NUTRIENTS AND ORGANIC

MATTER IN WASTEWATER

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Environmental Engineering

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ABSTRACT

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Nutrients and Organic Matter in Wastewater

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The aim of the project was to test if three different systems of treating wastewater were able to treat the wastewater from mineral processing , and if they were to reduce the amount of nutrients and organic matter in the tested process water. This project was implemented in the greenhouse in the laboratories of Tampere University of Applied Sciences. This final thesis is a part of a TAMK Research, Development and Innovation project. The project results could be used for further studies in research projects concerning wastewater treatment methods.

The systems tested were modifications of biological treatment methods. One of them was a coarse filter system made of willow branches, called the Willow stack Tower. The second system was an ebb-flow system based on a modification of the willow branch filter, called the Ebb-Flow. The third system tested used wastewater as food for algae; this system is called the Algae Turf Scrubber.

The analyzed parameters were total nitrogen, phosphate, total organic carbon and biochemical oxygen demand over a period of five days. There were two test runs made in the testing process. In the first test run the experiment was done with untreated wastewater from mineral processing . In the second test run mining wastewater enriched with nutrients was applied in all the systems.

The results show that the concentration of total nitrogen remained constant though the testing process and the phosphate precipitated with heavy metals. Biochemical Oxygen Demand removed value is higher in the Willow Stack Tower and Ebb-Flow system than in the Algae Turf Scrubber.

In conclusion, the three systems tested do not seem to work well. Testing of the three systems concerned should be continued, since e.g. Total Organic Carbon content in the test procedure concerned gave confusing results.

Key words: Mining Water, Mineral Processing Water, Organic Matter, Total nitrogen, Phosphate

CONTENTS

ABBREVIATIONS AND TERMS

AAS	Atomic Absorption Spectrophotometer
ATS	Algae Turf Scrubber
BOD	Biochemical oxygen demand
BOD_5	Biochemical oxygen demand during 5 days
C	Carbon
COD	Chemical oxygen demand
EF	Ebb-flow system
K	Potassium
N	Nitrogen
Na	Sodium
Ni	Nickel
NO_3^--N	Nitrate Nitrogen
P	Phosphorus
PAOs	Phosphorus accumulating organisms
pH	Logarithmic H^+ concentration
PO_4^{3-}	Phosphate
TC	Total Carbon
TIC	Total Inorganic Carbon
TN	Total nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
WST	Willow stack tower
Zn	Zinc

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1 INTRODUCTION

The main aim of this project is to test if three different systems of treatment wastewater were able to treat the mining waste water from mineral processing , Willow Stack Tower (WST) , Ebb-Flow (EF) system and Algae Turf Scrubber (ATS), are able to treat the mining waste water and reduce the amount of pollutants and nutrients from it. This project was done during February 2013- June 2013 in the greenhouse in the laboratories of Tampere University of Applied Sciences (TAMK).

The research results are presented in this project. In this thesis the nutrient concentration and organic matter are discussed. Pollutants and toxicity were measured by Paula Ruipérez Leguina. In her thesis, two different ecotoxicity test has been done (how the mining wastewater affects to a aquatic medium and in a terrestrial medium). Sulphates were analyzed by the spectrophotometer and the heavy metals (Zn, Na, Ni and K) were measured by Atomic Absorption Spectrophotometric analysis AAS.(Ruipérez, 2013)
Algae analyses (biomass, lipids, carbohydrates, algae species) and analyzing pH were done by Stefan Sprock. (Sprock, 2013)

This report contains the results of the nutrients and organic matter in the untreated and treated wastewater. The purpose is to test if the three systems (two biofilters and the ATS) are able to treat the mining wastewater of and reduce the amounts of nutrients and organic matter from it. The system dimensions are explained in Alberto Freire's Thesis (2012) for the biofilter systems and Gerbrand Grobler thesis (2013) for the algae system. The systems were built on a small scale in the TAMK laboratory and two experiments were done. Each test run lasted three week and it was necessary to analyse the initial values and the evolution of the concentration of the nutrients, TOC and BOD; so every week samples were taken and analyzed the same day.

The results will be published as Thesis documents in Theseus database and they can be used for future projects for students. (Viskari, 2013.)

2 MATERIALS AND METHODS

2.1 Wastewater from Mineral Processing

The mining wastewater used in this project comes from Talvivaara mine, The Talvivaara mine is located in Sotkamo in Eastern Finland. The company uses bio-heapleaching as a method of recovering metals from sulphide ore. This is an exploitation system of metal extraction using bacteria in presence of water and air. It is a simple operation system and it produces high value products. The main product that is obtained is nickel but there are other metals that are extracted as zinc, cobalt and copper.(Talvivaara, 2013)

The figure 1 shows the production process in Talvivaara. The process consists in four steps: mining, crushing, bioheapleaching and metals recovery. The mine whose water is used in this project works with a biological process to extract the metals from the ores in presence of air and water. After the crushing of the rocks, the mineral are stacked in bioleaching stacks. There the metal extraction starts. The biological process name is bioheapleaching. It consists in the mineral leaching in the main leach platform during 14 months. The leaching platforms were inoculated with endemic bacterias that are naturally growing in the ore because of that they are well adjusted to the prevailing environmental conditions. The amount of bacteria that is inoculated are in the range between 106 to 108 cells / ml. These bacterias are either mesophilic or thermophilic. The biological oxidation of the pyrite and cryolite that are present in the ore is an exothermic reaction which releases substantial amounts of energy. Temperature can increase until 500ºC during the leaching. Several physical, chemical and microbiological process parameters can be modified in order to enhance and speed up the metal recovery process. To reach and maintain the temperatures required for enhanced sulphide mineral leaching, different microbial populations are required to be present over time and the microbial growth rates need to be optimum. (Talvivaara, 2009)

When the leaching finishes, the metals recuperation is done by precipitation. Nickel, zinc, copper and cobalt from the pregnant leach solution are precipitated and filtered. After the metals are removed, the solution is further purified and returned to irrigate the heaps. The solution is collected at the bottom of the heaps and either recirculated through the heap or fed to metals recovery. (Talvivaara, 2009)

