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SOME QUALITY FACTORS OF RIVER WATER

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ABTRACT

The purpose of this thesis was to study the essential factors, which determine the surface water qualities, more emphasizing Eurajoki river water. Particularly, this thesis focused on the humus removal and optimization of different coagulant chemicals: $Fe_2(SO4)_3 \cdot 6H_2O$, $FeSO_4 \cdot 6H_2O$ and $Al_2(SO4)_3 \cdot 3H_2O$. Chemical Oxygen Demand – COD and Biological Oxygen Demand – BOD measurement procedures were performed in order to accompany the studied goals. In addition, electric machinery measurement AAS –Atomic Absorption Spectroscopy and UV Spectrophotometer were used for Iron and Phosphorus content determinations respectively. Eurajoki River is one of rivers which have been studied about water qualities in Satakunta region. Content in thesis hopefully contributes to future restoration programs. All experiments were conducted in SAMK chemistry laboratory during October and November 2016.

According to the experimental results, iron (III) based coagulants are most effective in coagulation and flocculation process, which was clearly seen visually and by-COD_{Mn}-determination. Important is to carry out humus coagulation under optimal reaction conditions, e.g pH between 4 to 5. Also modified BOD method including lactose bacteria, was tested in order to determine dissolved organic substances. Results were relatively logical and reliable.

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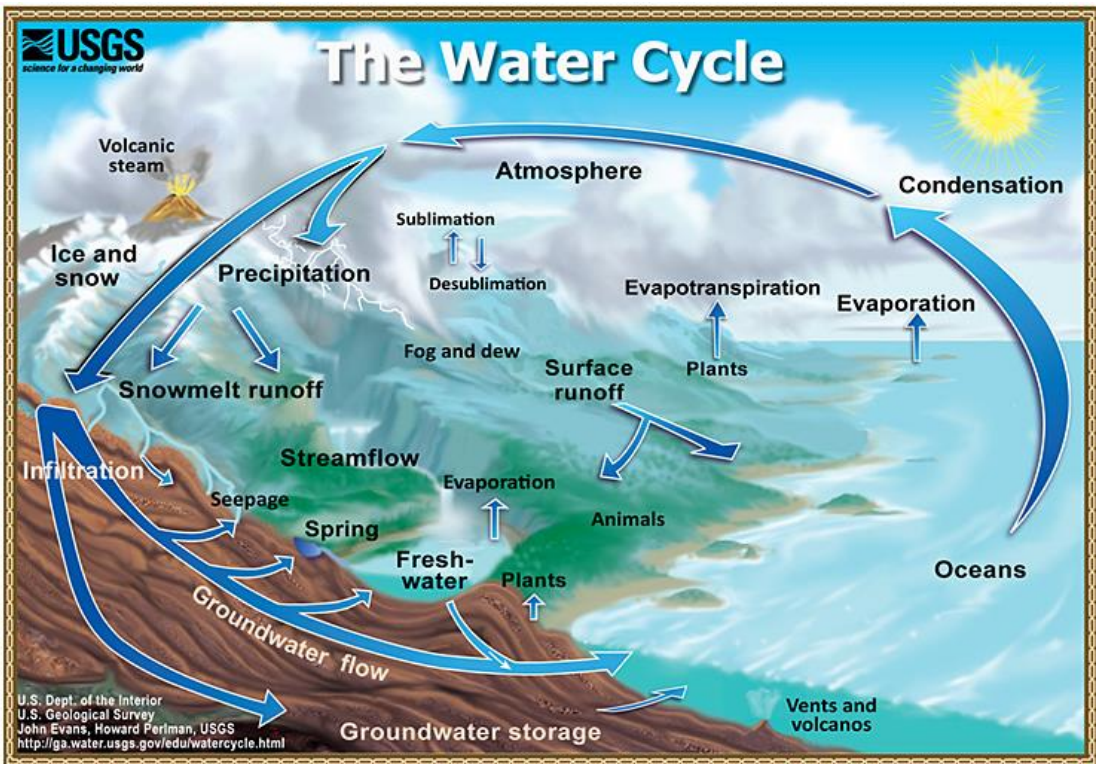
1 INTRODUCTION

Finland is one of the best life quality countries worldwide so attention to natural water resources is considerably prioritized in its environment conservation aspect. Thesis mainly focuses on Eurajoki river water in Finland regarding its qualities such as humus substances, phosphorus, and iron and surrounding regions that contribute river water characteristics. Humus exists in water body is the most concern in this thesis, which is an important decisive factor influencing coagulation process even though Eurajoki river water is not in use of drinking water production. The information of Eurajoki river water in English is inadequate available; therefore, this thesis work provides specific basic qualities, which is also for future reference usage. Experiments of COD_{Mn} had been done several times to deduce natural organic matter situation. BOD was conducted to depict its method effectiveness of bacteria degradation. Äyhönjärvi Lake is water sources used to produce drinkable water for residents living in Rauma, Finland so its humus content was tested with COD_{Mn}. Studies of natural organic matter – NOM and phosphorus removals are needed for river, lake restoration and management to have applicable approaches to conserve high quality water sources.

2 SURFACE WATER SOURCES

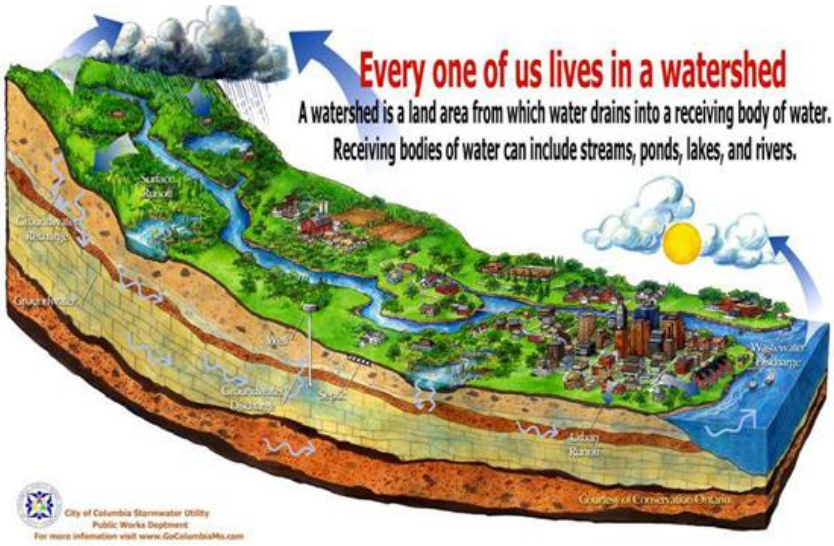
2.1 General Surface Water Sources

Fresh water flowing on the land surface is a contributor in the hydrological cycle happening in the Earth. The water evaporation from ocean causes the inland rainfall – precipitation. This element forms the surface flows which are called particularly streams, rivers, wetland and lake. Water precipitation partly penetrates into soil and beyond to ground water. The subsurface flows feed to surface water. The intersection of ground water and surface water is called hyporheic zone. (Walter Dodds & Matt Whiles 2010, 76, 80).



Picture 1 A summary of water cycle (USGS Science for Changing World 2016).

Drainage basin - Watershed is land-area that drains the stream-flow, rainfall into the common outlet channels from the higher point to lower point, which forms surface water sources. Water of river and stream-flow qualities is affected by the watershed routes due to human activities, nature phenomenon, and animal habitats. (Website of USGS Water Science School 2016)



Picture 2 Example of watershed (Website of City Columbia Missouri. 2017)

The experimental work concentrates on the Eurajoki river water and a part of work is done with Äyhönjärvi lake water. Rivers flow from higher elevation to lower one because of gravity. Beneath the land surface with a definite depth, there is saturated soil where the ground is saturated with water. If the rivers pass through the saturated area, the water from ground will seep out and join with river flow.(Website of USGS Science of Changing World 2016). A lake is formed by the cumulative surface water runoff or seeping out of groundwater. The inflow of water entering the lake is faster than outflow to river or groundwater or evaporation. (Website of USGS Water Science School 2016)

2.1.1 Eurajoki River

Eurajoki river flow originates from Pyhäjärvi lake, see figure 3 below, and dividedly runs to the Bothnian Sea - Bothnian Sea has basin countries Finland and Sweden and flow to Köyliönjoki River. The Pyhäjärvi lake is 50m higher than the sea level. The length of river is 52km; size of watershed land-area is 1336km^2. Water from Kokemaenjoki River has run to Eurajoki river in dry season since 2000. (Romakkaniemi 2011, 8).

Picture 3 River basin surrounding Lake Pyhäjävi, Lake Köyliönjäarvi, Köyliönjoki River and Eurajori river -dark blue route. (Website of Jarviwiki. Year Unknown)

2.1.2 Äyhönjärvi Lake

Picture 4 Äyhönjärvi Lake (Places To Walk In The Rauma Area 2013)

Äyhönjärvi lake is located in Lajo area, Rauma town. Surrounding the lake is residential place and vegetation. This lake is used for drinkable water in Rauma. (Places to walk in Rauma area 2013)

3 SURFACE WATER QUALITY CRITERIA

3.1 Water Quality Characteristics

In natural water, there are chemical constituents existing. Some of them are beneficial e.g calcium (Ca^{2+}) and some are harmful. Constituents can be organic, mineral chemicals and the concentration is measured in laboratory in mg/l unit.
Raw water has variety of dissolved mineral elements such as calcium, sodium, iron, magnesium, carbonate, bicarbonate, sulphate, chloride.
Physical properties of natural water are important in water treatment such as original water pH, turbidity, electrical conductivity, hardness, alkalinity, dissolved oxygen, dissolved solids, colour, temperature, taste and odour.
Algae, aquatic plants, bacteria, virus and other micro-organism constituents present in raw water, which determines water quality. Typically algae and plants mostly occur in surface water. Too large amounts of them brings bad taste and odour to water and possibly change pH level.
Surface water rarely has radioactive constituents, like radon (Rn-226), which could be present in some groundwater sources originating from the bed rock. If they are in surface water and sea water, they are caused by human activities. (American Water Works Association 2009, 116 ,127 & 128)

3.1 General Surface Water Quality

3.1.1 Runoff Water Quality

Runoff flow is made from the excess amount of water on land surface and also comes from storm (storm-water runoff). Runoff is essential factor contributing the river, lake water qualities. The urbanization activities; animal natural actions; disasters; nature movements such as wind, rainfall, snowing; different types of elements that runoff passes through such as soil, vegetation, land. They affect the runoff qualities. Runoff can contain nutrients such as nitrogen, phosphorus, bacteria, chemicals, metal, organic compounds and sedimentation. It determines the characteristics of a certain river, lake. (Website of USGS Science Water School 2016).

3.1.2 The Impacts of Agricultural Runoff

The section 2.1.1 describes the stream-flows, which constitute Eurajoki River, in particular is Lake Säkylän Pyhäjärvi. Köyliönjärvi, where Köyliönjoki river flows into, is known to be contaminated with nutrients originating from agriculture (eutrophication). This type of lake has oxygen depletion, i.e. lack of dissolved oxygen, due to the occupying of nutrients which slows down the water quality improvement. Nutrient load from cultivation region and animal husbandry run off 55% - phosphorus content and 39% - nitrogen content to Lake Säkylän Pyhäjärvi. Phosphorus in lake water body has been ranked high especially in winter period, so restoration programs has been implementing. (Kirkkala 2014, 23&27)

Picture 5 Köyliönjärvi lake (Google 2016)

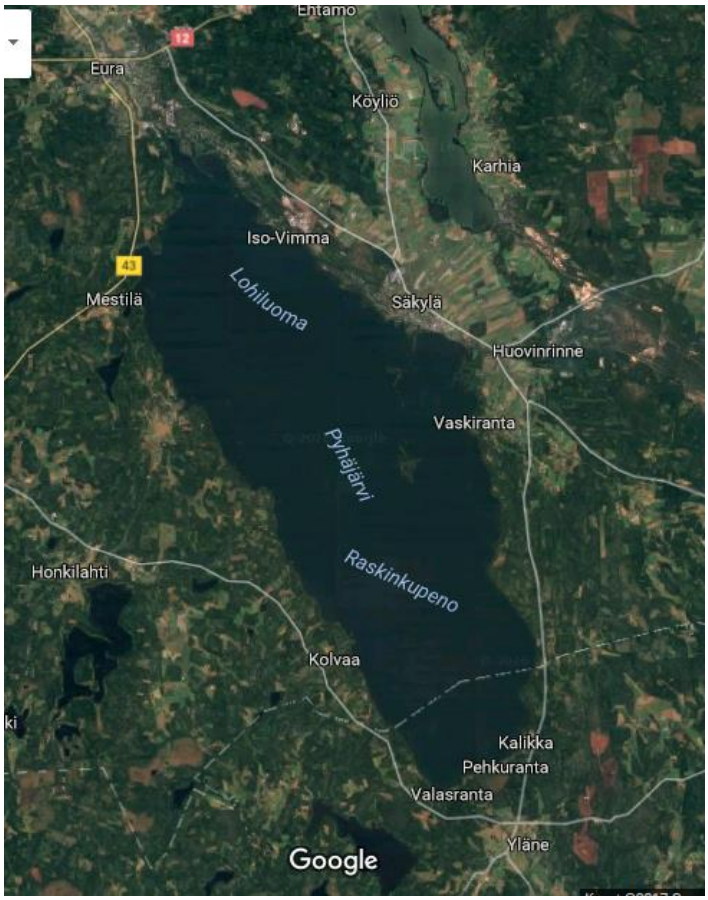
As it can be seen in picture 5, there are fields around the lake that can trigger the cultivated agricultural runoff to the river. In the past research, the lake had hypertrophic level of chlorophyll a and nutrients even though the exceed amount of phosphorus did not effect to water quality. Chlorophyll a is the element for the photosynthesis of plant and algae. Maximum phosphorus content was 170 mgP/m^3 (0.17 mgP/L) in summer 1998 (Sarvala, Ventalä, Helminen, Hirvonen, Saarikari, Salonen, Sydänoja & Vuorio 2000, 40). The algae expand basing on factors such as sufficient amount of

nutrients (phosphorus, nitrogen), sunlight, pH, temperature. (Website of Department of Ecology State of Washington, “year”)

