Biological water treatment - simultaneous removal of thiosalts and nitrogen compounds

Srebreniković, Tarik

Master's thesis / Diplomski rad

2020

SVEUČILIŠTE U ZAGREBU
RUDARSKO-GEOLOŠKO-NAFTNI FAKULTET
RUDARSTVO Zbrinjavanje i odlaganje otpada

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R 219

Zagreb, 2020

Sveučilište u Zagrebu
RUDARSKO-GEOLOŠKO-NAFTNI FAKULTET
HR-10000 Zagreb, Pierottijeva 6, p.p. 390

OBRAZAC SUSTAVA UPRAVLJANJA KVALITETOM

KLASA: 602-04/20-01/21
URBROJ: 251-70-03-20-3
U Zagrebu, 17.02.2020.

Tarik Srebreniković, student

RJEŠENJE O ODOBRENJU TEME

Na temelju Vašeg zahtjeva primljenog pod KLASOM 602-04/20-01/21, UR. BROJ: 251-70-03-20-1 od 03.02.2020. godine priopćujemo temu diplomskog rada koja glasi:

BIOLOGICAL WATER TREATMENT- SIMULTANEOUS REMOVAL OF THIOSALTS AND NITROGEN COMPOUNDS

Za voditeljicu ovog diplomskog rada imenuje se u smislu Pravilnika o diplomskom ispitu doc. dr. sc. Anamarija Grbeš, docentica Rudarsko-geološko-naftnog fakulteta Sveučilišta u Zagrebu.

Voditeljica
(potpis)
Doc. dr. sc. Anamarija Grbeš
(titula, ime i prezime)

Predsjednik povjerenstva za završne i diplomske ispite
(potpis)
Doc. dr. sc. Želimir Veinović
(titula, ime i prezime)

Prodekan za nastavu i studente
(potpis)
Izv. prof. dr. sc. Dalibor Kuhinek
(titula, ime i prezime)

Sveučilište u Zagrebu

Diplomski rad

Rudarsko-geološko-naftni fakultet

Biological water treatment- simultanoeus removal of thiosalts and nitrogen compunds

Tarik Srebreniković

Rad izrađen: Sveučilište u Zagrebu
Rudarsko-geološko-naftni fakultet
Zavod za rudartsvo
Pierottijeva 6, 10 000 Zagreb

Sažetak

Smanjenje koncentracija dušikovih komponenti I tiosoli u rudarstvu je izuzetno važno za održiv razvoj ekosustava I ljudskog zdravlja. Cilj ovog rada je sastaviti I testirati probno postrojenje za simultano uklanjanje dušikovih spojeva I tiosoli. Sva ispitivanja su napravljenja za kompaniju Boliden Mineral AB, u gradu Boliden, Švedska. Ovo ispitivanje je izuzetno važno za Boliden, s obzirom da je krajnji cilj kontinuirano usavršavanje I poboljšavanje kvalitete I očuvanje okoliša. Rad je izvršen u periodu of 25. veljače do 15. kolovoza 2019. godine. U prva tri mjeseca probno postrojenje se prilagođavalo potrebama. U periodu od 14. Lipnja do 27. Srpnja izvršena su sva mjerenja I zabilježena opažanja. U ovom radu uklanjanje je bilo djelomično uspješno. Dušikovi spojevi su uklonjenji u većim koncentracijama nego tiosoli. Ovim radom biti će istaknuti I opisani problemi I rješenja za što uspješnije buduće uklanjanje ovih komponenti

Ključne riječi: dušikovi spojevi, tiosoli, denitrifikacija, probno postrojenje, kemijska denitrifikacija, oksidacija, Boliden

Završni rad sadrži: 44 stranice, 2 tablice, 23 slike i 28 referenci.

Jezik izvornika: Engleski

Pohrana rada: Knjižnica Rudarsko-geološko-naftnog fakulteta, Pierottijeva 6, Zagreb

Mentori: Dr.sc. Anamarija Grbeš

Ocjenjivači: Dr.sc. Anamarija Grbeš
Dr.sc. Mario Klanfar
Dr.sc. Zlatko Briševac

Datum obrane: 20. Veljače, 2020 , Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb

University of Zagreb Master's Thesis
Faculty of Mining, Geology and Petroleum Engineering

Biological water treatment- simultanoeus removal of thiosalts and nitrogen compunds

Tarik Srebreniković

Thesis completed at: University of Zagreb
Faculty of mining, Geology and Petroleum Engineering
Mining department
Pierottijeva 6, 10 000 Zagreb

Abstract

The reduction of nitrogen compounds and thiosalts in mining industry is extremely important for sustainable management of ecosystem and human health. The goal of the present thesis was to assemble and test a pilot water treatment plant for simultaneous removal of nitrogen and thiosalts compounds at Boliden Mineral AB in Boliden, Sweden. This pilot project is important part of Boliden Mineral AB environmental policy to constantly improve environmental performances of mineral processing. The work is undertaken at Boliden in period February 25 – August 15, 2019. In first three months of work the pilot plant was assembled, followed by the plant testing from June 14 to July 27 (in total 24 work days of testing). With this work removal is achieved partly. Nitrogen compounds are removing more than thiosalts. Thesis will state problems and solutions for better removal of these compounds.

Keywords: nitrogen, thiosalts, denitrification, oxidation, chemolithotropical denitrification, pilot
Thesis contains: 44 pages, 2 tables, 23 figures, i 28 references.
Original in: English
Archived in: Library of Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, Zagreb

Supervisors: Assistant Professor, Anamarija Grbeš, PhD

Reviewers: Anamarija Grbeš, PhD
Zlatko Briševac, PhD
Mario Klanfar, PhD

Defence date: Ferbruary 20, 2020 , Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb

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1 INTRODUCTION

1.1 Problem

Economic growth, improvement of standard and growing world population requires metals, both, primary and recycled. However, the demand for metals should be met with the sustainability in the perspective. That requires production oriented to strong profitability, safe work places and especially good environmental performances (Boliden, 2019).

Water pollution and deficiency of drinking water are some of the major threats to sustainability. Deficiency of drinking and non-polluted water affects production of food and energy and the existence of the life. The biggest causes of surface water pollution are intentional and planned releases of the wastewaters (Deletic, 2019) (Sobota, 2016).

Direct emissions to water bodies from Europe's large industrial sites have decreased in recent years. Industrial sectors with large-scale activities tend to have a higher proportion of direct releases to water, which require more intense on-site treatment. Examples of such sectors are pulp and paper, iron and steel, energy supply, non-ferrous metals and chemicals industry. Sectors with typically smaller facilities, and/or less polluted waste water (eg. manufacturing and food and drink production) report higher proportions of their releases to the sewer system, often similar in pollutant-loading as releases from domestic sources. The largest environmental pressures caused by direct releases of pollutants to water bodies come from single large or clusters of smaller, thermal power plant, coke ovens and chemical manufacturing plants (EEA, 2019).

According to EEA in 2016. Swedish industry combined was responsible for 95,48% of water used. Most significant pollutants are metals such as lead, mercury, nickel, and cadmium and non-metallic pollutants such as organic carbon (TOC), nitrogen and phosphate (Figure 1-1). The trends in emissions showing a decrease (EEA, 2019).

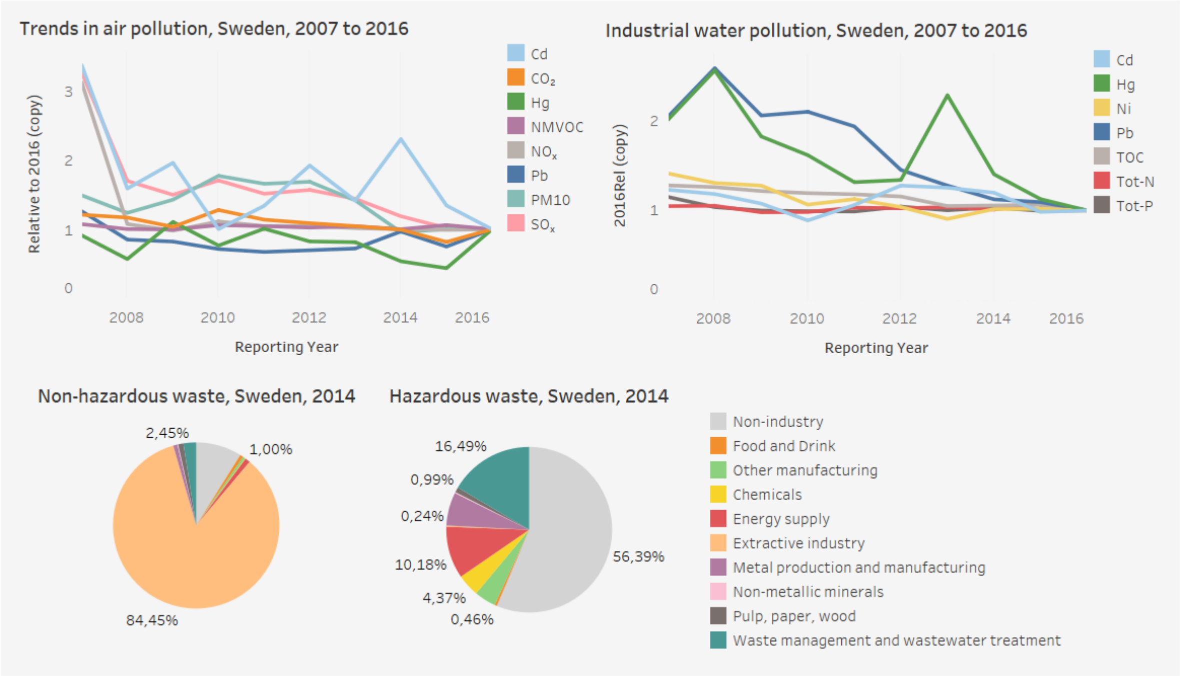
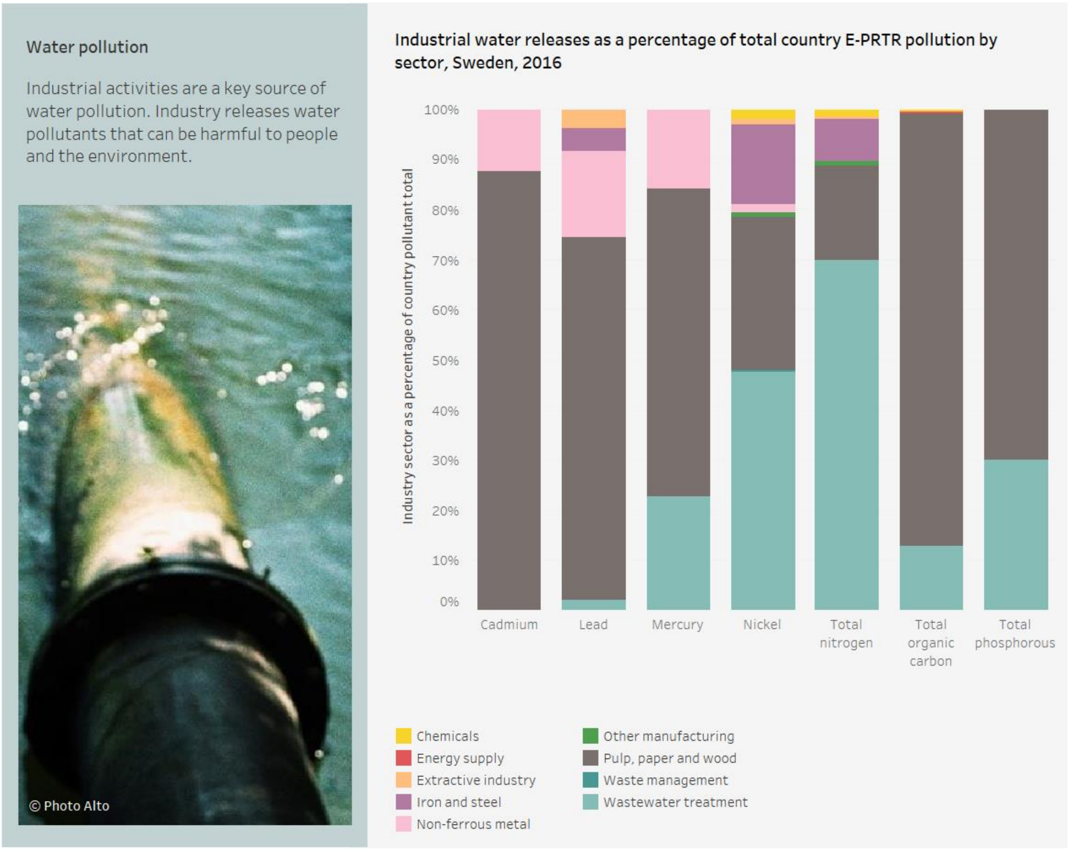


Figure 1-1 Industrial pollution profile of Sweden (EEA, 2019)



Water pollution

Industrial activities are a key source of water pollution. Industry releases water pollutants that can be harmful to people and the environment.

