else stored at + 4°C. Because both of the coagulants used here are acidic and therefore cause a drop in pH, the pH was to be adjusted subsequent to adding of the coagulant dose. Lime solution was used to raise the pH which is prepared at Rusko water treatment plant in daily basis.

Flocculator 2000 produced by Kemira for flocculation testing was use as laboratory coagulation-flocculation device. Flocculator 2000 has 6 parallel agitators and cylindrical glass beakers which allows 6 simultaneous analyses to be done. In this study, triplicate sampling was used to ensure the quality of the results. Therefore, 2 total analyses could be completed at once.

Beakers of 1l were filled with 600ml of sample water following with desired dosage coagulant. The last step before agitation was to adjust the desired pH. Agitators were then placed on the decanters and samples were agitated with the set period of time. All the samples were agitated equally and let settle for 1 hour. For the effect of agitation, separate tests were done.

The Flocculator 2000 allows programming of the agitation by microprocessor controlled agitators. In this project, following agitation program was used (which later on is referred as “normal settings”);

1 min 250 rpm (fast mixing)
15 min 50 rpm (slow mixing)
1h settling

After the settling period, necessary volume of sample for each analysis of residues was carefully pipetted from the surface of the flocculated water. It was ensured that settled flocks were not disturbed in the process.

During the first stage the optimal pH was to be found. 600ml of test water was transferred into 1000ml beaker. Predetermined dosage of coagulant was added, which was that dosage which is currently set for each water purification plant (Polso 55mgl^{-1} / PAX 14, Kämmenniemi 65mgl^{-1} / PAX 14, Kauppi 55 mgl^{-1} / Aluminium sulphate), and the desired pH was adjusted before agitation described above took place with continuous pH measurement.

The optimization of the pH was based on the results attained from following analyses of Al, TOC, UVA-254, turbidity and HPSEC. The optimal dosage was found following the same procedure but while adjusting the pH continuously on the optimal level the dosage of coagulant was to be decreased.

13. The effect of pH

There are two different mechanisms affecting the optimal pH to be found. Firstly the pH has a great effect upon the hydrolysis process of monomeric aluminium species (20, 1), which means that the solubility of aluminium to the water is dependent on the pH. Aluminium is estimated to be least soluble at pH 6,2 (13).

Secondly adjusting the pH will affect the charge on humic substances due to protonation reactions. When the pH decreases, the charge on the humic substances will decrease, effecting the stability of the colloids (1). At the optimal pH less coagulant is needed to form insoluble complexes or to neutralization (20), thus, the lower the dosage of coagulant, the more sensitive the floe is to the changes of pH. It is also possible that if pH is too high (above 6), colloids in water will re-stabilize.

It is not evident that both solubility of aluminium and the charge decrease of humic substances, are optimal at same pH, but can vary for different parameters. Therefore, in some cases, range of pH can be proposed instead of one exact value, or, optimal pH is chosen as the result of cumulative analyses. This kind of results can be found also in this research.

14. NOM (Natural organic matter)

Large part of the natural organic matter is derived from terrestrial ecosystems, such as soils and vegetation (16). The rest is from aquatic ecosystems. Most of the NOM is consumed by other organisms for the growth but some of it is not easily degraded and that fraction is accumulated in aquatic systems (12). Most often NOM is studied as a matter of TOC, total organic carbon (14).

There are three types of organic matter in natural waters, which are dissolved, colloidal and particulate organic carbon. (12,14). Most commonly the dissolved organic matter (DOM) is studied which can be defined as that fraction smaller than 45µm diameter (Standard Methods for the Examination of Water and Wastewater

1992), and is measured as the concentration of dissolved organic carbon, DOC (13).

Colloids are particles with size of 10^{-8} – 10^{-6} m of diameter. Particulate NOM (particulate organic carbon; POC) are organic particles such as plant debris and inorganic particles absorbed into organic particles (14), whereas TOC is DOC and POC together. (13)

DOM can be derived in six fractions, which are hydrophilic acids, bases and neutrals and hydrophilic acids, bases and neutrals (15). Colloids can be hydrophobic and hydrophilic and are micro particles or macromolecules. They are small enough to have Brownian motion (14) which gives pericinetic aggregation where suspended particles with small size are assumed to have continuous random movement, or Brownian motion which is given by Stokes-Einstein equation (4**.)**

$$Di=kT/(6\pi ai\mu)$$

Where k stands for Boltzmann’s constant, T for the absolute temperature, ai for the radius of a particle and μ for the viscosity. (4)

NOM can also be divided into humic and non-humic fraction where humic fraction is hydrophilic and non-humic fraction is less hydrophilic in character. (11, 12) In the context of coagulation, humic substances have strong effect on coagulation, since they are macromolecules containing both colloids and dissolved substances (14).

Fraction	**Chemical group**
Hydrophobic	
Strong acids	Humic and fulvic acids, HMM alkyl monocarboxylic and dicarboxylic acids, aromatic acids
Weak acids	Phenols, Tannins, IMM alkyl monocarboxylic and dicarboxylic acids
Neutrals	Hydrocarbons, aldehydes, HMM methyl ketones and alkyl alcohols
Hydrophilic	
Acids	Hydroxyl acids, sugars, sulfonics, LMM alkyl monocarboxylic and dicarboxylic acids.
Bases	Aminoacids, purines, pyridines, LMM alkylamines
Neutrals	Polysaccharides, LMM alkyl alcohols, aldehydes, ketones

Figure 14.1. Fractions of NOM and their chemical groups (16).

Humic substances are defined based on their isolation (16) with acids and bases. After alkaline extraction humic remains, after acidification, humic acid precipitates and the organic material remaining in solution is called fulvic acid (16). Last to are the major constituents of any NOM sample from aquatic environment (16), thus fulvic acid is more soluble than humic acid (13).

Molecules of humic substances can differ, although can have group of similar building blocks. There are several hypothetical structures for the chemical composition of humic substances.

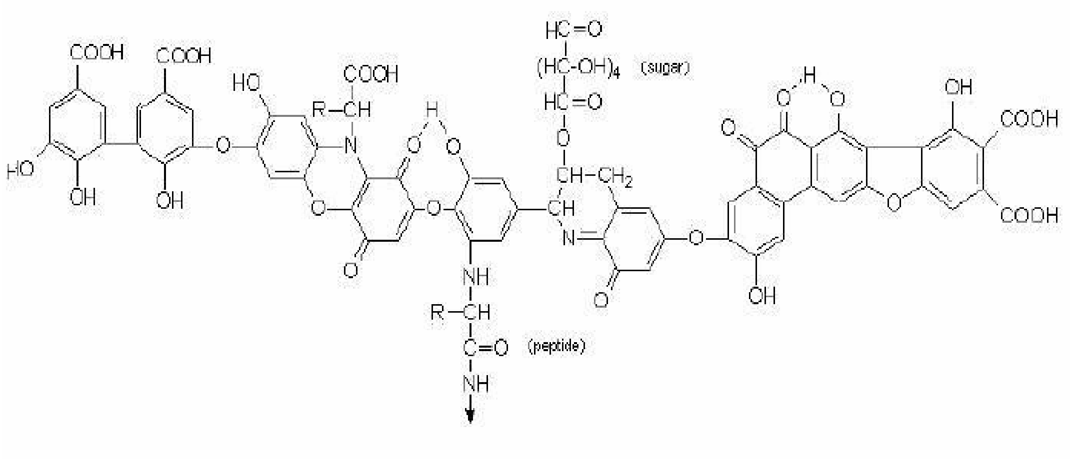

Figure 14.1. Proposal for humic acid structure in aqueous environment after Stevenson, 1982. (16)

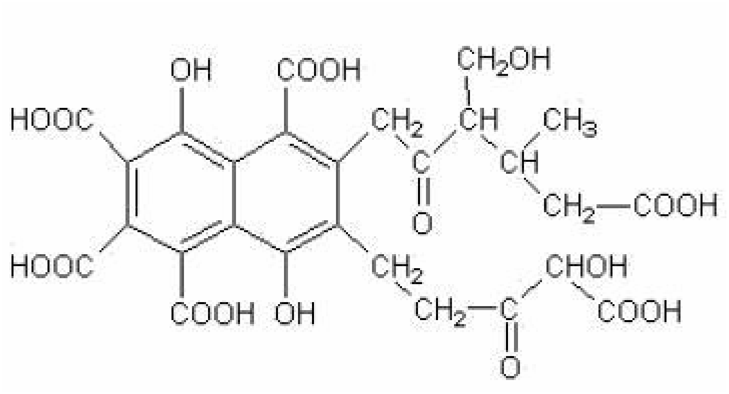

Figure 14.2. Estimated structure for humin acid acquired from Buffle 1997 (16)

Size of the humic substance has effect on efficiency of coagulation and removal by other means of water treatment processes (16) . Size can also effect adsorption of humic substances onto minerals such as activated carbon and partitioning of organic pollutants.

Of the parameters studied here which are TOC, UVA254, turbidity and HPSEC MSD, represent both qualitative and quantitative information of concentrations of NOM in water.

15. The effect of mixing

In most of the studies investigating flocculation, both rapid phase of mixing and slow phase of mixing has been utilized. Many studies carried out by different scientists show that the time used for mixing had significant impact upon the charge neutralization of the system (8) as well as other mechanisms that take place in coagulation-flocculation.

The time used for rapid mixing phase has impact on the destabilization of the colloidal structures and the aggregation of the particles in the slow-mixing phase (8). In order to simplify the previous, rapid-mixing can be referred as coagulation and the slow-mixing as that part of the process where flocculation takes place.

16. Sedimentation

After mixing tests the samples were left to settle for the sedimentation to take place for time period of one hour. This period of time was found to be long enough for the flock have settled reasonably efficiently on the bottom of the beakers. Obviously, any longer sedimentation time period would give better results especially in turbidity measurements, but one hour is time effective enough for this project. After the flock inside the beaker has been settled it is clearly visible as dark yellow substance.

After sedimentation the water sample for the measurements is taken carefully from the surface of the beakers. The flock settled on the bottom can easily become disturbed and mixed again with the water. Therefore it is the most crucial that water is taken from the surface of the sample in a careful manner. It is also important that the beakers are not accidentally shaken during the sedimentation or sample collection.

17. The effect of temperature

In many studies, as well as in practice, it has been noticed that flocculation is several times more effective with higher temperatures than it is at lower temperatures. This phenomenon is more likely to be due to physical than chemical factors taking place in the process.

As the water temperature decreases the stage of the water changes towards freezing which consequently has effect on the viscosity of the water, which is found to be one of the important factors that change the effectiveness of flock formation in coagulation and flocculation systems.

Mpofu et al, 2004, studied effect of temperature upon flocculation of kaolinite dispersions. They found that supernatant polymer viscosity and hydrodynamic diameter of polymers decreased with increased temperature. They also found that the optimal temperature for coagulation is 20^{o}C.

Kang et al, 1995, studied effect of low water temperature on flocculation kinetics by flocculation of kaolin clay with ferric nitrate. They found that low water temperature has a pronounced detrimental effect on flocculation kinetics, which would lead to decreased performance in comparison to the performance at room temperature.

18. Limit values

Social- and health ministry of Finland have set regulations concerning concentrations of different substances in municipal drinking water. The following statement is from degree 461/2000 by Ministry of social and health “Drinking water must not contain micro-organisms, parasites or any substance in such concentration that will be dangerous to human health”. (5)

In this study the focus is on the recommendations, since regulations for drinking water do not exist in case of most of the water quality parameters covered in this study, such as residue TOC or aluminium. Instead of that, only recommendations have been set. Generally, companies which offer drinking water purification services are following these recommendations as they would have been set as regulations.

Recommendations for the drinking water are always applicable only to the water that is ready to be led for the people to use, which also means that the recommendations do not have to be yielded yet at the coagulation and flocculation phase. However, the results gathered during this thesis study are being compared particularly to these recommendations, in order to achieve as realistic results as possible, and find such conditions for where the least strain would be set to the subsequent water treatment, furthermore, where more organic matter could be removed trough coagulation and flocculation while as little concentration of residue aluminium as possible would be present in the water.

The limit values set by Ministry of social and health are presented in figure 18.1.

Substance	**Max concentration**	**Remark**
Aluminium	200 µg/l	
Turbidity	To be approved by water users and no unusual changes	
TOC	No limit value	1
Color	To be approved by water users and no unusual changes	

Figure 18.1 Limit values concerning drinking water.

Remarks

1: TOC concentration has no limit value. During the preparation of the directive limit value of 4,0mg/l was proposed, but was not confirmed. Therefore that concentration in question may be considered as a limit value. TOC is to be decreased because it forms organic chlorine compounds with chlorine and organic chlorine compounds have harmful health effects.

19. Analytical methods

Several different parameters, namely TOC, UVA245, turbidity and HPSEC were studied to find the efficiency of coagulation and flocculation process in different kinds of circumstances. These parameters stand for the residue organic matter in water. In addition concentration of residue aluminium had to be analyzed to adjust such circumstances where aluminium coagulants would be least soluble, and yet most effective to remove NOM from water.

After the coagulation and flocculation was over, water samples were collected for each analyze from the subsurface of the water, no more than from the depth of 2 cm. Samples were always collected in same order to avoid fluctuation in the results due the settling trough time.

19.1 TOC (Total organic carbon)

TOC (total organic carbon) is an useful measure of quantitative and qualitative information about presence of organic matter in water. It is an indirect measure of organic carbon atoms in water but it does not present any information about the nature or structure of the organic matter. Generally it exists in natural water due to humic substances and degraded matter from animals or vegetal sources. TOC can also present fertilizers, pesticides and such in contaminated waters. (28)

Organic carbon is analyzed by combustion of the sample in a presence of catalysts, and is represented as carbon dioxide formed in the combustion. Carbon dioxide is measured with IR-spectrophotometer. Inorganic carbon (IC) is removed from the sample as carbon dioxide from acidified sample. Thus, TOC is obtained by subtracting concentration of IC from the concentration of TC (23). The error in the analyze can be increased due to the evaporation of some organic compounds. (10) Here TOC is tested with Shimadzu TOC5000 (A), which utilizes combustion non-dispersive infrared gas analysis method and high purity air as a carrier gas.

19.2 TOC Measurement

The samples are collected from near the surface ensuring that they are presenfigure and do not have contamination of other organic sources. 100µl of strong hydrochloric acid is added to each sample before analyze. Sample is placed into auto sampler with the blank sample in the beginning and utilizing 3 minutes period for bubbling the sample with synthetic air to remove IC. This procedure follows the standard method SFS –EN 1484 used at Rusko laboratory.

19.3 Molecular weight distribution and high performance size exclusion chromatofigurey (HPSEC)

High Performance size exclusion chromatofigurey (HPSEC) is used to determine the molecular weight distribution of organic matter in water. It is useful tool in optimization of water treatment process. Possibly UV-specific detector is used. (16). The primary theory of the size exclusion chromatofigurey is based on size differences of molecules. HPSEC is a high performance liquid chromatofigurey applied with SEC (size exclusion chromatofigurey). Advantages of HPSEC are that it is relatively fast in comparison to previous methods and pre-treatment of sample is not required. Also, very small volume of sample is enough for detection. In the column silica and polymeric gels are used due to their low reactivity. However it is possible that some charge repulsion effects occurs during the sampling as well as interactions with the organic compounds. (16)

The charge and the structure of organic matter in sample water can be effected by the eluent used in the analysis, thus it is the most important that the choice of right eluent is done. Even tough manufacturers recommend distilled water for the mobile phase, many studies show that it is not the most convenient for the Finnish surface water samples. Instead of distilled water, 10mmol sodium acetate is used giving resolution that can be used, since it will show the profile distinct to the sample itself, which is hardly possible with other eluents. (16)

For detection, it is most common that UV-vis detection with wavelength of 254 is used. They are easy to use and fast and generally available in normal laboratories. Regardless of few disadvantages, currently it is the most feasible method in comparison to others, such as exsiccation emission matrix fluorescence detection or online DOC analyzer (16).

Standards used for the measurements are chosen by the hypothesized structure of the NOM in the sample. Globular protein standards can be applied, but are not the most recommendable due to the over-prediction of NOM fractions. Instead of them, random coil structure standards are used because NOM molecules often have similar shape. Such standard is, for example, polystyrene sulphonate (PSS). The results are found to be most reliable since they are equal to established methods which are vapor pressure osmometry and field flow fractionating. (16)

19.4 HPSEC measurement

HPSEC analyses were conducted in order to determine the NOM MSD (molecular size distribution). The samples were filtered with a Gelman 45µm membrane and fractionating of the size exclusion was run with Shimadzu LC-20A system with a TSKgel G3000SW 7,5mm (ID) x 30cm column. Eluent used was sodium acetate (0,01 M) with flow rate of 1ml/min. The volume of the injected sample was 30µl. The same method is used at Rusko laboratory.