There are some impact routes affecting to the surface water quality. Fertilizer content commonly phosphorus, which leads to the eutrophication, algae growth bloom and oxygen depletion. Irrigation, clearing and cropping change the natural landscape and water system. It can increase the salinity level in river and on land. The salt runoff makes surface water more salinity. High salt-elements cause the damage of ecology in river water. (Website of FAO Corporate Document Repository 2016)

Sedimentation is an influential factor to water quality of river, lake. It derives from tillage when the soil surface is disturbed and dissociated. The wind carries away soil light particles into the lake, river. The water erosion accompanies the sediment to the stream. Sediment contains nutrients, which causes the eutrophication. This is favorable environment for the algae growth leading to the elimination of rooted-plants in water body. Moreover, algae expansion prevents the oxygen penetration causing the inadequate oxygen level for fresh water ecology. Suspended solids determine the turbidity level of water. The mist level of water body increases when the turbidity indicator increases. Suspended solid particles run off from cultivated field possibly include the pesticide, pathogen that can exist in water. (Website of Agriculture and Agri – Food Canada. 2014)

3.1.3 The Impact of Vegetation Cover to Surface Water Quality

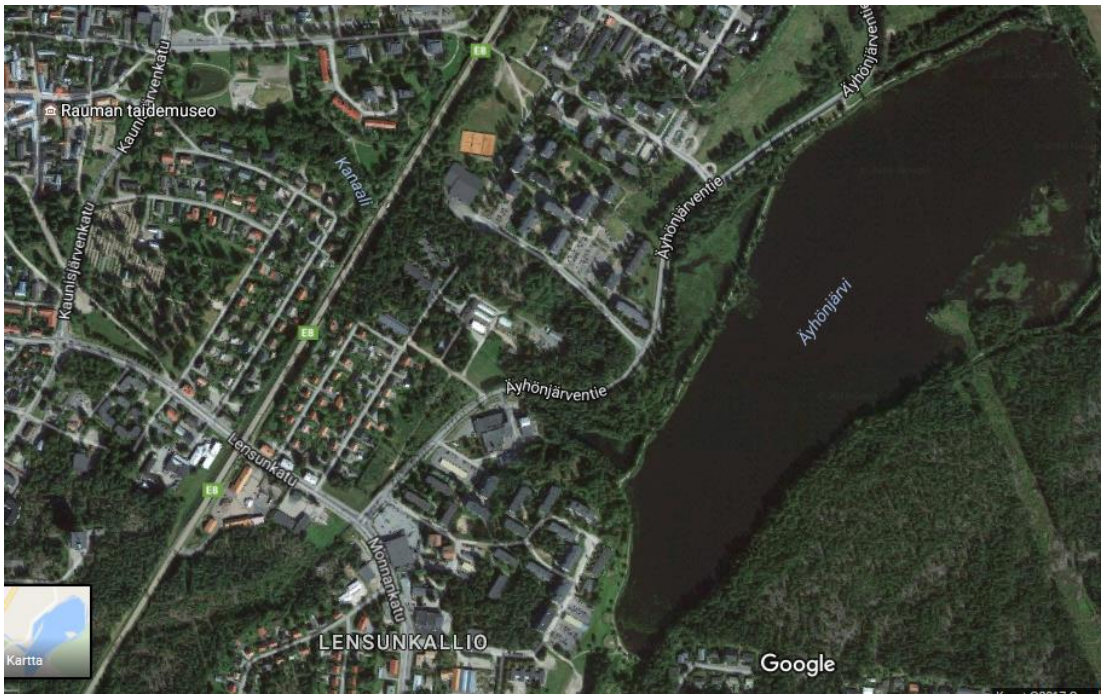


Picture 6 Pyhäjärvi lake (Google Map. 2017)

Pyhäjärvi lake is surrounded by vegetation area. The vegetation cover is the area full of trees, shrubs locating at the stream-bank. The area can be higher than the river water flow. The vegetation helps to prevent the agricultural runoff and non-pollutant sources entering the surface water. Vegetation absorbs the nutrients.

It functions as a filter to limit the release of sediment, nutrient, unexpected materials runoffs toward surface water region. The stream stabilization is remained. Water temperature should be at acceptable level. Low temperature is practical condition for water to absorb and sustain the dissolved oxygen amount. The nutrients tend to attach to the plant's root and be able to supply the needed nutrient for plants. It prevents the eutrophication to surface water. (Hutchens 1998, 2)

3.1.4 The Impact of the Urbanization



Picture 7 Äyhönjärvi Lake (Google Map. 2017)

Äyhönjärvi Lake is located nearby residency area. Urbanization means human activities such as construction, building, transportation, factories affect to water quality and aquatic habitats. When land cultivation increases, fish community declines. Temperature of water body goes up due to upland runoff, which can change habitat of some sensitive aquatic species. Food chain is interrupted when streams are altered. (Cahill, Thomas H, Adam, Michele, Horner, Wesley .2012.41)

Picture 8 Eurajoki River runs through agricultural fields and residential area.(Google Map 2107)

4 CHEMISTRY IN WATER

4.1 Alkalinity

This term expresses the water capacity of attracting H^+- ions in order to neutralize the acidity in water body. pH is high, when alkalinity level is high. Ions in water acting as alkalinity contributors are bicarbonate (HCO_3^-) , carbonate (CO_3^{2-}) and hydroxide (OH^-) . Chemical reactions below describe the H^+- absorption:

$$HCO_3^-(aq) + H^+(aq) \leftrightarrow CO_2(aq) + H_2O(l) \quad (1)$$

$$CO_3^{2-}(aq) + H^+(aq) \leftrightarrow HCO_3^-(aq) \quad (2)$$

$$OH^-(aq) + H^+(aq) \leftrightarrow H_2O(l) \quad (3)$$

H^+- ions represent as acidic character, which decreases pH. They are absorbed by alkalinity ions and produce mainly CO_2 and water. (Stanley E 2010, 59)

4.2 Origin of Calcium in Water

Calcium (Ca) presents naturally in water as Ca^{2+}, or more precisely bound in calcium hydrogencarbonate ($Ca(HCO_3)_2$). Calcium exists in soil, rocks in different forms of minerals, e.g. as limestone ($CaCO_3$), gypsum ($CaSO_4.2H_2O$), $CaSO_4$ and dolomite $CaMg(CO_3)_2$ produce Ca^{2+} ions into water. Calcium ions contribute water hardness as pH stabilizer:

$$Ca(HCO_3)_2(aq) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2\,CO_2(aq) + 2\,H_2O(l) \quad (4)$$

CO_2 gas dissolves in water and form bicarbonate ions:

$$CO_2(g) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq) \quad (5)$$

Calcium ions combine with bicarbonate ions.

$$Ca^{2+}(aq) + 2\,HCO_3^-(aq) \leftrightarrow Ca(HCO_3)_2(aq) \quad (6)$$

Carbon dioxide CO2 which originates mainly from organic matter degradation continually dissociates and presents in water with high level. The chemical reaction above tends to shift from left to right. (Manahan 2010, 63)

5 SURFACE WATER PURIFICATION

Surface water purification refers to municipal water treatment. Drinkable water from faucet is purified from river, lake and reservoir water sources. The sources could be either originally having good qualities or get polluted. They can have various components existing in water body such as excess metals, bacteria, oil, food residuals and so on. The raw water treatment plants guarantee the residents receiving non-poisonous, clean, safe drinking water every-day. Importantly, the purification processes oblige the allowed amount of chemical in drinking water and effectively eliminate the listed dangerous pathogen – virus and bacteria. (Website of Lentech 2016)

5.1 Surface Water Purification Process

This is the first step of treatment process, which is also called water intake. The pumps and pipeline system is installed to transfer raw water to the plant. The pumps and pipeline needs assuring the hygiene in order not to cause the contamination to the inflow. It depends on the chosen materials, construction, and flaw detection (Website of Filtronics Municipal and Industrial Filtration System. 2013).

In primary stages of conventional techniques, the influent is transported to the screening making up by the screen bars. The types of screening basing on the spacing of screen bars so as to retain the large solid objects e.g tree branch or trunk, leaves, small aquatic animals and litter in surface water inflow. The spacing of screen bar for surface water is 20mm to 40 mm. When the clogging is starting, the screen is cleaned off either manually or automatically. The plant operators set up the proper inflow velocity so that complete clogging will not occur. (Website of Lenntech Water Treatment 2016).

In secondary stage, if water is acidic or alkaline, operators will adjust pH of natural water by base chemical e.g. lime (CaO), soda (Na_2CO_3). Then, coagulation and flocculation are most important decisive processes in treatment plant. They are well-explained in part 6.2 below in this thesis. Ferric sulphate ($Fe_2(SO_4)_3$) is widely used coagulant. Afterwards, water with precipitated particles enters to sedimentation tank – settling process or – in the case of flotation- flocs are lifted up to the water surface and removed by mechanical devices. Staying time of floc or the depth of basin determines the efficiency of sludge removal in water. Cleaner – upper layer of water

exits from sedimentation basin. This outflow water comes to filtration section in which remained floc is removed with different methods: activated carbon pore, sand, membrane filtrations. This process is explained in part 6.3 below in this thesis.

Tertiary stages emphasize on disinfection of water before distributing to consumers. To ensure water quality, pathogen is eradicated by several approaches: usages of chlorides, ozone, UV – ultra violet radiation. Then, with different water utilization purposes, there are supplemental processes to attain final expected water qualities. For example, water is re-mineralized and disinfected for drinking use.(Website of Filtronics Municipal and Industrial Filtration System. 2013).

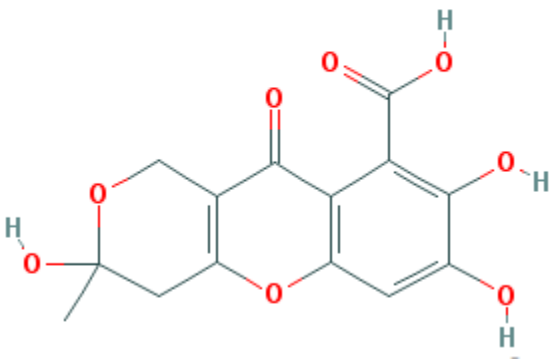
6 NATURAL ORGANIC MATTER IN RAW WATER

6.1 Humic Substances in General

Humic substances are the natural organic matter (NOM) material residue deriving from decayed vegetation – plant in soil. The soil water carries the NOM to the surface water. These substances include humic acid, fulvic acid, humin fractions. The fundamental elements in humic substances are C: 45 – 55%; O: 30-45%; H: 3- 6 %; N: 1-5%; S: 0-1%. The properties of these substances affect to water quality. (Stanley E 2010, 77). Briefly explaining, humic acids are insoluble-water compounds in condition of pH less than 2, acting at least partially soluble at higher pH.

Natural raw water pH varies typically between 6.0 and 7.0, it is slightly acidic.

Their colors are dark brown and black. Fulvic acids are soluble compounds in water under all pH condition. Their colors are light yellow to yellow-brown. Humin is not soluble in water in any value of pH and it has black color. (Jerzy Web, year unknown).



