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**Studies on the reactivity activation of zero-valent iron (ZVI) with
hydrogen peroxide for nitrate reduction in mine water**

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FOREWORDS

This Master Thesis was conducted as a part of the iMineWa project of Green Chemistry Laboratory in Mikkeli, from Lappeenranta University of Technology during the end of the year 2015.

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ABSTRACT

Lappeenranta University of Technology
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Studies on the reactivity activation of zero-valent iron (ZVI) with hydrogen peroxide for nitrate reduction in mine water

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The emission of mining wastewater with high concentration of nitrate leads to the risk of the aquatic ecosystem, being detrimental to human health and excess nutrients of water bodies. The aim of this thesis work was to improve the reactivity of zero-valent iron (ZVI) on the reduction of nitrate to ammonium in mine water. The selected method for the reactivity improvement of ZVI surface was a ZVI/ H₂O₂ system. Preliminary tests were performed to demonstrate the feasibility of ZVI/ H₂O₂ system. The effect of pH value, iron mass and hydrogen peroxide concentration on nitrate reduction were evaluated by batch experiments. The effect of adding iron oxide waste with ZVI was tested as well. The result of this thesis indicated that nitrate reduction rate achieved 99.5% with the experimental setups in optimized conditions. Thus, it was possible to increase the nitrate reduction rate at near neutral pH conditions by adding a strong oxidant, H₂O₂.

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LIST OF ABBREVIATIONS

AMD	Acid mine drainage
ANFO	Ammonium Nitrate Fuel Oil
ZVI	Zero-valent iron
IX	Ion exchange
RO	Reverse osmosis
ED	Electrodialysis
TFC	Thin film composite
EDR	Electrodialysis reversal
TiO ₂	Titanium Dioxide
UV	Ultraviolet
3D	Three-Dimensional
REDOX	Oxidation-Reduction Reaction
ORP	Oxidation reduction potential

1. INTRODUCTION

The content of this chapter is to describe the motivation and objectives of this master thesis by giving an overview about the nitrate problems and possible treatment techniques. Furthermore, the thesis outline is also presented below.

1.1. Motivation and objectives of the thesis

The mining industry has an enormous influence on global economy. Various mining products play important roles in most industrial societies for human development in everyday life, for example electronics, machinery, construction materials and many others (BRGM 2001). With abundant natural mineral resources, the European mining industry has a long standing history, particularly in Finland (GTK 2013). The Siilinjärvi mine of Finland have the biggest apatite production for manufacturing fertilizers. However, the mining wastewater from the production line of nitric phosphate fertilizer still contains a large amount of nitrate and phosphate, which is considered to cause many troubles to environment.

The presence of nitrate in surface water and groundwater around mining areas leads to the risk of ecosystems, which results in the excess nutrients of water bodies (eutrophization) (Katri et al. 2007). As a result of eutrophication, the water body creates a dead zone, where living organisms cannot survive any more. The presence of nitrate in waters have impact in human health by causing diseases, such as “methemoglobinemia” - “blue baby syndrome” in newborn children, liver damages and there is a high risk of bladder and ovary cancers (Samarghandi et al. 2013).

Due to the risks of nitrate, several treatment techniques were investigated in order to remove nitrate from water. These include ion exchange (IX), reverse osmosis (RO), biological denitrification, electrodialysis (ED), electrodialysis reversal (EDR), photocatalytic reduction, adsorption and chemical denitrification (Jensen et al.2012). While the group of physicochemical technologies can remove nitrate with high efficiency, however the generation of concentrated nitrate require further treatment

and residual disposal. Biological denitrification processes are slower when compared with the physicochemical ones and require huge infrastructure and manufacturing. The technique of adsorption with natural materials is a simple design, whereas some adsorbents are costly.

Chemical reduction method by ZVI/H₂O₂ system was selected in this thesis for nitrate reduction in mine water from a phosphate mine managed by Yara Oy. The main objective of this thesis work is to study the reactivity activation of ZVI with the addition of hydrogen peroxide (H₂O₂) and the optimization of pH, ZVI load and H₂O₂ concentration in nitrate reduction reaction as well as the influence of the addition of iron oxide waste as a possible iron source.

1.2. Thesis outline

This thesis work consists of nine chapters described as following:

Chapter 1 presents the motivation, objectives and outline of this study. In the literature section, the following chapter 2 gives the general overview of mines and mining wastewater characteristics regarding European and Finnish mining industry (Siilinjärvi mine). Chapter 3 discusses the nitrogen cycle and the problematic of nitrate in the water. Moreover, six developed treatment technologies to remove nitrate from wastewater are indicated in Chapter 4. For example, the photocatalytic reduction by UV-light and titanium dioxide recognized as photocatalyst and adsorption with bioresources like agricultural waste, for example, were presented. Chapter 5 analyzes the mechanism of chemical denitrification process, especially the redox reaction of ZVI with H₂O₂.

In the experimental section, Chapter 6 describes the materials and methods used, including the experimental setup, laboratory procedures and analytical techniques. In Chapter 7, the results and discussion is reported, being divided in three sections:

preliminary tests; the optimization of ZVI reactivity activation with H_2O_2 , which consists on the studies of the effect of pH, effect of ZVI dosage and effect of H_2O_2 concentration in nitrate reduction; On the last section, the iron/ H_2O_2 system is tested with iron oxide waste and ZVI, alone and combined for comparison purposes. Furthermore, the conclusions of the thesis are shown in Chapter 8. Ultimately, Chapter 9 presents the possible subjects for further research studies.

LITERATURE PART

2. GENERAL OVERVIEW OF MINES AND MINING WASTEWATER CHARACTERISTICS

Mining activities includes the extraction of mineral substances and some nonrenewable resources like natural gas and petroleum from the earth. Besides metals, coal, gravel, gemstones, limestone and clay are extracted from ores. The mining industry has a powerful influence on global economy (BRGM, 2001). Different mining products play important roles in most industrial societies for human development in everyday life, such as electronics, machinery and construction materials for buildings and roads.