The values are found by calculating the height of the chromatograms peaks. The height of the peak can be referred as the amount of NOM in particular fraction of molecular size. (16). The peak with the lowest retention time reflects the highest molar mass whereas the peak with longest retention time reflects the lowest molar mass. Total amount of NOM in the sample can be found from the sum of the heights of all of the peaks. (16)

There are 7 peaks in general chromatogram, largest of them being the peaks III, IV and V. They represent molecules which are smaller than 3000 Da. (Active carbon filter books from Tampereen Vesi)

The sizes of the peaks are presented as Daltons (Da). Peak I represents the molecules lighter than 5000 Da, Peak II represents MW 4000-5000 Da, peak III is 3000-4000 Da, peak IV 1000-3000 Da, peak V is 500-1000 Da. Peaks VI is derived from peak V after processing of the water as well as peak VII which is present only from April till end of August. This information is based on the records of Rusko laboratory.

19.5 Turbidity

Turbidity indicates the clarity of water while it can not be referred as color in water. Suspended materials tend to increase turbidity in water. This can include all kinds of impurities such as silt, bacteria, algae, viruses, macro-molecules, which means all kinds of material derived from organic soil matter, etc. Turbidity is measured with the amount of light passing through a sample of water. (1)

Solids found in drinking water reduce effect of chlorinating and give a way for the growth of undesired micro-organisms. Therefore, high concentration of suspended matter is not acceptable in drinking water.

In this study, turbidity was measured with HACH 2100 AN IS turbidity meter. Results are shown as NTU (nephelometric turbidity unit),where N stands for nephelometry.(21)

Nephelometric turbidity meters are designed to distinct also very low concentrations of turbidity in water. The detection angle is 90^o which is found to be very sensitive for particle scatter. The name nephelometer or nephelometric turbidity meter is used to distinguish them from generic turbidity meters which utilize the measurement of the ratio of transmitted to absorbed light. (21) In figure 19.1 theoretical functioning of nephelometric turbidity meter is being presented.

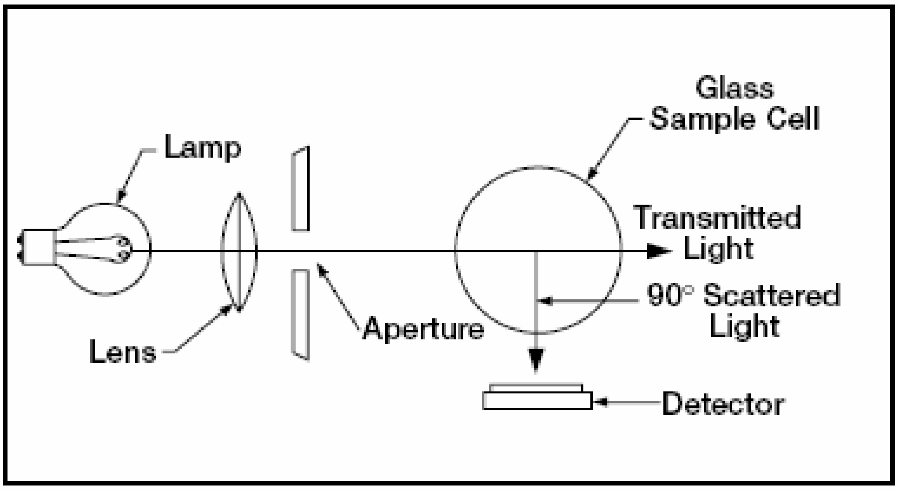

Figure 19.1. Schematic drawing of nephelometric turbidity meter. where turbidity is determined based on the light scatter at 90° angle from the incident beam (21)

19.6 Aluminium

There is always some undesirable aluminium remaining in the samples after the coagulation. At different pH levels, aluminium is more soluble than on the others. To achieve quantitative information of the remaining Al it was analyzed by means of photometry. The method is based on the standard method SFS 5763 (*Veden happoliukoisen alumiinin määritelmä*) used by Tampere Water, which is suitable to analyze aluminium from drinking water which is treated with some alum coagulant. All the samples were diluted 1:10 due the high concentrations of aluminium in them which is normal at this stage of water purification. (Information is based on the results attained at Rusko water laboratory from the samples which are collected from the flocculation stage from the plants)

Heating of the 25 ml of each diluted sample brings the monomeric, inorganic and organic complexes, polymers and aluminium adsorbed into particles to react with pyrocathecol. Preserved with acid, sample is heated for 20min in an incubator and left to cool down. When the reagents are added, the present aluminium with pyrocathecolsulphonalein forms a blue solution, with pH in range of 6.1 to 6.2. The measurement is done with the wavelength of 580 nm and the results present the concentration of aluminium as mg/l. The maximum error in the results is given as 5%.

19.7 UV-absorbance

Natural dissolved carbon (DOC) is commonly predicted with photometric methods by using the wavelength of 254 nm. (UVA254) Also, it's reactivity to form disinfection by-products can be predicted. There is a possibility for some other compounds present in analyzed sample to contribute in the measurement. UVA254 is an easy measurement a simple and very fast way to provide accurate quantification of organic carbon in water.(2)

UVA254 gives the proxy of aromatic content of dissolved organic carbon (DOC) , which is mostly humic material, in water (14). Aromatic carbon is highly reactive during the chlorination of water in water purification systems. (2)

20. Results: Optimal pH

As for the aim of the study, for water samples from each water purification plant, optimal pH to remove NOM was to be found. Also, the solubility of aluminium had to be considered, thus, the optimal pH was that pH where the values were the lowest possible for each analyze. In this project, the results for TOC and aluminium analyses had priority to other analyses which were the turbidity- and UV254 analyses.

The results of the analyses are presented in the figures below. The pH were the figure shows the lowest values for all the analyses, or at least for TOC and the residue aluminium, were chosen to be the "optimal pH" for the process.

Treatment plant	Optimal pH found	Dosages tested
Polso	5,5	50g/m^3, 55g/m^3
Kauppi	5,7	50g/m^3, 55g/m^3
Kämmenniemi	6	65g/m^3, 50g/m^3

Figure 20.1. Optimal pH levels found for each plant

20.1 Optimal pH for Kämmenniemi

The results for the analysis for the water collected from Kämmenniemi water purification plant are presented in the figures below. The TOC was lowest at a pH 6 but did not rise when pH increased. All the other parameters follow closely the same form. The results from aluminium analyses are presented in figure 20.2. Regarding these results aluminium becomes less soluble at higher values of pH which is typical for metals. Results from residue aluminium analysis and turbidity analysis gave similar results which can be seen similar shape curves from the figure 20.1, thus both aluminium and turbidity were at lowest at pH 6. Also, regarding these figures and giving the TOC and Aluminium the primary position in selecting the optimal pH, optimum results were attained when coagulation took place at a pH 6. A pH 5,7 also gave fairly good results, but at pH levels lower than that the results were no longer acceptable. Many the parameters show that especially at pH 5,5 the flocculation process were no more ideal. Similar results was attained with tests done with Kämmenniemi water at dosage of 50g/m^3 (Appendix), where pH 6 was found to be optimal considering TOC and residue aluminium being the priority parameters.

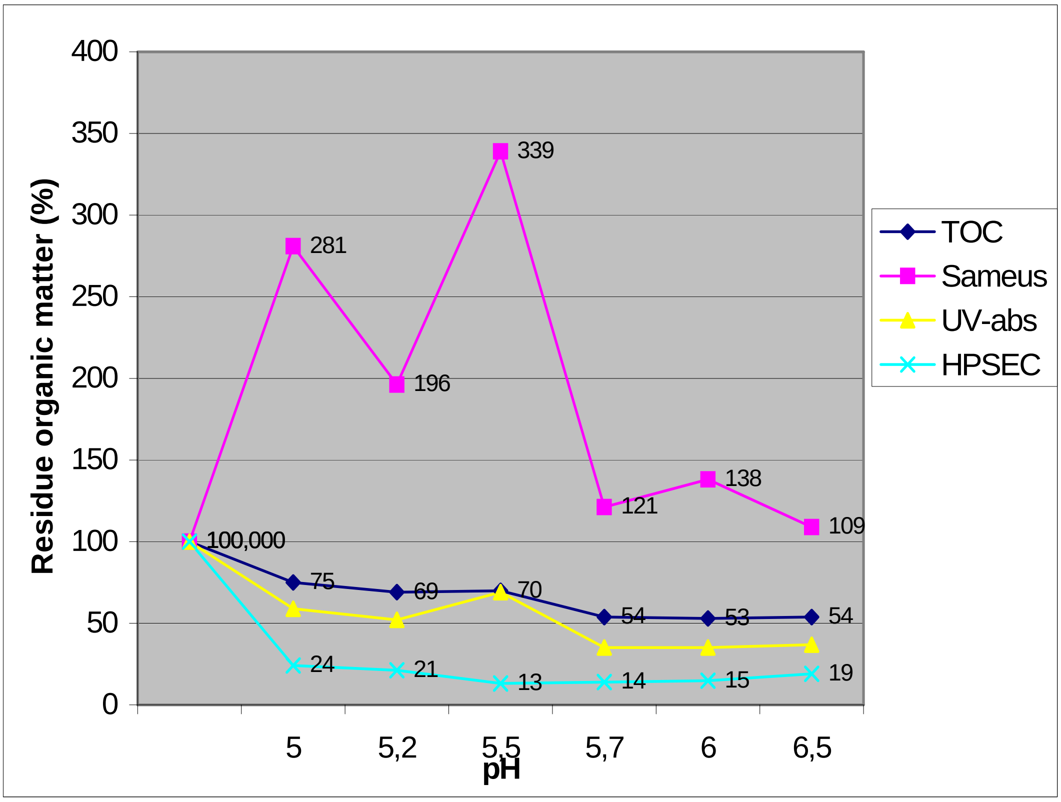

Figure 20.1 Percentage residues of different parameters with dosage of 65 g/m^3 of polyaluminium chloride where the 100% describes the amount of organic matter in Kämmenniemi raw water.

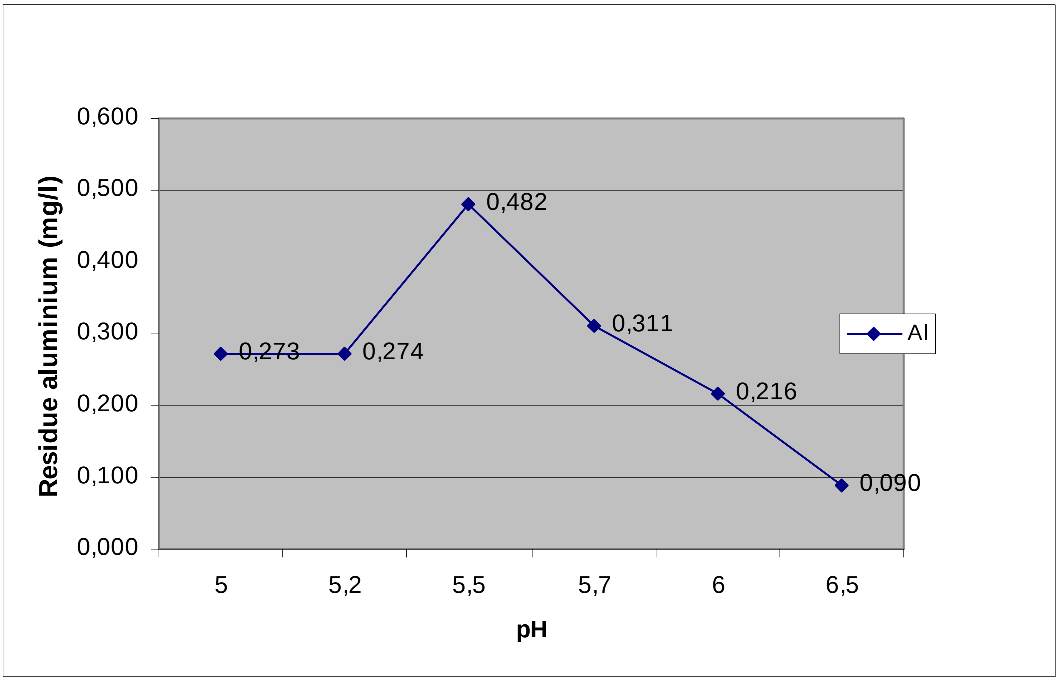

Figure 20.2 Residue aluminium for Kämmenniemi water at different pH values with dosage of 65g/m^3

20.2 Optimal pH for Polso

Polyaluminium chloride is used as coagulant at Polso water treatment plant. The optimal pH-evaluation was rather easy, because of the behavior of TOC and also other parameters.

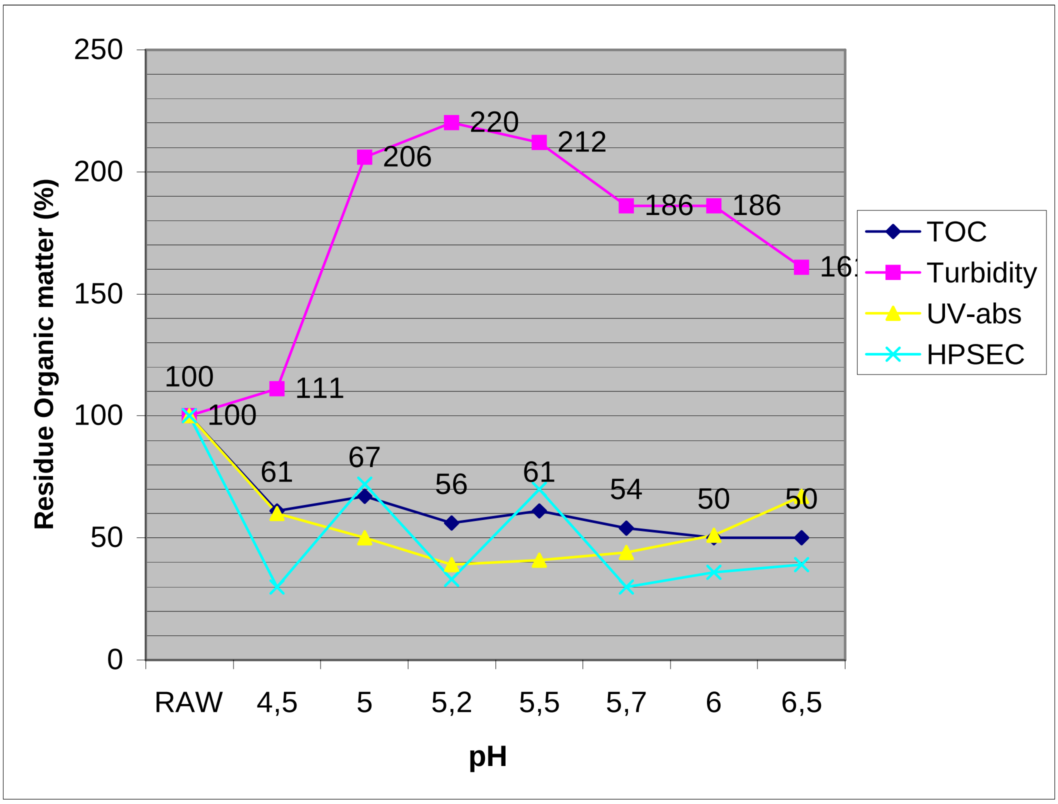

Figure 20.3 Percentage residues of different parameters after dosage of 50 g/m^3 of polyaluminium chloride where the "RAW" is the amount of organic matter in raw water from Polso.

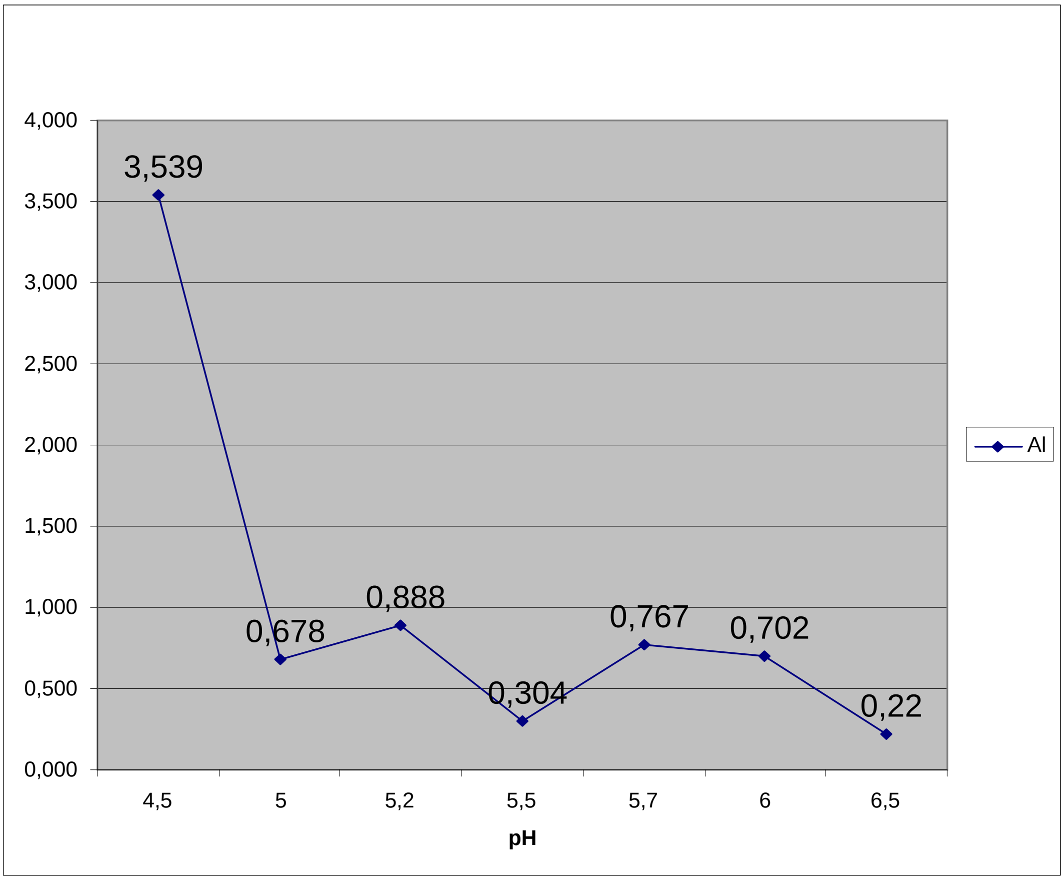

Figure 20.4 Residue aluminium at different pH levels with coagulant dosage of 50g/m^3 for Polso water (concentration is mg/l) .