Picture 9 Fulvic acid compound: $C_{14}H_{12}O_8$ (Website of PubChem .2016)

The coagulation in raw water and wastewater purifications occurs relying on the important environmental trait of metal ion binding between humic substances and coagulant chemicals. The metal cations of coagulant form with the molecules of natural organic matter (NOM) to create larger solid particles. Iron and aluminum coagulants

are common-effective chemicals used in treatment plants. (Stanley E Manahan. 2010. 78)

The natural organic matter in water body comes from the decomposition of aquatic organisms, animal manure or the growing of living organism, biomass. The humus substances in water are usually components of humic acids and fulvics acids. These acids compounds contain the functional groups: carboxylic and phenolic groups, which can become negative charges chelating with metal ions of coagulants.(American Water Works Association.2010.6)

6.2 Humus

This thesis concentrates on the humus fraction in soil affecting to surface water quality. Humus is generally another name of humic substances. Humus makes the surface water turn into light or dark-brown color depending on amount of it. This component is significant important for the soil's health and acts as glue adhering soil particles. Agricultural land benefits from the humus characteristics such as water-holding capacity, oxygen penetration, and nutrient binding. Soil and agricultural run-offs are the actors transporting the humus to the rivers, lakes. (Website of Science Encyclopedia. Year unknown).

In natural water body, the functional groups of humus covalently bond with metal ions; therefore, organic particles will have partly inorganic traits and vice versa. The presence of NOM in water results the production of by-product of disinfection; when chloride is added into water having organic matters. Natural organic matter – NOM negatively affects to raw water quality; for instance, the color, odor, taste will change or more by-products are formed. Extra chemicals for treatment process are needed; the efficiency of disinfection processes e.g UV- treatment is reduced because some NOM particles are able to absorb the UV- light. The adverse impacts can bring few disadvantages to membranes, water flux, and increase pressure for operations. Microbe is present in water and they can use residue short-chain NOM as food source, which likely expands the microbe population and pathogen in treatment. This is why disinfection is necessary to inactivate microbes and by-products in treated water.(America Water Works Association 2010, 7)

7 HUMUS REMOVAL

7.1 Interactions of Particles – Water

Raw water naturally contains suspended, colloidal, dissolved compounds; bacteria, algae, pathogen are considered as bio-colloidal. Much of them have size less than 1 micrometer, which hardly settles down on their own. Hydrophilic is the compound bonding with water and it can be either inorganic or organic materials. So the chemical coagulants are needed to form agglomerates.

Crucial principle for coagulation taking place is surface charge of particles in water. Natural organic matter – NOM is macromolecules, which include carboxylic group as functional group and can donate the H^+ as the below equation illustrates:

$$R - COOH(aq) \leftrightarrow R - COO^-(aq) + H^+ (aq) \tag{7}$$

Above equation also indicate the NOM substances induce negative charge, which bind positive ion of coagulants like ferric iron (Fe^{3+}) or aluminium (Al^{3+}) see below.

There are other formations of surface charge particle in water comprising metal oxides – crystal, inorganic functional group, clay/mineral. Nevertheless, as already told in part 5.2, this thesis mainly concentrates on humus – natural organic matters. (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 143)

Particles in water often have negative surface charge. They bind with cation layer of ions which has positive charge. It accords to electrostatic forces that are about attractive and repulsive interaction within charged particles.

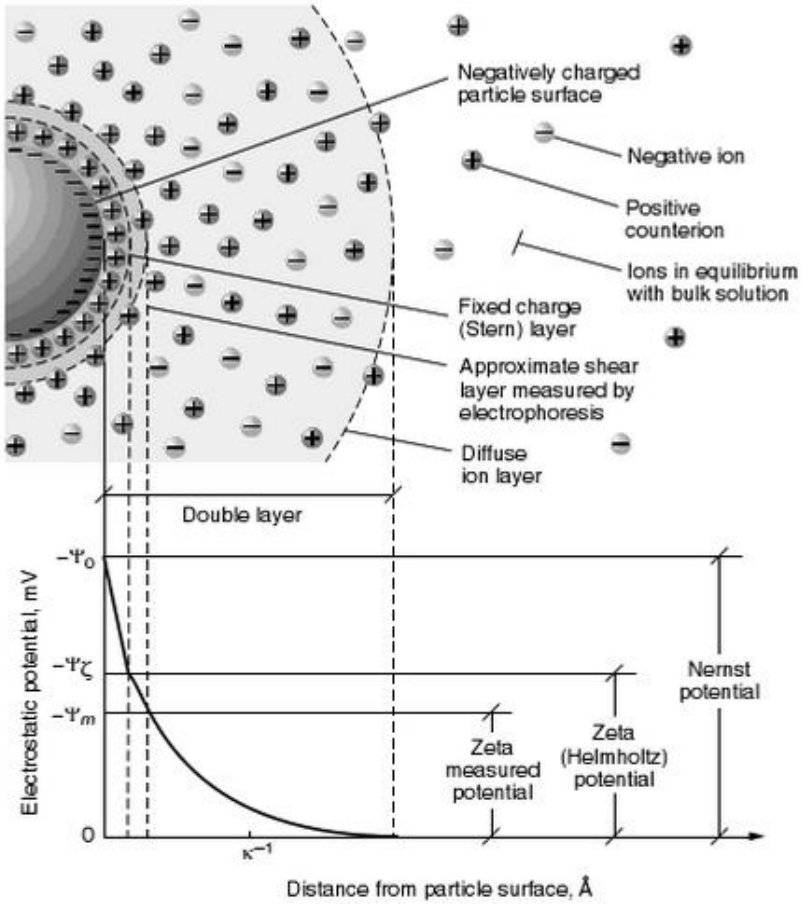


Figure 10 Structure of electrical double layer (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 145)

As the figure 10 illustrates, basically, negative surface charged particle attracts positive charged particle due to electrostatic force and create first layer – fixed charge (Stern) layer. Electric field induces a certain force that can repel the negative particles - anion and attract positive ones. Then, charged particles are in equilibrium state and form electrical double layer - EDL. EDL varies depending on the aqueous/solution characteristics. (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012. 145)

In addition, Van der Waals bonding is a factor creating the attraction interactions between particles. This is a weak electric force, which is able to attract one molecule with another near-by molecule in any kind of state (gas, liquid, solid). Particles in water (pH 6 -8) are mostly negative surface charged; they tend to repel one another. The electrons in atoms are moving and they make molecules slightly either positive or negative at other ends. The Van der Waal force must exceed the repulsive forces

caused by net negative charged particles. In result, the molecules are attracted to each other in water. (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012. 146).

7.2 Coagulation and Flocculation Stages

This stage indicates the chemical treatment to freshwater sources. The highly efficient selected chemical - coagulant is added into raw water inflow after screening. Dissolved and suspended materials attach to coagulant compounds to form the larger visible particles. These particles gradually settle down owing to the increase of mass. The mixture is mixed to balance equally concentration inside the buffer and exert force to agglomerate the large particles into solid clusters. Some of clusters are at the bottom and some float on the top of buffer. Coagulation – Flocculation combination process supports the sedimentation - filtration to work effectively. (Website of Sustainable Sanitation and Water Management. 2011)

The desirable floc size is crucial in filtration section. If there are too large flocs, it will diminish the filtering rating. Otherwise, if it is too small, it is unlikely to settle down or form agglomerates; in this case the aeration produces air bubbles and very small flocs attach onto the air bubbles and starts floating. The capacity of flocculator plays a decisive role for the floc size. The plant operators adjust the flocculator velocity suiting with the water temperature/viscosity and this depends on the season in a year. (America Water Works Association. 2010. 102)

7.2.1 Coagulations and Flocculation Formation

The chemistry experiments conducted in SAMK laboratory were carried out by using inorganic metallic coagulants: hydrated aluminum (III) sulfate – $Al_2(SO_4)_3 \cdot XH_2O$;and hydrated iron (III) sulfate - $Fe_2(SO_4) \cdot 6\ H_2O$ or hydrated iron(III) chloride – $FeCl_3 \cdot 3H_2O$.

Purpose of coagulant addition is to destabilize colloidal and suspended solids, dissolved organic matters in raw water. These compounds are absorbed onto the surface of coagulant particles following charge neutralization.

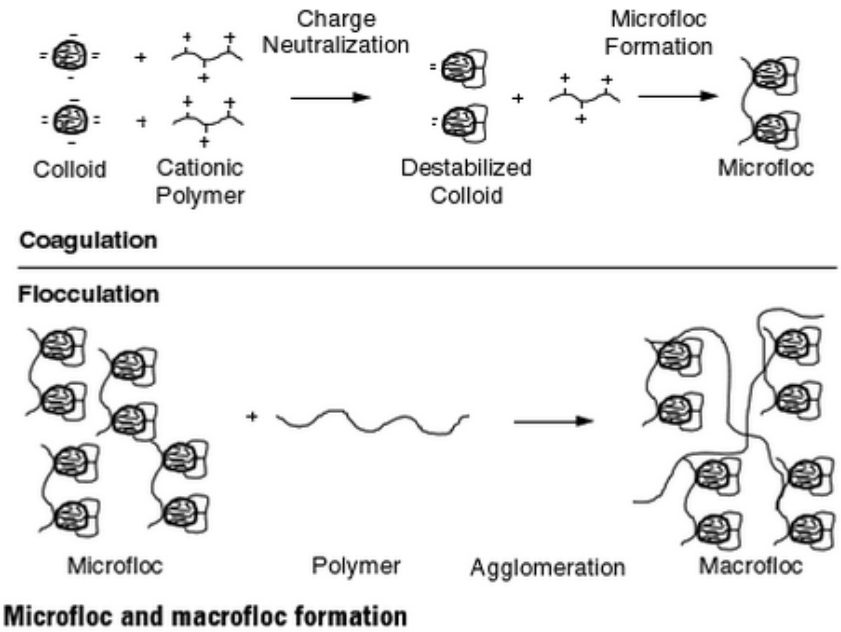


Figure 11 Microfloc and macrofloc formation (AWWA.2009.50)

In solution, metal ions in coagulants exist as Al^{3+} and Fe^{3+} react with water to form various molecules. Basically, $Al(H2O)_6^{3+}$ and $Fe(H2O)_6^{3+}$ molecules – hydrated metal ions are attained but concentrations of them diminish steadily due to chemical reactions so as to reach the most stable state of metal ions. Therefore, there are subsequent reactions occurring in water solution.

For instances:

$$Fe(H_2O)_6^{3+}\ (aq) \Leftrightarrow Fe(H_2O)_5OH^{2+}\ (aq) + H^+\ (aq) \quad (8)$$

$$Fe(H_2O)_5OH^{2+}\ (aq) \Leftrightarrow Fe(H_2O)_4(OH)_2^+\ (aq) + H^+(aq) \quad (9)$$

$$Fe(H_2O)_4(OH)_2^+\ (aq) \Leftrightarrow Fe(H_2O)_3(OH)_3(s) + H^+(aq) \quad (10)$$

Over all reaction formula is hence:

$$Fe(H_2O)_6^{3+}\ (aq) \Leftrightarrow Fe(H_2O)_3(OH)_3(s) + 3H^+(aq) \quad (11)$$

The metallic coagulants make water solution shift toward acidity and they will give off H^+ obeying Brönsted acid-base until the hydrated metal ions achieve stability - precipitation. (Mahana 2010,62)

Insolubility of diversified ferric molecules in aqueous solution is wider than alum ones; so it is more effective for precipitated-solid particles absorb the NOM. Ferric coagulant is commonly utilized in water treatment plants. pH influences on the coagulation process. Hydrolyzed alum and ferric salts contain strong acidic property which effects to alkalinity and lowers down the pH value of raw water. Alum and ferric coagulants have distinguished optimum pH range of solubility (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 153 &156). Optimum pH for iron-base coagulant is from 5 to 8.5 and alum-base coagulant is between 5.5 – 7.7 (Yonge 2012, 8 & 13)

Depending on natural water characteristic; alkalinity level, which is acid neutralization indication is different and H_2SO_4 acid sulfuric is created. If alkalinity is too low to neutralize pH, base chemical is added to raise desired pH number. NaOH, $Ca(OH)_2$ or Na_2CO_3 are added. Considering ferric coagulant is used, the below chemical reactions taking place (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 153.156):

$$Fe_2(SO_4)_3 \cdot 9H_2O(aq) \rightarrow 2Fe(OH)_3(s) + 3H_2O(l) + 6H^+(aq) + 3SO_4^{2-}(aq) \qquad (12)$$

$$Fe_2(SO_4)_3 \cdot 9H_2O(aq) + 6NaOH(aq) \rightarrow 2Fe(OH)_3(s) + 9H_2O(aq) + 3Na_2SO_4(aq) \qquad (13)$$

(Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 153&156)

Coagulant dosage is decisive parameter to get the optimum pH number. Over-dosing causes the water solution more acidic, pH drops down. Proper dosage gives effective NOM removal process and economically usage chemical resources. Relying upon the raw water quality, recommended alum dosage is 10 – 150mg/L and ferric dosage (($Fe_2(SO_4)_3 \cdot 9H_2O$) is 10 – 250 mg/L; $FeCl_3 \cdot 6H_2O$ is from 10 – 250 mg/L. (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 156)

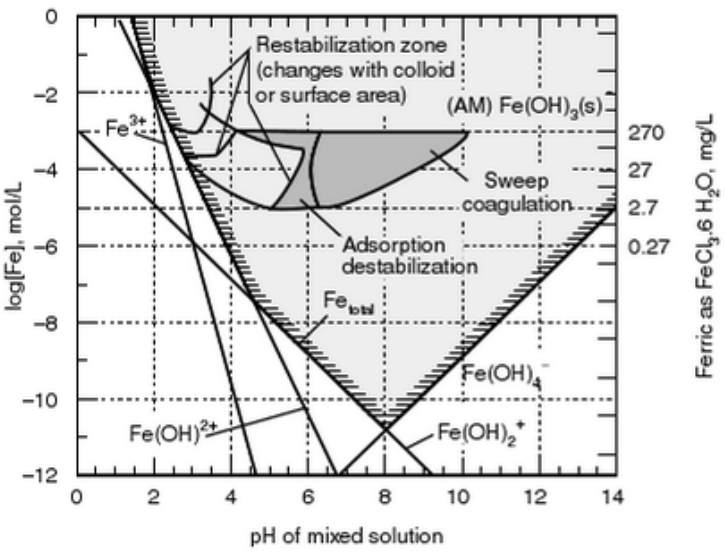


Figure 12 Solubility of Fe(III) at 25°C indicating the relation between pH and coagulant dosage.