2.1. European mining industry

With abundant natural mineral resources, the European mining industry has a long standing history. The extraction and supply of minerals play a key role in the European economy and society during thousands of years. In spite of European mining has decreased over the last 150 years, the consumption of mining products for industry has still increased rapidly in recent years. Relying on a great deal of raw materials the European manufacturing industries ultimately evolve into the hundreds of thousands of products and enterprises. Nowadays, the most of mining projects are usually related to the extraction of mineral deposits for instance nickel, copper, zinc, cobalt, lead, gold, silver and platinum (GTK, 2012).

Comparing with the other continents, Europe is not a main producer for metals. Basic mineral deposits are located in Ireland, Sweden, Finland, France, Serbia, Romania, Slovakia, Spain and Portugal. Coal is mainly produced in Poland and Germany. Some ore deposits are so rich that deserve the exploration of international mining companies. For example, one large mineral deposit of iron, copper and nickel is situated in Finland and Sweden in the Baltic Sea region (Vos et al.,2005). Between the boundary of Czech Republic and Germany there is another major polymetallic ore deposit

named “Erzgebirge”, with a variety of silver, sulphides, pitchblende and others. The lower carboniferous carbonate rocks of Ireland have plenty of limestone, sphalerite, galena and dolomite, producing lots of zinc and lead. The Iberian pyrite belt which belongs to the south Portuguese zone hosts a great amount of sulphides, copper, lead, zinc silver and gold. The main mineral deposits in Europe are shown in Figure 1.

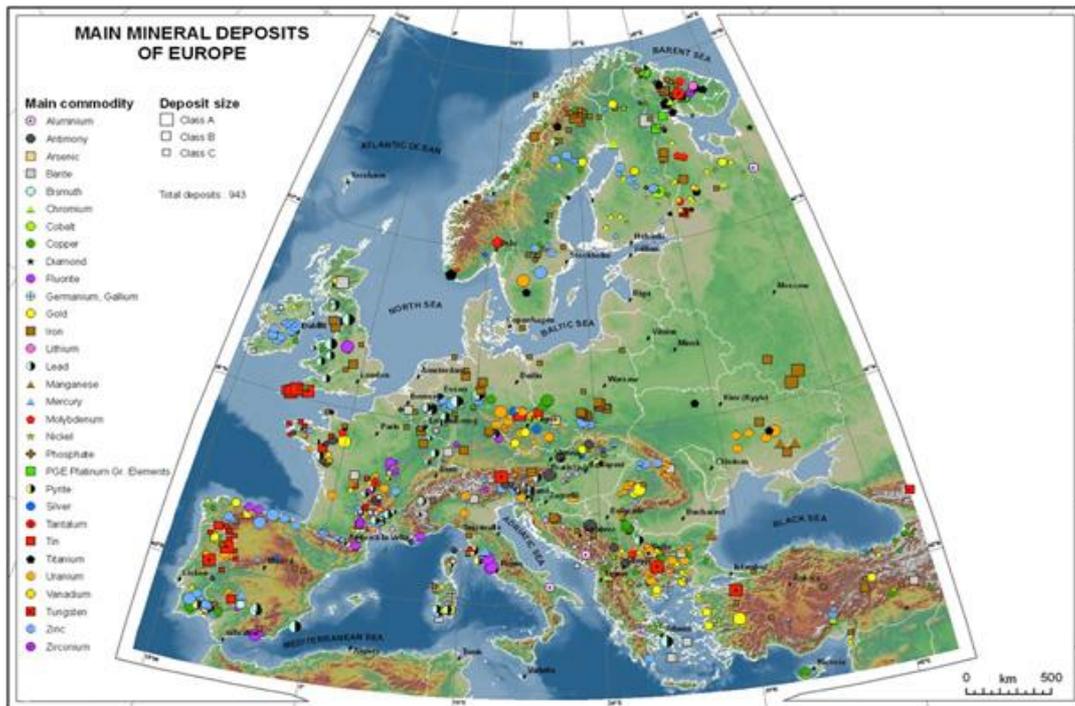


Figure 1. Main mineral deposits of Europe (Euromines,2008).

2.2. Finnish mining industry

With a long tradition, Finnish mining history can trace back to 500 years ago when iron ore mining started. The metallurgical technologies of Finland are well known through all around the world. New technology like the flash smelting method for refining of copper concentrates were invented and turned into the world’s leading one (GTK, 2013). There are several world class rich mines in Finland such as nickel ores in Pechenga, copper ores in Outokumpu, nickel in Kola Peninsula which belongs to Norilsk Nickel, zinc at Kokkola, chromium at Kemi and iron at Raahe (Finnish mining. 2012). The mineral deposits in Lapland are very rich holding reserves of a

number of massive uranium, rare earth minerals, gold, nickel, phosphorus and platinum metals. The primary industrial minerals exploited in Finland are limestone, talc, apatite and carbonates (National report). Finland produce the largest amount of talc in Europe which is one of the most important material in paper industry as pigment. The largest apatite production for manufacturing fertilizer is the Siilinjärvi mine. Figure 2 represents the location of the metal ores in Finland.