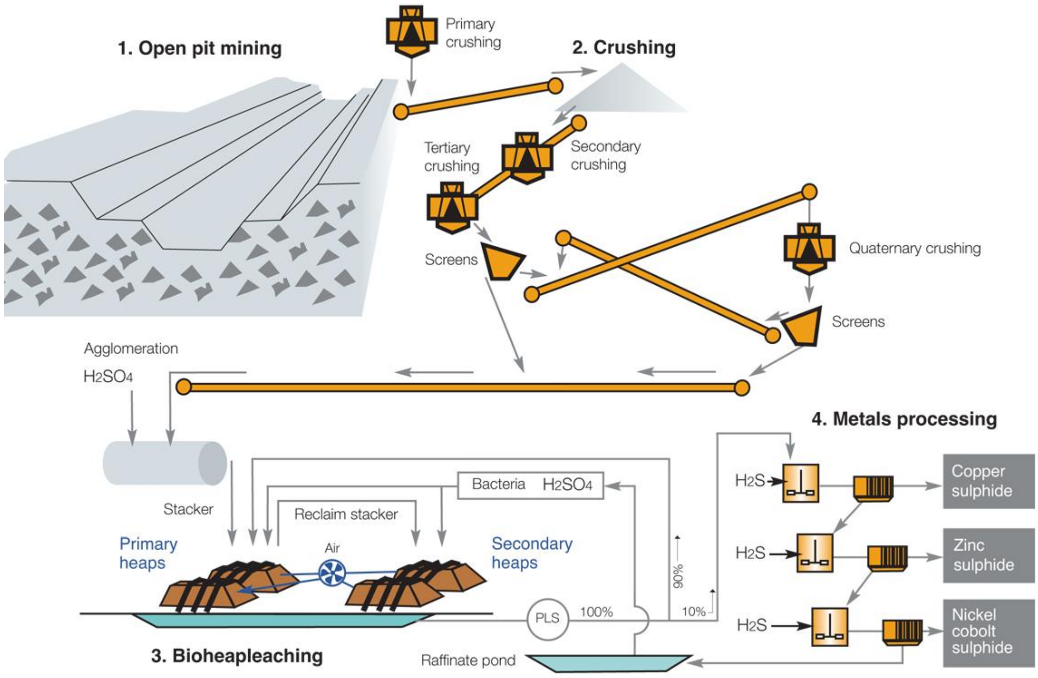

FIGURE 1. Production Process in Talvivaara (Talvivaara, 2010)

The unknown wastewater comes from process operation and the concentration of metals and sulphate are shown in table 6 in Appendix 1. Also the table 6 shows that the pH of the wastewater is low. The value of the pH is 3 in tank one and in tank three the pH is 3,9.

2.2 Analyzing Methods

During this project the parameters of Total nitrogen, Nitrate, Total Phosphorus, Phosphate, Total Organic Carbon and Biochemical Oxygen during five days were analyzed with this different analytical equipment in TAMK laboratories.

2.2.1 Total Nitrogen and Nitrate

The reason to analyze total nitrogen is because nitrogen removal is a good way to prevent rivers and lakes eutrophication. (Jokela et al., 2002). The removal of total nitrogen could be done by using nitrification reaction, denitrification reaction or bacteria autoconsuption. Nitrification is the biological conversion of ammonia-nitrogen to nitrate-nitrogen. For this process is necessary bacteria called *nitrosomonas* and oxygen. Denitrification is a process where the nitrate-nitrogen is converted to nitrogen gas. The reactions removing nitrogen are presented in figure 2. (Fernández M., 2010)

NITRIFICATION

$$NH_4^+ + \frac{3}{2}O_2 \xleftrightarrow{microorganism} NO_2^- + 2H^+ + H_20$$

$$NO_2^- + \frac{1}{2}O_2 \xleftrightarrow{microorganism} NO_3^-$$

$$NH_4^+ + 2O_2 \xleftrightarrow{microorganism} NO_3^- + 2H^+ + H_20$$

DENITRIFICATION

$$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- \xleftrightarrow{microorganism} \frac{1}{10}N_2 + \frac{3}{5}H_20$$

BACTERIA AUTOCONSUPTION

$$C_5H_7NO_2 + 5O_2 \xleftrightarrow{microorganism} CO_2 + NH_3 + 2H_20$$

FIGURE 2. Nitrification, denitrification reactions. (Fernández M., 2010)

There are some parameters whose effects change the rate of nitrification. Temperature impact on the fixed film nitrification rate at 20 ºC was 1.108% per ºC when oxygen is limited. However, if there is enough oxygen the value will increase until 4.275% per ºC. (Songming Zhu et al., 2002). Other parameter is pH. The optimal pH is 7.5, but in the range of 5.0 to 9.0 pH there is a 13% increase on the nitrification yield when pH increase in one unit. (F. Fdz-Polanco et al., 1996).

The analysis of the concentration of total nitrogen and nitrate in the wastewater is done with the Spectrophotometer.

An spectrophotometer consists of two systems, one is the spectrometer which produces the light with a determinate wavelength and the other is the photometer which measures the intensity of this light. The cell is situated between the spectrometer bean and the photometer. The photometer sends a signal to a display device. Normally a galvanometer is used in this kind of system. It is necessary to measure the light absorbed by the liquid. For changing the colour of the sample, a reactive is added and the colour will be lighter or darker depending on the concentration. The amount of light absorbed is linked with the concentration of the sample. For the analysis the wavelength has to be chosen correctly. (Principles of Spectrophotometry, 2013.)

The method "Lange LCK 138" is used for the determination of TN whose range of application of this method is for water and wastewater. The sample pH was between pH 3-12 and the temperature of samples and reagents varied between 15 ºC and 25 ºC. However the ions concentration of 400 mg/l COD or 800 mg/l of Cl^- can cause interferences. The samples were taken of the effluent and analyzed the same day therefore preservation of the samples was not required. Some of the samples have been diluted due to the fact that the range of this method is 1-16 mg/L. (HACH Total Nitrogen ,2007)

Inorganically and organically bonded nitrogen is oxidized to nitrate by digestion with peroxodisulphate. The nitrate ions react with 2.6-dimethylphenol in a solution of sulphuric and phosphoric acid to form a nitrophenol.(HACH Total Nitrogen, 2007)

The nitrate method used was HACH method 8039. The range of the measurements: 0.3 – 30 mg/L NO_3^--N. Sometimes the samples have been diluted. Cadmium metal reduces nitrates in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt. The salt couples with gentisic acid to form an amber colored solution. Test results are measured at 500 nm. (HACH Nitrate, 2007).

2.2.2 Total Phosphorus and Phosphate

Removal of phosphates from wastewater is important in order to protect lakes and rivers from eutrophication. Conventional biological treatment processes remove about 50% or less of the phosphate. To increased the amount of phosphate removed is necessary a chemical treatment whose efficient is 90%. Phosphate release occurs on addition of a carbon source to the carbon-starved bacteria, lowering pH or both. (Fuhs, Min Chen, 1975).

The biofilter system has to be on alternating conditions of aeration/no aeration for phosphorus to accumulate in the microorganisms. The microorganisms use the phosphate to grow.