Figure 1-2 Contribution to water pollution in Sweden (EEA, 2019)

The structure of contribution (Figure 1-2) to emission of pollutant into the water is showing that industry of minerals (extractive industry, iron and steel and non-ferrous metal) contribute to emission of metals and nitrogen, ranging from 25% (emission of lead) to 10% (emission of nitrogen).

1.2 Problem description

Presence of the nitrogen in the surface water causes environmental issues such as acidification (decreased pH of the water ecosystem) and eutrophication (loss of dissolved oxygen due to extensive growth in ecosystem). Its presence in drinking water is harmful to human (nitrite compounds cause health issues) (Deletić, 2019).

Emission of nitrogen into the waste water from the minerals sector most often is associated with blasting using explosive mixtures such as ammonium-nitrate and fuel-oil ANFO (Forcit, 2019). Extracted raw material- containing nitrogen (from undetonated explosives)- is transported and processed in a mineral processing plant. Objective of mineral processing is to liberate useful minerals from the waste rock (using comminution i.e. size reduction in crushers and mills), and to separate the waste and useful minerals using concentration/separation techniques such as gravity concentration, magnetic separation and/or flotation. Most of these techniques use water as a media. In final step, the concentrate is dewatered (Wills, 2015).

Depending on the process, ore type, and chemicals used, the water can be recycled or ends up as a waste-water, containing dissolved compounds originating from process and ore. Over the last decade, nitrogen removal processes have generated much attention due to understanding of risks that can occur as a result of high nitrogen concentrations in water flows. A number of methods have recently been described for removal of nitrogen compounds by bacteria assisted methods (Sobota, 2016).

1.3 Background

Thesis work has been done for Boliden Mineral AB in the time from 26th February until 17th August 2019. All measurements were done in Boliden Process Technology Laboratory. The equipment for the pilot project is located at the Concentrator plant. Concentrator plant is facility which processes ore brought from the mine and extracts most of the valuable mineral or metal from the ore. The Boliden area today is home to the Renström, Kristineberg and Kankberg underground mines, as well as the Maurliden open-pit mine. In this area, ores can contain copper, zinc, gold, lead and silver. Also, Kankberg mine is a gold and tellurium mine. Mines contain polymetallic mineralisations of volcanogenic sulphide minerals. When it comes to nitrogen compounds, they are delivered into Concentrator during transport of ore extracted by using explosives. Boliden area also has a concentrator and a leaching plant for gold and tellurium production. Concentrator is important for extraction of valuable minerals containing copper, zinc, gold and silver. Extraction is achieved by various processes e.g. grinding, gravimetric separation, flotation, leaching. The concentrates are then delivered to smelter in the area, lead smelters in Europe and tellurium costumers in Asia. Waste components are brought to tailings ponds (Boliden, 2019).

In mining industry mineral processing is very important. The main goal is to produce maximum value from raw material. One of the stages in mineral processing is enrichment. In enrichment process, value of minerals is improved by washing and/or separation. One of the techniques in enrichment is flotation (Metso, 2018). Flotation process is controlled by reagents addition and adjusting pH value in the pulp. The pulp is provided with oxygen by aeration process to separate precious minerals from the gangue minerals to produce mineral concentrates. Gold and silver are extracted by leaching.

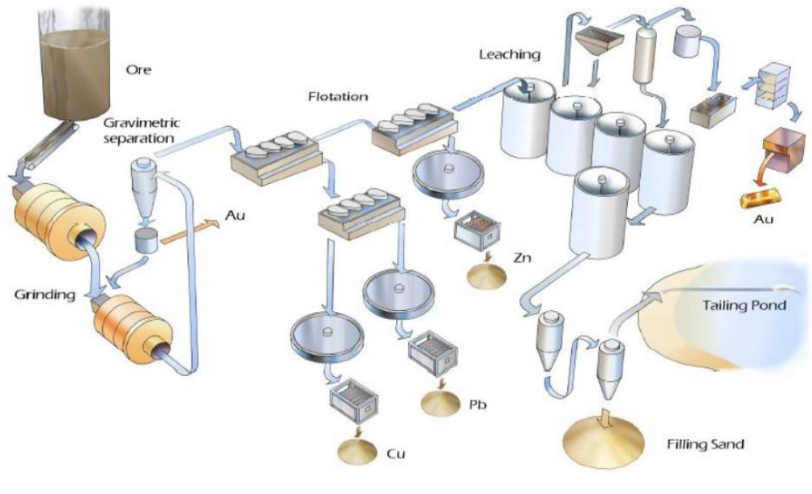


Figure 1-3 The Concentrator process. (Forsberg, 2011)

Concentrates of copper and gold from the mines are processed in the Rönnskär smelter, while zinc concentrates are supplied to Odda in Norway and Kokkola in Finland. In figure 1-3 The Concentrator process is shown.

1.4 Objectives and methods

The main objective of this thesis was to achieve simultaneous removal of nitrogen compounds and thiosalts from the Boliden area concentrator's water using chemolithotrophic denitrification. This means decreasing total concentration of nitrogen compounds in the water after the bioreactor. Also, simultaneously thiosalts concentrations will be decreased. A pilot plant was assembled to treat process water using MBBR (moving bed biofilm reactor), overflow tank, thickener and mixing tank. Solids from income water were removed using a thickener. It was achieved with flow rate adjustments and with thickener. This pilot was running continuously.

A literature review was done to identify values of process parameters for running the pilot and to achieve successful nitrate and thiosalts removal. Firstly, literature review was done on chemolitotrophic denitrification. This was done by reviewing scientific articles, internal reports of Boliden Mineral AB, and interviews with process engineers. Kankberg mine was visited, where mine water is treated by conventional MBBR denitrification and nitrification processes.

From the pilot plant, samples were taken and analysed in Boliden laboratory. There were preliminary results from the plant, which were analysed so further approach could be defined. In preliminary analyses, initial values are defined of nitrogen compounds, tiosalts and other. Also, mechanical and chemical characteristics were done, in order to regulate flow rate in pilot plant.

2 THEORY

2.1 Nitrogen compounds in the environment

Nitrogen appears naturally in the environment as an elementary atom or in compounds. As compound nitrogen can appear in water in form of nitrate, nitrite, ammonium, or ammonia. (Milinkovic, 2015.)

Nitrogen is one of the most important elements for nutrition of plants. In natural waters, presence of nitrogen compounds often indicates organic pollution. One of the nitrogen compounds are nitrate, nitrite, ammonium. Since nitrates are tasteless, odourless and without flavour, water must be chemically tasted to determine nitrate contamination (Milinkovic, 2015).

As it was said before, nitrogen is a component of ammonium nitrate fuel oil (ANFO), which is main component in explosives. Explosives are used for blasting the ore to make it easy to transport and process. Residuals of undetonated explosives could be found in wastewater from the processing plant and they have to be removed before this water could be discharged.

2.2 Toxicity of nitrogen compounds

One of the most toxic nitrogen compounds is nitrite. Signs of nitrate poisoning are: diarrhoea, vomiting, hypertension, higher mortality rate of new-borns, spontaneous abortion etc. (D.W.Koren, 1999). Also, nitrite increases a risk of such diseases as, gastric cancer and cardiac diseases (Di Capua et al., 2019).

Also, nitrates can affect environment. One study has shown that nitrogen compounds can lead to heavy plant growth due to its nutrient properties, so accordingly nitrate can be directly used as a nitrogen source by aquatic plants and thus increases risk for eutrophication (Jermakka, 2015). Another study has shown that higher concentrations of nitrates are significant factor in coastal areas where nitrogen compounds are responsible for water pollution (Filipovic, 2013). High concentrations of nitrate are also toxic to aquatic freshwater animals (Filipović, 2013) (Jermakka, 2015).

2.3 Nitrification

Nitrogen compounds removal requires two main processes in which compounds are transformed. In case of higher content of ammonium, nitrification process needs to be explained. Regarding, one of the most important biological processes for nitrogen compounds transformation is nitrification process. Nitrification is the biological oxidation of ammonium (NH_4) to nitrate (NO_3), widely applied in ecosystems for ammonium (NH_4) removal from during drinking water production and wastewater treatment. In drinking water production nitrification is employed to treat ground waters with ammonium concentrations to produce biologically stable water for distribution (Subba Rao, 2017) (Lawson, 2018). Nitrification is a two-step process in which nitrite is formed as an intermediate. The microorganisms responsible for effecting the transformation are *Nitrosomonas* and *Nitrobacter*. The reaction proceeds according to the equations shown below (Koren, 1999):

$$17NH_4+O_2+24HCO_3\rightarrow 13NO_2+4H_2CO_3+28H_2O+4C_5H_7O_2N \quad (\textit{Nitrosomonas.}) \qquad (2\text{-}1)$$

$$NO_2+7NH_4+4H_2CO_3+6HCO_3+2O_2\rightarrow 6NO_3+14H_2O+2C_5H_7O_2N \; (\textit{Nitrobacter}) \qquad (2\text{-}2)$$

2.4 Denitrification

With nitrification, denitrification process is one of the most important biological processes for nitrogen compounds transformation. Denitrification is a biological process of reduction of nitrates and nitrites to nitrogen oxides or nitrogen gas. Process proceeds in anoxic conditions. In denitrification process nitrate is oxidizing component (electron acceptor) as denitrifying bacteria utilize oxidized nitrogen compounds as terminal electron acceptors in place of oxygen (Koren, 1999)(Milinkovic, 2015). The process is facilitated by specific bacterial species, e.g. *Pseudomonas, Paracoccus, Alcaligenes,* and *Bacillus*. These bacteria can be heterotrophic or autotrophic depending on whether they gain their energy from oxidation of organic or inorganic compounds(Di Capua et al., 2019).

The nitrate ion is reduced to dinitrogen gas under the influence of heterotrophic bacteria in anoxic conditions (Milinkovic, 2015). According to the following equations [1]:

$NO_3^- + 2\ H^+ + 2e^- \rightarrow NO_2^- + H_2O$ (Nitrate reduction) (2-3)

$NO_2^- + 2\ H^+ + e^- \rightarrow NO + H_2O$ (Nitrite reduction) (2-4)

$2NO + 2\ H^+ + 2e^- \rightarrow N_2O + H_2O$ (Nitric oxide reduction) (2-5)

$N_2O + 2\ H^+ + 2e^- \rightarrow N_2 + H_2O$ (Nitrous oxide reduction) (2-6)

2.5 Thiosalts in the environment

Thiosalts in the environment are formed during mining activities by different processes, including grinding and flotation of sulphidic ores. Thiosalts are formed due to oxidation of sulphide minerals, but mainly pyrite (FeS2). Following equation describes formation of thiosulfate (Sundkvist, 2015):

$$2\ FeS_2 + 3.5\ O_2 + 4\ OH^- + H_2O \rightarrow 2\ Fe(OH)_3 + 2\ S_2O_3^{2-} \quad (2\text{-}7)$$

It has also been found that formation of thiosalts can occur under poor oxygen conditions, especially when ore slurry environment is alkaline. The process of thiosalts formation is not well-understood, but it is supposed that the main reasons are that sulphur and polysulphides as sulphur are not thermodynamically stable at high pH values. Therefore, formation of thiosulphate can occur through disproportionation reactions in an oxygen-free environment according to following equations (Sundkvist, 2015):

$$4S^0 + 4\ OH^- \rightarrow 2HS^- + S_2O_3^{2-} + H_2O \quad (2\text{-}8)$$

$$4S^0 + 6OH^- \rightarrow 2S^{2-} + S_2O_3^{2-} + H_2O \quad (2\text{-}9)$$

$$FeS_2 + OH^- \rightarrow 0.5\ HS^- + 0.25\ S_2O_3^{2-} + 0.25\ H_2O + FeS \quad (2\text{-}10)$$

$$FeS_2 + 1.5\ OH^- \rightarrow 0.5\ S^{2-} + 0.25\ S_2O_3^{2-} + 0.25\ H_2O + FeS \quad (2\text{-}11)$$

As shown from the equations above, a disproportionation of the sulphur content means that sulphide in the form of HS^- or S^{2-} is formed in neutral and alkaline solutions. It can be assumed that formation of other types of thiosalts such as tri-thionate ($S_3O_62^-$), tetrathionate

($S_4O_6^{2-}$) and other higher polythionates ($S_nO_6^{2-}$) can occur through the same type of disproportionation mechanism (Sundkvist, 2015).