In the evaluation of optimal pH-value it was found that at pH 5,5 that concentration of many parameters was efficiently decreased. TOC and UV-absorbance is at lowest and turbidity reaches the second lowest value when pH is 5.5. These results are presented in figure 20.3 for the residue organic matter and in the figure 20.4 for residue aluminium. Tests which were run with coagulant dosage of 55 g/m^3 support the proposal for the optimal pH.

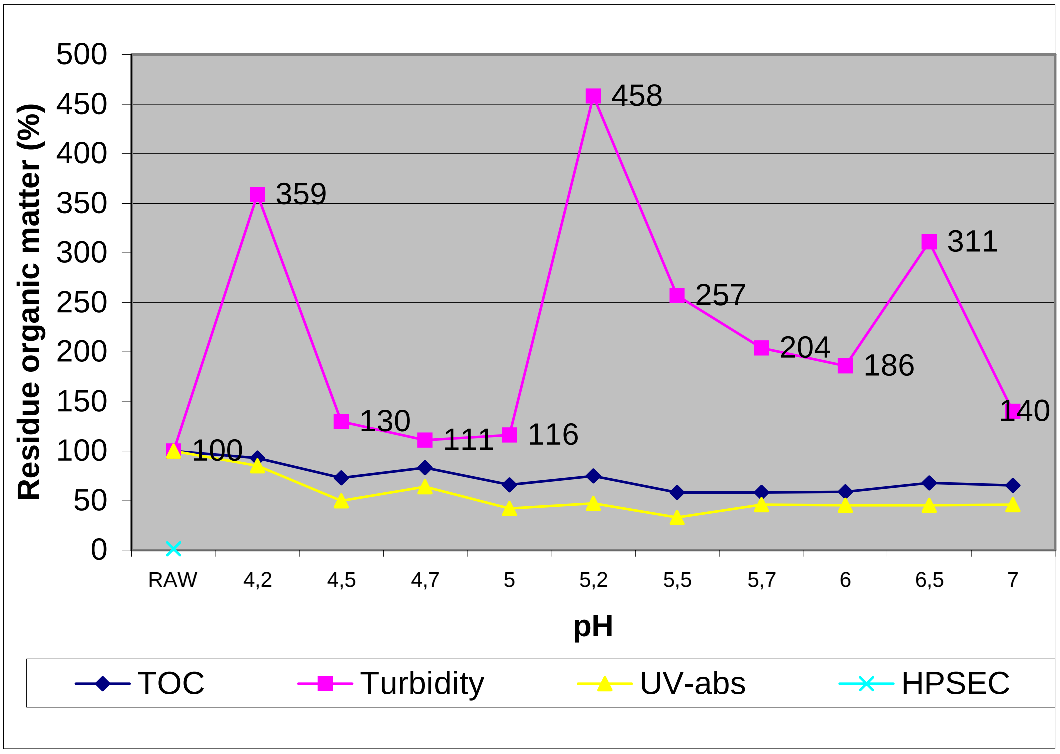

Figure 20.5 Percentage residues of different parameters after dosage of 55 g/m^3 of polyaluminium chloride where the "RAW" is the amount of organic matter in raw water from Polso. (HPSEC not available)

With the dosage of 55 g/m^3 more variation between the parameters has been found in comparison to the tests done with 50 g/m^3 dosage. Results from the analyses done for the tests with both dosages; 55 g/m^3 and 50 g/m^3 , are evaluated to facilitate the finding of optimal pH which was found to be pH 6.5. At dosage of 55 g/m^3 TOC is very low at pH 5.5. Turbidity becomes unstable at lower pH levels than pH 5.2 but while still resisting reasonably low level at pH 5.2. UV-absorbance is also found close to optimal at this pH value.

20.3 Optimal pH for Kauppi

Aluminium sulphate was used as coagulant for water from Kauppi water purification plant. The results for each parameter analyzed to find the optimal pH varied in range of 5.2 to 6. TOC was found to be the lowest at 5.7, turbidity at 5.5, UV 254 at 5.7 and Aluminium at 5.7. In this kind of situation it is difficult to determine an exact value for the pH, especially when the prioritized parameters are the most variable. However, it would be safe to maintain the pH at 5.7, where the

TOC is as low as possible in respect to the lowest aluminium result. Overall, all the results were found to be optimal at pH 5.7.

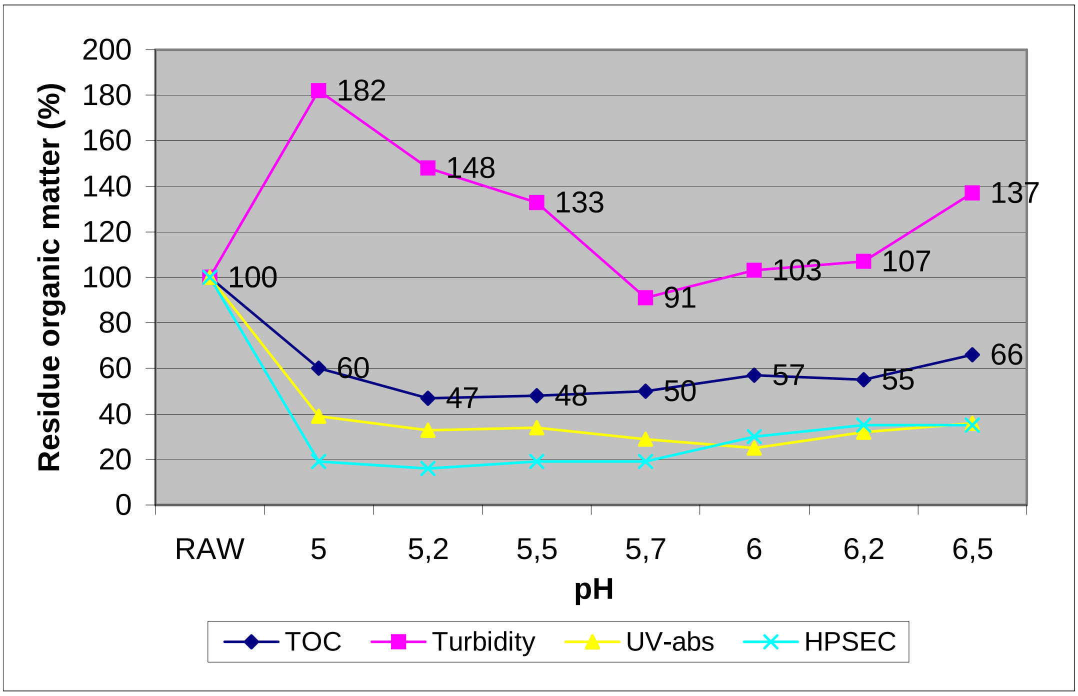

Figure 20.6 Percentage residues of different parameters after dosage of 55 g/m^3 of polyaluminium chloride where the "RAW" is the amount of organic matter in raw water from Kauppi.

The figure 20.6 presents the results of the tests done with Kauppi water. Based on those results, it can be noted that pH 5.7 are optimal for Kauppi water. At this particular pH value the amount of TOC is at lowest and also other parameters are found to be reasonably low.

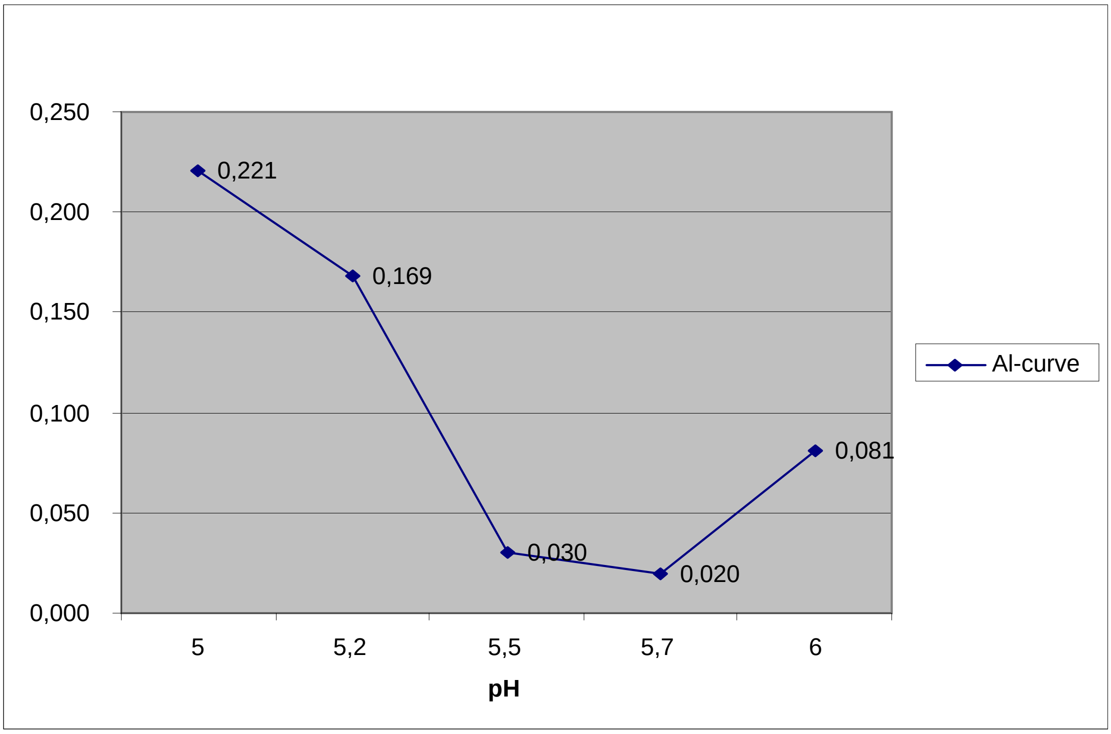

Figure 20.7 Residue aluminium at different pH levels for Kauppi water with dosage of 50g/m^3(consentration is mg/l).

The figure 20.7 for residue aluminium with coagulant dosage of 50 g/m^3 and variable pH values can be found to support the conclusion that 5.7 is indeed the optimal pH-value for Kauppi water.

To ensure that this conclusion is in fact correct, also several tests with dosage of 55 g/m^3 has been used to determine the optimum pH. Furthermore, pH-value of 5,7 was found to be optimal also with dosage of 55 g/m^3. It was found that TOC results are at moderate level, turbidity is at lowest and UV-absorbance is moderately low at optimal pH 5.7.

21. Results: Optimal dosage

The tests to find optimal dosage are conducted with a similar jar-test method as the tests to optimize the pH. In this section, pH was maintained at the optimal level previously found, and the tests were passed trough with smaller dosages of coagulant. The results for each water purification plant are presented below. The optimal dosage was in every case chosen based on the result where the dosage was the lowest possible while results for residue TOC, UVA254 and Turbidity would still resist at the same level or lower as with the original dosages at each water purification plant. Also, the residue aluminium in samples had to be minimal.

21.1 Optimal dosage for Kämmenniemi

At Kämmenniemi plant the coagulant dosage is generally higher than at the other water purification plants. Until now, the amount of polyaluminium chloride fed into the system has been $65g/m^3$. In the figure 21.1 presented below the concentration of TOC can be found along with the results of turbidity and UVA254 at optimized pH 6. These results can be found to give support to the expectations set by Tampereen Vesi where it was assumed that it is possible reduce the PAX-14 consumption also at Kämmenniemi plant.

As well as amongst themselves, results can be compared with the respective results of the raw water used at Kämmenniemi plant. The TOC levels at Kämmenniemi have been measured to be approximately 8,98. The value can vary trough the seasons. The advantage to conduct the optimization at spring-time is that the TOC levels are at the highest of that time of the year.

Raw water turbidity was measured several times and found to be between 0,250-0,550NTU. In the coagulation-flocculation process, the turbidity tends to rise due the interaction of the particles during the coagulation and flocculation and formation of larger flocks.

While looking at the figure below it is evident that decrease in the coagulant is appropriate and can be done. Minimum dosage giving applicable results from all TOC, UVA254 and turbidity is found to be $45g/m^3$. At low dosage as $40g/m^3$ the coagulation is no more taking place sufficiently which can be seen as a rise in both TOC and UVA254.

The results for the residue aluminium give important information as well, however it seems to be more difficult to understand the behavior of the aluminium with different dosages. The results for the residue aluminium analyses for the optimal dosage are presented in figure 21.1.

While the results do not give a symmetrical figure it can still be seen that when the dosages are decreased the residue aluminium also tends to decrease, although there is no uniform pattern supporting this conclusion.

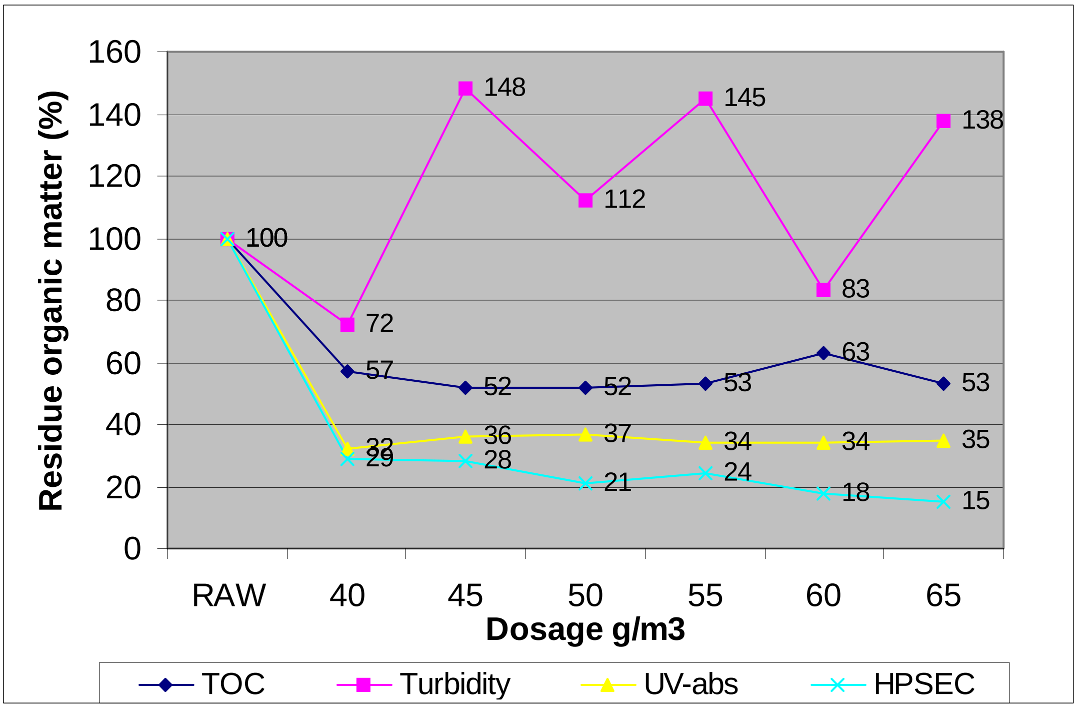

Figure 21.1 Residual organic matter at different dosages of polyaluminium chloride and at constant pH 6 for Kämmenniemi water.