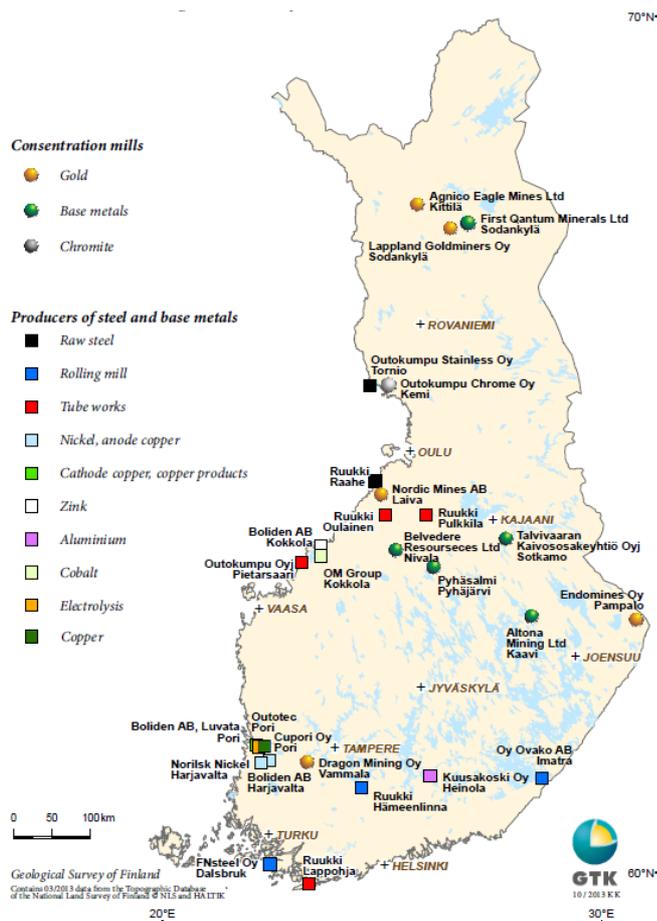


Figure 2. Metal concentration mills and producers of steel and base metals (GTK2012).

2.3. Siilinjärvi mine

Siilinjärvi carbonatite, shown in Figure 3, is one of the worldwide oldest carbonatite deposits *in situ* with 4.2% of phosphorus pentoxide (P_2O_5) whose age is over 2600 million years. The area of apatite rocks is 14.5 km long, width up to 650 m and depth

is over 800 m from surface (YARA,. The Siilinjärvi deposit started to operate in 1979. Currently the mine is owned by Yara, which is a global supplier of mineral fertilizers and industrial chemicals. The factory has three production units: a phosphate mine, sulphuric acid, phosphoric acid and nitric acid plant and a fertilizer plant. Two open pit operations (Särkijärvi and Saarinen) are performed in order to produce fertilizers, phosphoric acids and apatite concentrate. Regarding the tailings management the pond zone keeps more than 5 km away from concentrator. After the purification process the mine water with no harmful substances is circulated back to the concentrator. However, the mine water from the production line of nitric phosphate fertilizer still contains a large amount of nitrate and phosphate.



Figure 3. Yara – Siilinjärvi open pit mine

2.4. Mine water

Mine water is considered to be one of the most serious issues in water treatment. The water is generated from mining processes and are usually acidic and highly polluted by various toxic metals, which affect the quality of surface water and ground water (Banks et al., 1997). Acid mine drainage (AMD) is a threat to the environment usually generated by rainfall and snow melt on abandoned mines, tailings, heap leach piles

and waste rocks. As a result, ground minerals are oxidized and the contained compounds are dissolved into the water. Without control, AMD may leach into groundwater (MINEO Consortium, 2000). Because of the hydrological cycle system, the produced contaminant of surface water may also directly flow down to ground water. Separated by different production operations, there is another type of mining waters – effluents (Wang et al., 2014). Effluents are the waste streams, which are produced during the refining operation process. With a large number of very fine solids and dissolved compounds, the effluents are injected into tailing ponds. The slurry contain plenty of salts and metals which are abstracted by natural minerals and waste rock. However, there are lots of various toxic chemicals like cyanide in effluents that are used for extraction operations (Azapagic, 2004). A mining operation sketch is shown in Figure 4.

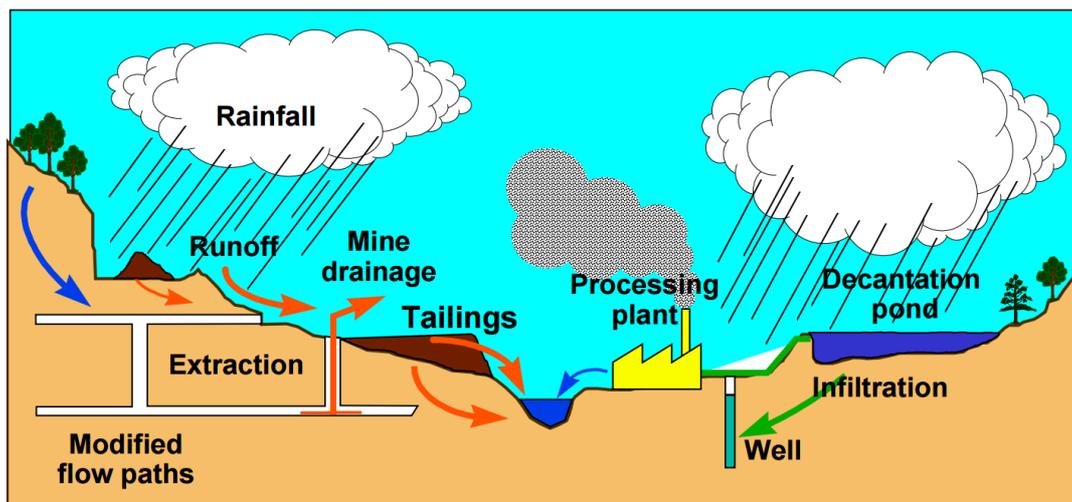


Figure 4. General sketch model of surface and groundwater contamination by mining operations (MINEO Consortium., 2000)

To monitor water management in the mining industry, some procedures have to be controlled: decrease the requirement of water volume during the whole process, purify the polluted water and leachates, prevent the contamination of groundwater and surface water (Charbonnier et al., 2001). If the water is contaminated by toxic mining water, people who are exposed to it would get health issues, like skin rashes or diarrhea, among others. Even fishes and other living organisms would be ultimately killed in the river.