The shaded area in figure 12 provides process of donating proton (H^+) of iron (III) ion in solution until it attains stable form ($Fe(OH)_3$)). pH adjustment and appropriate chemical dosage determine the favorable coagulation – "sweep coagulation". Shaded area refers the precipitate formation of iron (III). Darker shaded region practically illustrates the wanted results in water treatment plants where they can reach the best optimization of both parameter pH and dosage. Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 152). The optimum pH for iron-base coagulant is from 5 to 8.5. (Yonge 2012, 8)

7.3 Clarification Processes

7.3.1 Sedimentation

Sedimentation is the process in which floc, suspended solid particles, mineral from influent water settles down to basin bottom by gravity. Turbulence of inflow reduces when these particles are removal. They accumulate at the bottom and generally are called sludge. Sludge is taken out to disposal or reuse places. The retention time of water and depth of basin determine the efficiency of particle removal. (Dave & Mike 2009, 81)

Beside those suspended particles of which are easily flocculating and aggregating the size as discussed in “Coagulation and Flocculation Formation” section above. There are discrete particles; these particles do not interact with their neighbor matter. They settle down independently and low concentration and are not able to form floc. They are removed in pre-sedimentation before coagulation. When flocculating particles amount increases, they adhere together and create solid layer called blanket of particles. This layer gradually settles down as well as combines with its beneath particles. Inflow water continually entry to basin and create more “blanket” layers. These layers are slowly and become bulky solid at basin bottom. (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 195)

7.3.2 Filtration

Outlet water flow from sedimentation basin enters filtration section. The purpose is to get rid of remained suspended particles, small flocculates that cannot settle down, and dissolved metals. Micro-organism, pathogen are removed in this process. There is various filtration media which are most effective to absorb different size of particles, which is called rapid filtration.

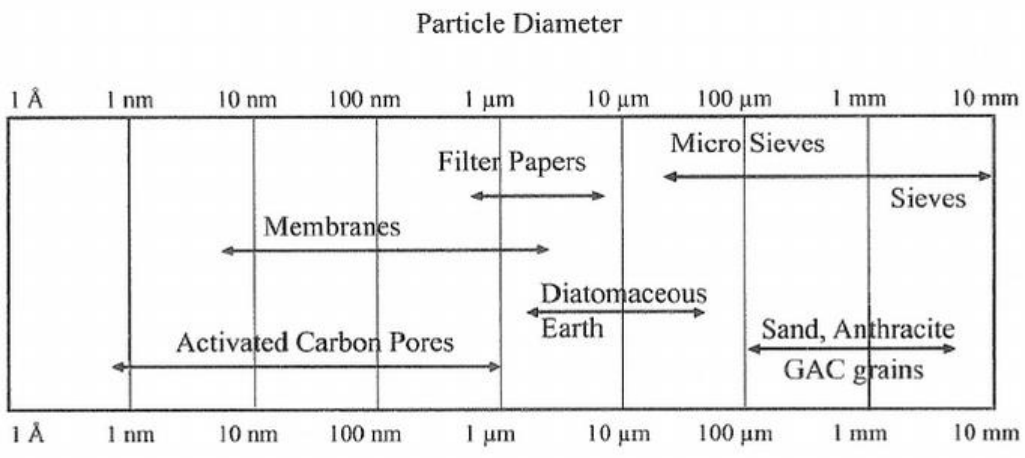


Figure 13 Size Range of Different Types of Filter (AWWA 2010, 122)

Influent water passes through the filter media from top of chamber. Solid matters in water are absorbed onto surface of media. Granular activated carbon filters are able to absorb larger organic compounds and chlorides from water. A proper amount of activated carbon and slow water rate enhance the filtration effectiveness. The longer

time water in filter bed, the more unwanted particles is absorbed onto media. (Website of Water Professionals. Year unknown). Anthracite is a less impurities, highest carbon content coal and less dense than sand. It is placed on sand layer setting up dual media filtration. Denser mineral than sand e.g. garnet, ilmenite are laid under sand forming trio media filtration. One layer of media sometimes is arranged e.g. only sand or anthracite. (Kerry, David, John, Trussel, Geo Howe, Hand, Crittenden, Trussel & Tchobanoglous rge 2012, 235)

Other options are membrane filtrations which have the same purpose as granular activated carbon is to remove water's contaminants by applying pressure to water solution. Microfiltration, ultrafiltration are commonly used in water treatment plant. Membrane filters use thin porous organic polymer materials as filter media such as polyvinylidene fluoride (PVDF), polysulfone (PS), polyethersulfone (PES). On the other hand, reverse osmosis (RO) is modern widely effective process separating unnecessary dissolved particles out of water. This system is also used to desalinate sea water and brackish water. (Howe, Hand, Crittenden, Trussel & Tchobanoglous, 289&328)

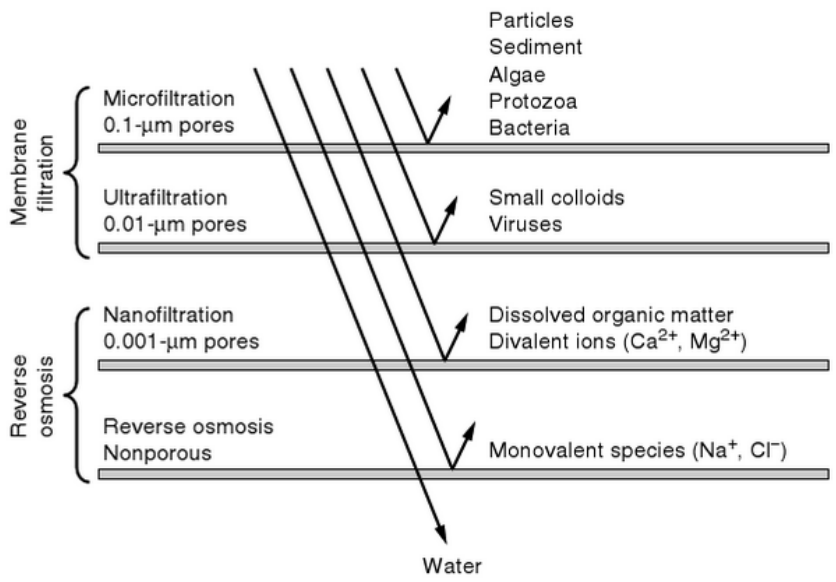


Figure 14 Pressured – Driven Membrane Classification (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 284)

8 ION EXCHANGE

This process is widely used in power plants, which removes humic substances, dissolved matter and undesirable ions. Process utilizes synthetic resins to strip away contaminants and give into water source necessary ions. In addition, ion exchange acts as water softening. There are two fundamental types: cation and anion exchanges.

Cation exchange absorbs positively charged ions e.g. Ca^{2+} , Mg^{2+} and release resin ions e.g. Na^{+}, H^{+}. In order to get rid of humic substances/total organic compounds, anion exchange is applied. Resins take away negatively charged organic matter and exchange resin ions e.g Cl^{-}, OH^{-} . (America Water Works Association 2009, 329, 331 & 339)

8.1 Absorption Process

To specifically remove synthetic organic chemicals, compounds causing odor – taste – color, disinfection by-product, natural organic matter, some heavy metal. Common absorbent material is e.g. activated carbon, granular alumina, and synthetic polymeric absorbent. Matter - adsorbate attaches on surface of absorbent until it reaches saturation state, then it gradually desorbs. (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 371)

9 DISINFECTION

Disinfection is an important stage that raw water purification must have so that drinking water is distributed without pathogen – organisms cause disease to human.

9.1 Chlorination

Chlorine gas (Cl_2) or sodium hypochlorite (NaOCl) are disinfectants used in treatment. Either of them is injected into water to deactivate microbe.

$$Cl_2\,(g) + H_2O(l) \rightarrow HOCl(aq) + HCl(aq) \quad (14)$$

(Kerry, David, John, Trussel, George 2012, 532)

Hypochlorous acid – HOCl is produced and it dissociates into H^+ and OCl^-

$$HOCl(aq) \Leftrightarrow H^+\,(aq) + OCl^-\,(aq) \quad (15)$$

HOCl and OCl- have disinfecting capacities and deactivate pathogenic organism in water, which forms chloride ions – Cl^- (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 532).

If NH_3 exists in water, there are combined chlorine formed and nitrogen gets oxidized to N_2 gas and nitrate – NO_3^-.

$$2NH_3(aq) + 3\,HOCl(aq) \rightarrow N_2(g) + 3H_2O(l) + 3HCl(aq) \quad (16)$$

$$NH_3(aq) + 4HOCl(aq) \rightarrow H^+(aq) + NO_3^-(aq) + H_2O(l) + 4HCl(aq) \quad (17)$$

(Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 535)

Sodium hypochlorite is commonly utilized in disinfection process because chlorine liquid contains hazardous factors:

$$NaOCl(aq) + H_2O(l) \rightarrow HOCl(aq) + Na^+(aq) + OH^-(aq) \quad (18)$$

(Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 532)

9.2 Ozone

Using ozone as disinfection agent to deactivate micro-organism, ozone – O3 is oxidized to oxygen O2. Contrasting to chlorination, O3 in water decays over time and in final forming radical hydroxyl – $HO^{\cdot}$ such as hydroperoxyl - HO_2-.

$$O_3 + (\text{microbes}) + 2H^+ + 2e^- \rightarrow O_2 + H_2O + (\text{inactive microbes}) \qquad (19)$$

(Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 538, 539)

9.3 Ultraviolet Light

The wavelength range of ultraviolet light used in disinfection is between 200nm to 300nm, which induces high energy that can penetrate to DNA in living organism. Therefore, it can inactivate microbes in water owing to DNA transformation and prevent reproduction of living cells. (Howe, Hand, Crittenden, Trussel & Tchobanoglous 2012, 544)

10 COD – CHEMICAL OXYGEN DEMAND AND BOD – BIOLOGICAL OXYGEN DEMAND

10.1 Definition of Dissolved Oxygen

Dissolved oxygen -DO is the most important element in natural water, which is fundamental realistic indicator to define water quality and effect to aquatic living organism. Oxygen in water mostly comes from oxygen (20.95%) in atmosphere. It penetrates into water body until getting saturated. Photosynthesis produces oxygen when consuming CO_2 and sunlight. However, this oxygen amount from photosynthesis does not take into account much compared to oxygen from atmosphere; because respiration takes place in night-time. Water temperature, partial pressure and salt content can affect to oxygen content in water. High temperature makes oxygen escape from water and low temperature retains it. Sea water has less dissolved oxygen than surface raw water. Degradation of plant, algae in water take ups dissolved oxygen and releases carbon dioxide and water. (Manahan 2010, 55)

10.2 COD – Chemical Oxygen Demand

This thesis has done experiments to determine COD- and BOD- values. BOD - Biological Oxygen Demand is explained at part 7.3.

Chemical Oxygen Demand measures required oxygen to oxidize organic matter in raw water, which produces carbon dioxide and water. It usually has strong oxidizing agent and under acid condition. KMnO4 – strong oxidizing agent and H2SO4 – acid solution are used in this thesis' experiments. COD is one of water quality indicators to know the degree of pollution in water body. High COD means sample water contains high content of organic compounds and DO is depleting. Reduction of DO causes serious negative effect to aquatic creatures e.g fish kill. Low COD refers excess DO amount can cause supersaturated state in water. (Website of RealTech Inc 2015)

10.3 BOD – Biological Oxygen Demand

Biological Oxygen Demand is a measurement to determine needed oxygen which is consumed by micro-organism, particularly bacteria to decompose organic matters in raw water. Tested samples are at rest in dark place about 5 or 7 days so as to measure reduction of DO content. Low BOD indicates water sample less polluted – less organic compounds and high BOD is opposite. Plant grows fast due to excess nutrients; decay of plant and algae; urban runoff can occupy DO in water. Bacteria consume DO to decompose organic matter which triggers DO content diminishes. Aquatic living organism lacks of oxygen for their natural activity. (Website of Apec Water Free Drinking Water. Year Unknown)

EXPERIMENTAL PART

11 GENERAL INTRODUCTION

This section mainly focuses on experiments done in SAMK chemistry laboratory, where COD_{Mn} and BOD were analysed including procedures and results. Sample water used in experiments was deionized water, tap water, Äyhönjärvi lake water, Eurajoki River water and pure water.