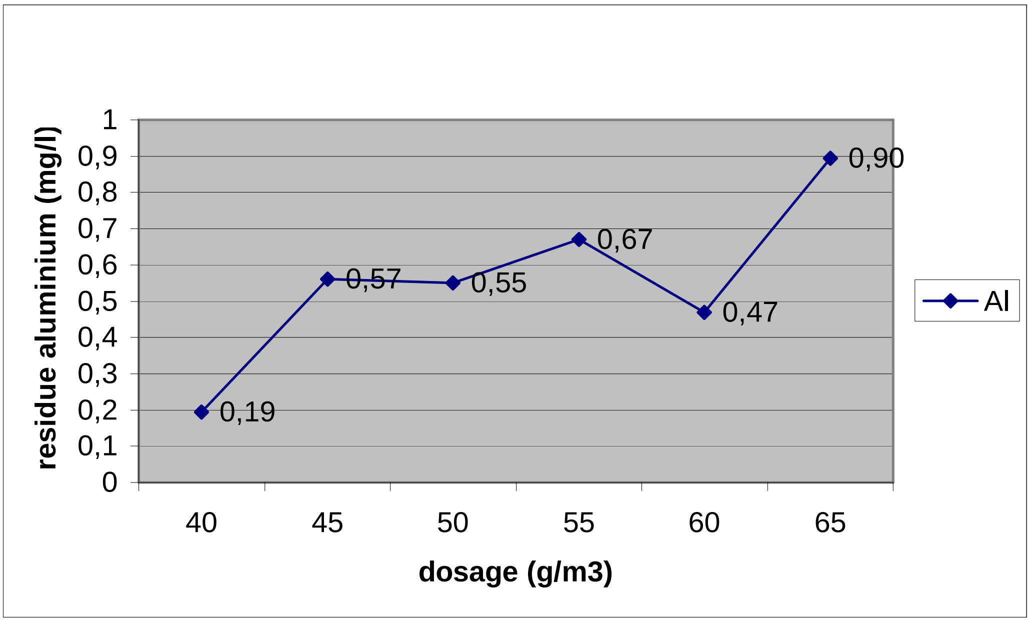

Figure 21.2 Residual aluminium at pH 6 for different dosages for Kämmenniemi water

21.2 Optimal dosage for Polso

To find optimal dosage for Polso Water Purification Plant tests were runned at optimal pH with dosages of 40, 45, 50 and 55 g/m^3, where the last dosage mentioned is the one currently used. The results from different analyses are presented in figures 21.3 and 21.4 for residues after coagulation-flocculation tests. In Figure 21.3, the residue organic matter is presented in comparison to raw-water. Respective results for raw water are presented as 100%, where TOC is 9.88mg/l, turbidity is 0.576 NTU, UVA254 is 0,351. These numbers are calculated as average of analyses conducted in weekly basis during the period from 7.2.2007-3.5.2007. Figure 21.3 consists of the concentrations of residue aluminium after coagulation-flocculation.

With coagulant dosage of 55g/m^3 and at optimal pH found to be 6,5 at Polso, after coagulation-flocculation the TOC was reduced to 68% (6,765mg/l), UV254 to 44% (0,152), and turbidity increased to 310% (1,79 NTU). Residue aluminium was 0,376mg/l which is well above the recommendation limit set by Finnish official.

Optimal results were achieved at dosages of 50g/m^3 and 45 g/m^3. With dosage of 45g/m^3 the residue organic matter was less but with dosage of 50g/m^3 the residue aluminium was lower. With 45g/m^3 TOC was reduced to 47% (4,670mg/l), UVA245 to 32% (0,110) and turbidity to 64% (0,37 NTU) but residue aluminium retained at 0,480mg/l. When coagulant dosage was set to 50 g/m^3, the residue TOC was found to be 49% (4,837mg/l), UVA245 to be 89% (0,227), and turbidity 161% (0,93 NTU) in comparison to raw water. Residue aluminium was 0,227 mg/l which from all the results is closest to the recommendation limit.

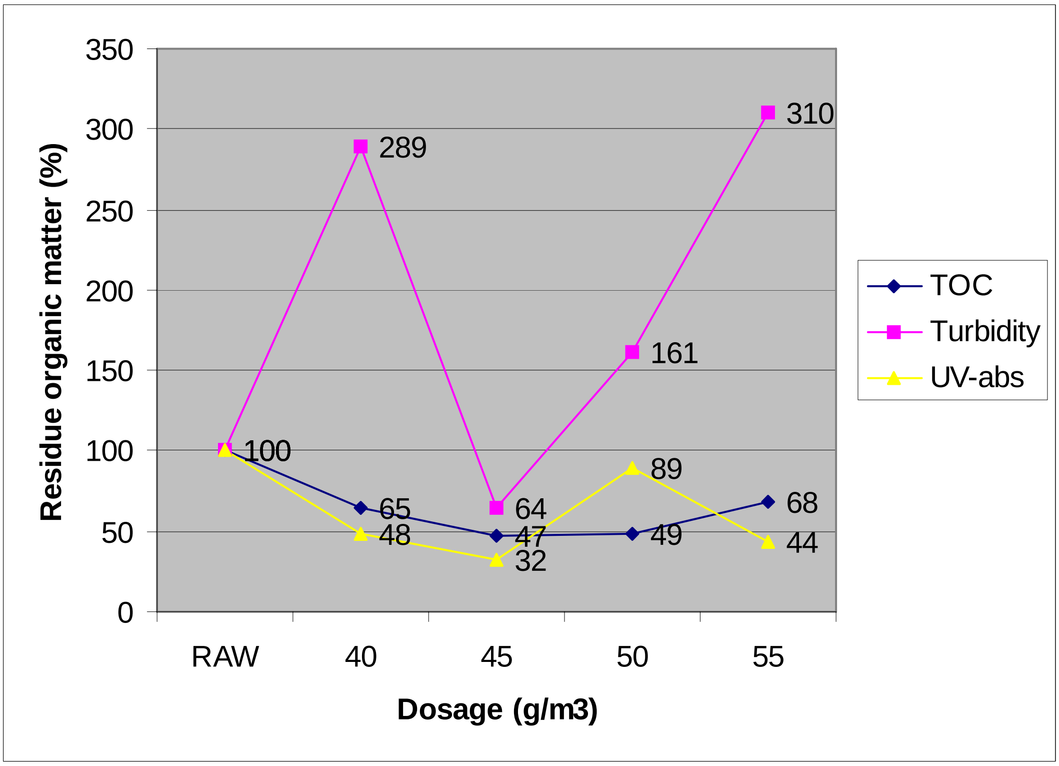

Figure 21.3. Residual organic matter after coagulation-flocculation process at pH 6,5 and with different dosages in comparison to respective results for raw water in Polso case.

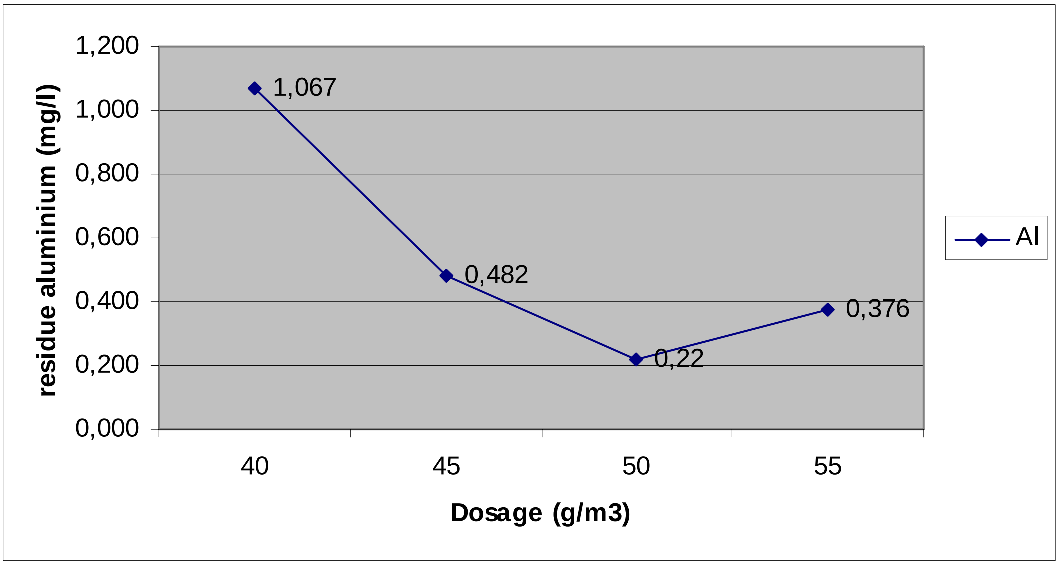

Figure 21.3. Residual aluminium after coagulation-flocculation process at pH 6,5 and with different dosages for Polso water.

21.3 Optimal dosage for Kauppi

At Kauppi, aluminium sulphate is used as coagulant and the dosage is currently 55g/m3, which was to be optimized. The tests were done at the optimal pH found to be pH 5,7 but the dosage was lowered in steps of 5g to find the optimal dosage. The results were compared to the respective results found for the raw water. The results for residue organic matter can be found in the figure 21.4 below presented as percentages where the respective result for raw water is 100%, where TOC is 8,177mg/l, turbidity 0,614NTU, UVA254 0,269 and HPSEC is 28996 mAU.

At current dosages it was found that the TOC can be reduced to 50% (4,061mg/l) from the TOC in raw water stated as 100% (8,17mg/l), Turbidity decreased to 91%, (0,55 NTU), UVA254 to 29% (0,078) and HPSECto 19% (5532 mAU). Residue aluminium in the samples was 0,315mg/l which is quite high result.

In comparison to the results found at the current dosages, and to the decrease from raw water tests runned at dosage of 50g/m^3 was found to be the most optimal. TOC decreased to 44%, turbidity to 90% UVA254 to 12% and HPSEC to 31% (6362 mAU) from the respective results of raw water. Residue aluminium was 0,199mg/l being the lowest result achieved in analyses and also below the recommendation limit set by Finnish officials. Thus, with coagulant dosage of 50 g/m^3 only results from HPSEC were higher than with dosage of $55g/m^3$.

With dosages lower than $50g/m^3$ the results were already rising above the results with current dosage apart from turbidity which was found lowest at dosage of 45 g/m^3(decrease to 65%). At dosage of 40 g/m^3, surprising results were found, where all the analyses gave very high results. Also, the affect of soluble aluminium towards turbidity can be noted from the figures. With small dosage of $30g/m^3$ too high concentrations of NOM was found after treatment.

Thus, optimal dosage was found to be 50 g/m^3 at pH 5,7 at Kauppi and is recommended to be used at the plant.

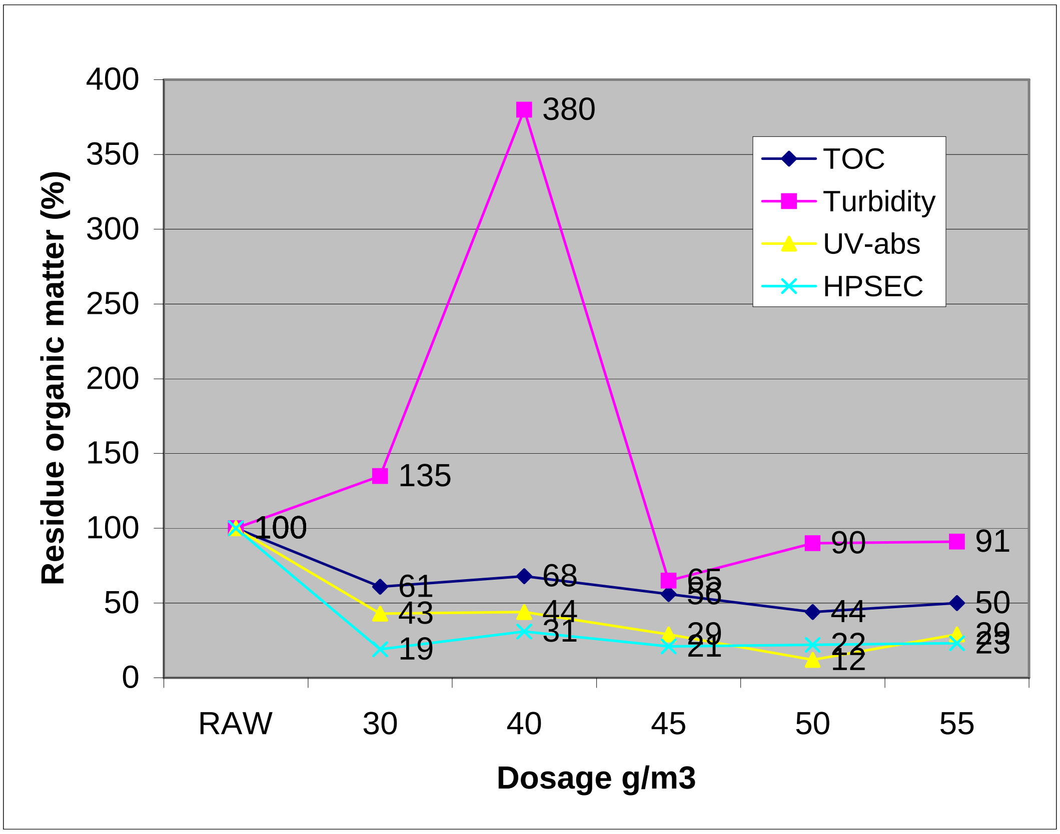

Figure 21.4. Residual organic matter at different dosages of aluminium sulphate and at constant pH 5,7 for Kauppi water.

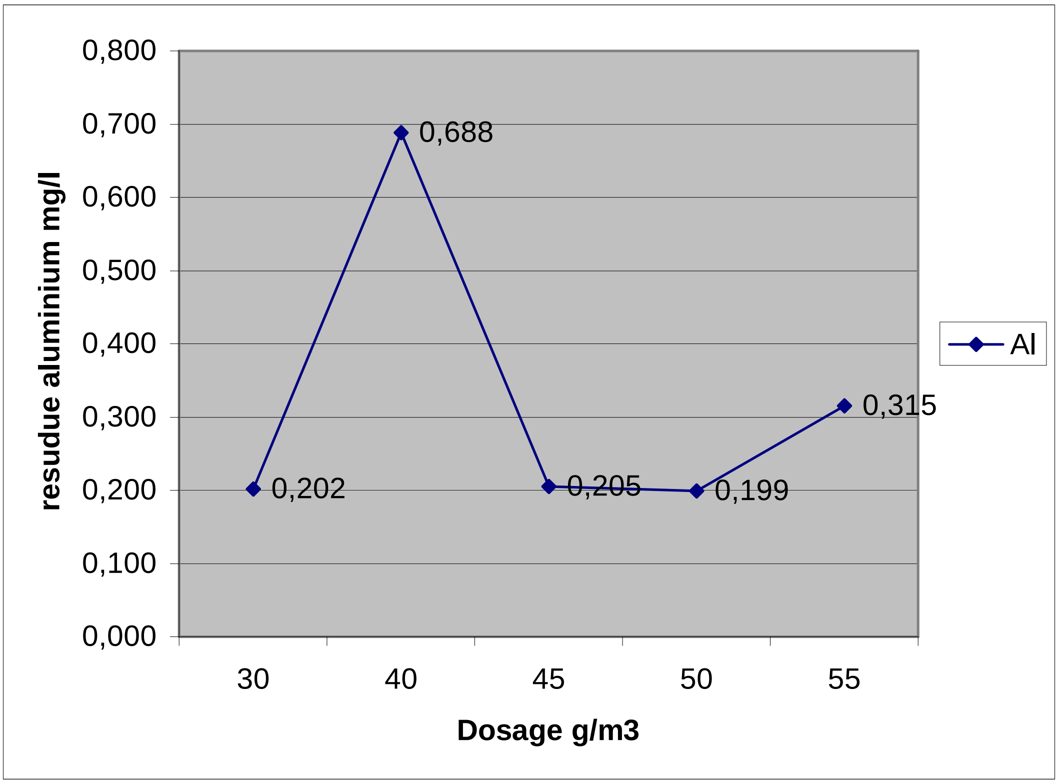

Figure 21.5. Residual aluminium at different dosages of aluminium sulphate and at constant pH of 5,7 for Kauppi water.

22. Results: HPSEC analysis

The results attained from the HPSEC analyses are similar to the results in a lot of other research been done in the subject. From the figure 22.1. It can be found that the larger molecules that are presented in peaks 1-3 are easily removed at water purification. Medium sized molecules are removed moderately, and the smallest ones are retained or even grow in number. The removal of the smallest molecules is a common problem in water purification process found by many.

22.1 Results achieved from the HPSEC analysis for Kämmenniemi

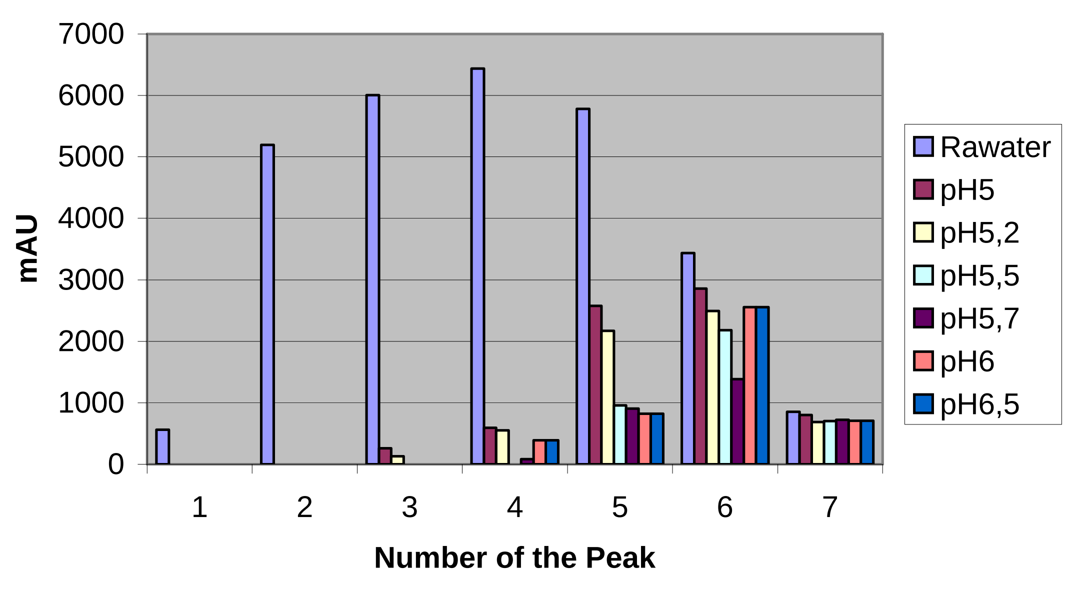

Figure 22.1 Distribution of the peaks at different pH values for Kämmenniemi water at dosage of 55g/m3

From the figure 22.1 can be found the optimal pH to remove the molecules. At the case of Kämmenniemi water coagulated with Polyaluminium chloride optimal pH is found to be between pH 5.5 and 5.7 since at that range of pH also both large and medium sized molecules were removed efficiently. At pH 5.7 also very small molecules which are presented at peak 6 were removed moderately. Smallest molecules presented by the peak 7 have not been removed at any pH value. The dosage used was same for all the samples presented here, 55 g/m^3.