3. THE PROBLEMATIC OF NITRATE IN THE ENVIRONMENT

3.1. The nitrogen cycle

Nitrogen is one of the crucial nutrients for the survival of life (Patil et al. 2013). The Earth atmosphere has abundant nitrate resources, in addition to dinitrogen gas (N_2), nitrogen occur in many various forms, such as nitrate (NO_3^-), ammonium (NH_4^+) and ammonia (NH_3) and the conversion from one form to another under different processes (Anne et al., 2010).

Nitrogen undergo through many complex chemical, biological and physical changes among the atmosphere and the land in a continuous cycle (Carbin et al., 2009). This kind of biogeochemical cycle is known as the nitrogen cycle. The primary transformations participate in the nitrogen cycle including fixation, ammonification, nitrification and denitrification, and it can be represented schematically as the image in Figure 5.

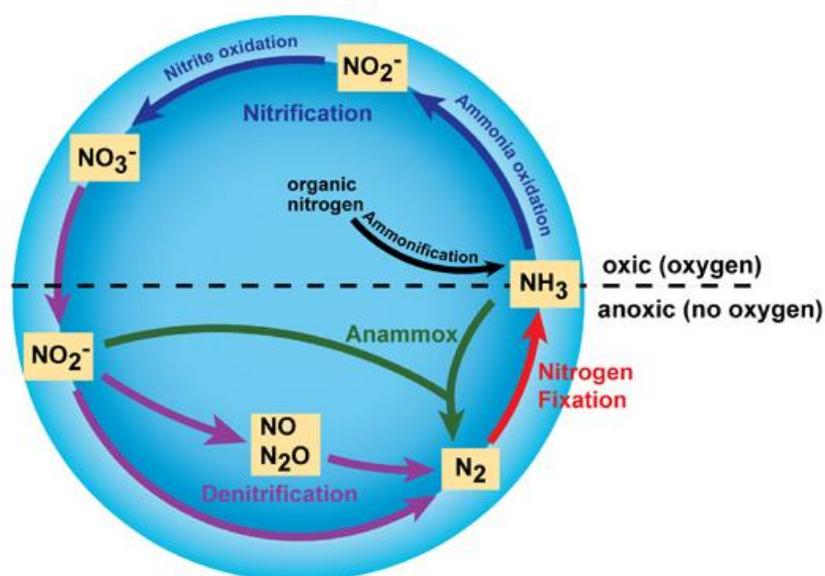


Figure 5. Major transformations in the nitrogen cycle (Anne et al., 2010)

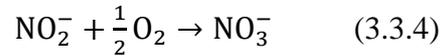
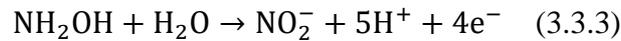
Nitrogen cannot be absorbed as a nutrient for most living organisms in gaseous state

(N₂), but only when it is converted into biological available nitrogen. Nitrogen fixation is the process to convert N₂ into NH₃ by nitrifying bacteria, as it can be seen in equation 3.3.1.



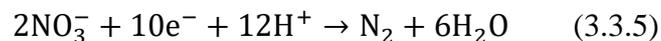
When an organism dies, bacteria and fungi will decompose it and convert N₂ into NH₃ in the ecosystem. This decaying process is called ammonification and the NH₃ becomes available for plants in the nitrogen cycle.

Ammonia (NH₃) is then transformed into NO₃⁻ by aerobic bacteria during the nitrification process, which is accomplished in two distinct steps as following equations 3.3.2, 3.3.3 and 3.3.4:



The first step in nitrification is when Nitrosomonas bacteria oxidize NH₃ to NO₂⁻ via intermediate hydroxylamine, by microorganisms called ammonia-oxidizers (Anne et al., 2010). The second step is carried out by Nitrobacter, as nitrite-oxidizing bacteria, which oxidize (NO₂⁻) to NO₃⁻.

Denitrification is an anaerobic process that reduces nitrate NO₃⁻ to N₂, and it is represented in equation 3.3.5. The process is performed by various species of anaerobic bacteria, such as Bacillus, Paracoccus and Pseudomonas.



3.2. The problem of nitrate

As a crucial water pollutant, nitrate becomes a common environmental problem of the world (Katri et al., 2007). Nitrate is part of the natural composition of plants and is required for planting vegetables as fertilizer, but excessive use of fertilizers will be harmful to water resources (Patil et al., 2013). The largest sources of nitrate pollution are digestion tanks from animal wastes, organic and chemical fertilizers in agricultural activities. Farmers usually keep manure in large storage underground, which easily leads to excessive nitrates leaching (Lee et al. 2010). Excess of nitrogen-based fertilizers are used by farmers to improve the cultivation of plants, causing groundwater contaminated with nitrate. All these sources increase the concentration of nitrogen compounds in water in the most industrialized countries. For example, the concentration of nitrate in 1000 lakes got twice higher over than 10 years ago in Norway. In many parts of Europe, river nitrate concentrations have raised 15 times in the past hundred years (Global Nitrogen., 2004).

As it was referred previously, nitrate contamination is harmful to water ecosystems leading to eutrophication. Nitrate, as a sustainable source of nutrients, helps algae bloom growing rapidly in coastal zone. When the algae die, they consume the oxygen present in the water, causing a dead zone, where living organisms cannot survive. There are several hypoxia areas all around the world, for example, the Baltic Sea, the Yellow Sea and the Gulf of Thailand, but the Gulf of Mexico is the most famous one, which is loaded by the nitrate-rich Mississippi River owning the size from 3,000 to 8,000 square miles (Global Nitrogen., 2004).