"In anaerobic condition, Phosphorus accumulating organisms (PAOs) take up easily biodegradable substrate quickly from the bulk and store them in form of polyhydroxyalkanoates accompanied with degradation of polyphosphate and consequent release of phosphorus. In the subsequent aerobic condition, PAOs grow aerobically and take up phosphate from the bulk to recover intracellular polyphosphate level by using polyhydroxyalkanoates stored anaerobically as carbon and energy sources". (Zheng Bei et al., 2008) Phosphorus removal reaction is shown in Figure 3.

$$\mathrm{n_1 Organic\ materia} + \mathrm{n_2}\ \mathrm{O_2} + \mathrm{n_3} NH_3 + \mathrm{n_4} PO_4^{3-} \xrightarrow{microorganism} \mathrm{n_5\ New\ cells} + \mathrm{n_6 CO_2} + \mathrm{n_7} H_2O$$

FIGURE 3. Phosphorus removal reaction. (Fernández, M., 2010)

The analysis of the concentration of total phosphorus and phosphate in the wastewater is done with the HACH Lange Spectrophotometer.

The method "Lange LCK 349" is used for the determination of TP . The range of application of this method is for wastewater, drinking water, boiler water, surface water and process water. The sample pH was between 2-10 and the temperature of samples and reagents varied between 15 ºC and 25 ºC. The high concentration of some ions could cause interferences. The table that shows these concentrations is in the Instructions guide, HACH Lange method. LCK 349. Phosphorus total. Phosphate ions react with molybdate and antimony ions in an acidic solution to form an antimonly phospho-molybdate complex, which is reduced by ascorbix acid to phosphomolybdenum blue. The range of the measurements: 0.05 – 1.50 mg/l PO_4-P. Sometimes the samples have been diluted. (HACH Phosphorus total, 2007).

As it is said the phosphate is analyzed by the HACH method 8048. the waveweight to measured it is 880nm. The range of this method is 0.02 to 2.50 mg/L PO_4^{3-} so in this case is necessary to dilute the sample. The principle of this method is that the ortho-phosphate reacts with molybdate in an acid medium to produce a mixed phos-phate/molybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. A blue color will develop if phosphorus is present. when the concentration is higher, the color blue is darker. (HACH Phosphorus, 2007).

2.2.3 Total Organic Carbon

Total Organic Carbon (TOC) is the amount of organically bound carbon present in water. The TOC could have effects on the environment, human health, and manufacturing processes. (Ramalho, 1977).

The TOC analyzer calibration is done according to the manufacture's instruction (Shimazu). Calibration curve is established by analyzing $C_8H_5KO_4$ for TC and $NaHCO_3$ for Total Inorganic Carbon (TIC). The standard solution of Total Carbon (TC) and TIC were placed to the automatic sampler of Shimazu TOC 5000A and analyze the standard solutions and samples according to separate instructions. The analyzer calculates the TOC as a subtraction of TC-TIC automatically.(Instruction manual of TOC Shimazu, 2013).

2.2.4 Biochemical Oxygen Demand

Biochemical oxygen demand is used as a measure of the quantity of oxygen required for oxidation of biodegradable organic matter present in the water sample by aerobic biochemical action.. The BOD value is most commonly expressed in milligrams of oxygen consumed per liter of sample during 5 days of incubation at 20 °C. (Ramalho, 1977).

There are some factors that disturbed the analysis of the BOD_5. The presence of algae die and algal cells contribute to the increase of total organic of the sample. It causes the BOD values grow higher. It is recommended doing the BOD test a pH 7,2. If the pH is not adjust to 7.2 the values obtained are lower. (Ramalho, 1977)
The reaction rate constant k is directly affected by temperature. This relation was given by the Van't Hoff-Arrehenius equation:

$$\frac{\partial \ln k}{\partial T} = \frac{E}{RT^2}$$

where k is reaction rate constant; T , temperature; R, universal gas constant; and E is the activation energy for the reaction.

Domestic wastewater does not normally contain any toxic substances. There are sufficient nutrient salts and suitable microorganisms present. These conditions enable the BOD_5 determination of the undiluted sample using the OxiTop® Control and the OxiTop® measuring system.

Take the measuring range and volume of sample from the OxiTop® Controller or from Table 1. (BOD_5 Operating manual, 2006)

TABLE 1. Nitrification inhibitor drops, function of measuring range.

Expected BOD value [mg/L]	Amount of sample to be used [mL]	Factor (*)
0 – 40	432	1
0 – 80	365	2
0 – 200	250	5
0 – 400	164	10
0 – 800	97	20
0 – 2000	43,5	50
0 – 4000	22,7	100

To choose the correct range, the amount of the Chemical Oxygen Demand (COD) has to be calculated. The COD result was 31mg/L. The BOD is lower than the COD so initially in this project has worked with a range of values (0-40mg / l). After the correct range was chosen and check that the temperature of the sample was between 15 and 21ºC.(Ramalho, 1977 and BOD_5 Operating manual, 2006)

3 DESCRIPTION OF THE SYSTEMS AND SET UP

The systems tested were modifications of biological treatment methods. One of them was a coarse filter system made of willow branches, called the Willow stack Tower. The second system was an ebb-flow system based on a modification of the willow branch filter, called the Ebb-Flow. These two systems are biofilters. It is well known that aged refuse has a high porosity and specific area. In these aged refuse, over time, bacteria become to acclimate at high concentrations. (Zhao et al., 2006; Shi et al., 2007) These biofilters are a low-cost alternative. (Jokela et al., 2002). The third system tested used wastewater as food for algae; this system is called the Algae Turf Scrubber.

3.1 Willow Stack Tower

The first system used to treat wastewater is willow stack tower which uses microorganisms that grow on the willow surface to the wastewater treatment. Willow branches are used to increase the surface area for microorganisms. (Freire, 2012)

Willow stack tower is being used to remove contaminants from landfill leachate and leachate created on compost field. This WST consisted of a wooden frame with three In regular use during summer 2009 in Pälkäne, leachate was treated in the tower until it was satisfactory in reduction of unwanted substances and was then transferred to the septic tanks for sedimentation from where it continued to the soil filtration and finally to the water bodies. (Hepokorpi et al., 2010).

FIGURE 4. Willow Stack Tower
(Photo, Lorena Lorilla 2013)

In the system visualized in figure 4, there is a WST storage tank with mining wastewater that is constantly spreading and flowing over the willow. The spray system distributes the water by all the willow. This spray system was built with a silicon pipe with some holes. It is necessary to clean this frequently because the holes were closed constantly due to the solids on water. The pipe is on the top of the tower and also a cover closes the tower to prevent the evaporation. The aeration is necessary so this cover could not be totally closed. (Freire, 2012).

The samples were taken of the effluent and analyzed the same day therefore preservation of the samples was not required.