2.6 Degradation of thiosalts by oxidation

Degradation and transformation of thiosalts is important to be discussed in this work in order to fully understand how removal of thiosalts is achieved. Thiosalts have been found to be relatively stable in neutral and alkaline solutions, even at oxygen solutions. For a quick and complete oxidation to sulphate with air a catalyst in the form of sulphur oxidizing microorganisms is normally required. The following equations describe oxidation of thiosalts with oxygen as oxidant (Sundkvist, 2015).

$S_2O_3^{2-} + 2\ O_2 + H_2O \rightarrow 2\ SO_4^{2-} + 2\ H^+$ (thiosulphate) (2-1)

$S_3O_6^{2-} + 2\ O_2 + 2\ H_2O \rightarrow 2\ SO_4^{2-} + 4\ H^+$ (trithiosulphate) (2-13)

$S_4O_6^{2-} + 3.5\ O_2 + 3\ H_2O \rightarrow 4\ SO_4^{2-} + 6\ H^+$ (tetrationate) (2-2)

2.7 Chemolithotrophic denitrification

Chemolithotrophic denitrification is process of simultaneous removal of nitrogen compounds and thiosalts. Chemolithotrophic denitrification recently gained increasing interest (Di Capua et al., 2015). In the mining industry, thiosulphate is used for gold leaching as an alternative to cyanide. Thiosulphate can occur in effluents together with nitrate (Di Capua et al., 2017). Thiosulphate is discharged as a product of sulphide oxidation (Di Capua et al., 2015). .

In chemolitotrophical denitrification thiosulphate has been shown to be highly bioavailable and efficient source of energy for sulphur-oxidizing denitrifiers. It is assumed that activity of sulphur-oxidizing denitrifiers is most successful at circum-neutral pH values(Di Capua et al., 2017). .

Thiosulphate is one of the sulphur compounds that is widely used as electron donor for autotrophic denitrification (Di Capua & Pirozzi, 2019). In addition, it has been shown that thiosulphate can be successfully used as an electron donor for the removal of high NO_3^- concentrations. S_2O_3 used as electron donor produced 11.067 mg/l of SO_4 by reduction of 1 mg of NO_3-N. It was observed that denitrifying biofilms cultivated on $S_2O_3^{2-}$ showed outstanding performance (Di Capua & Pirozzi, 2019).

2.8 ADSOX Process

ADSOX process is a configuration of chemolithotrophic denitrification process for simultaneous removal of thiosalts and nitrogen compounds in waste water where the content of thiosalts is considerably larger than stoichiometric demand for nitrogen removal. One part of the thiosalts oxidize because of nitrogen compounds, and in the same time nitrogen compounds reduces in nitrogen gas because of tiosalts. ADSOX process main feature is its control philosophy. Oxygen is constantly added to water. Oxygen level in water is measured using an on-line electrode. Increasing supply of oxygen increases oxidation of thiosalts, but hinders denitrification. UV-measurements at 214 nm show peak of adsorption for nitrite, nitrate, and thiosalts. Adjusting oxygen addition to minimize the top of the adsorption peak simultaneous removal of nitrate and thiosalts could be achieved.

Oxygen concentration should be kept in range around 0.3-1.5 mg/L (Sundkvist, 2014). ADSOX process includes on-line pH measurement in water, which is supplied with adequate pH-regulator, so it is retained within range 6.5-7.5. *Thiobacillus denitrificans* grow optimally at pH between 7.5 and 8 (Di Capua et al. 2017). Another article suggested that denitrification with thiosulphate as an electron donor at acidic conditions. The study showed that the reaction proceeded at pH as low as 5.75 (Di Capua et al. 2017).

The ADSOX process has following advantages in comparison with heterotrophic denitrification process
(Sundkvist, 2014):

1. Denitrification and oxidation of thiosalts is achieved in one step
2. This method is ecologically suitable considering that only oxygen source, carbon dioxide and trace elements are needed. There is no using of organic compounds such as methanol, ethanol, acetate etc.
3. The process proceeds at neutral pH. Neutral water typically contains low concentrations of dissolved metals, so it is less toxic for bacteria than acidic water. The water after ADSOX process could also be directly discharged to the recipient.
4. This method can be used for water treatment at temperatures of 0˚C, so denitrification can be achieved efficiently at lower temperatures comparing it with

conventional denitrification that requires an organic substrate source. These makes ADSOX especially attractive for mines in Northern climate

5. Lower capital and operational costs, considering that fewer process steps are needed.

The equation below describes the stoichiometric relation between the species involved in the ADSOX process (Sundkvist, 2014):

$$0{,}844\ S_2O_3^{2-} + NO_3^{-} + 0{,}347\ CO_2 + 0{,}0865\ CO_3^{2-} + 0{,}0865\ NH_4^{+} + 0{,}434\ H_20 \rightarrow$$

$$0{,}0865\ C_5H_70_2N + 0{,}5\ N_2 + 1{,}689\ SO_4^{2-} + 0{,}697\ H^{+} \qquad (2\text{-}3)$$

As could be seen from the Equation 18 above the molar ratio between S_2O_3 and NO_3 is 0,844 which is required for biomass growth. Typically, in waste water from mines and ore plants, molar ratio between thiosulphate and nitrate is significantly larger and is in interval between10 and20). Typically the carbon sources used for autotrophic denitrification are $NaHCO_3$, $CaCO_3$, or simple CO_2 (Sundkvist, 2015). Reduced sulphur compounds or hydrogen could serve as electron donors. Examples for sulphur oxidizing based bacterial cultures are *Thiobacillius denitrificans* and *Thiomicrospira denitrificans*. As electron donors, for example, elemental sulphur or thiosulphate ion S_2O_3 function. Thiosulphate produced during processing of sulphidic ores could serve as an electron donor for removal of nitrate that comes from blasting. Thiosulphate has been shown to be easily assessable and quickly consumed by denitrifying bacteria (Sundkvist, 2015).

2.9 Theoretical nitrate and ammonium removal

Engineers in Boliden developed the equations for theoretical removal of nitrate and ammonium. With theoretical stoichiometric relations for thiosulphate (S_2O_3), tetrathionate(S_4O_6) and dextrin –equivalents assumption, maximum nitrate and ammonium reduction capacity can be calculated. In following equations stoichiometric relations for denitrification process with thiosulphate, tetrathionate and dextrin are shown (Forsberg, 2011):

- With thiosulphate

$0.8413\ S_2O_3^{2-} + NO_3^- + 0.0865\ NH_4^+ + 0.4325\ HCO_3^- + 0.08175\ H_2O \rightarrow 0.0865\ C_5H_7O_2N + 0.5\ N_2 + 1.6825\ SO_4^{2-} + 0.3365\ H^+$ (3-4)

- With tetrathionate

$0.4807\ S_4O_6^{2-} + NO_3^- + 0.0865\ NH_4^+ + 0.4325\ HCO_3^- + 0.6826\ H_2O \rightarrow 0.5\ N_2 + 0.0865\ C_5H_7O_2N + 1.9229\ SO_4^{2-} + 1.5383\ H^+$ (3-17)

- With dextrin

$0.1220\ NH_4^+ + 0.15503\ C_{12}H_{22}O_{11} + NO_3 \rightarrow 0.1220\ C_5H_7O_2N + 1.25\ HCO_3^- + 0.500\ N_2 + 0.711\ H_2O + 0.3720\ H^+$ (3-5)

$S_2O_3^{2-} + 2\ O_2 + H_2O \rightarrow 2\ SO_4^{2-} + 2\ H^+$ (3-6)

Chemical oxidation of thiosulphate by dissolved oxygen (eq. 16) in the feed water causes losses of denitrification capacity. With these equations and calculations nitrate and ammonium removal can be predicted based on amount of dissolved oxygen and thiosalts in income water.

3 WATER TREATMENT PROCESSES

Water treatment processes is used for removal of pollutants from wastewater. Based on the main operational principle waste water treatment processes could be divided into mechanical, physical, chemical and biological. These processes could are utilized with many different combinations (Yoo, 2001).

The goals of water treatment processes are transformation of materials into secure end products, which can be disposed into natural waters without any negative effects. Secondly, protection of plants, animals and humans. Thirdly, recycling and recovering the valuable materials available in waste waters (Samer, 2014).

3.1 Mechanical and chemical treatment of water

3.1.1 Sedimentation

Sedimentation is used as a stage of pre-treatment process for removal of solids and for achieving clear overflow for further treatment processes. Sedimentation process is described as separation of suspended particles, which have higher mass than water. This process is based on the gravity force and is affected by difference in density of particles and fluid. Sedimentation is used in wastewater treatment systems for several reasons, for example for removal of the following (Carlsson, 1996):

1. Grit and particulate matter in the primary settling basins,
2. sludge from the bioreactors,
3. chemical flocs in the chemical treatment step.

Main goal of sedimentation process is to remove, progressively, all of the solids from suspension and to sediment these solids (Carlsson, 1996).

3.1.2 Thickening

The thickener separates suspended solids from a mixture using gravity settling. The purpose of thickening is to increase the concentration of solid particles in underflow (Nasab, 2014). Thickeners can run continuously or semi-continuously. They have reservoirs in which fluid is taken up and the concentrated product is collected at the bottom (Nasab, 2014). Forces that are affecting separation are gravity, buoyancy and friction. Also, factors which are influencing these forces are liquid density, solid density, particle size and shape, flocculation of particles and separation velocity. The main purpose of thickening is to increase the concentration of solid particles in underflow, or to get clearer water phase in overflow. In thickening process three zones are formed during the time in thickener. From top to bottom, first zone is zone of clear water, which is later drained away as overflow from thickener. After that, zone of sedimentation (disturbed sedimentation) occurs, and it is significant that concentration of solid particles is higher than previous zone. Last zone is thickened zone. Density in that zone is growing to the bottom. Also, the level of the inlet of the suspension is located under zone of clear water, in zone of sedimentation. Thickened sludge as underflow is moved by rakes which are moving slowly. In this project, zone of clear water is needed. It is needed for bioreactor, so there will be no solids in bioreactor. Solids can affect further processes in bioreactor. They can slow down process of simultaneous removal; also it can affect bacteria's. Also, sludge can agglomerate on carriers, and in the reactor.

3.1.3 Coagulation and flocculation

Coagulation and flocculation process are used to speed up sedimentation process if it is needed. Coagulation and flocculation are often used as first pre-treatment process stage to remove solids. Coagulation and flocculation are one of the most commonly applied techniques to achieve efficient solid-liquid separation in water treatment (Hua Wei, 2018). Coagulation is the process where destabilization of a given suspension or solution is affected. The function of coagulation is to overcome those factors, and to disturb the stability of given system and to make it unstable (Bratby, 1980). On the other hand, flocculation is the process where destabilized particles, or particles formed as a result of destabilization, are combined and they make contact and they form larger agglomerates, see Figure 2 (Bratby, 1980). Coagulation and flocculation processes are applied for removal of colloidal particles from water which are characterized as very small by dimensions ($1x10^{-6}$ m), and negatively charged which allows their long-lasting stability in colloidal suspensions and prevents sedimentation of particles. Colloidal particles have high degree of dispersion and high contact area. Dispersion degree is defined as ratio of total area of dispersed phase and total volume of dispersed phase (Habuda- Stanić, 2013). This process is based on dosage of chemical matters e.g. coagulants, which causes destabilization, aggregation and mutual connection of colloidal particles, after what result is sedimentation of those particles by gravitation. This process contains two segments. Coagulation is neutralization of negative charged ions in colloid particles, respectively their destabilization, and flocculation which means aggregation, mutual connection and sedimentation of colloidal particles (Habuda- Stanić, 2013).

As it is said, destabilization of negatively charged colloidal particles is caused by coagulant. Coagulants are chemical matters, which in water medium hydrolyse, they release chloride or sulphate ion and hydrogen ion, and as result, voluminous metal hydroxide precipitate generates. In figure 3-1. Flocculation process and forming of bigger particles is shown.