At pH 6 which was chosen as the optimal pH for Kämmenniemi water purification plant based on the results achieved from aluminium and TOC analysis, the results for HPSEC analyse are less appropriate, however being better than results from the analysis at even lowered pH values, such as pH 5. or 4.5.

22.2 Results achieved from the HPSEC analysis for Polso

The HPSEC results for Polso water has been analyzed with polyaluminium chloride dosage of 50g/m^3. The results are presented in the Figure 22.2. In case of

Polso, all the heaviest molecules which are presented as peak 1 in the figure were removed. At pH 4.5 and 5 peak 2 has retained unexpectedly high which is likely to present an error in the results. At higher pH levels, the peak 2 presenting heavy molecules, was removed. Molecules having medium mass were partially removed from all the samples but at pH 4,5 and 5 they have retained at high volume, which again can be treated as an error. Instead of that, small molecules were most efficiently removed at those same pH levels, which is surprising.

Most efficient pH to remove all sizes of molecules would be pH 5.2, which is lower to that pH found optimal in Kämmenniemi case.

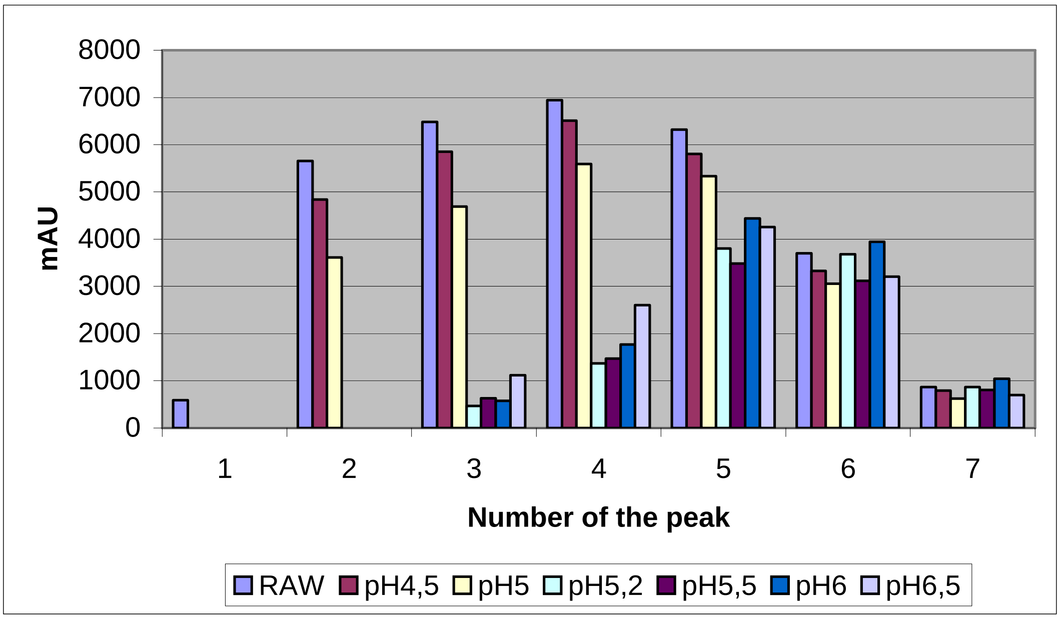

Figure 22.2 Distribution of the peaks in the chromatogram at different pH levels at dosage of 50mg/l for Polso water, where some problems may have occurred while analyses of pH 4,5 and pH 5.

22.3 Results achieved from the HPSEC analysis for Kauppi

The results from the HPSEC analyses for Kauppi water are presented in the figure 20.6 below. The results do not vary highly trough the different pH values but are at lowest at pH 5.2. which is the same pH found optimal in Polso case. Optimal pH based on the TOC and aluminium analyses was found to be 5.7 in case of Kauppi which is slightly higher than the optimal pH found with analyses of HPSEC.

The figure no. 22.3 represents the distribution of the peaks at different pH values. It is possible to see that at pH 5.2 the peaks 1-3 presenting the large molecular size are being completely removed. Medium sized molecules (peaks 4-5) are removed well and the smallest particles are removed only slightly at pH 5.2. At the optimal pH 5.7 determined for Kauppi water the results for HPSEC MSD analysis are somewhat higher. Large molecules were removed apart from peak 3 where slight peak was visible at pH 5.7. Medium sized molecules were removed moderately and the smallest particles tended to retain, or even slightly increase, as it was in case of the small molecules at pH 6.2. At pH 5.2 slightly less of small molecules were found present in the sample.

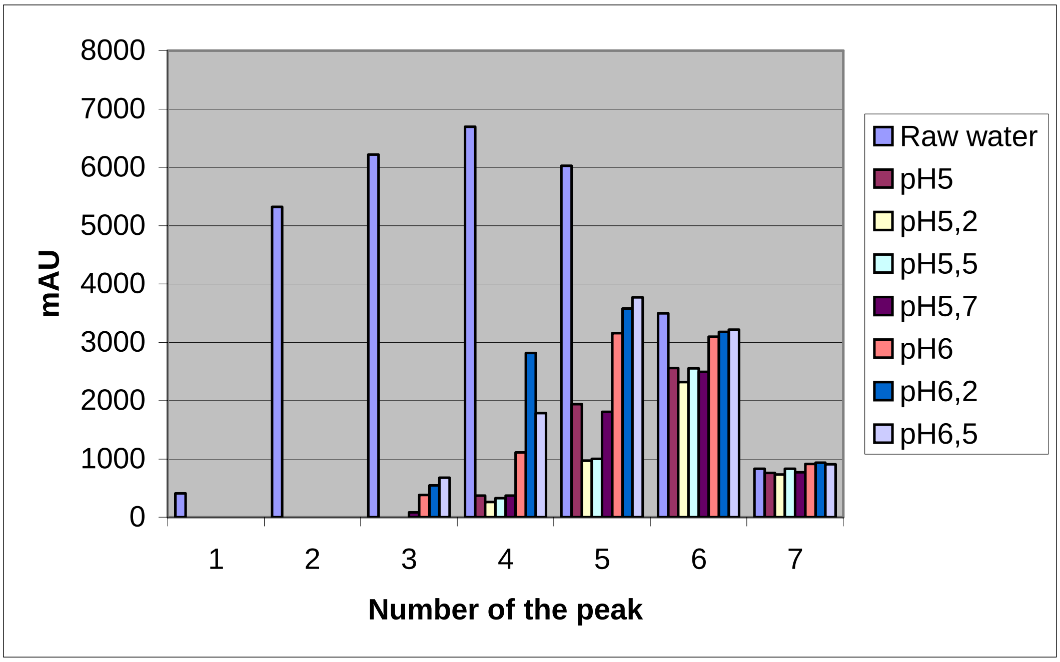

Figure 22.3. Peak distribution for different pH values with polyaluminium chloride dosage of 55 g/m^3.

23. Results: Effect of mixing

The results achieved from tests using different mixing settings are compared to raw water results. The mixer was set to have four different mixing programs and at these settings the optimum dosage (50 g/m^3 of coagulant for each plant) and pH is used for Kauppi, Kämmenniemi and Polso waters was used.

During previous tests the settings for the agitation program had been rapid mixing at 250 rpm and slow mixing at 50 rpm. These settings were the default settings in the mini-flocculation device used in this project.

Raw-water	**Kauppi**	**Kämmenniemi**	**Polso**
TOC	8,177	8,890	9,880
Turb.	0,61	0,59	0,58
UV-abs.	0,269	0,292	0,341

Figure 22.1. Raw-water figure for each plant

Raw water measurements for Polso and Kämmenniemi were done by personnel of Tampere water during 07.02.2007-03.05.2007 the raw-water values used in this work are averages from that time period.

Since in Kauppi water purification plant there is no production at the moment for water, regular laboratory testing of the water quality is not done by Tampere Water. The raw water values used for Kauppi are taken separately while working in Rusko treatment plant.

23.1 Effect of mixing for Kämmenniemi

In the figure 23.1 presenting the results for the tests of effect of mixing different parameters are stated as follows; F in the figures stands for fast mixing which in the program tested lasted for 1 minute. S stands for slow mixing, which lasted for 15 minutes. Sedimentation time was set to be one hour. Thus, the time frames were exactly the same as in the previous tests done in this project.

In the figures 23.1 and 23.2 the result values achieved from the analyses have been compared to the respective concentrations of NOM and aluminium found in the raw waters from each plant.

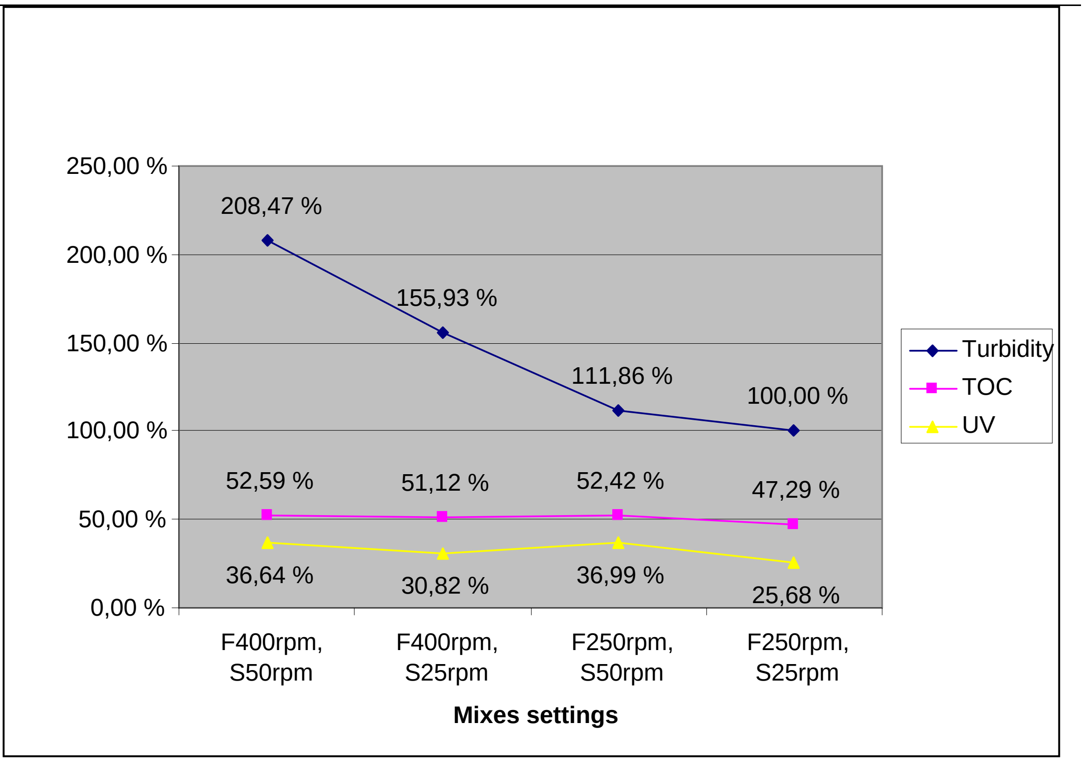

Figure 23.1 Results for the effect of mixing tests for residue organic matter. Apart from the mixing, the conditions were set to be those found optimal for Kämmenniemi water in previous tests.

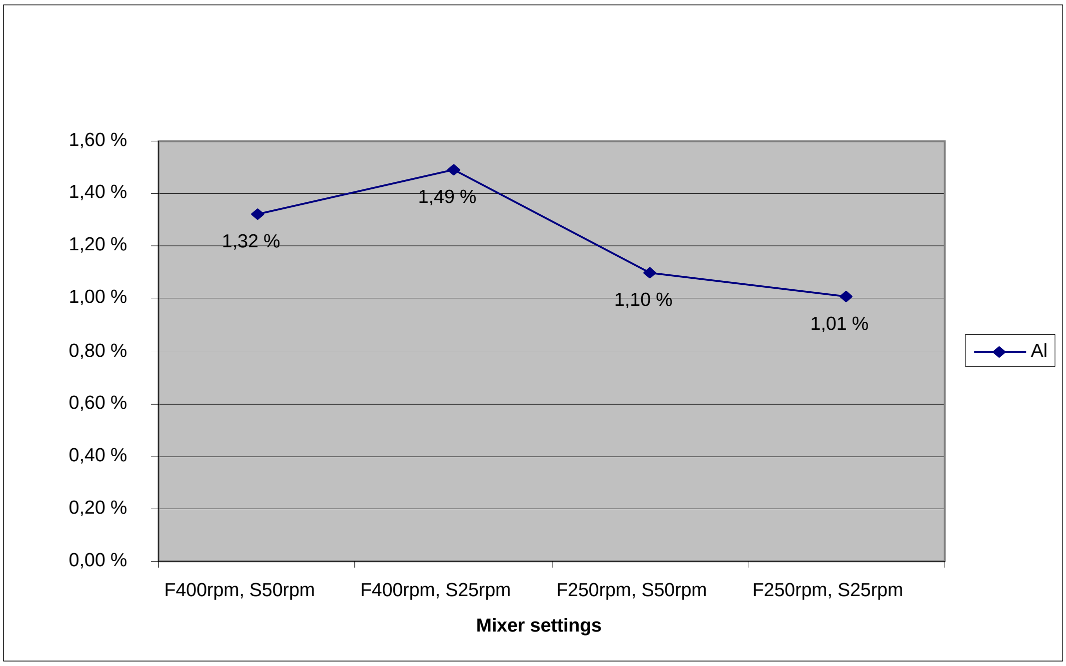

Figure 23.2. Percentage of residue aluminium at Kämmenniemi after coagulation and flocculation took place in cold water. 100% is the dosage of 50 g/m^3 of coagulant.

23.2 Effect of mixing for Polso

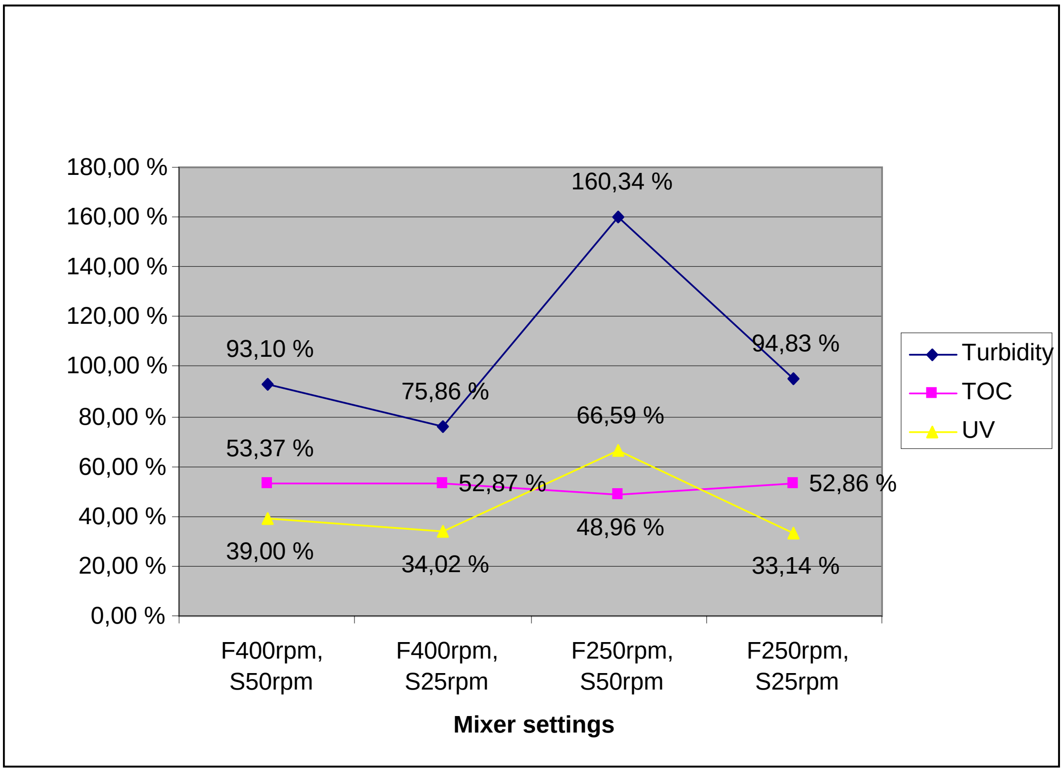

Figure 23.3. Results for the effect of mixing tests for residue organic matter. Apart from the mixing, the conditions were set to be those found optimal for Polso water in previous tests.