12 WORKING PROCEDURES IN EXPEWRIMENTAL PART

Electrical equipment involved in experiments is introduced below.

Analytical test methods, which are illustrated in appendixes.

Picture 15 Atomic Absorption Spectroscopy – AAS (Website of Lab – training Experience Beyond Books. 2017)

Picture 16 Laboratory Water Bath for COD_{Mn} measurement (Website of Memmert Experts in Thermostatic)

Picture 17 Ultraviolet Absorbance machine for Phosphorus measurement (Website of Scintek 2017)

13 HUMUS REMOVAL - COD_{MN}

13.1 Deionized Water

13.1.1 $Fe_2(SO4)_3 \cdot 6H_2O$ Coagulant.

Äyhönjärvi Lake Water:

Table 1 COD-and $KMNO_4$-Values of Tap and Äyhönjärvi Lake Water.

	COD_{Mn}(mg/L)	$KMnO_4$(mg/L)
Tap Water	4.4	17.38
Äyhönjärvi Lake	11.6	45.8

Eurajoki River Water:

Four samples: original Eurajoki river water; clean layer liquid taken from river water reacted with $Fe_2(SO_4)_3 \cdot 6H_2O$ coagulant 10mg/l, 50mg/l and 100mg/l solutions

Table 2 Humus Removal of River Water at Different Coagulant Dosages.

	COD_{Mn} (mg/L)	$KMnO_4$(mg/L)	pH
Original River Water	7.64	30.18	6.6
Clean Liquid 10mg/l	7.16	28.28	6.8
Clean Liquid 50mg/l	3.8	15.01	6.15
Clean Liquid 100mg/l	2.16	8.532	5.05

Deionized water has no metallic compounds but still have organic materials. (Website of Formula Botanica. Unknown year). This is why consumption of $Na_2S_2O_3$ in this deionized water is 1.835 ml. Organic matter in deionized water is a sub-factor

making KMnO4 got oxidized, which resulted 30.178. COD_{Mn} of clean liquid 10mg/l is the highest compared to other samples due to low coagulant dose, which barely form flocs – brown particles according to theory of floc formation 7.2.1. Settling process hardly occurred. Therefore, organic suspended materials remain scattered. The COD_{Mn} decreases from 10mg/l to 100mg/l since organic compounds likely attach to positive charge of coagulant.

Picture 18 Iron coagulant colors water yellow-brown. Notice deposit formed at largest dosage (the right bottle).

13.2 Pure Water

13.2.1 $Fe_2(SO_4)_3 \cdot 6H_2O$ coagulant

Pure water was used in COD_{Mn} measurement. Three samples were successful to define COD_{Mn} in optimized pH range. Calcium Oxide (CaO) was added to achieve desirable pH. Then $Fe_2(SO_4)_3 \cdot 6H_2O$ coagulant was added into river water samples 125mg/l and 50mg/l.

Table 3 Analytical Values of Eurajoki Raw Water

	COD_{Mn}(mg/L)	$KMnO_4$(mg/L)	pH
Eurajoki River Water	3.36	13.27	7.01
125mg/l	2.32	9.16	4.33
125mg/l	3.08	12.17	3.28
50mg/l (no Cao addition)	4.88	19.28	5.6

Iron – base coagulants:

Pure Water – distillation water has organic or volatile materials, which consumed $Na_2S_2O_3$ solution 1.87ml. pH in water determines solubility of material existing in water body such as metals, nutrients. CO_2 is a factor affecting to pH with reaction between water and CO_2. pH level increases because plants and other organism take up CO_2 for their photosynthesis which releases glucose and oxygen, less H_2CO_3 product. Bacteria can use oxygen to decompose organic matters in water body, which likely makes COD_{Mn} smaller in case pH 7.01 comparing to pH 6.6. After several freshwater pH measurements, pH level of Eurajoki River fluctuates from 6 to 7 range. It could be cellular respiration happens, which produce CO_2.

The difference of Eurajoki river water COD_{Mn} numbers between table 2 and 3 could be affected by not being preserved. It is advised water samples should be preserved so that degradation would be prevented and eliminate reducing interference (Cl^- or $Fe2^+$) (Goerlitz & Brown.1984.20). River water was stored in a big bottle with capsulate. Possibly more oxygen from air penetrated water when opening bottle, which decreased COD_{Mn} in table 3.

Table 4 Quality Parameters of Oulu River Water (Matilainen 2007, p. 31)

		Raw Water			Treated Water	
		Average	min	max	Average	Average
					HINTTA	KURKELANRANTA
Temperature	**°C**	8	0	19		
Colour	**mg/l Pt**	87	60	140	<5	<5
pH		6.8	6.3	7.0	8.5	8.4
$KMnO_4$	**mg/l**	51	42	74	3,9	3,2
TOC	**mg/l**	12.2	10.0	17.2	2.0	2.1
Abs. 254nm*	**1/m**	49.7	38.6	70.9	1.8	1.8
Turbidity	**NTU**	2.37	0.56	7.70	0.17	0.15

* measured 1.1.-30.6.2005

Table 2 provides the COD_{Mn} of Eurajoki river in middle of October: 7.64 and $KMnO_4$ is 30. Compared to Oulu river water which is used in Hintta and Kurkelanranta Water Treatment Plants have KMnO4 51mg/l as average number and 42mg/l as minimum number before treating process see table 4.

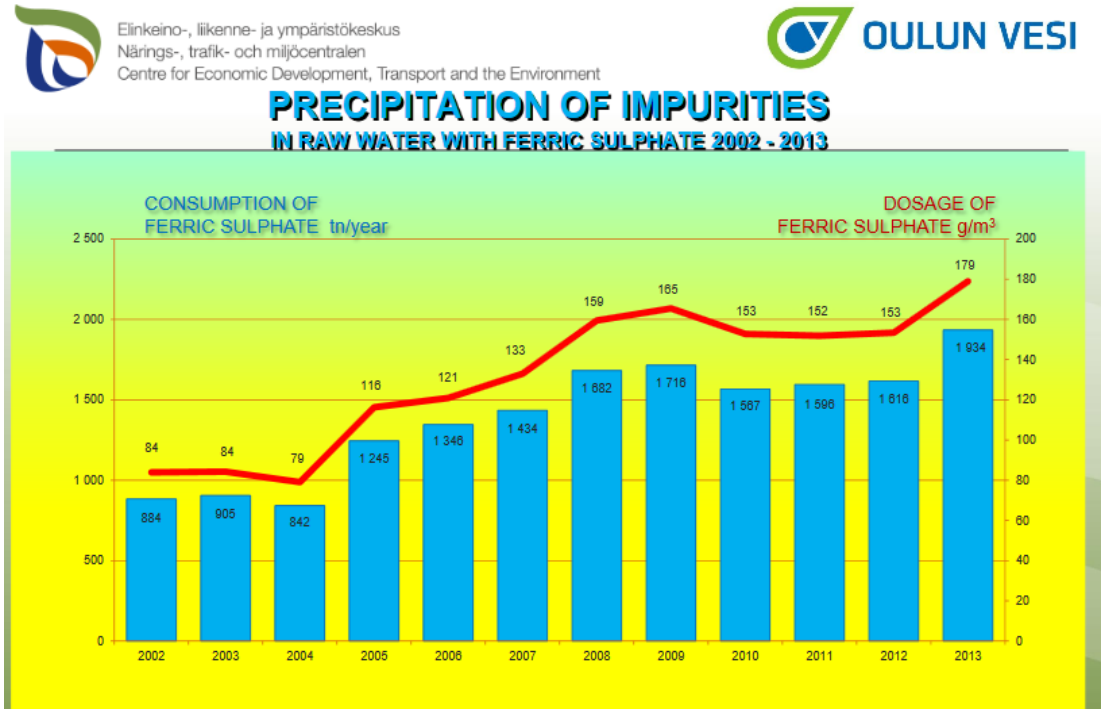


Figure 19 Precipitation of impurities in raw water with ferric sulphate 2002-2013 (Kaisa Vahanen.2013)

Owing to achieve the water quality target of Oulu Water - work total organic compound 2.1mg/l. Amount consumption of coagulant increased to 1934 tn/year and dosage was 179 g/m^3 in 2013, see figure . Ecological status of Oulu is at moderate. The total organic compounds in Oulu river water is 1 – 1.9 mg/l measured in 2013. (Kaisa Vahanen 2013)

Therefore, the COD_{Mn} of Eurajoki in table 2 may indicate moderate river state. Eurajoki river water is not acidic, which maintains quite neutral pH. Peatland may not occupy the catchment area near Eurajoki river stream, which potentially increase dissolved organic compounds and lower down pH level. The lower pH the greater solubility of substances in water body, it could require more coagulant dose to form flocculation.

$KMnO_4$ results from table 2 & 3 of clean liquid layer samples 50,100, 125mg/l are less than 20mg/l. According to legislation from Oulu, quality of drinking water has

$KMnO_4$ under 20mg/l (Oulun Waterworks.2010.10). The efficiency of settling process depends on different concentration of coagulant added in to samples. 100 mg/l and 125 mg/l of ferric sulfate coagulant usually form flocs and settle down at bottom after few minutes e.g. approximately 5 minutes 35 seconds for 100mg/l sample (this timing was intentionally noticed in laboratory). Samples in table 2 except river water were stayed at rest in 5 days; and sample 125mg/l (table 3 - pH 4.33) formed flocs in fast way.

Picture 20 Sample after adding 125 mg/L iron coagulant after settling process occurred (Eurajoki river water + coagulant)

pH of solution samples could be a decisive factor determining settling efficiency. See table 2 & 3, pH is from range 4 to 5 after coagulant addition, which produces desirable COD_{Mn} or $KMnO_4$ numbers.

13.2.2 $FeSO_4 \cdot 6H_2O$ Coagulant

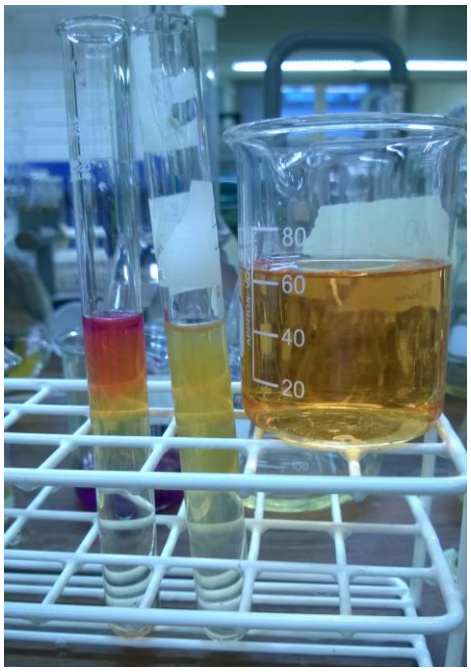
Four samples were made: Eurajoki river water; 10; 50; 100 mg/l coagulant mixed with Eurajoki river water. Top layer liquid of samples was taken for COD_{Mn} determination.

Table 5 Analytical values of Eurajoki river water after different sedimentation times

	COD_{Mn}(mg/L)			
		0.5 hour	1 hour	1.5 hour
Eurajoki River Water	4.96			
10mg/l		2.39	1.28	5.44
50mg/l		3.48	3.84	2.16
100mg/l		4	5.16	2.68

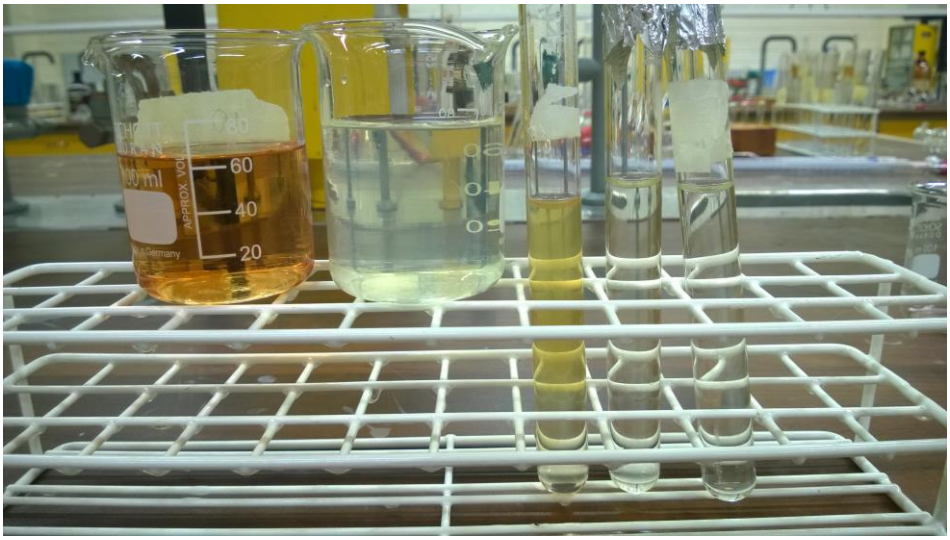
Picture 21 Samples of Eurajoki river water with 10 (left); 50 (middle); 100 (right)mg/l $FeSO_4 \cdot 6H_2O$ coagulant.