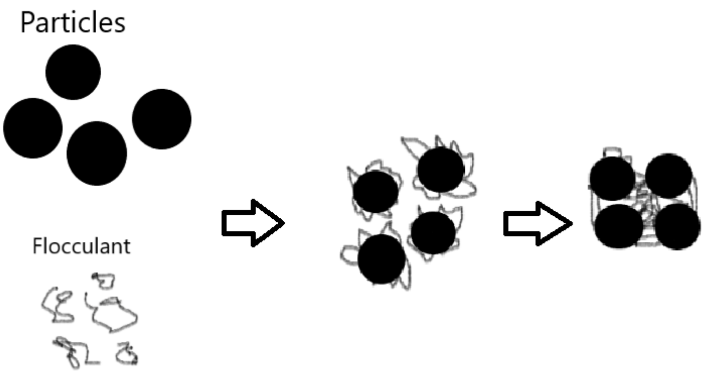


Figure 3-1 Flocculation process, forming of bigger particles

3.2 Biological processes

Biological treatment implies use and exploitation of bacteria species for removing pollutants. The primary idea is to cultivate many bacteria colonies (activated sludge, AS), which utilize pollutants for their own needs (growth and energy production), by creating the necessary conditions for their development. Different conditions, such as aerobic, anaerobic or anoxic, have different way of approach to the growth of specific bacteria. Biological process is followed by solids or liquid separation achieved commonly by gravitational sedimentation. Also, into biomass which can be removed by filtration. Microorganisms can grow spontaneously in the waste water, but their growth can be controlled with different operations such as aeration, hydraulic retention time, etc. Usually biological water treatment includes the removal of organic matter, which is measured as COD (chemical oxygen demand), or BOD (biochemical oxygen demand) (Piculell, 2016). As it is described there are several types of biological wastewater treatment process configuration. Those types are categorized into attached and suspended growth systems based, especially, on the mechanism by which the biomass is retained in the process. Attached growth, refers to microorganisms which are connected with extracellular polymeric substances, which they excrete, in cellule aggregates on carriers, as they form matrix structure of biofilm (Knezevic, 2015) (Piculell, 2016). Suspended growth system is also known as activated sludge. In active sludge system microorganisms grow in flocs, which are retained in the system by being separated from the treated wastewater by settling (Piculell, 2016). An important factor is presence of oxygen in biological water treatment. Aerobic treatment process, which means under presence of air, utilize those microorganisms which use molecular/free oxygen to assimilate organic impurities, convert them in to carbon dioxide, water and biomass or into nitrate in case of nitrification (Mittal, 2011). In other hand, anaerobic treatment process, takes place in the absence of air by those microorganisms that do not require air to assimilate organic impurities. Rather various organic and even inorganic materials may be used as electron acceptors during this process (Mittal, 2011).

3.2.1 Biofilms and carriers

Biofilms are defined as colonies of microorganisms that are connected to solid surface and are growing in almost any aquatic or humid environment. One of the most beneficial usage of biofilms is in wastewater treatment (Forsberg, 2011). Bacterial biofilms represent highly organized population of microorganisms concentrated on sub-surface connected with extracellular polymeric slimy matrix. Biofilms in wastewater treatment are using numerous mechanisms for removing biodegradable matter e.g. biological degradation, bio sorption, bioaccumulation, and bio mineralization (Singh, 2006). The way they are functioning contributes to efficient process wastewater purification (Knezevic, 2015). Biological processes of purification with biofilms are distinguished with numerous advantages e.g. big specific area for bacteria growth and high density of biomass. Systems with immobilized microorganisms are more flexible because they need lower space, they have lower hydraulic retention time, and in contrary provide higher retention time of biomass and increased capability for degradation of biodegradable compounds (Knezevic, 2015).

Extracellular polymeric substances are protecting bacteria's from dehydration and toxic substances and to facilitate the adhesion of the biofilm to the substratum (Piculell, 2016). Biofilm matrix contains: water (to 97%), microbial cells, excreted polymeric substances (EPS), absorbed nutrients and metabolites.

Forming of biofilm can be presented through 5 phases (see figure 3-2) (Knezevic, 2015):

1) Initial connection
2) Irreversible connection
3) Ripening 1
4) Ripening 2
5) Separation

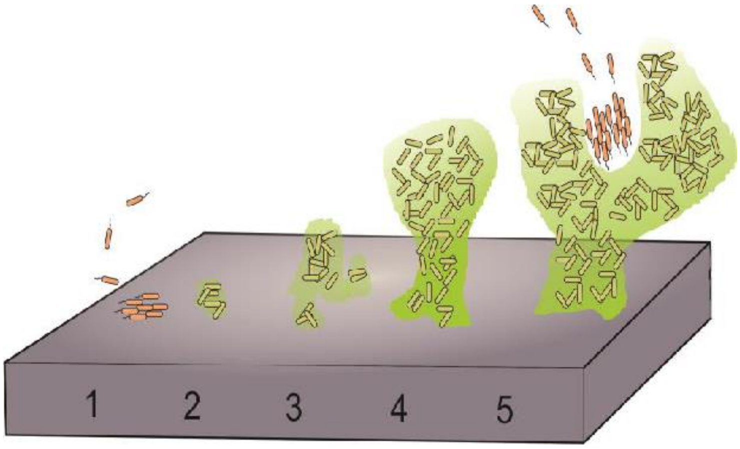


Figure 3-2 Forming of biofilm in 5 phases

Initial connection starts when surface of carrier is covered with nonorganic substances and organic molecules from water to which is exposed. After that cells, quick and efficient, with hemotax or „Brown's move“, get on surface of carrier where first connection to surface by Van der Waals force, electrostatic force, so with excreted polymers they connect for substrate on surface of carrier (Knezevic, 2015).

Irreversible connection is second stage of biofilm growth. It starts when microorganisms start to produce extracellular polymeric substance (EPS). By producing EPS cells remain firmly connected for surface, and real, irretrievably connection is possible if there is no, either chemical or physical stress (Knezevic, 2015).

After connecting with surface, cell continue regular reproduction, as new planktonic cells are attached, and as result is biofilm growing and generation of three-dimensional matrix. This stage of biofilm growth is known as ripening. In first stage initial bacteria are combining, after that bigger matrix is forming. Connected bacteria use nutrients from water for growth and production of EPS. Accordingly, they produce micro-colonies. During the biofilm growth it can be seen, that genetic expression is changed (Knezevic, 2015).

Bacterial biofilms represent heterogeneous bacterial communities, and their growth depends on conditions of environment (pH, temperature, osmosis. etc.). Biofilm growth is slow process. Sometimes it took few days until biofilm is structurally formed.

4 MATERIALS AND METHODS

Materials and equipment for experimental work were provided by the laboratory of Boliden Mineral AB. The conducted experimental work included laboratory analyses, as well as operation and control of the pilot plant by monitoring and adjusting different process parameters.

4.1 Materials and equipment

4.1.1 Wastewater for treatment

Wastewater from the processing plant originates from up-stream mineral processing operations and contains pollutants such as nitrates, nitrites, ammonium, thiosalts and cyanate (CNO^-) that are attributed mainly to flotation, leaching and tellurium production.

Typical properties of the wastewater are pre-measured to enable design of the experiments. The observations are done in period April 2nd -June 10th 2019. The wastewater in observed period have not shown high variations.

Main observed parameters are:

1. pH value, dissolved oxygen, temperature,
2. concentration of nitrogen:
    a. nitrates,
    b. nitrites,
    c. ammonium,
3. concentration of thiosalts:
    a. thiosulphate
    b. tri-thionate
    c. tetrathionate
4. Concentration of cyanate (CNO^-).

4.1.2 Pilot equipment

Pilot equipment (Figure 4-1) contains four main parts. Tailings pulp from the concentrator plant is mixed in mixing tank. Pulp is mixed to prevent accumulation of solids that can block water flow through the pump to thickener. Thickener contains one pump for underflow. The role of the thickener is to produce clear overflow which is going to be used for autotrophic denitrification. Thickened underflow is going to outlet. Overflow goes further to overflow tank. Overflow tank is important for controlling flow to bioreactor. It contains one pump. This pump is adjusted to constant flow that goes to the bioreactor. Bioreactor is the last stage of process.

Flow rates of process water:

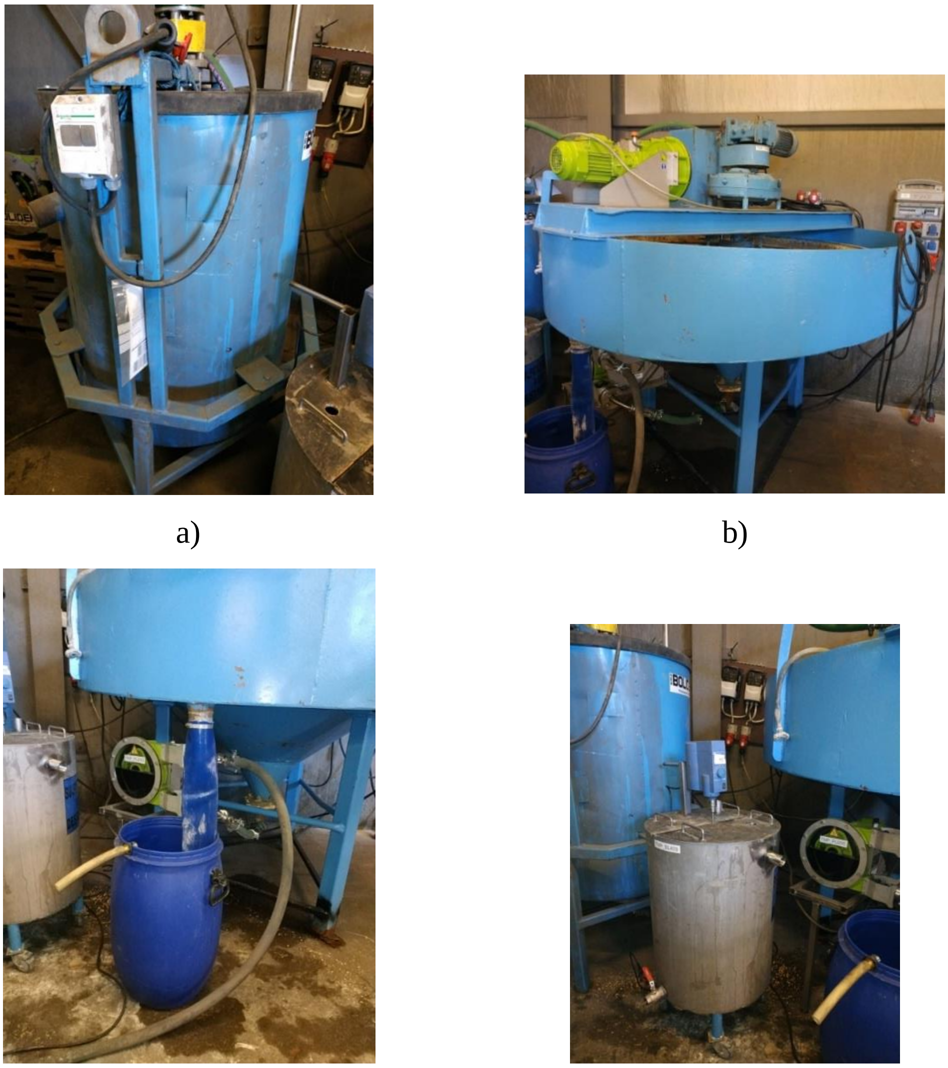
- from mixing tank into thickener - approx. 75 l/h,
- from thickener to overflow 60 l /h
- from thickener to underflow 15 l/h
- entering bioreactor 30 l/h

Bioreactor has agitator used for continuous and slow stirring of the content. The 10-cm layer of carriers at top of the bioreactor is not subdued to stirring due to slow speed of the agitator and constructive properties of the bioreactor. Higher speed of mixing can harm bacteria and affect the process.

Pipe from incoming water is placed at the bottom of bioreactor. Discharge opening is placed at the top of the bioreactor. It has metal net, to prevent carriers flowing out from bioreactor (see Figure 4-1).