3.2 Ebb-Flow

Ebb-flow system is a system working with the idea of maximizing the surface area of willow branches where the microbes grown. EF is a semi-close system which operates in batches. It is used the same configuration than Freire (2012) used for his thesis. In the WST the mining water is distributed spraying, but in the EF the system used is the siphon. There is a dual output system, which controls the flow through two ball valves. One of the outputs are directed to the tank where the willow is and the other is directed to the tank, to get a good homogenization of the storage tank. The wastewater is in the storage tank. (Freire, 2012).

FIGURE 5. Ebb-Flow System

(Photo, Lorena Lorilla 2013)

In WST and EF system the biofilm formation is developed in different steps: attachment, colonization and growth. First microorganisms exist primarily by attaching to and growing upon living and inanimate surfaces. The common feature of this attached growth state is that the cells develop a biofilm. Biofilm formation is a process whereby microorganisms irreversibly attach to and grow on a surface. There are Conditions that allow microorganisms to adhere to the surface. In the figure 6 the biofilm formation is showed.

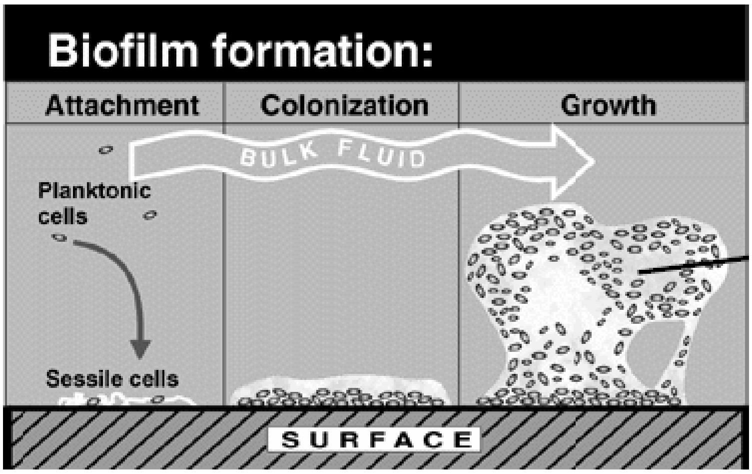

FIGURE 6 . Biofilm formation. (Rittmann, B. E. 2002, 208)

3.3 Algae Turf Scrubber

Algae turf scrubber is a system that uses an algae ecosystem as way of treating wastewater. The system uses string algae to capture the energy of sunlight and build algae biomass from carbon dioxide. The algae capture the nutrients from the wastewater as well as many toxic organic compounds can be degraded. As water travels down the ATS, pollutants are recovered through both biological and physical processes. Carbon dioxide (CO2), nitrogen (N), phosphorus (P) and other elements necessary for metabolic growth are rapidly removed from the water column through biological uptake. This speed however is highly dependent on the amount of light available to the algae. The uptake rates will increase under favourable conditions including light, water temperature, nutrient concentrations pH and correct flow rate. Removal of these compounds (CO2, N, and P) results in water quality changes within the ATS, including elevation of pH concentrations. (Gerbrand Globler, 2013).

The most important factors to take care are sunlight and a sufficient growing environment for the algae because of the fact that algae are a very sensitive organism and if they are not the correct ones the algae will not grow and they will die. pH is a very important factor to take care because if pH is low the algae will not grow.

The ATS consists of a sloped surface on which the substrate can grow and the water can run off by means of gravity. As the other two systems it was built in a small scale. This system has 4 lines where the water is constantly flowing.This wastewater is therefore distributed in equal pulses from which the algae obtains its nutrients. The results is that on the surface algae biomass are growing and meanwhile consuming pollutants. (Gerbrand Globler, 2013).

FIGURE 7. Algae Turf Scrubber
(Photo, Lorena Lorilla 2013)

3.4 Test Set up

There were two tests runs made in this project. In the first one, the three systems worked with untreated wastewater from mineral processing. The samples were taken weekly. In this test run total nitrogen, nitrate, total phosphorus, phosphate, total organic carbon and biochemical oxygen demand during five days were analyzed. After the 3 weeks running, the systems were stopped. There were some considerations for the next experiment. For example, the amount of water in the WST system and in the ATS decreased due to the evaporation and the sample taken. Also, the algae did not grow because the pH was low.

When the first test run finished the water in the system was changed to tap water for a couple of days for rinsing. Based on the results of the first experiment, the second test run started with recycling tap water enriched in order to keep the microorganisms and the algae could grow. . Then gradually the water was changed to mining water enriched with nutrients. It was necessary to add water enriched with nutrients because of the evaporation.

While the mining water was being added, foam with dark surface appeared in the systems. In the WST and in the EF system, the surface of the willow looked black. These systems was stopped before all the mining water were changed because the microorganisms died. On the other hand, when the first litre of mining water was added in the ATS, the pH decreased from 8 to 4 and the algae looked darker. Finally the algae died.

4 RESULTS

This report contains the results of the nutrients and organic matter in the untreated and treated water. Two experiments were done. The first one was done with wastewater from mineral processing. In the second test run mining wastewater enriched with nutrients was added in all the systems. These experiments could not be comparable so the results of the analysis of the nutrients and organic matter are presented in different graphs.

4.1 First test run

This thesis presents the results of the first experiment that was done only with wastewater from ore processing. In this test run total nitrogen, nitrate, total phosphorus, phosphate, total organic carbon and biochemical oxygen demand during five days were analyzed.

4.1.1 Total Nitrogen and nitrate

The spectrophotometer was used to measure the total nitrogen and nitrate, however the methods were different, so it is not possible to compare these results.

The graphs number 8 and number 9 show the results of the TN for the WST and the EF and in the other one are the results of the AST. The graph 8 shows that the initial concentration of TN is 5,75 mg/L and this value remains constant through the test run in the EF. However, the concentration of TN increases from 5,75 mg/L to 34,2 mg/L in the WST. The graph 9 presents the results of the TN measurement in the AST. This system was running for one week as it is said. The concentration of the total nitrogen increased between 7,69 mg/L and 11,6 mg/L.