Another concern of nitrate contamination is about health risk of human. Actually nitrate does not directly harm humans, only when it is reduced to nitrite in human gastrointestinal on the oxygen-free condition. Nitrite pass through the intestines into the bloodstream, then combines with hemoglobin molecules and converts hemoglobin to other form which cannot carry oxygen. If high concentrations of nitrate is completely reduced to nitrite, nitrate ions would weaken the capacity of blood to

transport oxygen that will result in a disease called as methemoglobinemia as well as “blue baby syndrome” in newborn children, even damage to liver and increase risks for cancer (Samarghandi et al., 2013). A study conducted by the epidemiological researcher also showed the high concentration of nitrate in drinking water increases the risk for bladder and ovary cancers.

3.3. Nitrate in mine water

The presence of nitrate in surface water and groundwater around mining areas affects the environment, leading to the risk of eutrophication (Katri et al., 2007). One source of nitrate in mine water is generated from blasting agents, like Ammonium Nitrate Fuel Oil (ANFO) explosives which contain a mix of ammonium nitrate and fuel oil. The explosion reaction of (ANFO) is shown below in equation 3.1.1 (Morin et al., 2009).



After the explosion, some residual chemicals like ammonium nitrate (NH_4NO_3) still remain on extracted waste rock and are flushed into water bodies by rainfall (Katri et al., 2008). Other nitrogen sources in the mine water are flotation chemicals, regulating agents for pH control, ammonium hydroxide and ammonium sulphate used in uranium precipitation as well as nitric acid for producing fertilizers from phosphate rock (Jack et al., 1992). The effluents from cyanide destruction in leaching process, which produces ammonia, also contribute to the increase of nitrogenous compounds in mine water. The equation of cyanide destruction reaction, equation 3.1.3, describes the cyanates (CNO^-) oxidized to ammonia and bicarbonates (Akcil et al., 2002).



4. TREATMENT TECHNOLOGIES FOR NITRATE REMOVAL

Since nitrate has high chemical stability and highly solubility, it is hard to remove from water by conventional treatment processes like coagulation, filtration and precipitation (Westerhoff et al., 2009). Other modern treatment technologies have been developed by scientists. These technologies can be classified into physicochemical, biological and catalytic methods (Jensen et al., 2012). The group of physicochemical treatment methods include ion exchange (IX), reverse osmosis (RO), electro dialysis (ED), adsorption and chemical denitrification. This kind of physicochemical treatment can remove nitrate with high efficiency, however they only generate concentrated nitrate and require further treatment and residual disposal. Biological treatment is approved as a useful biological denitrification process, which is the conversion of NO_3^- or NO_2^- into harmless gaseous N_2 by anaerobic bacteria. Nevertheless, there are several concerns: process conduct very slowly, produce undesirable bacterial contamination, require huge infrastructure and manufacturing. All of these treatment technologies have their own advantages and disadvantages, a hybrid process combining various technologies makes them work more efficiently.

4.1. Ion exchange

Ion exchange is the most widely employed treatment technology for nitrate removal, owing to its cost-effective and maneuverable characteristics. Ion exchange is a reversible exchange process of ions from ion exchanger in an electrolyte solution, which is usually applied to remove contaminants or hardness (Kabay et al., 2007). The direction of the exchange process is determined by two factors: the concentration of the ions in the solution, the selective attraction of the resin for the particular ions. Ion exchange resin is an insoluble matrix (bread-like materials), commonly fabricated from cross-linked polymers that remove ions from water for water softening and water purification processes (Westerhoff et al., 2009).

Anion exchange resin with a preferential affinity for nitrate is usually used for nitrate removal on which nitrate replaced chloride ions and sulfate ions in the solution (Jensen et al., 2012). However this kind of resins do have shortage, instead of nitrate most of them prefer to absorb sulfate, which reduces the efficiency of ion exchange process. Hence, the concentration and exchange capacity of sulfate and nitrate in the solution must be considered. After dealing with many liters of solution, it will led to the saturation of chloride in resin. In order to replace nitrate from the resin, the regeneration of the resin is needed. It can be carried out by a highly concentrated salt solution, like sodium chloride or sodium bicarbonate. Salts and organics in waste brine solution will foul the nitrate IX resins when the system operate for a long time. For the sake of keeping high-efficiency nitrate removal capacity, that requires disposal of waste brine. Figure 6 describes the process of ion exchange unit for nitrate removal.

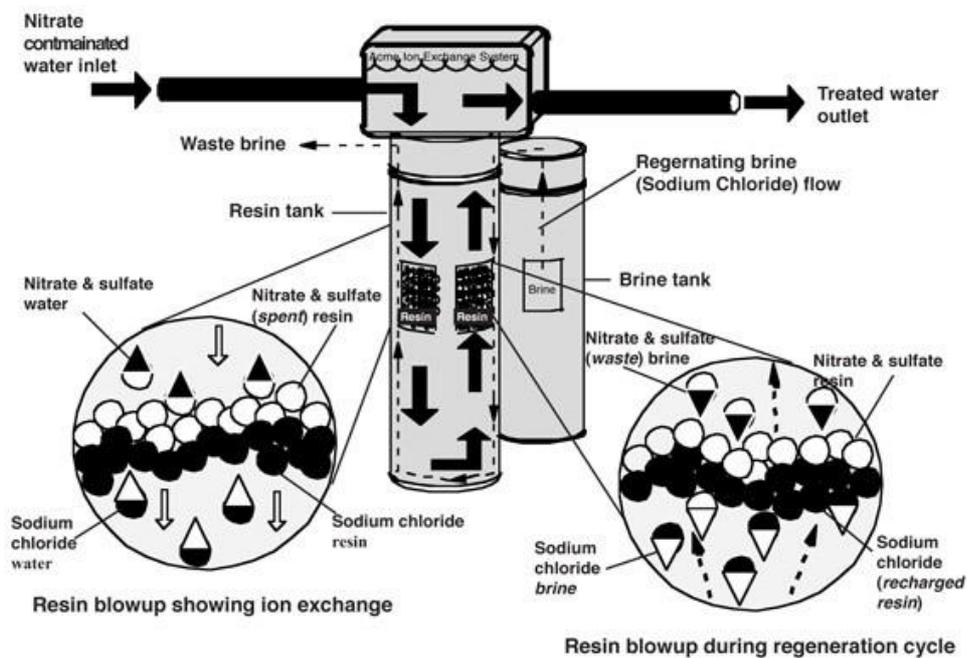


Figure 6. Ion exchange unit for nitrate removal (Swistock et al., 2016)