Bioreactor characteristics:

- Volume of bioreactor is 120 L.
- Volume of water and carriers in bioreactor: 115 litres
- Bulk volume of carriers: 60 litres
- The residence time: approximately 4 hours.



a) b)

c) d)

Figure 4-1 Pilot equipment (a - mixing tank, b – thickener, c – overflow tank, d - bioreactor)

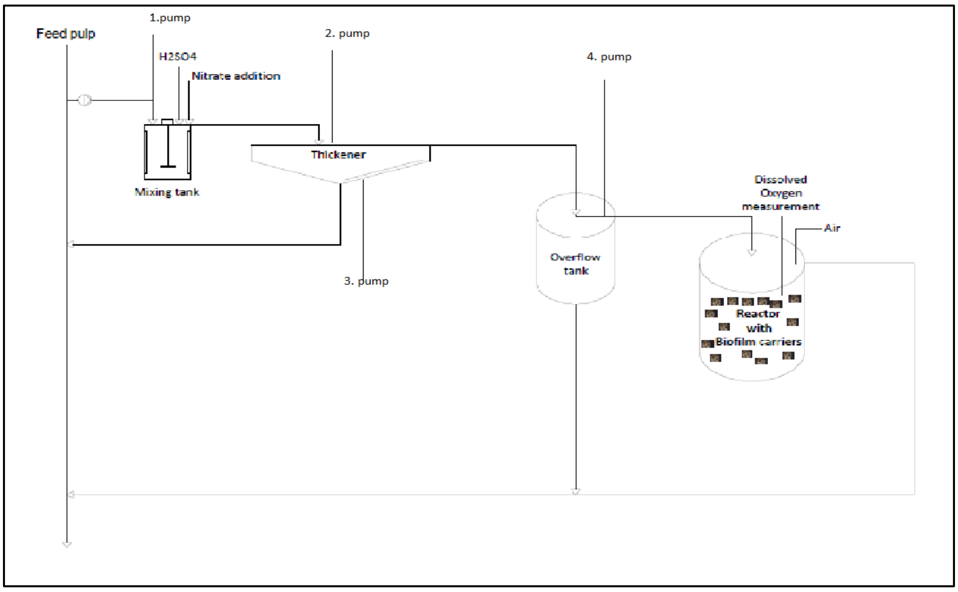


Figure 4-2 Process scheme of the pilot

The flow and conditioning are regulated using 4 pumps:

1. pump is pumping feed from waste water to pulp preparation tank.
2. pump is pumping water to thickener and
3. pump is responsible for underflow from thickener.
4. pump is smaller by capacity and dimensions, pumps overflow water from thickener, which is contained in overflow tank.

All pumps are calibrated by hand. First three are calibrated with 10 L bucket, and last one is in 1 L cylinder. (see Figure 4-2)

4.1.3 ADSOX biofilm carriers

For simultaneous removal of nitrate and thiosalts, AnoxKaldnes (K1) type of carriers are used (Figure 4-3). The carriers are made of high-density polyethylene (HDPE). On the surface, bacteria *Theobacillus denitrificans* is inoculated.

- volume of a carrier is 0,34218 cm^3
- density of a carrier is 0,9386 g/cm^3
- mass of a carrier is 0,3211 g
- bulk volume of a carrier is

Figure 4-3 AnoxKaldness K1 (Veolia, 2019)

4.2 Analyses

For the purposes of this work following parameters are measured: pH value, oxygen content, temperature, nitrogen content in nitrate, nitrite, ammonium, total nitrogen, chemical oxygen demand (COD), and content of phosphorus in phosphate. For the measurement Hach Lange spectrophotometer is used. The spectrophotometer provides concentrations of the measured parameters in the water. In addition, sulphate content, cyanate, and thiosalts are measured by standardized Boliden methods.

4.2.1 pH value, oxygen content and temperature

pH values are measured with portable pH meter from company “WTW”. Temperature was measured also with this meter. Dissolved oxygen content was measured with portable meter from Hach Lange “Hq30d”.

4.2.2 Standardized Boliden method

Thiosalts

In accordance with standard Boliden method, determination of the thiosulphate analysis is divided into four different reactions named as A, B, C, D (Forsberg, 2011). Reaction A generates the tetrathionate rate and reaction B the sulphate rate. The difference between reaction C-A and D-B generates the rate of tri-thionate. Average of the two differences provides an average tri-thionate concentration.

Previous work done at Boliden showed that tetrathionate ($S_4O_6^{2-}$) pentathionate ($S_5O_6^{2-}$), hexathionate ($S_6O_6^{2-}$) and higher polythionates can react with cyanide and carry out thiocyanate very rapidly, even in room temperature. Assuming that pH is controlled between 5-6 units and no catalyst is present, the reaction A is described by following equation:

$$S_nO_6^{2-} + (n-1)\,CN^- + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2HCN + (n-3)\,SCN^- \qquad (4\text{-}20)$$

Where, n – number of sulphur atoms.

From this equation, one mole of thiosulphate and sulphate is formed for each mole of polythionate.

In reaction B, catalyst is added, for instance copper (Cu_2^+), thiosulphate can form thiocyanate in association with cyanide. The reaction results in additional thiocyanate and thiosulphate, as an already present or intermediate species, during the cyanolysis of the polythionates.

$S_nO_6^{2-} + nCN^- + H_2O \rightarrow SO_3^{2-} + SO_4^{2-} + 2HCN + (n-2)SCN^-$ (4-21)

$S_2O_3^{2-} + CN^- \rightarrow S_2O_3^{2-} + SCN^-$ (4-22)

From these equation, one mole sulphite (SO_3^{2-}) and sulphate (SO_4^{2-}) is yield from one mole polythionate and thiosulphate accordingly. Again, the remaining sulphur forms thiocyanate. The products of the reactions A, B, C, D are measured with spectrophotometer. In figure 4-4 thiosalts analysis is shown.

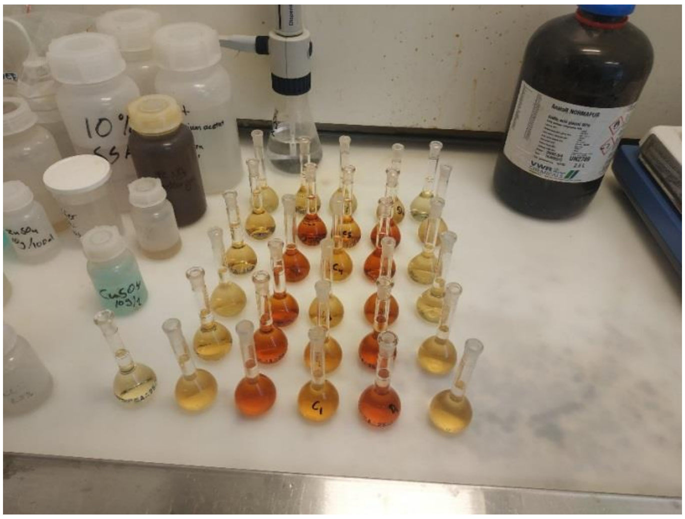


Figure 4-4 Thiosalts analysis

Sulphate

Sulphate is determined by standard Boliden method. By method, sulphate ions react with barium to form a fine-grained BaSO4 precipitate. Turbidity is then proportional to the sulphate content. Sulphate content is determined in Hach Lange DR3900 spectrophotometer with standard solutions at 450nm.

25 ml of sample is added into 100 mL volumetric flask. To sample, and to the blank sample, 5 mL of the buffer solution is added, and 0.3 g of $BaCl_2$. Buffer solution consists of 30g of $MgCl_2$, 5g CH_3COONa, 1g KNO_3, 20mL acetic acid + water to 1 liter. Deionized water is added to 100mL. After that sulphate concentration is measured (Boliden, 2019).

CNO measurement

Cyanate is unstable at neutral or low pH (R. B. Baird, 2017). By standard methods described in „Standard methods for the examination of water and wastewater procedure of cyanate measurement is to take or prepare at least 100 mL of sample. After that, it is needed to acidify 100 mL of sample by adding 0.5 mL of H_2SO_4 to a pH of 2.0 to 2.5. Next step is heating of sample to 90-95C and maintaining temperature for 30 min (R. B. Baird, 2017). After sample is cooled to room temperature, ammonia is measured again. Because of evaporation, deionized water has to be added up to 100 mL. Also, ammonia concentration must be determined on one sample before acidification (R. B. Baird, 2017). Difference between these two measurements is the amount of CNO in the sample. Also, depending on ore type leaching and type of ore refining method, in the results, it is shown that thiocyanate (SCN^-) can be found from the results of thiosulphate analysis which is described in later chapters.

Thiocyanate (SCN^-) can be formed biologically during cyanide detoxification or chemically during gold cyanidation as a result of the interaction of free cyanide (F. Di Capua F. P., 2019.). Also, *thiobacillus denitrificans*, are capable of complete denitrification with SCN^- as energy source . This has positively affected the results of the pilot experiments, as thiocyanate was used by the bacteria as energy source, as SCN^- will serve as one of the few energy sources in project.

4.2.3 Theoretical COD removal

Theoretical contribution of thiosalts to COD can be calculated. Following equations are showing thiosalts oxidation. From these equations contribution of thiosalts to COD can be calculated (Sundkvist, Jan-Eric, 2015.).

$$S_2O_3^{2-} + H_2O + 2\,O_2 \rightarrow 2\,SO_4^{2-} + 2\,H^+ \quad (4\text{-}73)$$

$$S_3O_6^{2-} + 2H_2O + 2O_2 \rightarrow 3SO_4^{2-} + 4\,H^+ \quad (4\text{-}84)$$

$$S_4O_6^{2-} + 3.5O_2 + 3\,H_2O \rightarrow 4\,SO_4^{2-} + 6\,H^+ \quad (4\text{-}95)$$

$$SCN^- + H_2O + 2O_2 \rightarrow CNO^- + SO_4^{2-} + 2\,H^+ \quad (4\text{-}106)$$

4.3 Research design

The properties of the wastewater, flow-rate and residence time were essential parameters for the design of this research. For that purpose, in period from April 2nd to June 7th 2019, initial testing and equipment adjustments were done. The most relevant parameters for design of this research are shown in table 4-1. The measurements are performed in mixing tank.

Table 4-1 Properties of the wastewater from the Concentrator plant

Parameter	**Observation**	**Ideal concentration for growth of the bacteria**	**Comment**
Ph	alkaline 9 (var. 2-12)	6.5-7.5, pH adjustment required	mostly constant properties, some inconsistencies in period May 3rd - May 10th
Oxygen	6 mg/L (var. 0.5-9 mg/L)	0.3-0.5 mg/L (?)	mostly constant properties
Temperature	18-19°C (var. 10-22°C	good survival in wide range of temperatures	seasonal variations
Nitrates (NO_3-N)	5 mg/L (var. 0.8-7 mg/L)	nutrient, higher concentrations preferable	mostly constant properties
Nitrites (NO_2-N)	0-0.1 mg/L	nutrient, higher concentrations preferable	mostly constant properties
Ammonium (NH_4-N)	3 mg/L (var. 0.8-5.5 mg/L)	n/a	mostly constant properties
Thiosulphates	50-60 mg/L (var. 0-150 mg/L)	n/a	mostly constant properties
Tri-thionate	0-170 mg/L	n/a	varies a lot
Tetrathionate	40-270 mg/L	n/a	varies a lot
Total nitrogen	30 mg/L (var. 0.5-47 mg/L)	-	total nitrogen was much larger than total sum of nitrate, nitrite and ammonium

The intention of the research design was to establish ideal conditions for growth of the bacteria. For that purpose, it was required to perform conditioning of the feed water pH using sulphuric acid and add nutrient for the bacteria (nitrates) into the mixing tank.

Total nitrogen was much larger than total sum of nitrate, nitrite and ammonium leading to assumption that water contained other sources of nitrogen, such as cyanate (CNO-) from cyanidation processes. Thus, the measurement of cyanates is added into research program.

4.3.1 Research set-up

pH conditioning

- H_2SO_4 addition until 7 pH
- 2 times in a day (in the morning and in the afternoon)

Nitrate addition

- NO_3-N target in mixing tank 15 mg/L (5 mg/L initial content in feed water)
- 750 mg potassium nitrate per hour required, in water solution pumped constantly

4.4 Pilot's operational procedure

4.4.1 The process

- The feed is controlled with pump 1: feed is mixed, and suspension is maintained
- Mixing is controlled with mixer controller and speed is adjusted.
- On the top of the preparation tank, acid and alkaline addition is set for manual addition
- Thickening process produces clear water for bioreactor, and the process is controlled in overflow tank
- Process of simultaneous removal of thiosalts and nitrogen compounds in bioreactor
- Water is leaving the bioreactor from outlet at the top

4.4.2 The procedure

a) in the morning

1. Take one sample from each: overflow tank, mixing tank and bioreactor
2. Measure pH, O_2, temperature in each: overflow tank, mixing tank and bioreactor
3. Adjust pH (add sulphuric acid) until pH-meter shows 7

4. Measure NO_3-N, NO_2-N, NH_4-N, COD, PO_4-P in each: overflow tank, mixing tank and bioreactor, in spectrophotometer.
5. Measure thiosalts, CNO-N, SO_4 in each: overflow tank, mixing tank and bioreactor, by standardized Boliden methods.

b) in the afternoon

1. Measure pH using pH-meter and adjust accordingly

c) check regularly the pumps and equipment

5 RESULTS AND DISCUSSION

5.1 Course of the experiments

The pilot project started in June. The experiments are performed in period June 11th – July 23rd 2019. In the beginning the intent was to run full ADOSX process in the pilot plant. Due to technical issues, it was not possible to run it. Parameters, such as, pH and oxygen should have been adjusted automatically with regulators. Because of technical issues, these parameters have been regulated manually.