The flocculation in this session was different from Iron (III) and Aluminum coagulants. It was barely to see suspension of solid matter and distinctive layers. Three solutions looked like mixture of coagulant and river water. Coagulant tended to present quite equally in decanters. Color of $FeSO_4 \cdot 6H_2O$ coagulant solution was light yellow. 50 and 100mg/l samples gradually become light orange possibly Fe^{2+} was oxidized by oxygen to Fe^{3+}.



Picture 22 Two tube river water samples with a lot of $FeSO_4 \cdot 6H_2O$ (more than 100mg/l) and $Fe_2(SO_4)_3 \cdot 6H_2O$coagulant

Three tube samples with more than 100mg/l $FeSO_4 \cdot 6H_2O$ was for extra phenomenon observation: Color was from pale green to orange possibly because of Fe^{2+} oxidation to Fe^{3+}. After $KMnO_4$ (purple color), H_2SO_4 addition before heating process; color was changed from orange to nearly colorless/pale green as proved at picture below. COD_{Mn} cannot be determined with these samples.



Picture 23 Iron (III) & (II) coagulants; light orange; colorless samples (left to right)

Here are thesis author's arguments for the phenomenon. Theoretically, Fe^{2+} ions were oxidized into Fe^{3+} by $KMnO_4$, see reaction

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \quad (20)$$

(The website of Meta – synthesis. 2017)

Two simultaneous color changes occurred: reduction of MnO_4^- to Mn^{2+} formed pale pink –almost colorless; oxidation of Fe^{2+} to Fe^{3+} formed orange. Color of final product solution is pale purple (pink) due to excess MnO_4^- and Mn^{2+} if reaction follows ratio Fe^{2+} : MnO_4^- : 5 : 1. (The website of Doc Brown's Chemistry. 2017)

In this case, sample solution had three color layers: nearly colorless/pale green; orange and pink, see picture 22. Maybe there were a lot of Fe^{2+} ions, more than ratio 5:1, orange layer appeared.

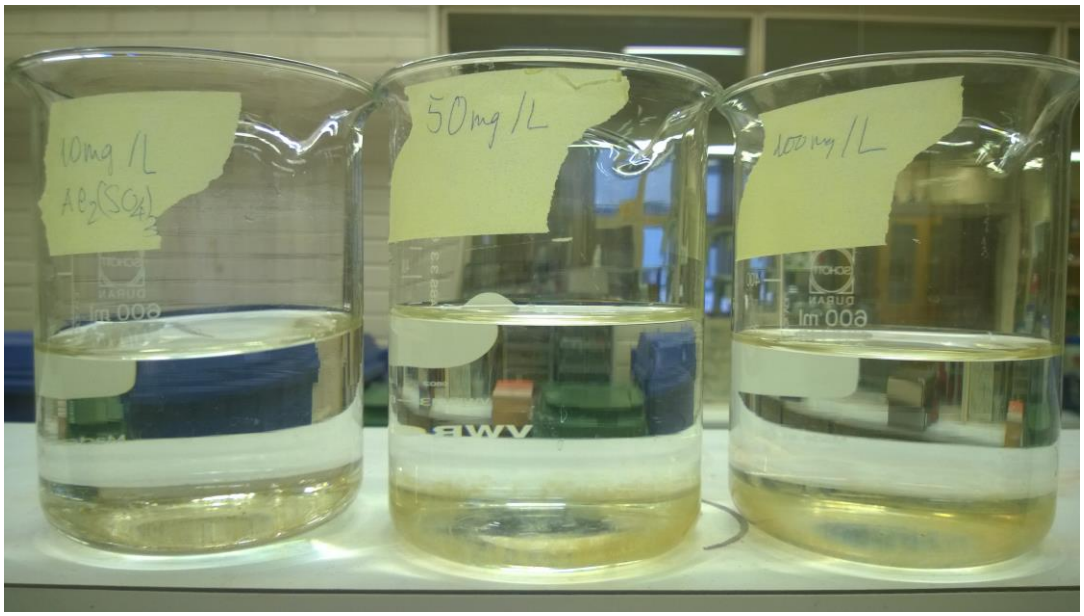
Fe^{2+} and Fe^{3+} can be existent in samples; it means Fe^{2+} was not necessarily oxidized. Additionally, Fe^{3+} could be reduced to soluble Fe^{2+} by humic acid -acidic solution (Libecki & Dziejowski 2010, 1091); natural organic matter – NOM is known as redox reactive, which chemically reduces soluble Fe^{3+} species.(Chen, Gu, Royer, Burgos. 2002. 173).

$$Fe^{3+} + e^- \Leftrightarrow Fe^{2+} \quad (21)$$

MnO_4^- was reduced completely into Mn^{2+}. It means there was no $KMnO_4$ residual and more water molecules formed in solution. This could be a reason to explain orange turned into nearly colorless/pale green.

13.2.3 $Al_2(SO_4)_3 \cdot 3H_2O$ Coagulant

Three different concentration of coagulant mixed with Eurajoki river water were made: 10mg/l; 50mg/l; 100mg/l. Top - upper clean layer liquid in each sample was taken to determine COD_{Mn}.



Picture 24 Flocs – brown particles at bottom of sample decanters with Al-coagulant concentration:10; 50; 100mg/l

Picture 24 illustrates that comparing to $Fe_2(SO4)_3 \cdot 6H_2O$, the organic matter aggregation of aluminum coagulant did not occur obviously. Amount of flocs was less visual. 10mg/l sample has brown particles at bottom, which can be seen by eyes.

Table 6 COD_{Mn}-values of Eurajoki River after different sedimentation times

	COD_{Mn} (mg/L)			
		1 hour	1.5 hours	2 hours
Eurajoki river water	2			
10mg/l		1.48	1.36	4.44
50mg/l		1.04	Cannot determined	Negative number
100mg/l		Negative number	Negative number	Negative number

Table 6 indicates that 50mg/l sample (1.5 hours) had same phenomenon that after adding $KMnO_4$ and H_2SO_4, sample color turned into orange, not having pink/light pink as picture indicates. Few seconds later, orange liquid was colorless, which resulted in not able to calculate COD_{Mn} – "cannot determined". This phenomenon was the same as three samples happened in part 12.2.2.

10mg coagulant/L sample may have insufficient amount Al^{3+} ions to bond with negatively charged organic particles so that creating rapid settling. Aggregation rule is explained in part 7, figure 9. Humus compounds possibly remained at equilibrium sample after 2 hours.

Samples gave negative COD_{Mn} because their consumption of thiosulfate ($Na_2S_2O_3$) was larger than pure water. Starch's structure is resemble to a coil, so I_3^- ions get inside "coil" starch and give dark blue color of solution.(Website of Virtual Chembook Elmhurst College 2003). KI and starch solutions in this experiment was made with pure water; possibly iodine bonded strongly with starch due to high concentrated iodine in sample. (Website of Titrations.Info 2014). This could require more titrated volume of thiosulfate to react with iodine so as to decolorize dark blue solution.

Picture 25 COD_{Mn} samples before heating.

13 PHOSPHORUS DETERMINATION

Experiment uses:

-Eurajoki river water sample

-Six standard solutions of potassium dihydrogenphosphate with different concentrations: 0.04M, 0.08M, 0.16M, 0.24M, 0.32M, 0.4M. Each of standard solutions is mixed with deionized water.

-Deionized water

Following the experiment procedure in appendix 2, six standard solutions potassium dihydrogenphosphate - KH_2PO_4 turn into blue colour.

Picture 26 Six standard solutions have blue colour.

Table 7 Standard Curve for Phosphorus.

Standard Solutions Concentration (mgP/l)	Phosphorus P Absorbance Value
0.04	0.169
0.08	0.217
0.16	0.248
0.24	0.274
0.32	0.309
0.4	0.369

Line graph below describes phosphorus contents in each standard solution. The equation is applied to calculate phosphate content in Eurajoki River water

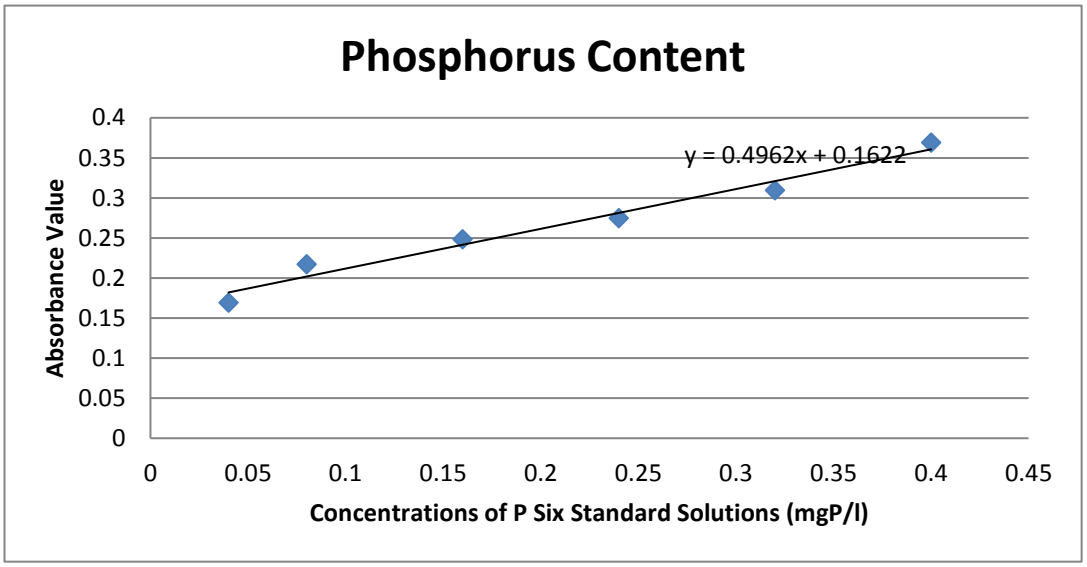
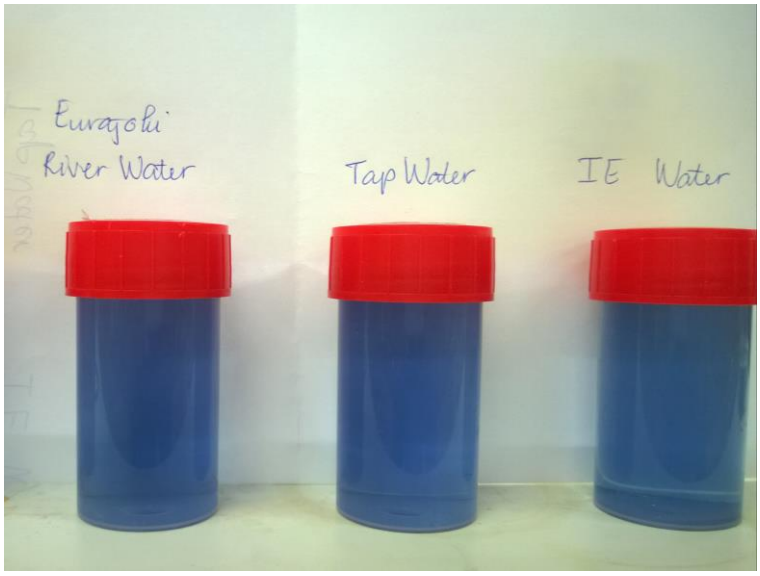


Figure 27 Phosphate Content Determinations.

Samples have blue colours indicating phosphate existence. During experimenting, deionized water is discovered to have phosphate and the absorbance value is 0.2217.



Picture 28 Eurajoki River water (darkest blue), tap water ad deionized water samples.