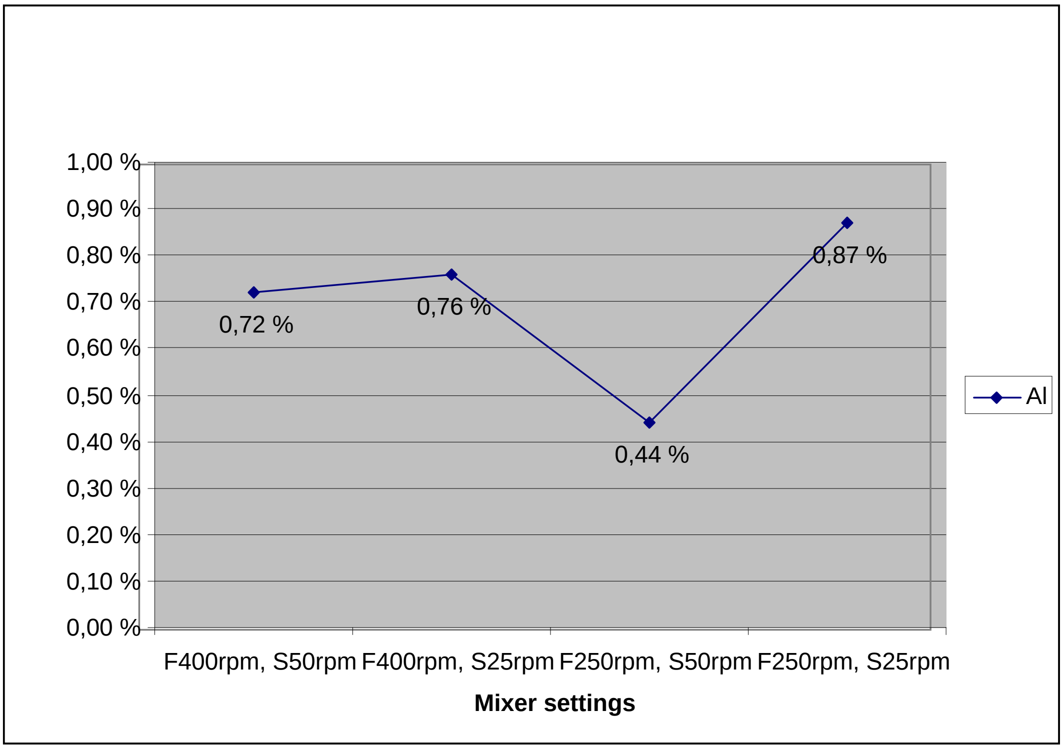

Figure 23.4. Percentage of residue aluminium at Polso after coagulation and flocculation took place in cold water. 100% is the dosage of 50 g/m^3 *of coagulant.*

The mixer settings of 250rpm at fast mixing, and 25 rpm at slow mixing seems to be most efficient. This supports the theory that the mixing speed at flocculation stage must be slow enough that the formed flock do not break. However the coagulation stage is supposed to prefer rather fast mixing speed to enable efficient mixing of water and coagulant. These results show that the rapid mixing for 250rpm is more efficient than 400rpm.

23.3 Effect of mixing for Kauppi

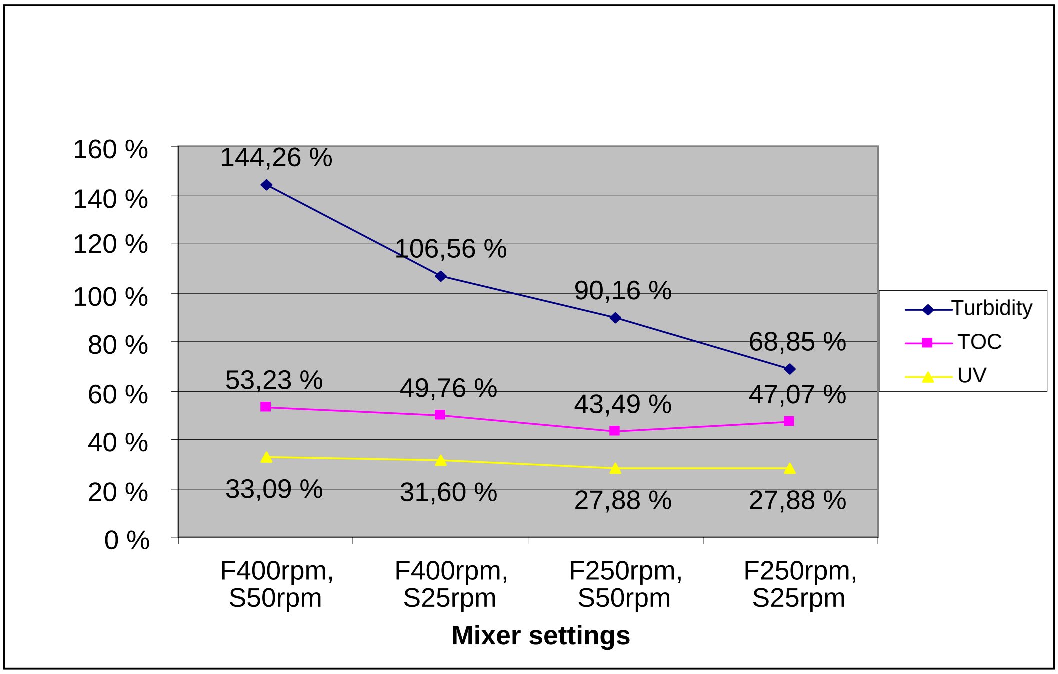

Figure 23.5. Results for the effect of mixing tests for residue organic matter. Apart from the mixing, the conditions were set to be those found optimal for Kauppi water in previous tests.

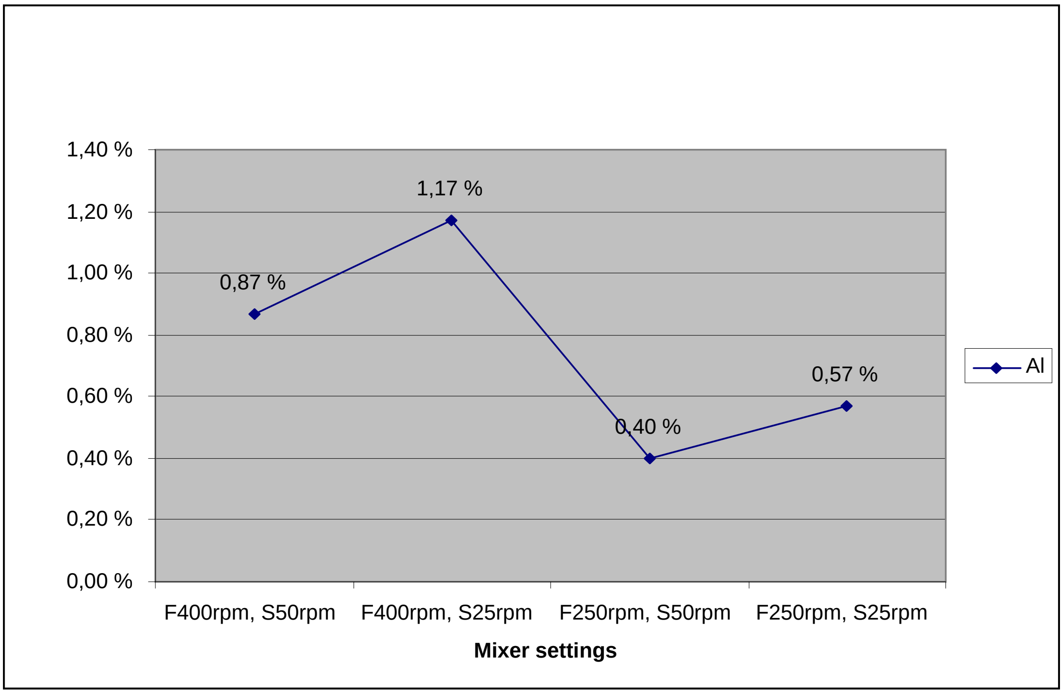

Figure 23.6. Percentage of residue aluminium at Kauppi after coagulation and flocculation took place in cold water. 100% is the dosage of 50 g/m^3 *of coagulant.*

The concentration at F250rpm, S25rpm is 0,287 mg/l. This is already almost valid for drinking water qualifications in terms of aluminium concentration. Aluminium concentration at Kauppi and Polso are lowest when rapid mixing is set to 250rpm and slow mixing 50rpm. The best over all settings seems to be still average fast mixing in coagulation stage and rather slow mixing in flocculation stage.

24. Results: Effect of temperature

In this study the effect of temperature is studied by making the flocculation tests with optimum dosage and pH at temperature of 7°C. The results gained at lower temperature are compared to results at room temperature. The change of results is shown in percentages.

24.1 Effect of temperature for Kämmenniemi

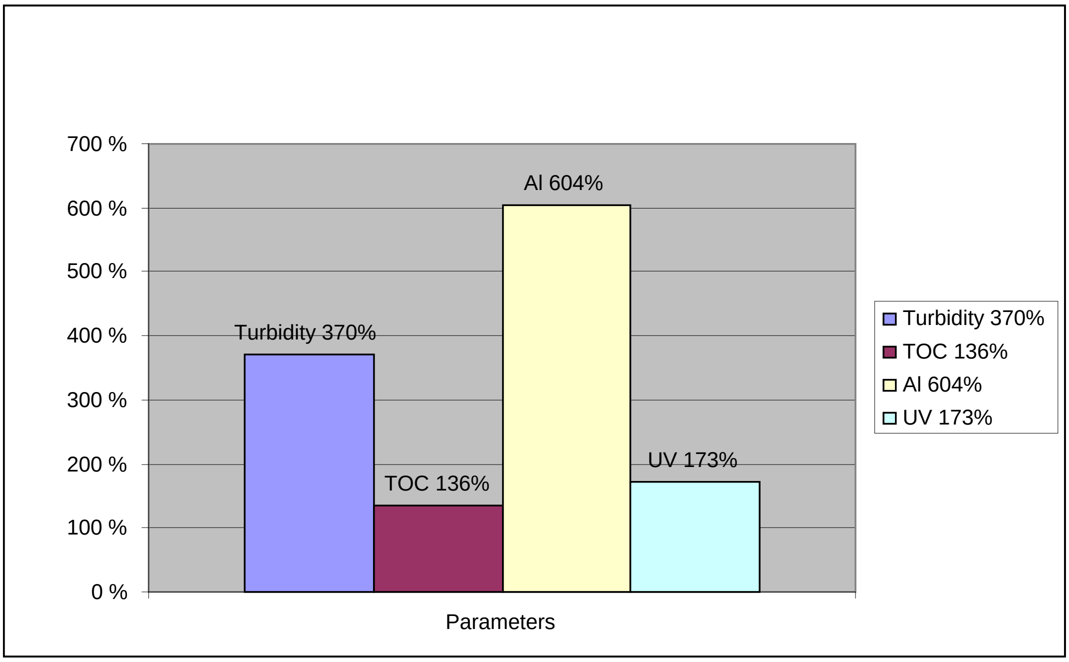

Figure 24.1. Change in Kämmenniemi results gained at low temperature compared to room temperature. 0% represents the optimum results gained at 20°C (room temperature).

24.2 Effect of temperature for Polso

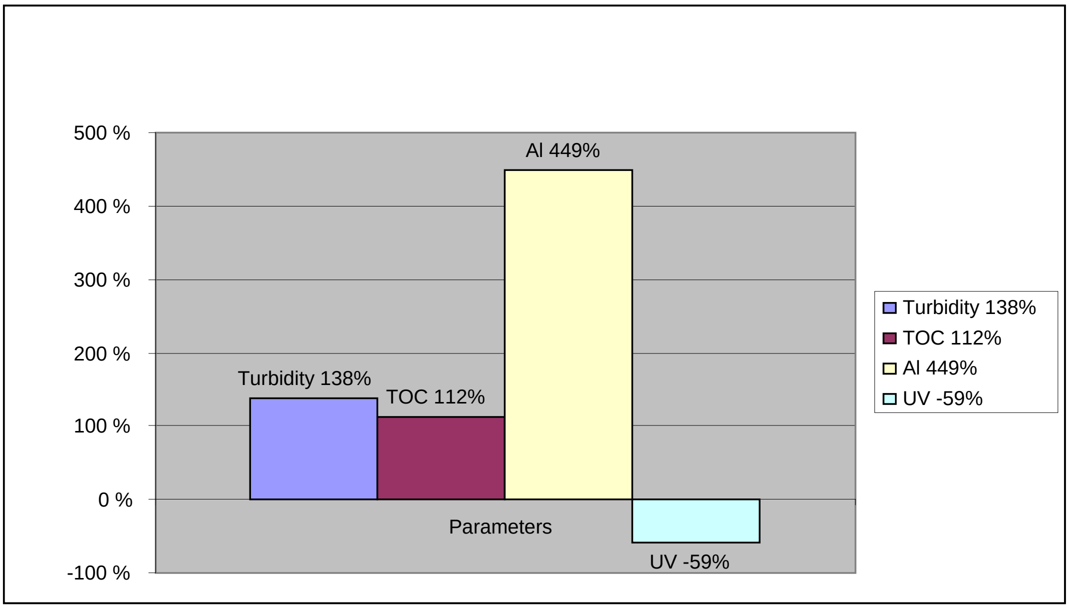

Figure 24.2. Change in Polso results gained at low temperature compared to room temperature. 0% represents the optimum results gained at 20°C (room temperature).

24.3 Effect of temperature for Kauppi

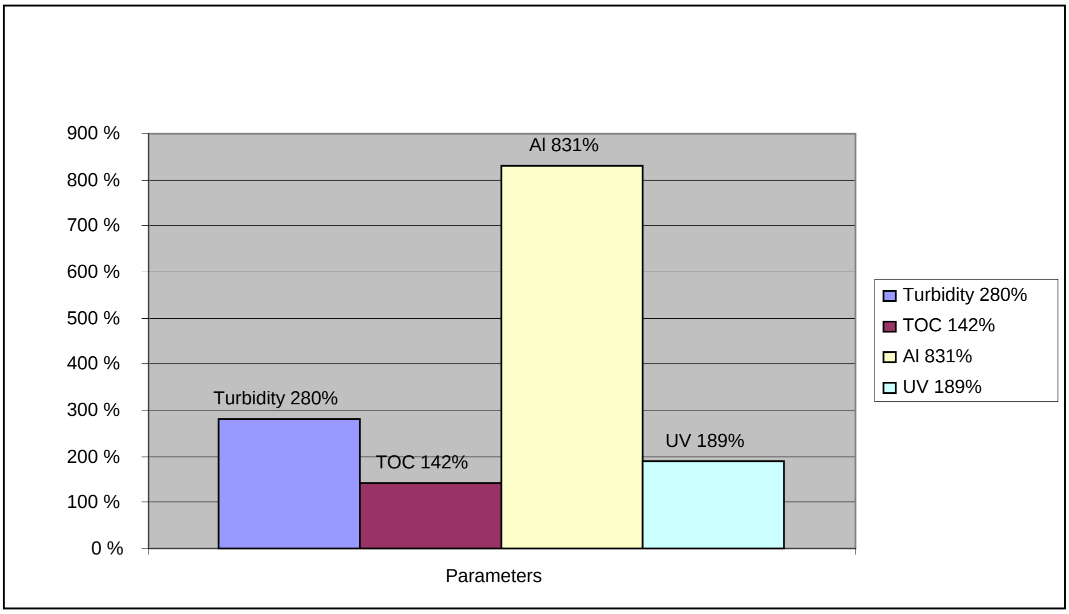

Figure 24.3. Change in Kauppi results gained at low temperature compared to room temperature. 0% represents the optimum results gained at 20°C (room temperature).

The results presented in figures 24.1, 24.2 and 24.3 confirm the theory that low temperature is not as effective for flocculation and coagulation as room temperature is. Each parameter gives higher concentrations of residue NOM and aluminium than at 20°C and therefore the water quality isn’t nearly as good as in the optimum situation.

Especially aluminium concentration remains high after treatment in low temperature. Same pattern of change in results is repeated with each case except the UVA254-value of Polso plant. After aluminium, turbidity is show second highest values. TOC show figure increase when water temperature is decreased. The most in figure parameter is UVA254.

25. Reliability and quality assurance

It is essential for reliability of any scientific research to have high quality analytical data and documenting. In this study several methods were utilized to ensure consistent high quality, which most importantly were avoidance of mistakes and consistency of performance while conducting analyses and documentation of the results.

Apart from that, practical tools to assure the quality were to use three parallel sampling (in some cases two) and treating mean of the results. If high variety between the results occurred, the one with most variety was deleted. This was done in addition with the quality control of each device used in the research. In some cases, results were double checked by repeating the flocculation tests and all the analyses.

All the analyses were conducted in as short period as possible after settling of the sample to maintain 1 hour of settling time for all the samples. Also, all the analyses were always conducted in same order to ensure their comparability between each others.

General SFS-standard methods were used where applicable to maintain consistency for the study. The standards are the same as used and accredited at Rusko Laboratory, as well as control samples and calibration of the devices.