Nitrate solution was added continuously during week days. The nitrate addition did not take place during, nights and weekends, so the Monday' measurements show low concentration of the nitrate.

5.2 pH value, oxygen content and temperature

5.2.1 pH value

The highest pH value in the mixing tank was 11,10. Minimum was 8,60. In the overflow tank, maximum was 10,00 with minimum of 8,00. In the bioreactor, maximum was 9,20 and minimum was 6,60 (Fig. 10). As expected, the water was alkaline due to upstream flotation process.

Ideal pH for *Thiobaccillus denitrificans* was 6,5-7,5 so the process required conditioning of pH by adding sulphuric acid two times a day into the mixing tank. That was the reason why the results have shown lower pH levels in the bioreactor and in the overflow tank are lower than in the mixing tank (Figure 5-1).

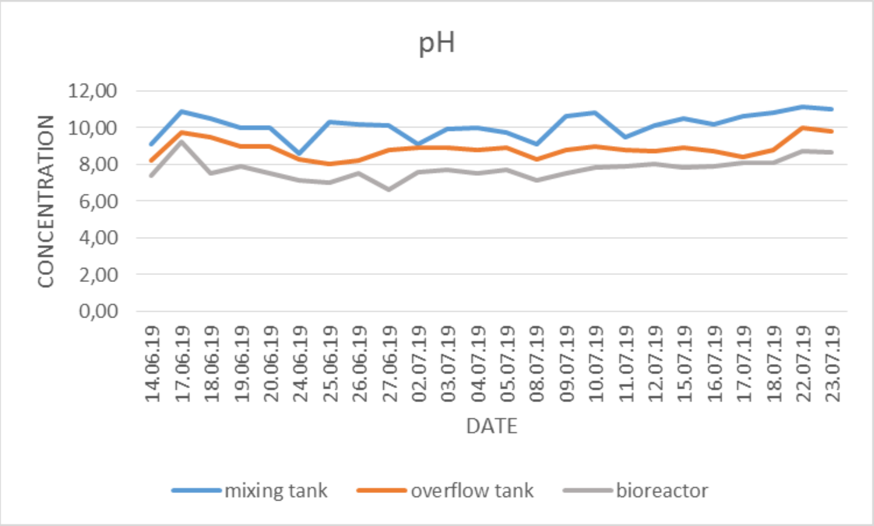


Figure 5-1 pH values

5.2.2 Oxygen levels

Oxygen levels were high in the mixing tank, lower in overflow and the lowest in the bioreactor (Figure 5-2). The highest oxygen concentration in mixing tank was 10,00 mg/L and minimum was 6,00 mg/L. Approximately oxygen levels in the mixing tank were around 7,50 mg/L. In the overflow tank the highest level was 5,20 mg/L, and the lowest 3,30 mg/L. Average oxygen concentrations in the overflow tank were around 4,5 mg/L Maximum dissolved oxygen content in the bioreactor was 7,50 mg/L and minimum is 0,10 mg/L. Most of the time, except in one occurrence, the oxygen concentrations in bioreactor was approximately 0,3 mg/L. In that one occurrence (July 15th), the oxygen concentration was 7,50 mg/L because it was added into bioreactor in uncontrolled and excessive manner.

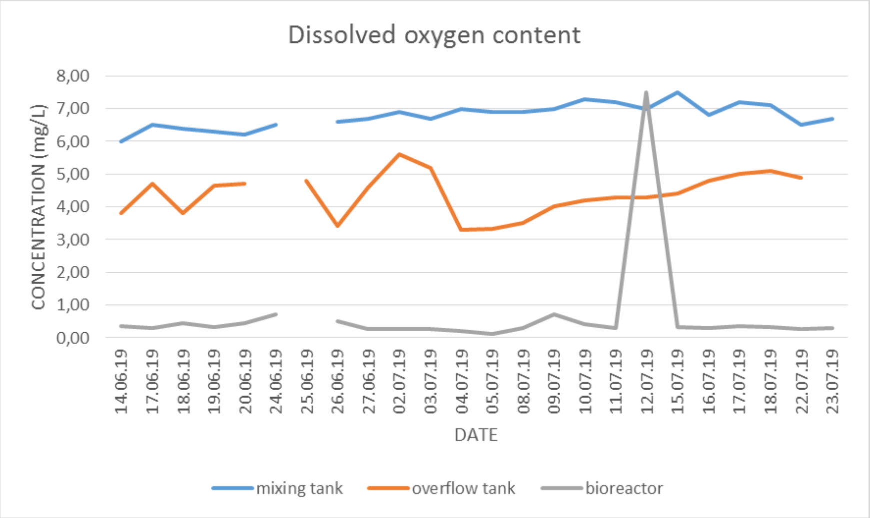


Figure 5-2 Dissolved oxygen content

5.2.3 Temperature

Temperature levels were mostly constant in the mixing tank, overflow tank and bioreactor (Figure 5-3). The highest temperature was 24,50°, and the lowest 18,10°. Temperature was slightly lower in the bioreactor compared to the mixing tank and overflow tank.

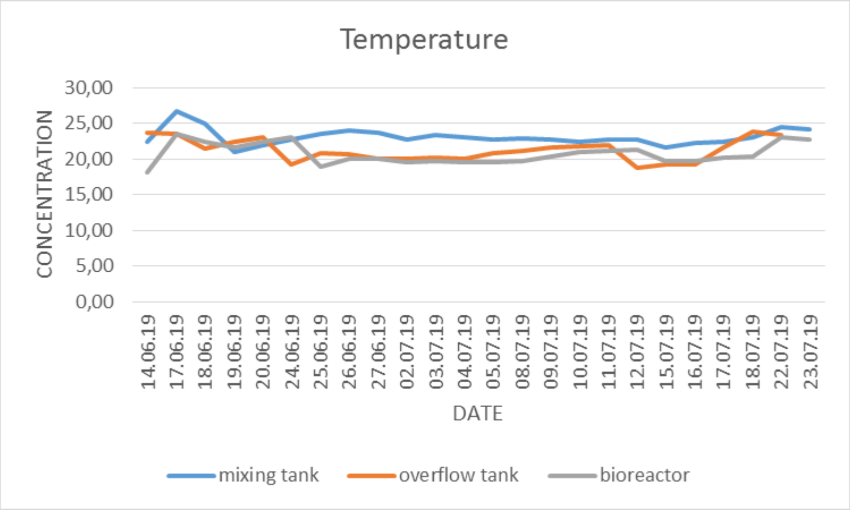


Figure 5-3 Temperature levels

5.3 Nitrogen content in nitrate, nitrite and ammonium

5.3.1 Nitrogen content in nitrate

During operation of the pilot NO_3-N, NO_2-N, NH_4-N were measured in three stages. From mixing tank, overflow tank and finally from bioreactor. From June 24th to July 23th, twenty-four daily measurements were performed (Figure 5-4).

- The highest concentration in the mixing tank was 16 mg/L, and minimum was 3,30 mg/L.
- In the overflow tank the highest was 12 mg/L and minimum was 2,00 mg/L.
- The highest concentration in the bioreactor was 7,50 mg/L with minimum of 0,35 mg/L.

Nitrate concentrations are decreasing from overflow tank to bioreactor in all measurements with exception on July 12th. The reason for that was oxygen addition, which was too high, so denitrification process was not achieved.

Potassium nitrate was added to get higher concentrations of nitrate; however, the results have shown that addition of nitrate in solution (solution dripping) was successful on June 27th, July 11th, July 16th, July 17th and July 18th, and that on other dates, the assumptions for the calculation of required nitrates were not correct. For example, if assumed that the concentration of nitrates in feed was 5 mg/l, while in reality it was lower, the calculation would not give sufficient mass of the nitrates to add into the mixing tank.

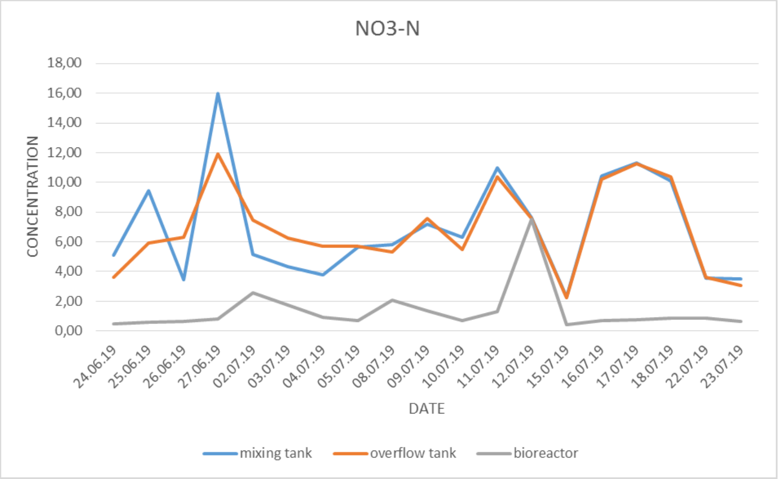


Figure 5-4 Nitrogen in nitrate concentrations

5.3.2 Nitrogen in nitrite content

Concentration of nitrites were higher in bioreactor and overflow, than in mixing tank where the nitrates were added. Existence of the nitrites indicated that the denitrification process was taking place (degradation of nitrate into nitrite) (Figure 5-5).

In 24 measurements, the highest NO_2-N concentration in the mixing tank was 0,15 mg/L, and the lowest was 0,20 mg/L. In the overflow tank the highest was 0,53 mg/l with the lowest of 0,22 mg/L. In the bioreactor the highest concentration was 0,85 mg/L. The lowest was 0,00 mg/L.

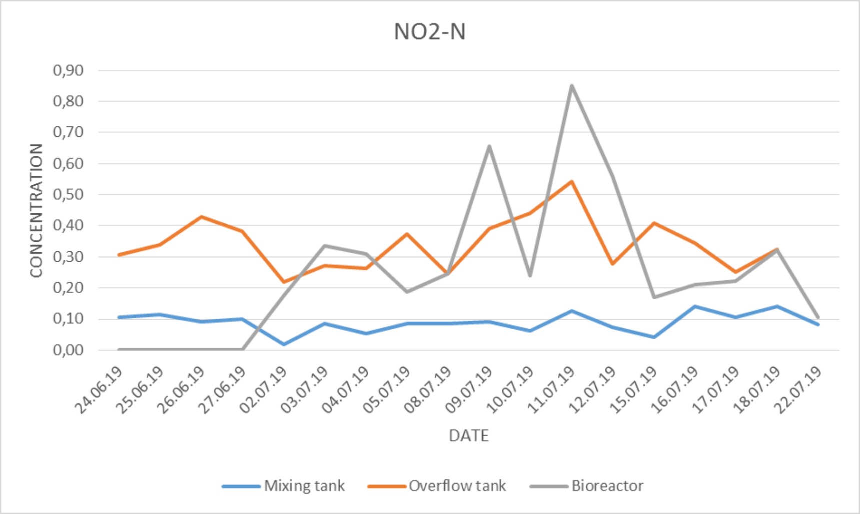


Figure 5-5 Nitrogen in nitrite concentrations

5.3.3 Nitrogen in ammonium

Concentration of ammonium behaved differently from what was expected - after the bioreactor, concentration of ammonium was significantly higher than in the mixing tank. As it was mentioned in previous chapters, it was assumed reason for that was inflow of the cyanate. At lower pH concentrations, cyanate was turning to ammonia (see Figure 5-6).