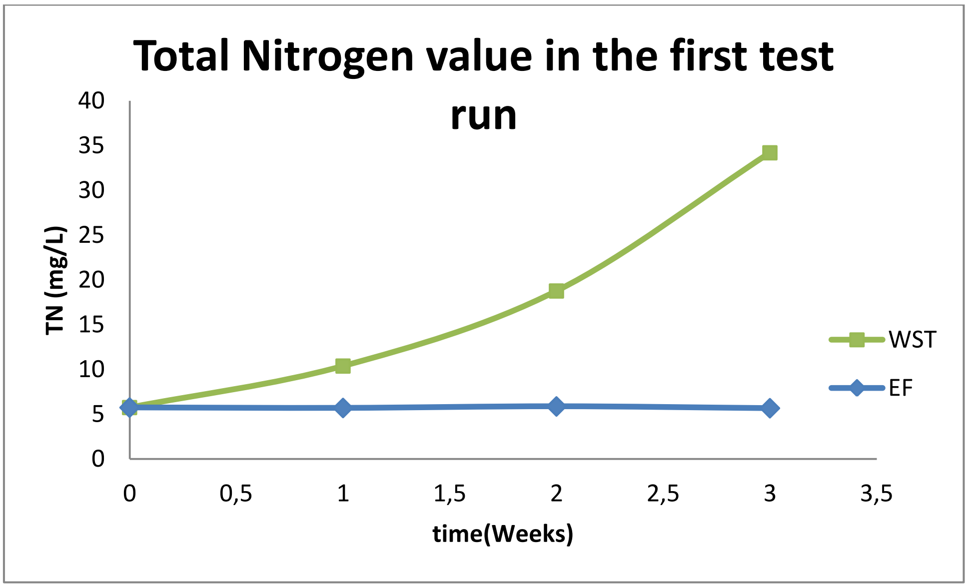

FIGURE 8. Analysis of Total Nitrogen in the first test run.

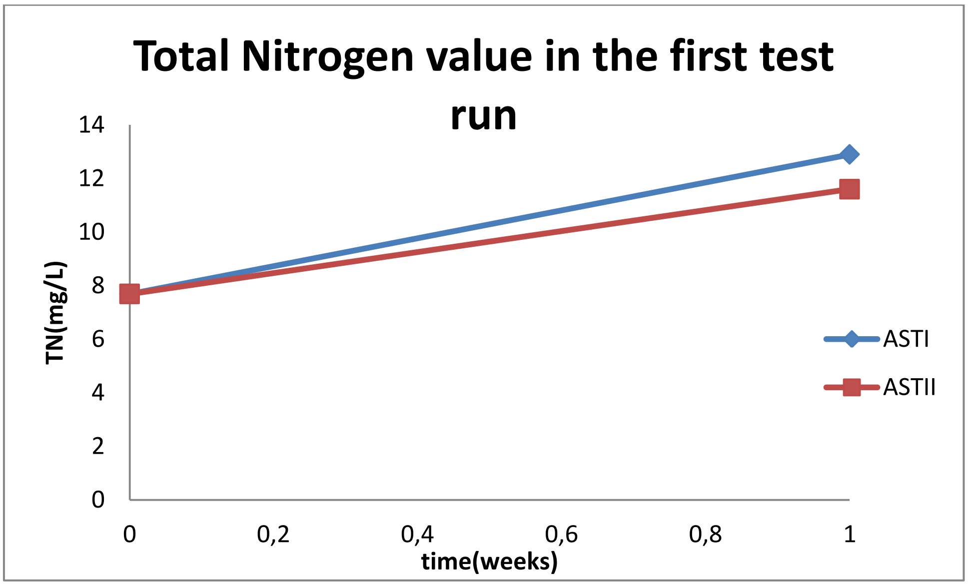

FIGURE 9. Analysis of Total Nitrogen in the first test run.

The results of the TN and the nitrate measured during the fail week were right because the total nitrogen was 7.13mg/L and 3.1 Mg/L NO_3^--N. However, in the first test run the analysis of the nitrate showed values higher than the total nitrogen. Some component of the wastewater from mineral processing interfering and there was precipitation. For this reason control tests were done with the waste water from ore processing from the systems (ATS, WST and EF as such), then known amount of nitrate added and measured. Stock solution for nitrogen was 1 mg/ml and known amount in the sample solution 10 mg/l total N. The table 2 presents the results of the TN.

TABLE 2. Total Nitrogen

TOTAL NITROGEN (mg/L TN)		
	Replicate 1	**Replicate 2**
$H_2O + NO_3^-$ N	10,8	10,8
ATS I	13,7	12,1
ATS I + NO_3^- N	21,7	21,7
ATS II	11,8	11,4
ATS II + NO_3^- N	20,3	19,1
WST	35,2	33,2
WST + NO_3^- N	43,3	41,7
EF	5,92	5,43
EF + NO_3^- N	15,2	14,2

The TN-measurement show that these values are reliable. However, the table 3 shows the results of the nitrate nitrogen. Some of these values are negative and in two cases (replicate 2 in WST and replicate 1 in EF), the concentration of NO_3-N with the amount of stock solution is lower than the concentration of nitrate nitrogen in the wastewater from ore processing. Therefore the NO_3-N results cannot be relied on and they cannot be compared with TN results.

TABLE 3. Nitrate- Nitrogen

NITRATE (mg/L NO_3 -N)		
	Replicate 1	**Replicate 2**
$H_2O + NO_3^-$ N	5,7	5,8
ATS I	-280	-260
ATS I + NO_3^- N	2632	1420
WST	-28	250
WST + NO_3^- N	686	10,1
EF	134	256
EF + NO_3^- N	36	460

4.1.2 Total Phosphorus and Phosphate

The HACH was used to measure the Total Phosphorus (TP) and the phosphate. The two methods were not comparable. During testing process there were negative values in the TP measurement. The problem was the same than between TN and NO_3-N measurements: the methods were not comparable. It was necessary to check the methods to know which of them did not work adequately.

The table 4 and table 5 show the P- measurement. In the first one there are the results of the phosphate which are reliable. In the other hand the concentrations of the total phosphorus, which are presented in table 5, are negative in some cases so in the second test run the Total Phosphorus should not be measured.

TABLE 4. Phosphate and Phosphate- Phosphorus

PHOSPHATE (mg/L PO_4^3)			TP(mg/L PO_4^3-P)	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2
H_2O + PO_4^3-P	3,32	3,69	1,08	1,20
ATS I	0,24	0,8	0,08	0,26
ATS I +PO_4^3-P	6,44	6,68	2,10	2,18
ATS II	0,52	0,48	0,17	0,16
ATS II + PO_4^3-P	7,42	6,5	2,42	2,12
EF	2,56	1,38	0,84	0,45
EF + PO_4^3-P	9,82	7,44	3,20	2,43

The results of the total phosphorus measurement are presented in table 5. There were differences between the duplicate and negative values. The high concentration of some metals present in the mining wastewater interfered in the method.(HACH Phosphorus total).