4.2. Reverse osmosis

As the second most commonly used nitrate treatment technology, reverse osmosis is a membrane separation process which is driven by osmotic pressure (Jensen et al., 2012). Its applications involve the removal of other ions, molecules and large particles

from water, including inorganic contaminants, microorganisms and organic matter (Symons et al, 2001). The reverse osmosis process works under pressure where nitrates or other target substances are retained on the pressurized side of the membrane and forcing pure water passes through a semipermeable membrane to the other side (Darbi et al, 2003). The RO process occurred owing to the pressure differential between two sides of the membrane (MWH, 2005). The thin film composite (TFC) membrane made from cellulose is commonly used for nitrate removal in RO units. Using thin film composite membranes can achieve the result that the concentration of nitrate reduction by 60% to 95%. While the nitrate level is higher than 30 mg/L, reverse osmosis technology will turn into low efficiency. Then, it is better to choose other treatment technology (Bebbee et al., 2006). In addition to concentration, other factors of RO should be taken into account, for instance, the pretreatment of water, materials of membrane, water temperature, osmosis pressure and the disposal of waste concentrate. The drawbacks of RO are its high cost and high energy consumption for unit operation (Bergman et al., 2007). The schematic RO process is shown in Figure 7.

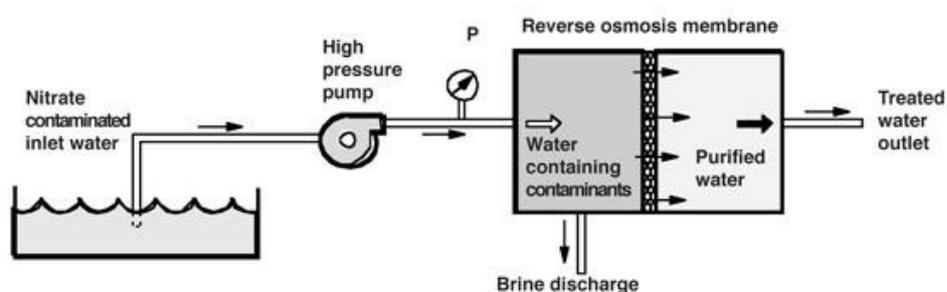


Figure 7. Scheme of the reverse osmosis process (Bryan et al., 2016)

4.3. Biological denitrification

In comparison with ion exchange and reverse osmosis method, biological denitrification treatment method is the most effective for nitrate removal, since it is economical with lower operating costs and does not change the content of other existing ions (Samatya et al., 2006).

In biological denitrification process, nitrate is microbially reduced to different nitrogen intermediates and ultimately to gaseous nitrogen, which steps can be generalized as below: $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$ (Soares, 2000). Each step of denitrification are associated with enzymes as catalyzer. The nitrate reduction process can be performed by two different kinds of electron donors: organic carbon electro donors like acetic acid or methanol; inorganic electron donors like reduced sulfur or hydrogen (Westerhoff et al., 2009). As a natural biological process, heterotrophic or autotrophic bacteria can be used to drive denitrification process as electron acceptor for reducing nitrates and release nitrogen gas (Shrimali et al., 2001). Moreover, as a respiratory process, energy sources such as an oxidisable substrate must be required in denitrification. An organic compound is the source of energy and carbon in heterotrophic denitrification, whereas an inorganic compound is the source of energy and carbon in an autotrophic denitrification (Haugen et al., 2002). Autotrophic bacteria grow slowly resulting in low efficiency of denitrification, so that heterotrophic process is more popular for applications. As an electron acceptor, oxygen has an inhibitory effect on denitrification competed with nitrate. Hence, the concentration of dissolved oxygen in the water should be lower than 0.1 mg/L for guarantee the reduction process occurs normally (Archna et al., 2012). In some particular cases, the biological denitrification processes arise under aerobic conditions (Rittman et al., 2001).

There are some limitations of this process. The residual contaminations presented in denitrified water, such as bacteria, residual carbon organics, is necessary to be removed (Haugen et al., 2002). The post treatment like filtration and clarification is helpful for that. The other key factor is temperature restrictions, low temperature can decrease denitrification (Archna et al., 2012). Low production rates of nitrate for biological treatment processes should be considered as well.

4.4. Electrodialysis and Electrodialysis Reversal

The application of electrodialysis (ED) technology in water treatment for nitrate removal became more popular recently. It provides the minimum requirement of

chemical and energy, the good selectivity to remove nitrate ions, high water recovery and a small quantity of residual (Archna et al., 2012). Electrodialysis is performed by passing a direct electric current through ion selective membranes where nitrate and other ions are transferred from a low concentrated solution (dilute) to a high concentrated solution (permeate, concentrate). The solution with high concentration of nitrate or other undesirable ions is considered to be a waste stream (Kabay et al. 2007).