The highest concentration in the mixing tank was 4,95 mg/L and the lowest was 1,45 mg/L. In the overflow tank the highest was 9,50 mg/L, and the lowest was 4,80 mg/L. The highest concentration in the bioreactor was 22,00 mg/L and the lowest was 9,15 mg/L. (Fig. 15)

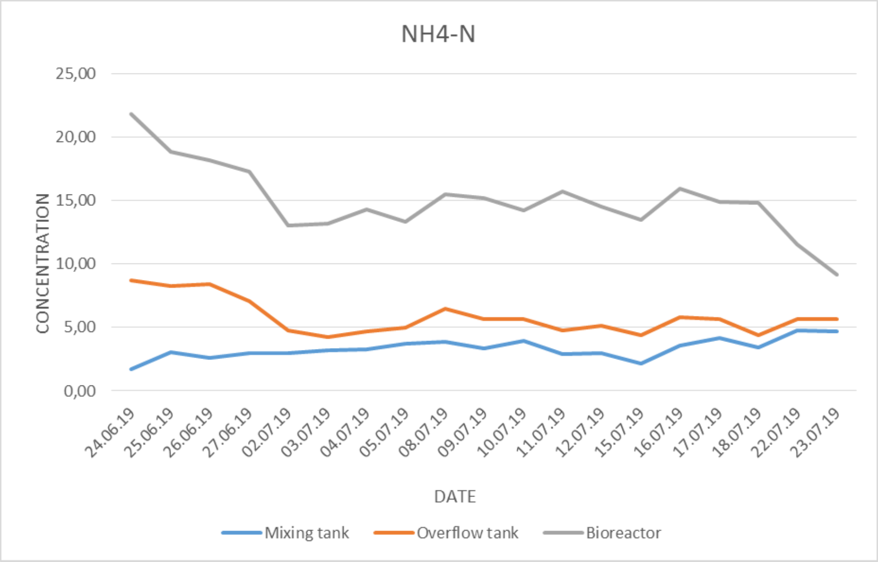


Figure 5-6 Nitrogen in ammonium

5.4 Thiosalts and chemical oxygen demand

5.4.1 Thiosulphate concentrations

As described in the previous chapter thiosalts analyses were performed by standardized Boliden method. Boliden rules forbid anyone without proper training to perform works involving cyanide. All measurements were done by engineers from the laboratory. From June 14th to July 12th, thirteen measurements were performed. The highest concentration in mixing tank was 225,00 mg/L, and the lowest was 0,00 mg/L. In the overflow tank The highest was 140 mg/L, and the lowest was 0,00 mg/L. The highest concentration in the bioreactor was 150 mg/L, and minimum was 20 mg/L. It can be seen that thiosulphate (S_2O_3) removal was not successful, with few exceptions, from June 16th until June 26th and on July 11th (see Figure 5-7).

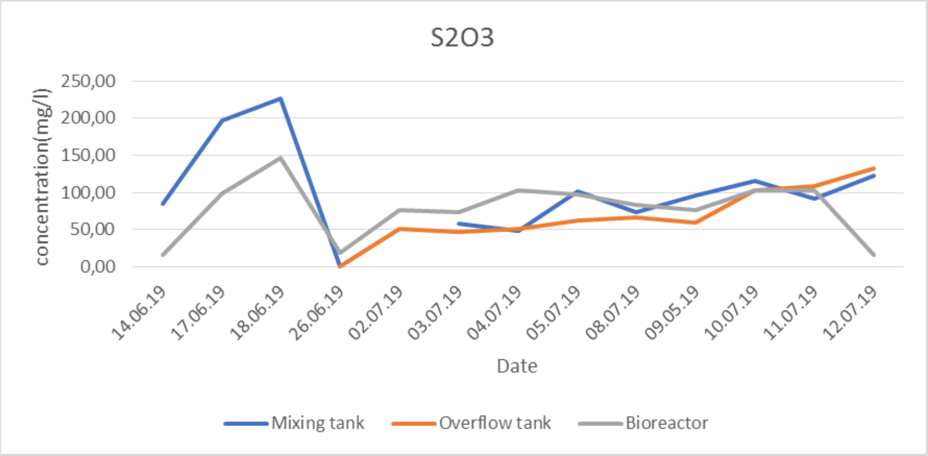


Figure 5-7 Thiosulphate concentrations

5.4.2 Tetrathionate concentrations

Figures 5-8 and 5-9 show rather successful removal of both, the tetrathionate (S_4O_6) and trithionate (S_3O_6).

The highest concentration of tetrathionate in the mixing tank was 320,00 mg/L, and the lowest was 45,00 mg/L. In the overflow tank the highest was 340,00 mg/L, with the lowest of 40,00 mg/L. In the bioreactor the highest concentration of tetrathionate was 250 mg/L. The lowest was 0,00 mg/L.

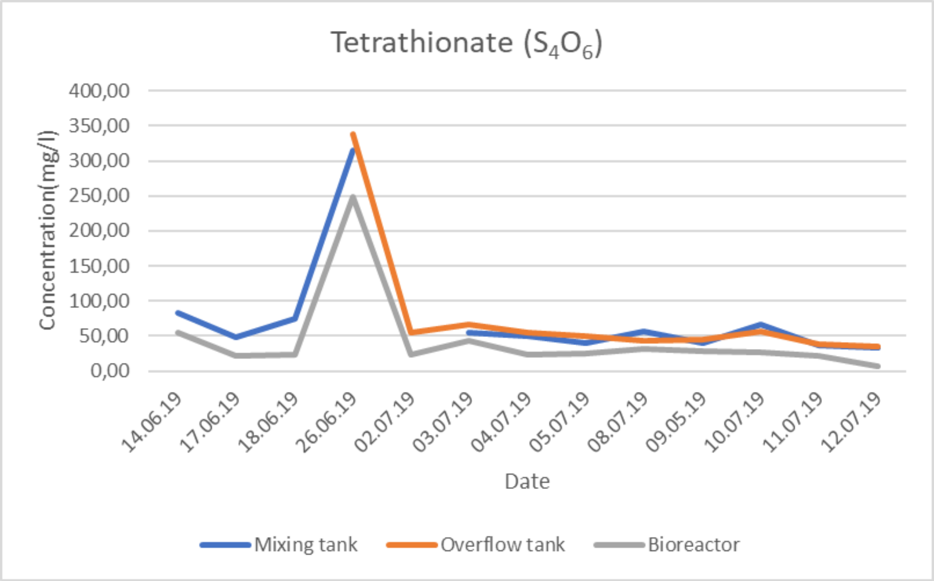


Figure 5-8 Tetrathionate concentrations

5.4.3 Tri-thionate concentrations

The highest concentration of tri-thionate in the mixing tank was 225,00 mg/L, and the lowest was 25,00 mg/L. In the overflow tank the highest was 140,00 mg/L, and the lowest was 0,00 mg/L. In the bioreactor the highest concentration of tetrathionate was 150 mg/L, and the lowest was 10,00 mg/L. (Figure 5-9)

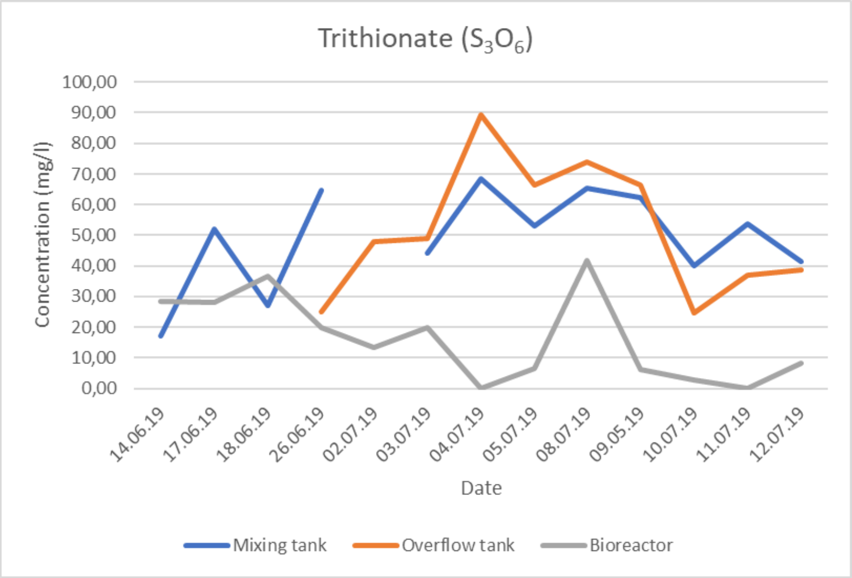


Figure 5-9 Tri-thionate concentrations

5.4.4 Chemical oxygen demand

Chemical oxygen demand or COD is a measurement of the oxygen required to oxidize soluble and particulate organic matter in water. COD was decreasing from the mixing tank towards the bioreactor. That was happening beacause oxidation of thiosalts concumes oxygen. Thiosalts increase COD of water, and after destruction of thiosalts water has lower COD (see figure 5-10).

- The highest concentration of COD in the mixing tank was 285 mg/L, and the lowest was 100,00 mg/L.
- In the overflow tank the highest concentration was 255,00 mg/L, with the lowest of 125 mg/L.
- In the bioreactor the highest concentration of the COD was 220 mg/L, and the lowest was 100,00 mg/L.

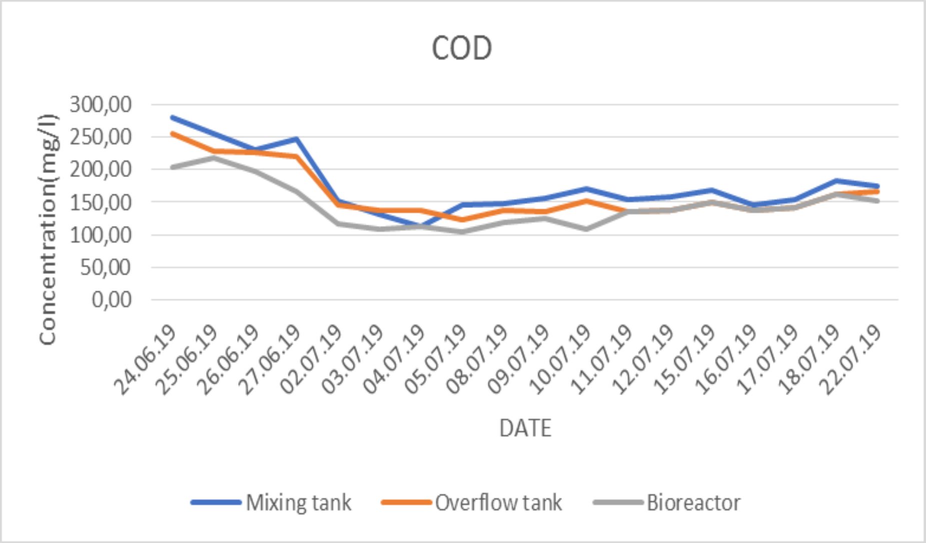


Figure 5-10 Chemical oxygen demand (COD)

5.5 Total nitrogen

Total nitrogen after bioreactor was lower than in the mixing tank (Figure 5-11). This can be related with the successful removal of the nitrate. Increased concentration of ammonium did not affect total nitrogen after bioreactor. It was expected that amount of cyanate and ammonium will correspond to each other. On July 12th nitrogen was not removed from bioreactor, and that's the only point where nitrogen amount was higher than in the mixing tank. The reason for this were too-high oxygen level in the bioreactor on that day.

- In mixing tank the highest concentration of nitrogen in total nitrogen was 39,00 mg/L, and the lowest was 20,0mg/L.
- In the overflow tank the highest concentration was 31,00 mg/L and the lowest was 20,00 mg/L.
- In the bioreactor The highest concentration was 28,00 mg/L. The lowest was 17,00 mg/L.

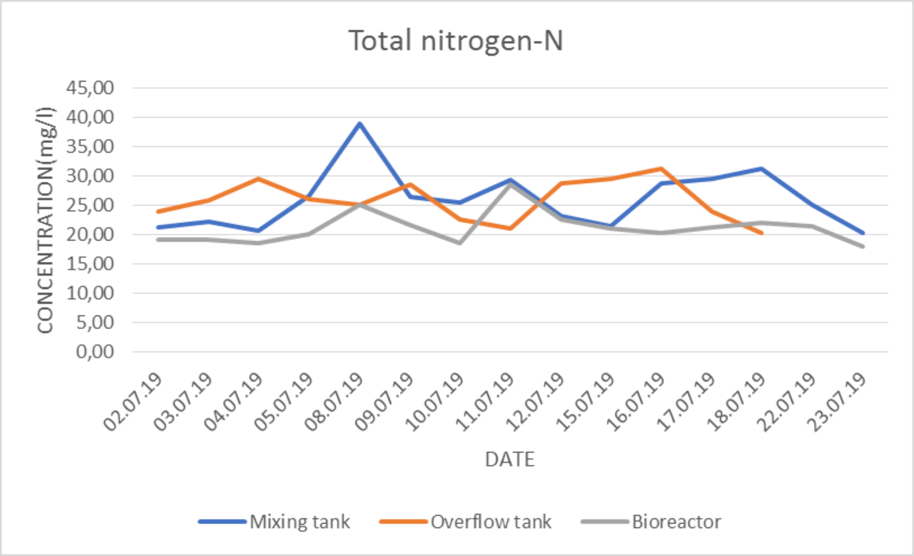


Figure 5-11 Nitrogen in Total nitrogen concentrations

5.6 Cyanate

Cyanate measurement was performed by standardized Boliden method. Concentration in bioreactor was lower compared to the mixing and overflow tank (Figure 5-12).

- The highest concentration of Nitrogen in cyanate, in the mixing tank was 22,00 mg/L and the lowest 17,00 mg/L.
- In the overflow tank the highest concentrations is 16,00 mg/L, and the lowest is 9,70 mg/L.
- In the bioreactor the highest is 7,50 mg/L. The lowest concentrations is 0,20 mg/L.