TABLE 5. Total Phosphorus

TOTAL PHOSPHORUS (mg/L PO_4^3-P)		
	Replicate 1	Replicate 2
H_2O + PO_4^3-P	1,09	1,12
ATS I	-0,11	0,058
ATS I +PO_4^3-P	0,404	0,37
ATS II	-0,084	-0,102

ATS II + PO_4^{3}-P	Abs >3,5	-0,018
EF	0,068	0,054
EF + PO_4^{3}-P	0,438	0,296

4.1.3 TOC

In the graph 10 there is the amount of total organic carbon presented in all the systems. The concentration of TOC increased in all the systems, but in the EF system the last value was strange. In the second week the concentration of TOC was 32,7 mg/L and suddenly the value decreased until 12,9 mg/L. On the other hand, the concentration of organic carbon increased from 2,8 mg/L to 53 mg/L in the WST during the first test run.

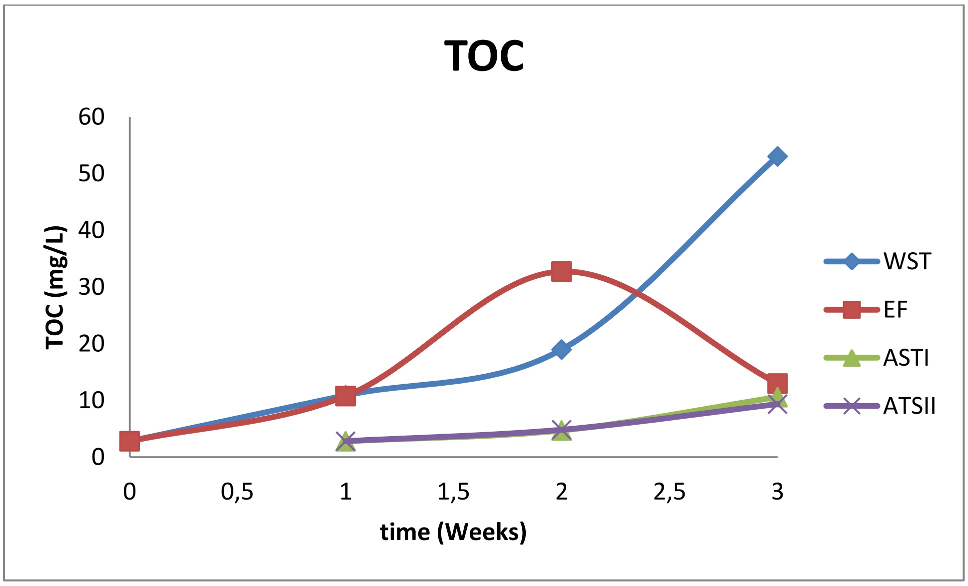

FIGURE 10. Concentration of Total Carbon Organic in the first test run.

4.1.4 Biochemical Oxygen Demand

In graph 11, the BOD_5 removed is showed. While in the EF the 65% of the biochemical oxygen is removed, in the WST the BOD_5 values removed is a little lower, around the 62%.

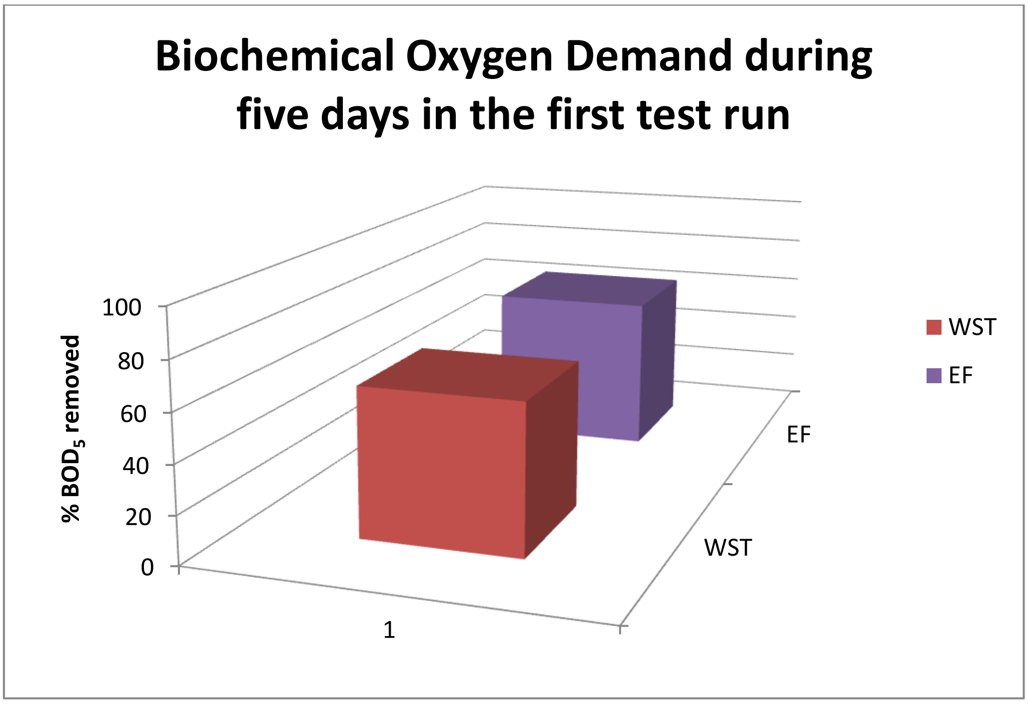

FIGURE 11. Biochemical Oxygen Demand during five days in the first experiment.

4.2 Second test run

The second test run started with recycling tap water enriched with nutrients in the cycle and then gradually mining water enriched with nutrients too was added. The graphs 12, 13, 14 and 15 show the concentration of the nutrients while the mining water enriched with nutrients was being added.

4.2.1 Total Nitrogen

The figure 12 shows the concentration of TN in the second test run. In all the systems the concentration of the nitrogen remained constant through the test. The concentration of the total nitrogen is around 40 mg/L.

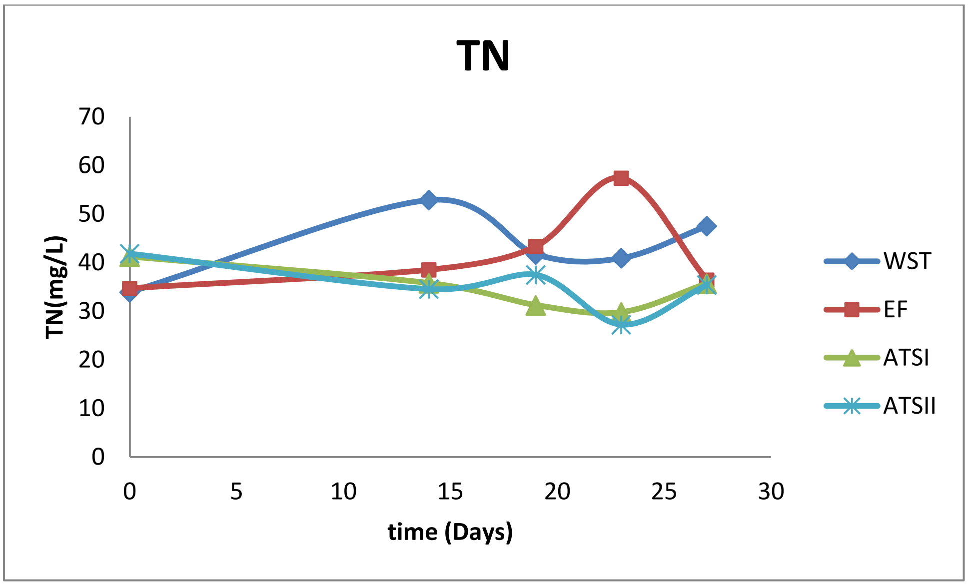

FIGURE 12. Concentration of Total Nitrogen in the second test run.