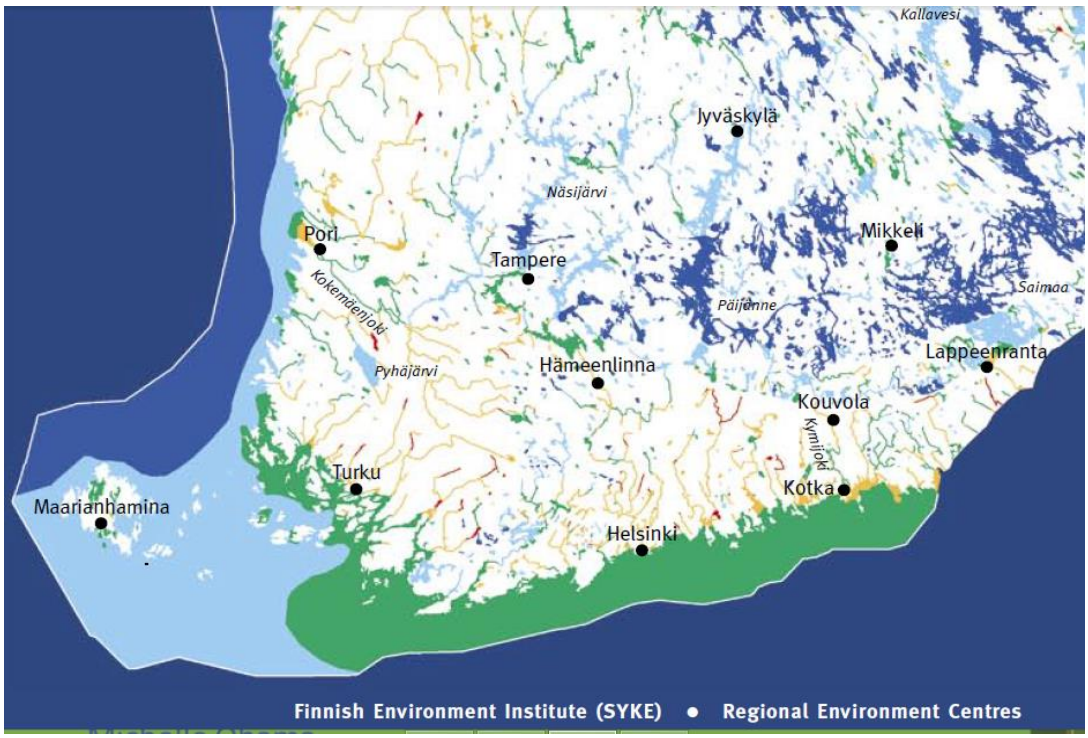
Otherwise, Eurajoki river water absorbance value is 0.3037 which is y variable and x is phosphate content in Eujajoki river water:

Applying equation: y = 0.4962x + 0.1622

- Phosphorus content in Eurajoki is:

- x = 0.285 mg P/l
- x = 285 µgP/l

Phosphorus (P) concentration in uncontaminated surface water is from 10 - 50µg P/l. The average phosphorus in Finland surface water was 15µg P/l in 1993.(Miettinen, Vartiainen & Martikainen 1997, 3244). Amount had increased generally $\frac{285}{15} = 19$ times in 23 years (1993 – 2016).



Picture 29 Situation of water quality of river, lake, sea in Finland 2000 – 2003. (Finnish Environment Institute. 2003.2); (dark blue: excellent; sky blue: good; green: satisfactory; yellow: passable; red: poor)

In order to have a focus on Eurajoki, below picture is cut from picture:

Picture 30 Zoom-in of Eurajoki river situation which originates from Lake Pyhäjärvi. (Finnish Environment Institute. 2003.2)

Color indicates that Köyliönjärvi has poor situation – red area near Lake Pyhäjärvi. Lake Pyhäjärvi is in good condition. Eurajoki river water route had yellow (passable) and green (satisfactory) colors in 2003. Phosphorous content possibly get influenced by eutrophication of Pyhäjärvi as stated in part 3.1.2, which makes sample taken has high value 285 µgP/l. According to table 8, its situation is in phase V (>100 µg/l). Criteria of general water quality classification can be seen in table 8. (Finnish Environment Institute. 2003.2)

Table 8 General Criteria for the Water. (Finnish Environment Institute. 2003.2)

Criteria for the general water quality classification

Variable	Unit	I	II	III	IV	V
		Excellent	Good	Satisfactory	Passable	Poor
Chlorophyll-a (lakes, rivers)	µg l^{-1}	< 4	< 10	< 20	20–50	> 50
Chlorophyll-a (sea)	µg l^{-1}	< 2	2–4	4–12	12–30	> 30
Total phosphorus (lakes, rivers)	µg l^{-1}	< 12	< 30	< 50	50–100	> 100
Total phosphorus (sea)	µg l^{-1}	< 12	12–20	20–40	40–80	> 80
Transparency	m	> 2.5	1–2.5	< 1	-	-
Turbidity	FTU	< 1.5	> 1.5	-	-	-
Colour	mg l^{-1} Pt	< 50	50–100 (< 200)[1]	< 150	> 150	-
Oxygen in surface water	%	80–110	80–110	70–120	40–150	serious problems
Oxygen depletion in hypolimnion		no	no	occasionally	frequently	common
Faecal coliforms or streptococci	nr in 100 ml	< 10	< 50	< 100	< 1000	> 1000
Hg in carnivorous fish	mg kg^{-1}	-	-	-	-	> 1
As, Cr, Pb	µg l^{-1}	-	-	-	< 50	> 50
Hg	µg l^{-1}	-	-	-	< 2	> 2
Cd	µg l^{-1}	-	-	-	< 5	> 5
Total cyanide	µg l^{-1}	-	-	-	< 50	> 50
Algal blooms		no	occasionally	frequently	common	abundant
Off-flavours in fish		no	no	no	common	common

1) humic waters in a natural state

14 IRON AND SULFATE (FROM COAGULANT) REMOVAL

14.1 Fe Determination by AAS – Atomic Absorption Spectroscopy

Six water samples made in this experiment of iron and sulfate content determination. Purpose is to find efficiency of coagulation settling down. They are mixture of Eurajoki river water and coagulant $Fe_2(SO4)_3 \cdot 6H_2O$ with three different concentrations 10mg/l, 50mg/l, 100mg/l. Afterwards they are let stay at rest for the particle settling in 5 days. The top layer of clean liquid water samples are taken for experiments.

Picture 32 Eurajoki River water with coagulant 10mg/l, 50mg/l, 100mg/l during settling.

Iron content is determined by AAS – Atomic Absorption Spectroscopy. The table below provides results of iron content.

Table 9 Iron content values

Coagulant Concentration Samples	10mg/l	50mg/l	100mg/l
Iron content (mg/l)	1.326	1.0585	1.552

Results:

100mg coagulant/l:

100 . $\frac{2 .55,85}{506}$ mgFe/L = 22.1 mgFe/l

Real Fe content value exists in tested water is 1.55mg/l => $\frac{1.55}{22.1}$ x 100% = 7%. It means that about 93% of Fe ions are adsorbed in to flocs, verify brown particles at the bottom.

50mg coagulant/l:

50. $\frac{2 .55,85}{506}$ mgFe/L = 11.03 mgFe/l

Real Fe content is 1.0585mgFe/l => $\frac{1.0585}{11.03}$ x 100% = 9.59%.

- 90.41% Fe in flocs and 9.59% in water

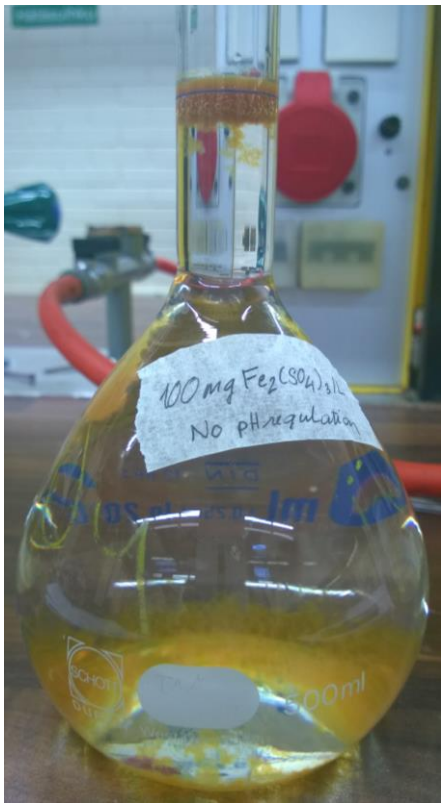
10mg coagulant/l:

10. $\frac{2 .55,85}{506}$ mgFe/L = 2.2 mgFe/l

Real Fe content is 1.326 mgFe/l => 1.326/2.2 x 100% = 60,3%

- 60.3% Fe in water and 39.7% Fe in flocs.

Molar mass of coagulant $Fe_2(SO_4)_3 \cdot 6H_20$ is 506 g/mol



Picture 33 Iron solution with 100mg $Fe_2(SO4)_3 \cdot 6H_2O$ per liter has flocs at bottom and top of liquid.

All three samples stayed at rest and there was no rapid mixing force applied as conventional coagulation and flocculation process stated in part 7.2. Therefore, there was no flocs- brown particle floating at the liquid surface in flask as Picture 28 illustrates. Picture 33 has flocs at the top of liquid due to a sudden mixing; air bubble is trapped. Mixing velocity is a factor affecting to coagulation; if velocity goes too fast, it can deform flocs and produce air bubble, which possibly lift up flocs to surface of water.

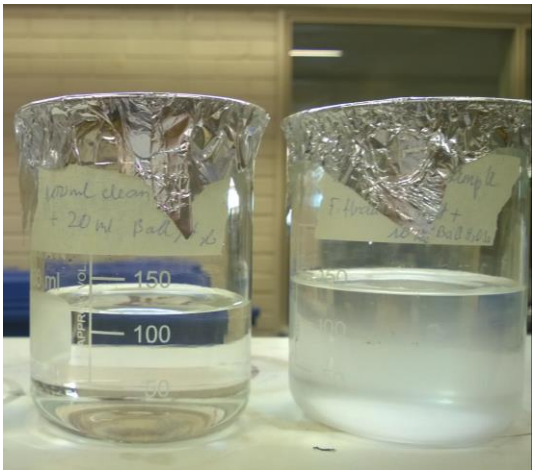
14.2 Sulfate Determination/Settling Process

This experiment is carried out with $BaCl_2 \cdot 2H_2O$ solution so as to form precipitate $BaSO_4$. Sulfate - SO_4^{2-} ions remain in water samples; therefore, there is chemical reaction:

$$BaCl_2(aq) + SO_4^{2-}(aq) \Leftrightarrow BaSO_4(s) \qquad (22)$$

$BaCl_2.2H_2O$ solution is added into three top layer of clean liquid water samples: 10mg/l (1), 50mg/l (2), 100mg/l (3) of coagulant $Fe_2(SO_4)_3 \cdot 6H_2O$.

Purpose of this experiment is to measure turbidity of three water samples mentioned above so that SO_4^{2-} settling process can be defined according to timing function.



Picture 34 Two Samples (100mg coagulant/L) with 20ml (left) and 40ml (right) of $BaCl_2 \cdot 2H_2O$ solution.

Table 10 Turbidity of the sample (100 mg Coagulant/L) after addition of different deposition chemical mounts

Time	100mg/l of coagulant $Fe_2(SO_4)_3.6H_2O$ Samples	
	40ml of $BaCl_2.2H_2O$ solution (right)	20ml of $BaCl_2.2H_2O$ solution (left)
After adding	50.2	5.6
1 hour	5.8	3.06
2 hours	6.1	1.1
3 hours	4.5	0.32

Table 11 Sample (50 mg Coagulant/L) turbidity results:

50mg/l of coagulant $Fe_2(SO_4)_3.6H_2O$	
Time	20ml of $BaCl_2.2H_2O$
After adding	8.3
1hour	3.6
2 hours	2.3
3 hours	0.34

Samples were filtrated by filtrate paper, not the same as samples in 14.1. Turbidity of filtrated liquid is 0.01. Sulfate – SO_4^{2-} which originates from mineral (gypsum – calcium sulfate) existing in soil, rock can be found in natural water. Adding coagulant increases dissolved ions such as SO_4^{2-} in samples. $BaCl_2.2H_2O$ solution formed precipitate $BaSO_4$. SO_4^{2-} content in water could not be done in laboratory beforehand.

Sample (3) - the right one in picture shows clearly two layers – a transparent and a stable colloid. From table 9, two samples show a significant difference in turbidity of first solution addition: right one is 50.2 and left one is 5.6. Noticeably, after one hour, turbidity of right sample decreased to 5.8; after 3 hours, turbidity is 4.5 comparing to the left is 0.32. Ba^{2+} and SO_4^{2-} ions are actors in water for turbidity measurement.

Settling of SO_4^{2-} is deduced to depend on sufficient amount of $BaCl_2{\cdot}2H_2O$ solution and timing, which has been done so far in this thesis. Ratio of $BaCl_2{\cdot}2H_2O$ to SO_4^{2-} is 3:2. pH might be a predominant factor influencing to removal process; unfortunately, pH adjustment was not done in this session.

Meanwhile, table 11 provides turbidity of 50mg/l coagulant after 3 hours is 0.34, which is relative with result in table 8 even though SO_4^{2-} ions is sample (2) is less than sample (3) due to difference of coagulant ($Fe_2(SO_4)_3{\cdot}6H_2O$) concentration. $BaCl_2{\cdot}2H_2O$ could be a promisingly reactive chemical used to remove sulphate in short time owing to physicochemical mechanism; especially when high dose of coagulant is consumed for flocculation and residual of barium could be as low as possible. Because Ba^{2+} is highly toxic element and its presence in water is limited. The effluent of treated water should have no content of barium.