Measurements of the cyanate have shown significantly lower CNO-N level after the bioreactor. Reason for this can be the ability of cyanate to turn into ammonium at lower pH conditions (pH in bioreactor was lower than in mixing tank). It was not possible to say whether cyanate is turning to ammonium due to lower pH values, reagents in water or bacterial activity.

Total sum of NH_4 and CNO in bioreactor corresponded to total sum in mixing tank. These results suggested that for more effective nitrogen removal aeration or an additional nitrification step may be required.

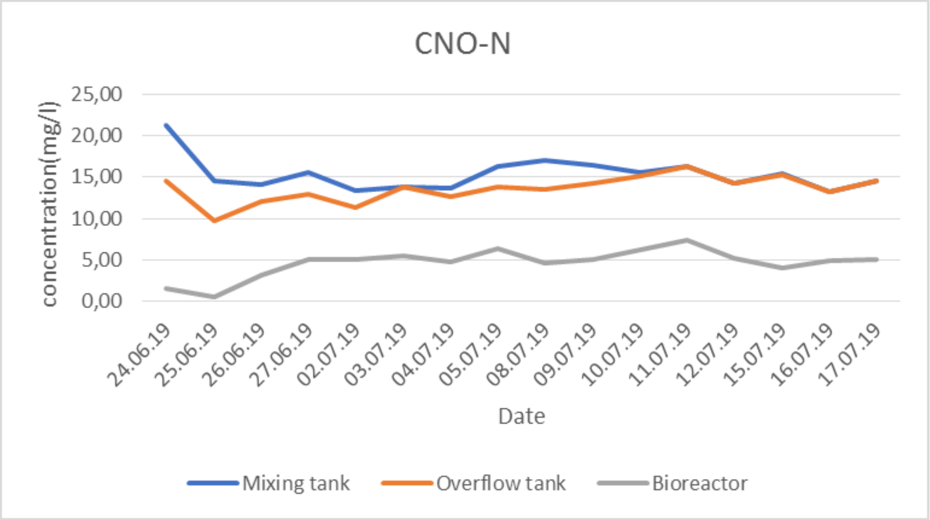


Figure 5-12 Nitrogen in cyanate concentrations

5.7 Sulphate

The source of the sulphate was the sulphuric acid that was used for pH conditioning in mixing tank and the degradation of the thiosulphates. The highest concentration of sulphate in the mixing tank was 1200 mg/L, and the lowest is 550 mg/L. In the overflow tank the highest concentration of sulphate was 1400 mg/L and the lowest is 500 mg/L. In the bioreactor the highest is 1200 mg/L and the lowest was 500 mg/L (Figure 5-13).

It was expected that the concentrations of the sulphate will be the highest in the bioreactor due to thiosalts oxidation, this however happened only occasionally (see Figure 5-13):

- sulphate levels were higher in bioreactor than in mixing tank on June 24th-27th, June 9th - 11th and July 15th-17th
- concentration of sulphate in bioreactor was lower compared than in the mixing tank on July 2nd, 3rd, 5th, 12th (when oxygen level in bioreactor was high), 22nd and 23rd
- concentration of sulphates was the highest in the overflow on July 10th

The reason why the concentrations of the sulphides behaved in unexpected manner could be because of the addition of the sulphuric acid into the mixing tank (higher levels in mixing tank and in overflow than in bioreactor); and/or because of the oxidation of the thiosulphates in the mixing tank due to mixing with air.

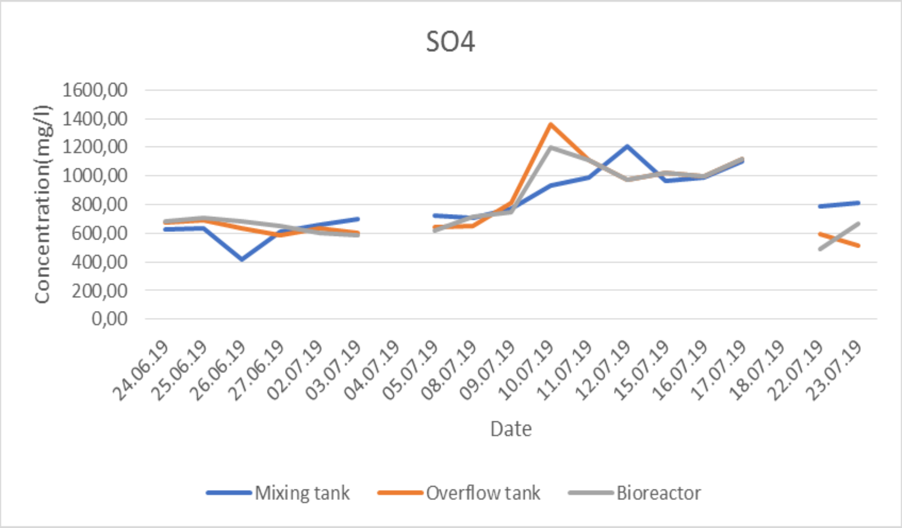


Figure 5-13 Sulphate concentrations

5.8 Phosphate

The phosphates were the highest in the mixing tank, and slightly lower towards the bioreactor implying that no significant consumption occurred (Figure 5-14). The highest concentration of phosphorous in phosphate in the mixing tank was 1,35 mg/L, the lowest was 0,60 mg/L. In the overflow tank the highest concentration was 1,40 mg/L and the lowest was 1,15mg/L. In the bioreactor the highest was 1,60 mg/L and the lowest was 1,00 mg/L.

In the beginning it was expected that bacteria *Thiobacillius denitrificans* will need some phosphate nutrient. The results imply that that bacteria are using other nitrogen based nutrients, if present, rather than phosphate.

On 4th July, the level of phosphate in the mixing tank was the lowest, and towards the bioreactor the level of phosphate increased significantly. At the same time:

- In mixing tank, at lower or the lowest points were levels of oxygen, nitrate, nitrite, thiosulphate, COD, total nitrogen and cyanate, while the level of the tri-thionate was the highest.
- In overflow, the concentrations of dissolved oxygen were low, and the concentrations of the nitrates, tri-thiosulphates, total nitrates and COD were higher than in the mixing tank.

- In bioreactor, the levels of nitrite, ammonium, and thiosulphates were increased or high, and the levels of the dissolved oxygen, nitrates, total nitrogen and tri-thiosulphates were the lowest. COD was the same as in the mixing tank.

The described situation on 4th July can be explained the best with the error of labelling. It is possible that a sample from mixing tank and from the bioreactors switched at some point, either at sampling, at measurement or at result writing. If that was the case, at that point, the level of phosphate would be the highest in the mixing tank and the lowest in the bioreactor. Taking in consideration absence of the nitrogen-based nutrients other than tri-thiosulphates, and favourable low oxygen levels, the bacteria probably ate phosphates and started denitrification, resulting with the denitrification products in overflow tank and bioreactor, and low phosphates. Unfortunately, that day the sulphates were not measured, however, other denitrification products were present as if the denitrification of tri-thiosulphates normally started.

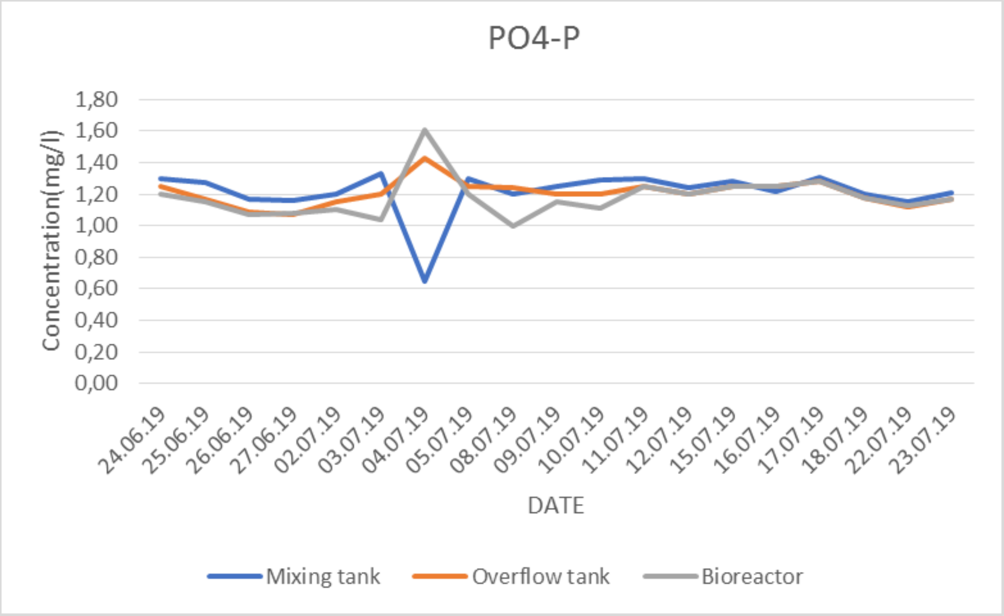


Figure 5-14 Concentrations of phosphates

5.9 Results of the theoretical nitrate and ammonium removal

According to the stoichiometry of autogenous denitrification reactions and thiosalts oxidation theoretical removal rate of nitrate by thiosalts was calculated. From these equations and from chemical ratios, following table (see Table 5-1) is showing total nitrogen reduction based on oxygen, thiosulphate, tetrathionate and dextrin concentrations. In this table it can be seen how much thiosulphate and tetrathionate can be reduced with oxygen and how much is left for nitrogen reduction. For example, theoretical nitrate reduction, based on levels of oxygen, nitrogen compounds and thiosalts, on July 11th was 23,89 mg/l and theoretical ammonium reduction was 2,56 mg/l. It can be seen in table that 9,68 mg/l of nitrogen in nitrate was removed from process. Under these theoretical conditions, in perfect case, process can remove 23,89 mg/l of nitrogen in nitrate. Therefore, 14,21 mg/l of nitrogen in nitrate (if there is this amount available) extra can be removed from the process based on these conditions. The measurements on July 26th have shown 6,33 mg/l of nitrate in overflow and the 0,67 mg/l in bioreactor. This actual removal was lower than theoretical concentration calculated because measured nitrate concentrations (nitrogen in nitrate in feed water= 11 mg/l) were lower than maximum theoretical (23,89 mg/l).

Table 5-1 Theoretical nitrogen removal based on thiosalts and dextrin for the best removal with complete measurements

Date	July 11th 2019
Measured	
Nitrate in feed water (mixing tank)	11
Nitrate in overflow	10,4
Nitrate in bioreactor	1,32
Total nitrogen in bioreactor	28,5
Nitrate reduction	9,68
O_2 concentration in feed water (mg/l)	7,2
$S_2O_3^{2-}$ concentration in feed water	92,5
$S_4O_6^{2-}$ concentration in feed water	37,1
Assume dextrin-equivalents in the feed water	27,3
$S_2O_3^{2-}$ reduction from O_2 in feed water	12,6
Calculated	
$S_2O_3^{2-}$, left for denitrification	79,8
NO_3-N reduction capacity, $S_2O_3^{2-}$	11,9
NO_3-N reduction capacity, $S_4O_6^{2-}$	4,8
NO_3-N reduction capacity, dextrin	7,21
Total theoretical NO_3-N reduction capacity	23,89
Total theoretical NH_4-N reduction capacity	2,56
Total theoretical N-reduction capacity	26,45

6 CONCLUSION

The testing of the assembled pilot plant has shown that simultaneous removal was achieved, however, with some room for the improvement. Total nitrogen, nitrates, COD, tri-thionate and tetra-thionate were successfully removed. The best removal of nitrate was achieved on June 26th (from 16,00 mg/L to 0,8 mg/L). The nitrite and thiosulphate were removed but not sufficiently.

The unexpected issues at operation and testing were:

- the oxygen addition was difficult to control, better suited equipment is required,
- the adjustment of the pH in mixing tank was difficult to control,
- in feed water presence of the cyanate was detected,
- presence of the ammonium in thickener overflow and bioreactor was detected, probably by the degradation of cyanate with change in pH from alkaline to neutral or bacterial activities,
- concentration of sulphate ion in outflow of the bioreactor were lower than expected and this requires better understanding.

Based on the observations and testing of the pilot plan the further improvement can be considered:

- improvement of the system for regulation of oxygen pressure,
- use of the automated pH controller for better adjustment and control of the pH,
- in-line analyses of the most relevant parameters in inflow and outflow of the plant for early detection of (undesired) changes in the process,
- in evaluation of the results it should be considered the residence time between inflow and outflow,
- development of the bioreactor with bacteria for degradation of the ammonium ion into nitrate ion.

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