Variation in results was estimated based on the same variation used at Rusko Laboratory. The calculation of variation is done for each analyze separately.

Documenting of the samples took place at Rusko Laboratory after the analyses. Documentation was done using MS Excel. Basic statistical principles were utilized while treating the results.

26. Cost of coagulant

The cost of PAX-14 for Tampere water is 501 €/1000kg. Aluminium sulphate, which is used in Kauppi, is not included in this chapter, because Kauppi treatment plant is not treating water at the moment.

The amount of water treated at Polso at year 2006 was 21868,1 m^3. At Kämmenniemi the amount was 42665,2 m^3. The used dosage of coagulant at Polso is at the moment 55 g/m^3, at Kämmenniemi 65 g/m^3 and at Kauppi g/m^3. At each plant the degradation of coagulant usage can be done. This leads to financial savings as well. Also the consumption of soda will decrease with the new dosages and this also saves money.

Dosage	**Polso annual cost**	**Kämmeniemi annual cost**	**Cost for dosage**
40g/m^3	438 €	855 €	40g/m^3 = 0,02004 €
45g/m^3	493 €	962 €	45g/m^3 = 0,022545 €
50g/m^3	548 €	1 069 €	50g/m^3 = 0,02505 €
55g/m^3	603 €	1 176 €	55g/m^3 = 0,027555 €
60g/m^3	657 €	1 283 €	60g/m^3 = 0,03006 €
65g/m^3	712 €	1 389 €	65g/m^3 = 0,032565 €

Figure 26.1 Costs for different dosages of PAX-14.

In this figure the cost for different dosages with year 2006 water amount is calculated. The optimum dosage is 50 g/m^3 of PAX-14 for both Polso and Kämmenniemi plants. When comparing the present dosage at Kämmenniemi to optimum found in this wok, the yearly savings in PAX-14 consumption are 320 €. At Polso the savings are 55 €.

27. Discussion

In this study, TOC, turbidity, UVA254, which represents NOM in water, and residue aluminium was analyzed for raw water taken from Kämmenniemi, Kauppi and Polso water purification plants in order to find optimal dosage of coagulant for the coagulation and flocculation system. The trial was made in order to reduce the amount of coagulant needed. To find the optimal dosage, the pH for the coagulation and flocculation processes had to be optimized as well, since pH has enhancing affect on the system at certain levels due to its effects on the behavior of NOM and to the solubility of aluminium.

Tests were run at laboratory scale in Rusko Laboratory during the spring 2007. The effect of pH was tested systematically at constant coagulant dosage. The range of pH tested was chosen based on the optimal pH range for the process given in literature (pH 5-7). After finalizing the analyses for pH, the optimal dosage could be found by running the tests in optimal pH but lowering the dosage as long as the results from the NOM analyses stayed as low as they are at the current dosage. When the NOM results became higher, the dosage had become too low.

27.1 Optization at Kämmenniemi water treatment plant

Kämmenniemi has a small water purification plant where amount of treated water during the year 2006 was 42665,2 m^3 (25) and the amount of treated water is increasing. It take’s water from Gulf Käälahti where seasonal fluxes have high effect on the NOM concentration in the water. Highest the NOM is at springtime. The water quality in Näsijärvi is generally good and at Kämmenniemi is average.

Eg. The TOC results for average during the spring 2007 in Kämmenniemi (8,89 mg/l) is slightly higher than in Kauppi (8.18 mg/l) but lower than in Polso (9,88 mg/l).

In case of Kämmenniemi analyses to find optimal pH were done for pH 5, 5.2, 5.5, 5.7, 6 and 6,5. at dosage of 65 g/m^3 which is the current dosage used at the plant. Based on the results presented in the figure 20.1 (residue organic matter at different pH) the decision for the optimal pH was made and it was found to be pH 6. In that pH TOC analyzed decreased to 53 % from TOC in raw water after coagulation and flocculation, which was lowest TOC found. Also other analyses for fractions of NOM gave low results at that pH. UVA254 decreased to 33% and HPSEC to 15%. Turbidity increased by 38, which is less than most of the other pH values. Residue aluminium was 0,213 mg/l at pH 6, but was found to be lower (0,090 mg/l) at higher pH (6,5) which refers to the common behavior of solubility of metals discussed in previous chapters.

Also, results achieved at pH 5,7 and 6,5 were close to optimal. At those pH TOC was slightly higher, both having 54% remaining from the raw water. Turbidity was found better at pH 5,7 and 6,5 than at pH 6. Results for molecular weight distribution (HPSEC) were found optimal at pH 5.5 (13%) but the increase to pH 6 was only 2%, when to pH 5.2 the increase was 8% and to pH 6.5 there was increase of 6%.

It was also noted that the optimal pH had greater role in the effect of coagulation when the dosage of coagulant was decreased for both behavior of the NOM fractions and for residue aluminium. Some analyses for various pH were also conducted with dosage of 50 g/m^3. In figures presenting those results (appendix). The results at pH 6 were also then found to the optimal, and the differences with other pH values were higher. It was also found at the effect of pH is better at pH above 6 than at the pH levels below pH 6.

Since the optimal pH was found to be pH 6, all the tests for the optimal dosage were conducted at that pH. Some extensive studies were conducted also at some other pH levels for the lower dosages. Currently, coagulation-flocculation system at Kämmenniemi receives 65 g/m^3 of polyaluminium chloride as coagulant. Tests run for lower dosages were done in laboratory scale at Rusko laboratory.

After the flocculation-coagulation at dosage of 65g/ m^3 of coagulant the TOC was decreased to 53% (4,749 mg/l) from raw water levels. Turbidity was 138% (0,81NTU), HPSEC 15% (4269 mAU), and UVA254 was 35% (0,102).

The results at dosage of 50 g/m^3 were found to be comparable to these results or even lower in some cases. The TOC had decreased to 52% (4,660 mg/l) which is 1 % less than with dosage of means 65 g/m^3 . That results also is closer to the 4,00 mg/l limit value recommended by Ministry of social affairs and health of Finland (recommendation yet under preparation), thus, it would be easier to decrease the TOC under 4,0 mg/l in subsequent processing of drinking water. UVA234 was 37% (0,108), HPSEC 21% (5977mAU) and turbidity 118% (0,66 NTU), but even then, the dosage could be lowered to 50 g/m^3 due to the TOC and aluminium results which are discussed below.

Results for aluminium decreased if the dosage was decreased until dosage of 50 g/m^3 where the residue aluminium after coagulation-flocculation was only 0,086mg/l. With dosage of 65 g/m^3 the same result was 0,216 mg/l which in fact is above the recommendation level of 0,200 mg/l set by Ministry of social affairs and health of Finland (discussed at chapter 12). At dosage of 45 g/m^3 of polyaluminiumchloride residual aluminium rose to 0,562 mg/l which would not be desirable.

At lower dosages than 50 mg/l TOC was still maintained having decreased to 52% (4,654 mg/l). However, other parameters studied begun to increase, which was considered as sign for improper coagulation-flocculation to be taking place. Molecular mass distribution (HPSEC) rose to 28%, turbidity to 148% and UVA254 resisted at 36%, still slightly lower at dosage of 45 g/$m^{3.}$

27.2 Optization at Polso water treatment plant

In Polso water purification plant, traditional method of contact filtering is utilized as a method to purify water. During the year 2006 21868,1 m^3 of water was treated at Polso plant, which is only a fraction of the annual average that Tampere Water processes (19 million m^3).

Alike at Kämmenniemi plant, polyaluminium chloride (PAX 14) is used as a coagulant. Currently 55 g/m^3 is fed to the system to coagulate the water. From those three water purification plants discussed in this study, Polso water suffers the highest concentration of NOM in it. In average, during the spring 2007, the parameters commonly studied were for raw water as follows; TOC was found 9.88mg/l, UVA254 0.341, and turbidity was 0.576 NTU. HPSEC results found for the raw water at Polso was 30557 mAU (total of the peaks).

In this study, Polso water was studied for its optimal pH and optimal dosage of polyaluminium chloride. The study was conducted in laboratory scale at Rusko laboratory. At first, optimal pH was to be found by studying the effect of varying pH levels with dosage of 55 g/m^3. The range studied was chosen based on the suggestions found in literature, which generally noted the optimal dosage to be in range of pH5-pH7. Some lower pH levels were also studied here. Overall, pH levels studied were 4.2, 4.5, 4.7, 5, 5.2, 5.5, 5.7, 6, 6.5 and 7.

Optimal pH was then justified to be 6.5, due to its effect to decrease the amount of organic matter and residue aluminium in it after coagulation-flocculation. In average, the amount of residue aluminium found in the samples after the process, was high.

The optimal dosage was then justified by choosing the optimal pH (pH6.5) and then feeding different dosages to the system, decreasing the dosage step-by-step-wise from the current dosage used. Both dosages 50 g/m^3 and 45 g/m^3 were found to be efficient. However, while dosage 45 g/m^3 gave excellent results for the decrease of organic matter, the concentration of residue aluminium was found unacceptably high. At dosage of 50 g/m^3 the residue organic matter wasn't decreased as efficiently yet better than at the current dosage. The residue aluminium was found lowest at that dosage.

In Polso, some difficulties were faced in laboratory coagulation and flocculation mainly due to the inexperience since the process was started with water from Polso, and it could be thought that while working with samples from Polso, the whole method utilized here was at a testing stage. However, the results achieved are being considerable.

HPSEC results have been discarded from the presentations of the results due to the low quality. The findings based on them could not have been trusted. HPSEC samples may have been collected too much below the surface of the flocculated water, or there may have been failure while freezing the samples. Also, some samples were not taken, therefore there was no result for them.

Economical savings from such decrease are not high and do not have effect on annual budget of business. Nevertheless, reduction of consumption in general can be noted to be valuable. In addition, dosage of coagulant has effect upon the formation of the flock, thus, the re-treatment of the flock will be more effective. There has been discussion above the health effects of the residue aluminium in drinking water. The amount of aluminium intake from the drinking water is no more than 1% of the total aluminium intake for Finnish person (27). However, finding the optimal conditions for the drinking water purification can decrease even that number.

27.3 Optization at Kauppi water treatment plant

Kauppi water purification plant is located in protected natural area of Kauppi forest near the city centre. The plant is used as reservoir and is not used in daily basis, due to its old age and weathering of the machinery. While there has been discussion to close the plant finally down, the machinery has still found to be working. Therefore, the closing down of the plant, and turning it Eg. to a museum has not taken place.

Coagulant used at the plant is aluminium sulphate in solid form. The dosage used is 55 g/m^3 currently. Water that the plant utilizes has somewhat lower concentration of NOM than is found in Kämmenniemi and Polso cases. Due to the fact that it is not in use, the quality of the raw water at Kauppi is not constantly followed. Therefore, some analyses of raw water were made for this study. In those analyses, TOC was found to be 8.177 mg/l, UVA245 was 0.269, turbidity was 0.614 and HPSEC was 28996 mAU.

The tests were done in laboratory scale in Rusko laboratory. After the coagulation-flocculation process the samples were studied for TOC, UVA245, turbidity and HPSEC which are considered to represent NOM in water. The results were studied as effect to reduce the NOM in comparison to the respective results analysed from raw water presented above. Residue aluminium was studied following standard method SFS 5763 in order to follow the solubility of aluminium.

To find the optimal conditions to reduce those parameters as low as possible, the coagulation-flocculation process was at first studied for the effect of pH. In extensive study, the pH optimal to the process was found to be 5.7. The result is lower than in other cases studied here, which is normal regarding the coagulants used in the plants. Aluminium sulphate generally has optimal pH lower than with polyaluminium chloride while regarding the literature the optimal range is the same for alum coagulants, from pH 5 to pH 7 (1, 15).

The study for the optimal dosage was done following to the study for the optimal pH. After dosing the samples with desired amount of the coagulant, pH was adjusted to be the optimized pH 5.7. The optimal dosage was selected based on the analyses for NOM and residue aluminium. Regarding the results, the optimal dosage would be 50 g/m^3, instead of the currently used 55 g/m^3 at pH of 5.7. It was found that at lower dosage of 50 g/m^3 different fractions of NOM were lowest. Furthermore, the solubility of aluminium was found to retain low, 0.199 mg/l, even below the recommendation limit set by Finnish officials which is set to be 0.200 mg/l, even tough it is not compulsory that the limits are fulfilled at this stage of water purification process due to the following processes, namely different methods of filtering, which yet will reduce the concentrations of all the parameters.

Therefore, as result to this study, it could be recommended that the reduction of coagulant in Kauppi case can take place at pH 5.7, but no dosage less than 50 g/m^3

should be fed to the system. While reducing the dosage, it should be taken in to the consideration that the effect of pH will play important role.

The cost savings of such decrease have no effect upon budget of Tampere Vesi due to the low market prize of any coagulant. Also, the health effects of aluminium coagulants are not considerable, due to the low residual concentrations of it in municipal drinking water already. However, the reduction of coagulant has effect on formation of flocks in the process and can ease the treatment and volume found after the process. Also, lower concentration of aluminium will lead to easier maintenance of the subsequent filter system. Based on the discussions with staff at Tampereen Vesi, soluble aluminium consequently can cause blockages in the filters, therefore requiring more careful washing. Blocked filters will, furthermore, have undesired effect upon the quality of the water leaving the treatment plant.

28. Conclusions

It has been found important to every now and then update the coagulant dosages at water purification plants, due to the changes that take place in natural surface waters. Optimization of the coagulation and flocculation process will lead to better quality of drinking water and easier maintenance of the subsequent processes that take place at the plants. Important parameters that have effect upon the efficiency of the coagulation and flocculation are type of coagulant, dosage of the coagulant and pH where the coagulation takes place. In this study, the focus was on the dosage and pH.

Here, study was made to optimize coagulation and flocculation process for Kämmenniemi-, Kauppi, and Polso water purification plants owned by Tampereen Vesi (Tampere Water). All the tests and analyses were done in Rusko laboratory in Tampere.

The water purification plants discussed here collect their water form Näsijärvi. In Kämmenniemi and Kauppi, polyaluminium chloride is used as coagulant, and in

Kauppi Aluminium sulphate is used. There were no changes made concerning the types of coagulants.

Regarding the results of this study, following recommendations can be given; At Kämmenniemi, the dosage can be reduced form 65 g/m^3 to 50 g/m^3. This can take place if the pH for the process can be set to be 6.In Kauppi, dosage can be reduced from 55 g/m^3 to 50 g/m^3 at pH 5.7 and in Polso, the reduction can also happen from current 55 g/m^3 to 50 g/m^3 at pH 6.5. It is important to notice that while the dosage is decreased, the effect of pH becomes more important, and the adjusting of it should not shift. These conclusions were based on the reduction of NOM and low solubility of aluminium at recommended dosages and pH.

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Appendix I.