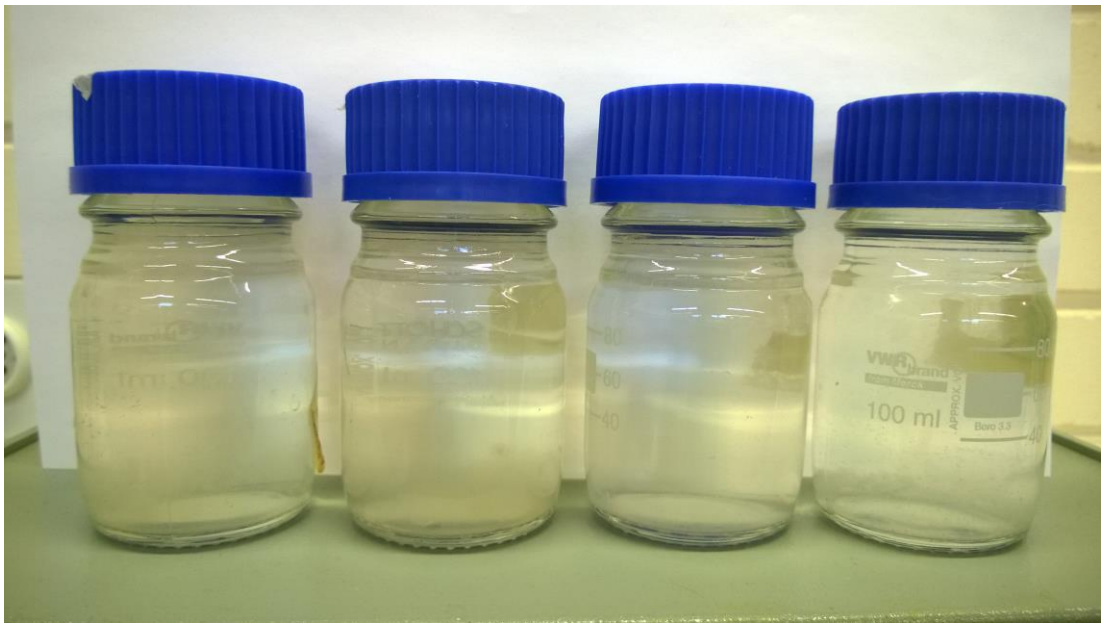
From table 10 & 11, it is assumed that if coagulant concentration from 50mg/l to 100mg/l, $BaCl_2{\cdot}\,2H_2O$ can be utilized for sulfate removal. The shortcoming is residual Ba^{2+} likely remains in water liquid when SO_4^{2-} completely precipitates Ba^{2+} in case of 50mg/l $Fe_2(SO_4)_3{\cdot}\,6H_2O$.

15. BIOLOGICAL OXYGEN DEMAND (BOD_7)

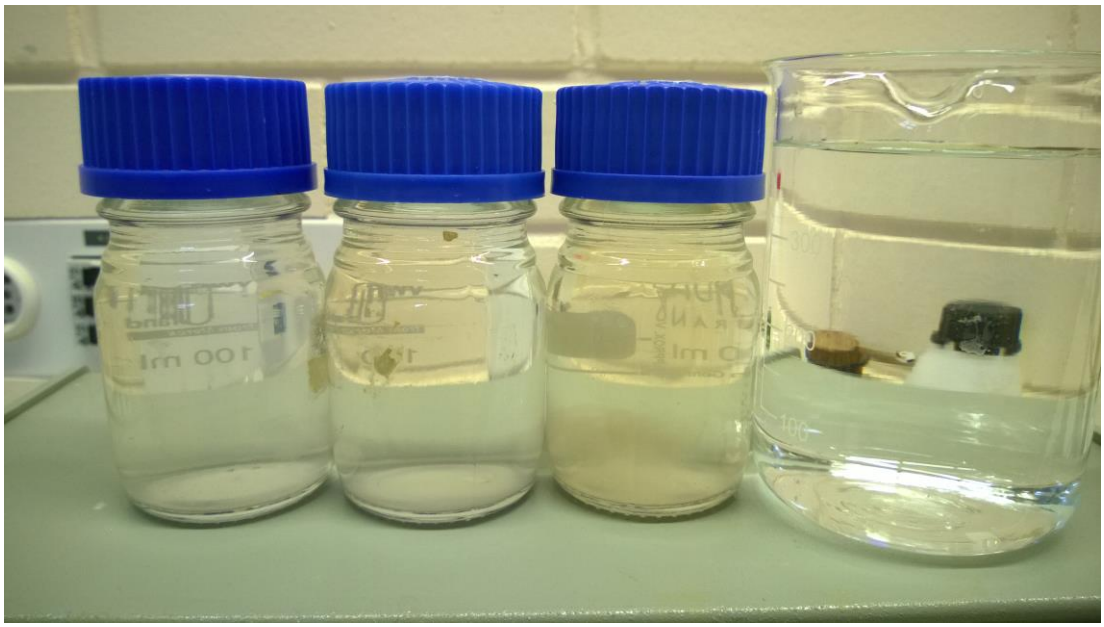
Five water samples were tested in this serial experiment: deionized water; tap water; Eurajoki river water; starch 10mg/l; starch 100mg/l. Samples were let at rest in dark place in 7 days to measure dissolved oxygen content in sample bottles. Two identical bottles were made for each sample. One bottle of each sample is opened after 4 days.

Table 12 BOD values of 4-day-samples.

BOD_4	Dissolved Oxygen Content (mg/l)		pH
	After Aeration	After 4 days	After 4 days
Deionized Water	8.71	6.6	3.83
Tap Water	7.6	4.41	3.95
Eurajoki River Water	8.54	5.66	3.92
Starch 10mg/l	7.14	4.2	3.77
Starch 100mg/l	7.62	0.58	3.79
Lactose Bacteria			3.59



Picture 35 BOD_7 samples: 2 Eurajoki river water samples and 2 deionized water samples (left to right)



Picture 36 BOD_7 samples: Deionized water; Tap water; River water; decanter of tap water without bacteria (left to right).

Table 13 BOD_7 results of all samples

BOD_7		Dissolved Oxygen Content (mg/L)		pH	
	After Aeration	After 4 days	After 7 days	After 4 days	After 7 days
Deionized Water	8.71	0.52	0.82	3.41	3.58
Tap Water	7.6	0.54	0.27	3.53	3.7
Eurajoki River Water	8.54	1.02	0.45	3.56	3.71
Starch 10mg/l	7.14	0.39	0.4	3.46	3.39
Starch 100mg/l	7.62	0.58	0.32	3.34	3.46

After 7 days, dissolved oxygen content in all samples decline genuinely. Bacteria uses nutrients such carbon, nitrogen, phosphorus, iron and other mineral in water to reproduce cell and membrane. The significant decrease of dissolved oxygen indicates rapid reproduction of lactose bacteria, which is a potential utilization in raw & waste

water treatment. There is small visual bacteria assembly at bottom of some bottles. pH level is quite acidly stable due to lactose bacteria and CO_2 in sample. This is aerobic environment so the reaction of degradation of organic matter:

$$\frac{1}{4} CH_2O + \frac{1}{4} O2\,(g) \rightarrow \frac{1}{4} CO_2\,(aq) + \frac{1}{4} H_2O(l) \qquad (23)$$

(Manahan 2010, 139)

Noticeably, dissolved oxygen content in starch 100mg/l sample after 4 days is 0.58 mg/L. Starch compound was decomposed by lactose bacteria, which made liquid in bottle transparent. It resulted in both bottles after 7 days; there was very small amount of bacteria existing. BOD test indicated that it can be used in determination of microbial decomposition in raw water under aerobic conditions.

16. CONLUSIONS

Generally, Eurajoki river water is medium polluted by phosphorus that originates from agricultural runoff and eutrophication effect of Köyliönjärvi Lake. It refers that river water body has got influenced by human activities. Organic matter state in river is still in acceptable level, which is demonstrated with experiments of three coagulant types with river water. Natural microbial decomposition proceeds itself quite effectively when COD_{Mn} of river water sample decreased in each time of measuring. BOD results provide prediction that Eurajoki river water contains high percentage of biodegradable organic matter that can be broken down by microbes. There is likely less non-biodegradable organic matter which is harmful to microbes and river water. Lactose bacteria are an effective media to break down organic matter basing on its population reproduction.

Iron (III) based coagulant shows its most efficiency during coagulation and flocculation within the most optimum pH 4 ~ 5. This can be useful when water treatment plant economically considers solution about consumption of coagulant annually.

Unfortunately, there are not much numerical results in aluminum – based coagulant session. This is reason why all chemical solutions involved in experiments ought to be careful made, calibrated and solid chemical should be dissolved completely in water. Deliberate instruction assists achieving reliable outcomes; for instance, Äyhönjärvi Lake COD_{Mn} gave realistic number: 11.6 mg/l. However, it is a worth researching and investigating various coagulants in order to produce best suitable method to purify different raw water sources. Moreover, nutrient loads exist in raw water must be monitored and controlled to restrain current state of eutrophication.

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APPENDIX 1

DETERMINATION OF COD_{Mn}

- Solution $KMnO_4$ + H_2SO_4 is poured into test tubes. These test tubes are heated to 100^oC in 20 minutes and cooled down and dried by pressured air.
- Adding 10ml of each sample waters into test tubes.
- Adding 2ml 0.002M KMnO4 solution into test tubes. Adding 0.5ml 4M H2SO4 solution. Mix the mixtures and capsulate these tubes by aluminum foil. Then heating them in 20 minutes. After that, test tubes are cooled down.
- Adding 1ml 0.1M KI solution and 5 drops starch to each test tube, which make samples become blue.
- Titrating each sample with 0.01M $Na_2S_2O_3$ until samples become colorless.
- Follow the below equation to calculate COD_{Mn}:

$$COD_{Mn} = (V_0 - V_1) . c . 800 . f$$

CODMn : Chemical Oxygen Demand, mg/l

V_0: Consumption of 0.01M $Na_2S_2O_3$ of blank test (either deionized water or pure water)

V_1: Consumption of 0.01M $Na_2S_2O_3$ of needed testing sample waters (lake, river)

c: Concentration of $Na_2S_2O_3$ = 0.01

f: Dilution factor (10 or 100)

- 0.5 ml; 2.5ml and 5ml of each coagulant chemical are added into each sample of 500ml river water.

APPENDIX 2

PHOSPHATE CONTENT DETERMINATION

- Potassium dihydrogenphosphate – KH_2PO_4 contains 0.008788 g KH_2PO_4/L ➔ 0.00200 gP/L = 2 mgP/L as Standard Solution (S1)
- Make six standard solutions (S1) with different volumes: 1ml, 2ml, 4ml, 6ml, 8ml, and 10ml in 50ml Erlenmeyer flask and add deionized water up to 40ml.
- Add 1ml ascorbic acid solution + 2ml acidic molybdate solution into six standard solutions under swirling and fill deionized water to have 50ml liquid in flask. Mix all the flasks.
- Six standard solutions correspond to concentration from 0.04 mgP/L to 0.4 mgP/L. Phosphorus is detected by UV – Spectrophotometer 880nm wave-length.
- Deionized water and Eurajoki river water are measured after that.
- Six standard solutions are plotted to have a standard curve, which should be a straight line. UV- absorbance in function of Phosphorus – P concentration in mg/l.

APPENDIX 3

IRON DETERMINATION BY ASS – ATOMIC ABSORPTION SPECTROSCOPY

- 0.5 ml, 2.5 ml and 5 ml $Fe_2(SO4)_3{\cdot}6H_2O$ coagulant are added into each 500ml Eurajoki River water flask.
- Three sample solutions stay at rest in 5 days
- Top – upper layer liquid of each sample is taken for AAS measurement to achieve Iron content.

SULFATE DETERMINATION

- Three samples solution in Iron Determination by AAS are filtered by filter papers.
- Dilute 0.15g $BaCl_2{\cdot}2H_2O$ in 1 liter of water – S1
- Add 20 and 40 ml of S1 into two 100mg/l coagulant filtrated samples (S2 and S3); add 20ml of S1 into one 50mg/l coagulant filtrated sample (S4).
- Observe the $BaSO_4$ deposition:

  $BaCl_2{\cdot}2H_2O$ (aq) + SO_4^{2-} (aq) ➔ $BaSO_4$(s)
- Measure turbidity of top – upper layer liquid of three samples.

APPENDIX 4

BOD – BIOLOGICAL DEMAND OXYGEN (MODIFIED METHOD)

- Deionized water; Tap water; River water; Starch 10mg/; and Starch 100mg/l are samples for BOD experiment.
- 10 ml Lactose bacteria adds to 90ml of each water mixes and aerating sample solution in 5 minutes.
- Each water sample has two identical bottles. 10 samples in final after aeration and being capsulated. They are placed in closet to prevent light.
- After 4 days, 1 sample of each category water is measured its dissolved oxygen.
- After 7 days, measuring dissolved oxygen of 10 samples.