ED treated the water in the multiples cell units, which consists of an anion exchange membrane and a cation exchange membrane located between two electrodes (Ted et al., 2005). The dilute feed solution should be pressurized into units. Then, influenced by an electric field, the solution is in an electrodialysis system, where the charge carriers change into motion. As the electrical potential difference, the negatively charged ions in the low concentrated solution move towards the positively charged anode passing through anion exchange membrane and the positively charged cations towards the negatively charged cathode passing through cation exchange membrane (Jingjing et al., 2011).

To separate nitrate or other ions from solution, the particular semi permeability membrane should be selected for the permeation of targeted ion. The charge balance must be maintained in the whole electrodialysis system as well, in order to keep the migration of anion and cation, where the electric current flows between them. The ED process results in a salt concentration increase in the concentrate stream with a depletion of charge carriers in the dilute stream (Kakay et al., 2007).

The whole ED system is shown at Figure 8. Different from other membrane based processes like RO, electrodialysis method has less quantity of dissolved species in the feed solution than of the fluid as well as the strength of higher feed recovery. Rather than in other membrane based processes, dissolved species are removed from the feed solution. The nitrate removal capacity of ED and RO process is nearly the same.

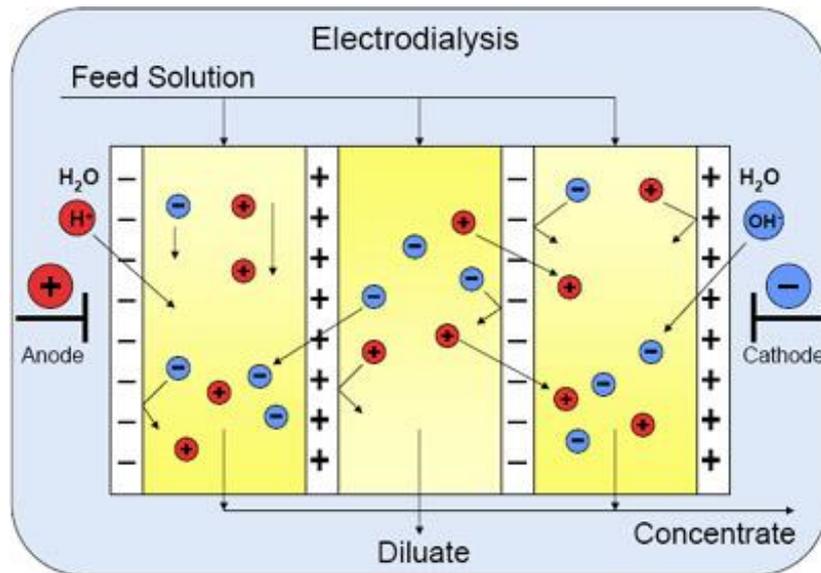


Figure 8. Electrodialysis (ED) for denitrification.

In order to minimize membrane fouling, the electrodesalination reversal (EDR) process is required, in which the polarity of the electrodes can be reversed several times per hour to convert the direction of ion movement. By means of reversing the solution flow direction, ions move in the opposite direction through the membranes, reaching the minimum heap (Ted et al., 2005). In comparison to conventional ED process, the electrodesalination process can decrease the formation of scale and the usage of chemicals, applied for nitrate rich water in drinking water treatment. The EDR process has high-efficiency for nitrate reduction when the nitrate concentration is in the range of 50 mg/L to 25 mg/L. There are some critical factors to be considered into EDR application, such as the pretreatment requirements, the system operation and the waste concentrate management.

4.5. Photocatalytic reduction

Photolysis disinfection and other light-based technologies are commonly used for water treatment in nowadays. Among them, photocatalytic reduction is gradually developed to split water for nitrate removal from water. The preliminary data demonstrate that photocatalytic nitrate reduction processes generate innocuous

nitrogen gas (N_2) as by-products and there is no need for extra treatment. Many scientists have studied that nitrate can be activated with light in the aqueous solution by a metal-loaded photocatalyst with a reducing agent as co-catalyst (Nubia et al., 2010). This method utilizes the properties of specific materials to absorb electromagnetic radiations and stimulate active sites, then to decline via charge transfer and light emission phenomena (Krisana et al., 2014). The photocatalytic reduction process is induced by “electronic holes” where free electrons exit by means of light-induced charge separation. Oxidation reactions subsequently occur to compensate for the formed electronic gap.

In general, the photocatalytic reduction of nitrates to nitrogen works in aqueous conditions. The process needs the addition of organic compounds, as active sites, which are hole scavengers that supply electrons to fill the electron holes in the valence band. Methanol, ethanol, formic acid, oxalic acid and sucrose all can be used as electron hole scavenger (Kobwittayaa et al., 2014). A number of research studies reported that formic acid is the best chemical agent for nitrate reduction over titanium dioxide (TiO_2). When formic acid is added, it brings out the formation of carbon dioxide (CO_2) and hydrogen as well as the reduction reaction. Moreover, the different pH conditions of formic acid lead to entirely different results. At acidic pH ($pH \approx 2.5$), the result achieves 98% conversion of nitrates to molecular nitrogen formation; in strong acidic conditions, the result brings the formation of nitrites and ammonium ions.

The reduction process could be achieved by using different kinds of photocatalysts (inorganic semiconductors), while TiO_2 and TiO_2 modified with iron, silver or copper as reducing agent are the best known choices (Krisana et al., 2014). Usually, TiO_2 photocatalyst is prepared by the simplified sol-gel technique where it is coated to form a thin film on the surface of materials, which are usually stainless steel sheets. The choice of using stainless steel sheets is due to the excellent corrosion resistance as well as good strength-deformation characteristics. (Nubia et al., 2010).

The photocatalytic reduction process for nitrate removal in water uses ultraviolet light (UV-light) as photo energy that brings out high energy consumption and it is very

costly for large scale industrial wastewater treatment. In Figure 9 is shown the schematic UV/TiO₂ photocatalytic reduction reactor. Several variables were discovered to affect the activity of process, for instance, total catalyst surface area, pH value and recombination rate (Ferro et al., 2003). Furthermore, the demand of additional processes act as the main shortage of the photocatalytic reduction, which is separation and recovery of the photocatalysts from the aqueous solution by using filtration or centrifugation.