4.2.2 Phosphate

The initial value of the concentration of phosphate in the AST is higher than in the WST and the EF, but in all the systems the amount of phosphate decreased. This could be seen in graph 13.

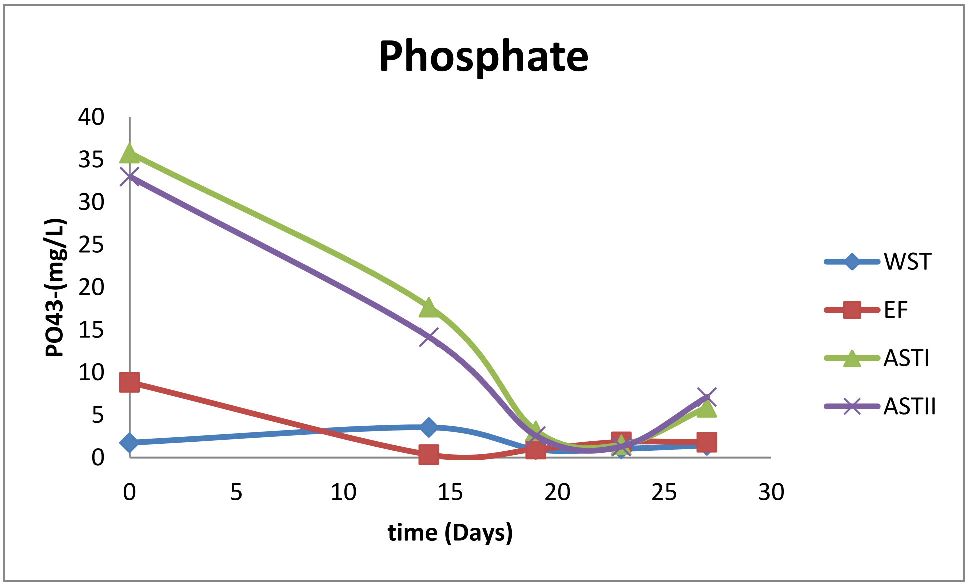

FIGURE 13. Concentration of Phosphate in the second test run.

4.2.3 Total Organic Carbon

In the graph 14 there is the concentration of Total Organic Carbon presented in all the systems. The value of the TOC decreased in the same rate in the WST system than in the ATS. In the graph 14 could be seen that the decrease of the concentration of TOC in the second test run is higher in the EF system;

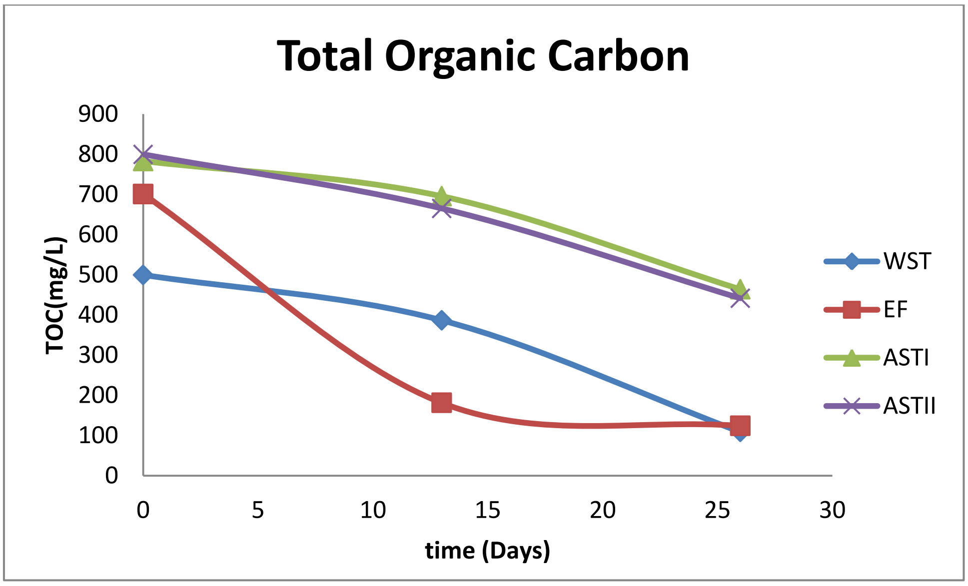

FIGURE 14. Concentration of Total Organic Carbon in the second test run.

4.2.4 BOD_5

The percentage of BOD_5 removed in the second test run are presented in graph number 15. While in the WST and in the EF the 80% of the biochemical oxygen is removed, in AST the BOD_5 values removed is lower.

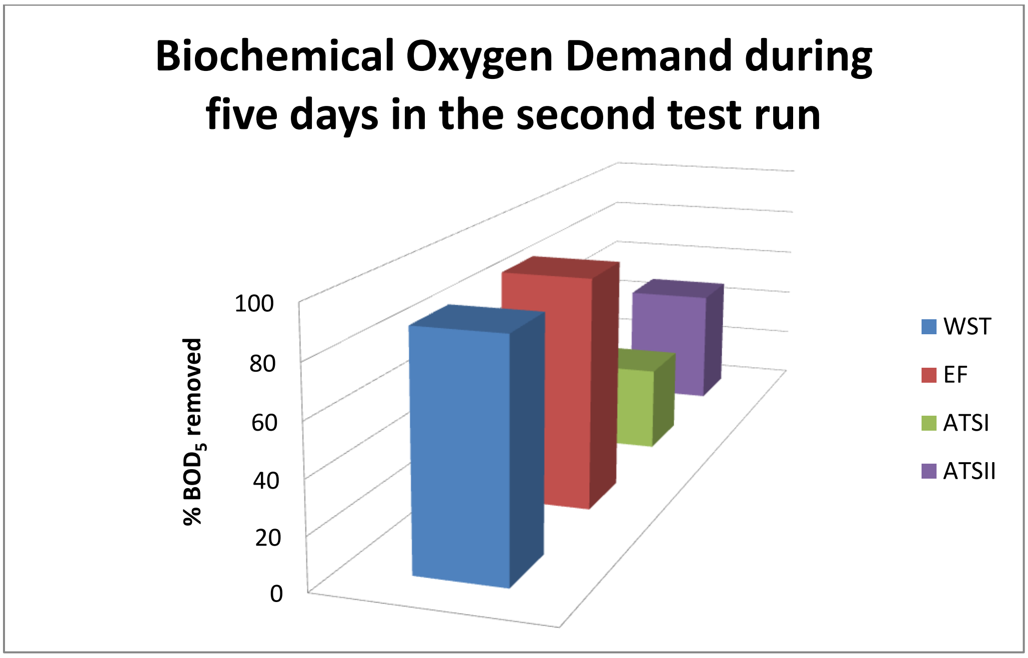

FIGURE 15. Percentage of Biochemical Oxygen Demand removed.