Kämmenniemi tables of results

KÄMMENNIEMI **Optimum is 50mg/l pH6**

Dosage	pH	Turbidity	TOC	Al	UV
40	5,5	1,11	5,095	0,178	0,107
40	5,5	0,98	5,011	0,297	0,127
40	5,5	1,60	5,516	1,607	0,150
Average		1,23	5,207	0,238	0,128
40	5,7	1,01	5,381	0,386	0,100
40	5,7	0,59	4,865	0,193	0,091
40	5,7	0,50	4,854	0,167	0,077
Average		0,70	5,033	0,249	0,090
40	6	0,39	5,087	0,136	0,091
40	6	0,28	5,017	0,200	0,091
40	6	0,60	5,102	0,247	0,095
Average		0,42	5,069	0,194	0,093
Dosage	pH	Turbidity	TOC	Al	UV
45	5,7	1,98	5,270	0,540	0,096
45	5,7	1,51	4,779	0,554	0,130
45	5,7	1,60	4,792	0,467	0,099
Average		1,70	4,947	0,520	0,109
45	6	1,30	4,697	0,639	0,094
45	6	0,90	4,679	0,850	0,116
45	6	0,40	4,587	0,196	0,104
Average		0,87	4,654	0,562	0,105
Dosage	pH	Turbidity	TOC	Al	UV
50	5	1,53	7,259	0,387	0,117
50	5	1,18	6,654	0,396	0,127
50	5	1,74	7,492	0,390	0,118
Average		1,48	7,135	0,391	0,121
50	5,2	1,30	6,047	0,543	0,100
50	5,2	1,37	5,581	0,404	0,108
50	5,2	0,97	5,811	0,492	0,111
Average		1,21	5,813	0,479	0,106
50	5,5	1,62	5,693	0,329	0,200
50	5,5	1,52	5,664	0,274	0,167
50	5,5	1,28	5,818	0,327	0,226
Average		1,47	5,725	0,310	0,198
50	6	0,42	5,642	0,480	0,107
50	6	0,77	4,359	1,480	0,111
50	6	0,79	3,980	0,620	0,108
Average		0,66	4,660	0,550	0,108
50	5,7	0,81	5,865	0,461	0,091
50	5,7	0,94	5,878	0,794	0,106
50	5,7				
Average		0,88	5,872	0,628	0,099
50	6,5	0,65	4,706	0,600	0,085
50	6,5	0,88	4,565	0,470	0,092
50	6,5	0,89	4,624	0,750	0,103
Average		0,81	4,632	0,607	0,093

Dosage	pH	Turbidity	TOC	Al	UV
55	5,2	1,60	6,737	1,951	0,153
55	5,2	1,46	6,679	2,442	0,151
55	5,2	4,31	6,327	2,728	0,160
Average		2,46	6,581	2,374	0,154
55	5,7	0,76	4,910	0,358	0,101
55	5,7	0,92	4,781	0,990	0,100
55	5,7	0,82	4,532	0,554	0,114
Average		0,83	4,741	0,634	0,105
55	6	0,59	4,690	2,177	0,107
55	6	0,90	4,902	1,442	0,099
55	6	1,06	4,496	1,364	0,093
Average		0,85	4,696	1,661	0,099
Dosage	pH	Turbidity	TOC	Al	UV
60	5,5	1,77	6,030	0,258	0,150
60	5,5	1,23	5,208	0,199	0,130
60	5,5	1,08	4,902		0,127
Average		1,36	5,380	0,229	0,136
60	5,7	1,02	5,113	0,769	0,114
60	5,7	0,57	4,500	0,408	0,115
60	5,7	0,79	4,895	0,614	0,196
Average		0,79	4,836	0,597	0,138
60	6	0,34	5,254	0,519	0,078
60	6	0,64	5,966	0,421	0,122
60	6				
Average		0,49	5,610	0,470	0,100
Dosage	pH	Turbidity	TOC	Al	UV
65	5	1,99	7,537	0,246	0,172
65	5	1,56	6,604	0,300	0,171
65	5	1,41	5,877		0,176
Average		1,65	6,673	0,273	0,173
65	5,2	1,06	5,894	0,274	0,144
65	5,2	1,27	6,079	0,273	0,161
65	5,2	1,13	6,329		0,154
Average		1,15	6,101	0,274	0,153
65	5,5	1,80	6,107	0,480	0,194
65	5,5	2,20	6,569	0,483	0,216
65	5,5	1,96	6,120		0,194
Average		1,99	6,265	0,482	0,201
65	5,7	0,71	4,865	0,229	0,085
65	5,7	0,94	5,058	0,393	0,126
65	5,7	0,47	4,477		0,093
Average		0,71	4,800	0,311	0,101
65	6	0,96	4,900	0,303	0,082
65	6	0,62	4,370	0,128	0,073
65	6	0,86	4,978		0,151
Average		0,81	4,749	0,216	0,102
65	6,5	0,69	4,999	0,990	0,125
65	6,5	0,66	4,838	0,800	0,089
65	6,5	0,56	4,660		0,107
Average		0,64	4,832	0,895	0,107

🟥 Large deviation from two parallel samples

🟨 Average

Appendix II.

Polso tables of results

Polso **Optimum is 50mg/l pH6,5**

Dosage	pH	Turbidity	TOC	Al	UV
40	5,5	0,56	4,615	0,486	0,091
40	5,5	1,32	6,149	0,676	0,147
40	5,5	1,77	6,557	0,829	0,176
Average		1,22	5,774	0,664	0,138
40	5,7	2,16	7,094	1,161	0,186
40	5,7	1,14	5,870	0,873	0,147
40	5,7	1,68	6,440	1,167	0,164
Average		1,66	6,468	1,067	0,165
Dosage	pH	Turbidity	TOC	Al	UV
45	5,7	1,37	7,371	0,355	0,134
45	5,7	1,84	6,567	0,304	0,220
45	5,7	0,68	5,748	0,643	0,138
Average		1,30	6,562	0,434	0,164
45	5,5	1,51	5,830	0,718	0,158
45	5,5	0,95	5,652	1,006	0,137
45	5,5	1,40	5,370	0,894	0,158
Average		1,29	5,617	0.718	0,151
45	6	0,46	4,526	0,517	0,104
45	6	0,37	4,352	0,173	0,078
45	6				
Average		0,42	4,439	0,345	0,091
45	6,5	0,39	4,777	0,581	0,116
45	6,5	0,36	4,563	0,383	0,104
45	6,5				
Average		0,37	4,670	0,482	0,110
Dosage	pH	Turbidity	TOC	Al	UV
50	4,5	0,79	6,032	3,490	0,265
50	4,5	0,58	6,027	3,588	0,194
50	4,5	0,56			0,157
Average		0,64	6,030	3,539	0,205
50	5	1,65	6,988	0,678	0,182
50	5	0,83	6,273	1,685	0,158
50	5	1,10	6,650		0,176
Average		1,19	6,637	0,678	0,172
50	5,2	1,33	5,459	0,888	0,130
50	5,2	1,20	5,550	1,302	0,115
50	5,2				0,154
Average		1,27	5,505	0,888	0,133
50	5,5	1,91	6,285	0,274	0,152
50	5,5	0,94	6,282	0,333	0,125
50	5,5	0,82	5,530		0,144
Average		1,22	6,032	0,304	0,140

50	5,7	1,20	5,600	0,640	0,158
50	5,7	0,95	5,136	0,894	0,137
50	5,7				0,158
Average		1,07	5,368	0,767	0,151
50	6	1,02	4,914	0,573	0,242
50	6	0,87	4,902	0,831	0,146
50	6	1,33			0,139
Average		1,07	4,908	0,702	0,175
50	6,5	1,21	5,000	0,252	0,167
50	6,5	0,88	4,837	0,188	0,321
50	6,5	0,69			0,193
Average		0,93	4,837	0,22	0,227
Dosage	pH	Turbidity	TOC	Al	UV
55	4,2	1,53	9,499		0,293
55	4,2	1,45	9,056		0,284
55	4,2	0,64	8,975		0,297
Average		1,49	9,177		0,291
55	4,5	1,17	6,755	0,352	0,150
55	4,5	0,58	7,109	0,335	0,168
55	4,5	0,50	7,742		0,198
Average		0,75	7,202	0,314	0,172
55	4,7	0,66	8,137	0,303	0,210
55	4,7	0,65	8,534	0,321	0,217
55	4,7	0,60	7,543	0,317	0,228
Average		0,64	8,157	0,314	0,218
55	5	0,49	6,685	0,381	0,144
55	5	0,77	6,520	0,433	0,147
55	5	0,76	6,290	0,472	0,140
Average		0,67	6,498	0,347	0,143
55	5,2	3,04	6,373	0,353	0,158
55	5,2	2,68	5,535	0,339	0,166
55	5,2	2,19	5,117	0,349	0,158
Average		2,64	7,416	0,347	0,161
55	5,5	1,48	5,274	0,375	0,099
55	5,5	0,94	6,783	0,335	0,121
55	5,5	1,48	5,155	0,341	0,116
Average		1,48	5,737	0,350	0,112
55	5,7	2,80	6,052	0,467	0,166
55	5,7	2,19	5,712	0,471	0,144
55	5,7	1,18	5,397	0,463	0,164
Average		2,06	5,720	0,467	0,158
55	6	0,95	5,155	0,363	0,127
55	6	1,19	7,064	0,301	0,144
55	6	1,92	6,523	0,368	0,125
Average		1,35	6,247	0,344	0,132
55	6,5	1,98	7,070	0,376	0,143
55	6,5	1,69	6,755	0,378	0,142
55	6,5	1,69	6,469	0,376	0,172
Average		1,79	6,765	0,376	0,152
55	7	1,42	6,685	0,397	0,150
55	7	1,34	7,022	0,377	0,164

55	7	0,44	5,431	0,377	0,115
Average		1,38	6,379	0,384	0,143

Large deviation from two parallel samples
Average

Appendix III.

Kauppi tables of results

Kauppi **Optimum is 50mg/l pH5,7**

Dosage	pH	Turbidity	TOC	Al	UV
30	5,2	0,88	4,986	0,367	0,113
30	5,2	0,48	5,140	0,283	0,104
30	5,2	0,74	4,966	0,327	0,105
Average		0,70	5,031	0,326	0,107
30	5,5	0,51	4,965	0,375	0,103
30	5,5	0,60	4,997	0,277	0,107
30	5,5	0,49	4,934	0,206	0,098
Average		0,53	4,965	0,286	0,103
30	5,7	0,79	5,105	0,144	0,112
30	5,7	1,01	5,133	0,259	0,119
30	5,7	0,70	4,920	-0,004	0,120
Average		0,83	5,053	0,202	0,117
30	6	1,01	5,626	0,358	0,139
30	6	0,82	5,495	0,712	0,120
30	6	1,64	5,337	0,913	0,139
Average		1,16	5,486	0,661	0,133
Dosage	pH	Turbidity	TOC	Al	UV
40	5,7	2,70	5,817	0,692	0,127
40	5,7	2,01	5,416	0,770	0,114
40	5,7	2,25	5,402	0,603	0,116
Average		2,32	5,545	0,688	0,119
40	6	2,25	5,353	0,997	0,115
40	6	1,75	5,279	0,704	0,115
40	6	1,43	5,039	0,663	0,106
Average		1,81	5,224	0,788	0,112
Dosage	pH	Turbidity	TOC	Al	UV
45	5,5	0,52	4,802	0,331	0,096
45	5,5	0,89	4,484	0,782	0,095
45	5,5				
Average		0,70	4,643	0,557	0,095
45	5,7	0,39	4,680	0,213	0,077
45	5,7	0,41	4,481	0,196	0,076
45	5,7				
Average		0,40	4,581	0,205	0,077
Dosage	pH	Turbidity	TOC	Al	UV
50	5	1,36	5,045		0,099
50	5	1,34	4,825	0,225	0,103
50	5	1,44	4,819	0,217	0,103
Average		1,38	4,896	0,221	0,101

50	5,2	0,81	4,674	0,167	0,121
50	5,2	0,62	4,306	0,201	0,097
50	5,2	0,61	4,011	0,138	0,098
Average		0,68	4,330	0,169	0,105
50	5,5	0,37	3,819	0,320	0,077
50	5,5	0,63	3,504	0,187	0,074
50	5,5	0,44	3,585	0,396	0,084
Average		0,48	3,636	0,301	0,078
50	5,7	0,65	3,682	0,230	0,090
50	5,7	0,68	3,677	0,213	0,071
50	5,7	0,32	3,420	0,155	0,064
Average		0,55	3,593	0,199	0,075
50	6	0,65	3,766	0,044	0,096
50	6	0,46	3,652	0,183	0,080
50	6	0,92	3,649	0,016	0,095
Average		0,67	3,689	0,081	0,090
Dosage	pH	Turbidity	TOC	Al	UV
55	5	0,94	5,576	0,185	0,094
55	5	1,01	4,800	0,246	0,108
55	5	1,42	4,351	0,212	0,114
Average		1,12	4,909	0,214	0,105
55	5,2	0,63	3,301	0,076	0,067
55	5,2	1,28	4,240	0,116	0,098
55	5,2	0,83	3,988	0,035	0,102
Average		0,91	3,843	0,076	0,089
55	5,5	0,90	3,741	0,452	0,096
55	5,5	0,76	3,922	0,577	0,090
55	5,5	0,81	4,038	0,869	0,087
Average		0,82	3,900	0,633	0,091
55	5,7	0,76	4,159	0,280	0,075
55	5,7	0,54	4,066	0,285	0,077
55	5,7	0,37	3,957	0,379	0,083
Average		0,56	4,061	0,315	0,078
55	6	0,40	4,409		0,062
55	6	0,80	4,553	0,203	0,070
55	6	0,69	4,923	0,135	0,066
Average		0,63	4,628	0,169	0,066
55	6,2	0,58	4,456	0,107	0,080
55	6,2	0,74	4,561	0,080	0,094
55	6,2	0,53	4,507	0,199	0,085
Average		0,62	4,508	0,129	0,086
55	6,5	1,00	5,990	0,423	0,107
55	6,5	0,72	5,277	0,362	0,099
55	6,5	0,80	4,817	0,510	0,087
Average		0,84	5,361	0,432	0,097

Large deviation from two parallel samples

Average

Appendix IV.

Effect of mixing tables

Kämmenniemi table

Mixing tests		Optimal dosage and pH			Kämmenniemi					
Dosage	pH	Turbidity	TOC	Al	UV	Name	Mixer settings			
50mg/l	6	1,24	4,788	0,671	0,111	S1A	Fast	400rpm	Slow	50rpm
50mg/l	6	1,22	4,562	0,649	0,104	S1B	Fast	400rpm	Slow	50rpm
Average		1,23	4,675	0,660	0,107					
50mg/l	6	0,47	4,095	0,391	0,075	S2A	Fast	250rpm	Slow	25rpm
50mg/l	6	0,72	4,313	0,616		S2B	Fast	250rpm	Slow	25rpm
Average		0,59	4,204	0,504	0,075					
50mg/l	6	0,87	4,412	0,736	0,087	S3A	Fast	400rpm	Slow	25rpm
50mg/l	6	0,96	4,678	0,757	0,092	S3B	Fast	400rpm	Slow	25rpm
Average		0,92	4,545	0,747	0,090					
50mg/l	6	Optimal dosage and pH	Optimal dosage and pH	Optimal dosage and pH	Optimal dosage and pH	Original	Fast	250rpm	Slow	50rpm
50mg/l	6					Original	Fast	250rpm	Slow	50rpm
Average		0,66	4,660	0,55	0,108					

Polso table

Mixing tests		Optimal dosage and pH			Polso					
Dosage	pH	Turbidity	TOC	Al	UV	Name	Mixer settings			
50mg/l	6,5	0,39	4,977	0,102	0,113	S1A	Fast	400rpm	Slow	50rpm
50mg/l	6,5	0,69	5,568	0,613	0,153	S1B	Fast	400rpm	Slow	50rpm
Average		0,54	5,273	0,358	0,133					
50mg/l	6,5	0,52	5,202	0,393	0,113	S2A	Fast	250rpm	Slow	25rpm
50mg/l	6,5	0,58	5,243	0,473	0,125	S2B	Fast	250rpm	Slow	25rpm
Average		0,55	5,223	0,433	0,113					
50mg/l	6,5	0,45	5,123	0,274	0,113	S3A	Fast	400rpm	Slow	25rpm
50mg/l	6,5	0,43	5,324	0,489	0,120	S3B	Fast	400rpm	Slow	25rpm
Average		0,44	5,224	0,382	0,116					
50mg/l	6,5	Optimal dosage and pH	Optimal dosage and pH	Optimal dosage and pH	Optimal dosage and pH	Original	Fast	250rpm	Slow	50rpm
50mg/l	6,5					Original	Fast	250rpm	Slow	50rpm
Average		0,93	4,837	0,220	0,227					

Kauppi table

Mixing tests		Optimal dosage and pH			Kauppi					
Dosage	pH	Turbidity	TOC	Al	UV	Name	Mixer settings			
50mg/l	5,7	0,79	4,380	0,402	0,093	S1A	Fast	400rpm	Slow	50rpm
50mg/l	5,7	0,98	4,325	0,463	0,085	S1B	Fast	400rpm	Slow	50rpm
Average		0,88	4,353	0,433	0,089					
50mg/l	5,7	0,40	3,748	0,261	0,075	S2A	Fast	250rpm	Slow	25rpm
50mg/l	5,7	0,44	3,950	0,312	0,085	S2B	Fast	250rpm	Slow	25rpm
Average		0,42	3,849	0,287	0,075					
50mg/l	5,7	0,62	3,952	0,68	0,084	S3A	Fast	400rpm	Slow	25rpm
50mg/l	5,7	0,68	4,185	0,486	0,086	S3B	Fast	400rpm	Slow	25rpm
Average		0,65	4,069	0,583	0,085					
50mg/l	5,7	Optimal dosage and pH	Optimal dosage and pH	Optimal dosage and pH	Optimal dosage and pH	Original	Fast	250rpm	Slow	50rpm
50mg/l	5,7					Original	Fast	250rpm	Slow	50rpm
Average		0,55	3,593	0,199	0,075					

Appendix V.

Effect of temperature tables

Kämmenniemi table

Low temperature mixing			7 degrees		Kämmenniemi	
Dosage	pH	Turbidity	TOC	Al	UV	Name
50mg/l	6	2,65	6,422	3,297	0,194	KÄMKA
50mg/l	6	2,83	6,551	3,478	0,200	KÄMKB
50mg/l	6	2,04	6,121	3,161	0,173	KÄMKC
Average		2,44	6,336	3,320	0,187	
Optimal in 20°c		0,66	4,660	0,55	0,108	

Polso table

Low temperature mixing			7 degrees		Polso	
Dosage	pH	Turbidity	TOC	Al	UV	Name
50mg/l	6,5	1,71	6,023	1,462	0,175	POLKA
50mg/l	6,5	1,55	5,859	1,215	0,157	POLKB
50mg/l	6,5	1,00	4,952	0,760	0,114	POLKC
Average		1,28	5,406	0,988	0,135	
Optimal in 20°c		0,93	4,837	0,220	0,227	

Kauppi table

Low temperature mixing			7 degrees		Kauppi	
Dosage	pH	Turbidity	TOC	Al	UV	Name
50mg/l	5,7	1,59	4,994	1,475	0,140	KAUKA
50mg/l	5,7	2,09	5,470	2,310	0,165	KAUKB
50mg/l	5,7	0,98	4,739	0,993	0,118	KAUKC
Average		1,54	5,105	1,652	0,142	
Optimal in 20°c		0,55	3,593	0,199	0,075	