5 DISCUSSION AND CONCLUSIONS

In Alberto's thesis the biofilters used are the same than in this project, the WST and the EF. In this case evaporation was a problem and in the WST the evaporation was higher than in the EF system as in this thesis. Total nitrogen, total phosphorus and BOD_5 were analyzed by Alberto Freire (2012). The amount of TN, TP and BOD_5 removed was higher in the WST than in the EF system.

5.1.1 First test run

During the first experiment the results obtained show in the graph 7 that the concentration of TN remains constant through the test run in the EF. However, the concentration of TN increases from 5,75 mg/L to 34,2 mg/L in the WST. These increased values were caused by evaporation of the mining water in the WST. In the AST the concentration of the total nitrogen increased between 7,69 mg/L and 11,6 mg/L in one week. As in the WST, these increased values were caused by evaporation. Other reason to explain this rise was that the willow and the algae released total nitrogen values in the effluent.

The nitrate-nitrogen was measured in the first test run; however, the analysis of the NO_3-N showed values higher than the total nitrogen. Some component of the wastewater interfering and there was precipitation, as well. For this reason control tests were done with the mining water from the systems (ATS, WST and EF as such), then known amount of nitrate-nitrogen was added and finally it was measured. Stock solution for nitrogen was 1 mg/ml and known amount in the sample solution 10 mg/l of Total N. Based on the results the TN-measurement showed that these values were reliable, but the results of the nitrate nitrogen were not reliable. The concentration of the metals interfering in this method was showed in the Instructions guide, HACH Method 8039, Nitrate. Based on the TN- measurement, it could be seen that the microorganism and the algae did not use nitrogen as nutrient so they did not grow.

The HACH was used to measure the Total Phosphorus and the phosphate. The two methods were not comparable. During testing process there were negatives values in the TP measurement. The results of the phosphate were reliable, however the analysis of the total phosphorus showed negative values in some cases. The main reason for this was that the high concentration of the sulphate and other metals like Zn and Ni in the wastewater interfered in the method.

In the first test run, the concentration of the TOC increased in the WST and in the AST. The main reason for this rise was the evaporation of the wastewater. Another reason was that the willow and the algae released carbon. On the other hand, the concentration of the organic carbon in the EF system increased during the first two weeks due to the evaporation. However, the concentration of the TOC decreased in the last week of the experiment. Total Organic Carbon content in the test procedure concerned gave confusing results, so it is necessary to continue the project.

The results of the BOD_5 removed is showed in graph 11. The efficiency of the willow to remove the BOD_5 is around 60%.

Based on the results of the first test run, the three biological treatment systems are not capable to treat the wastewater from mineral processing. The high concentration of heavy metals and sulphate and the low pH caused that the microorganisms and the algae could not grow.

5.1.2 Second test run

The second test run started with recycling tap water enriched with nutrients in the cycle and then gradually wastewater from mineral processing enriched with nutrients too was added in order the maintained the bacteria and algae alive. The concentration of TN in the second test run was constant for the different systems. The values were between 30 mg/L and 60 mg/L. It means that the microorganisms and the algae did not used the nitrogen as nutrient. Also, the concentration of phosphate decreased in all the systems. It was because of the precipitation of the phosphate with some heavy metals. Other option could be that the microorganisms and the algae used the phosphorus to grow, but based on the TN results it impossible because the microorganisms and the algae need TN and TP to grow.

The value of the TOC decreased in all the systems. The microorganisms and the algae used the wastewater enriched with nutrients as source of carbon. In the other hand, the percentage of BOD_5 removed in the second test run are presented in graph number 15.

While in the WST and in the EF the 80% of the biochemical oxygen is removed, in AST the BOD_5 values removed is lower. So the willow is efficient to remove the biochemical oxygen.

The results of the second experiment show that the three biological treatment systems used in this project are not capable to treat this wastewater from ore processing in these conditions. The high concentration of heavy metals and sulphate and the low pH did keep the microorganisms and algae alive. During the second test run, while the wastewater from mineral processing was gradually being added, the algae became darker and foam appeared. The algae died. Also in the WST and in the EF system appeared foam in the storage tank and the surface of the willow became black.

Based on the results of the concentration of the TOC it is necessary to continue testing because these results are confusing.

Therefore it is necessary to do a chemical pre-treatment to increased the pH and precipitate the heavy metals and sulphate. This treatment could be done in different ways. The first one is a chemical treatment that decreases the level of pollutants in the water and increase the pH. pH test was done in order to know how the metals and sulphates concentration vary when sodium hydroxide was added to precipitate them. The results showed that at pH 9 the concentration of sulphates is too high. However it could be one way to remove some pollutants and adjust the pH to keep the microorganisms alive.

Other option for pretreating the tested of the wastewater from mineral processing could be to dilute it in order to reduce the concentration of pollutants. This solution could be a good option when testing will be done in lab scale, but in a real scale is not economical due to big volumes of water to be treated.

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APPENDICES

Appendix 1. Talvivaara Water Analysis

TABLE 6. Talvivaara Analysis

		Metallianalyysit Liuos						
Näytepaikka	**pH**	**Al**	**As**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**
		mg/l	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**
TAMK3 AVOLOUHOS	3	175	0,54	318	0,26	1,38	<0.0121	<0.0121
TAMK1 AVOLOUHOS	3,9	207	0,6	378	0,3	1,63	<0.0121	<0.0121

	Metallianalyysit Liuos							
Näytepaikka	**Fe**	**Mg**	**Mn**	**Na**	**Ni**	**Si**	**Zn**	**U**
	mg/l	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**
TAMK3 AVOLOUHOS	1360	1736	1318	824	64,6	13	121	0,77
TAMK1 AVOLOUHOS	1595	2045	1559	952	77,7	15,4	143	0,82