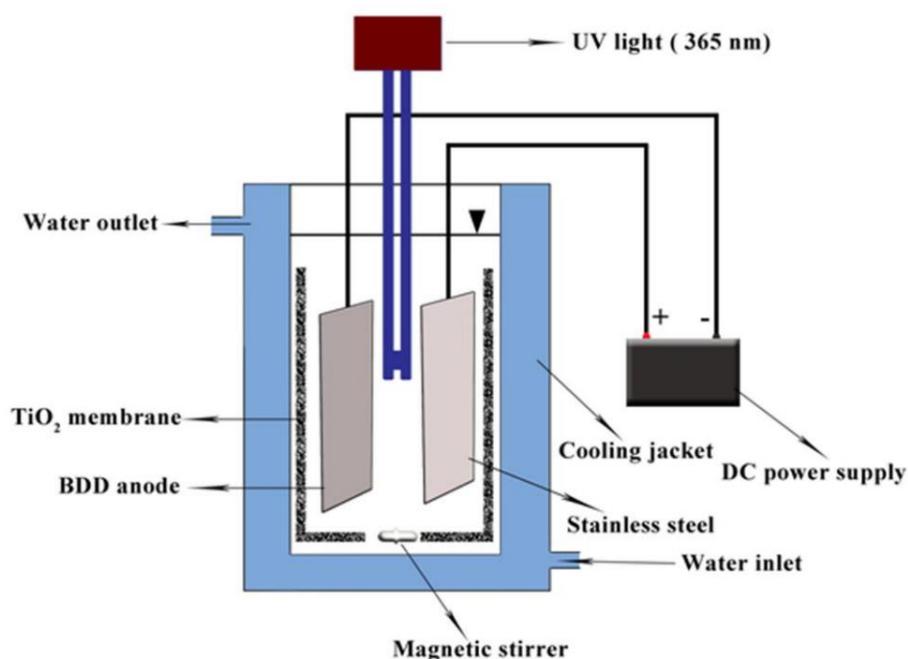


Figure 9. Schematic UV/TiO₂ photocatalytic reduction reactor.

4.6. Adsorption with natural materials

Adsorption is a physicochemical process in which a fluid (liquid or gas) is concentrated at the surface of a solid. The fluid substance being adsorbed is the adsorbate, while the solid bind with dissolved substance is called adsorbent. Various adsorbents are used for different systems, for instance, sediments and soils, activated carbon, metal oxides and biosolids (Mishra et al., 2009).

Many studies have proved that adsorption treatment technology is very feasible for removing nitrate from aqueous medium mainly owing to its simple design (Mishra et al., 2009). From the economical point of view of the industrial scale, some adsorbents are costly, thus more and more inexpensive natural materials especially bio-resources have been investigated in the preparation of adsorbents. Several natural materials with high potential are utilized for nitrate removal such as:

Biochar is a porous biomass-derived charcoal produced by thermal carbonization of biomass under exclusion of oxygen conditions which has a high density of negative surface charges and a high specific surface area. Biochar plays an important role in agronomic and environmental fields for water purification (Mishra et al., 2009). There are various sources of biochar produced by pyrolysis of biomass that can be used as adsorbent for nitrate removal, as well as materials such as woody materials (bamboo powder charcoal, moso bamboo), agricultural residues (wheat straw charcoal, mustard straw charcoal, pomegranate) (Kei et al., 2004; Wang et al., 2007; Mishra et al., 2014).

Activated carbon is a well-known adsorbent used for wastewater and gas treatments, since it is highly efficient with large surface area ($3000 \text{ m}^2/\text{g}$), high porosity and high degree of surface reactivity (Liang et al. 2011).

While activated carbon remains costly material, some studies observe that agricultural wastes as useful valuable adsorbents have become a better option to produce activated carbon, such as corn cob, palm shell, cherry stone, coconut shell, hazelnut bagasse, apricot stones and rice husk. Sugar beet bagasse which is obtained after sugar production as a by-product is illustrated as below. The produced activated carbons were used for nitrate removal from aqueous solution containing 300 mg/L of NaNO_3 by adsorption.

Chitosan refers to nitrogenous polysaccharide as a linear copolymer which is made up of glucosamide and N-acetyl glucosamine (Sowmya et al. 2014). Chitosan is biodegradable, biocompatible and non-toxic extract obtained by thermo-chemical deacetylation from abundant crustacean chitin, mainly from shellfish shells, insect

exoskeletons and fungi cell walls.

Natural zeolite was investigated in water treatment by scientists in South Africa. Based on experiments conducted by Mike and his co-workers, , surfactant modified natural zeolite is a very promising material to manage excess amounts of nitrates in ground water. With positively charged surface, surfactant modified zeolite will attract anionic pollutants such as nitrates via electrostatic interactions.

Natural clays as a natural scavenger of contaminants is used to clean and purify water. Wasse and his co-workers (2014) achieved 80% of nitrate removal rate by using acid activated bentonite clay as adsorbent. Acid activation treatment assists the modification of clay minerals via acid leaching process to improve their adsorbent capacity and increase the specific surface area as well as number of active sites of the solids.

5. CHEMICAL REDUCTION OF NITRATE BY ZVI/H₂O₂ SYSTEM

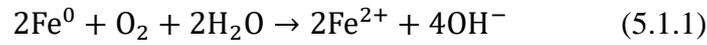
5.1. Chemical denitrification

Chemical denitrification is being considered as an emerging technique for nitrate removal from contaminated water. The potential of using nitrate chemical reduction for *in situ* groundwater and above-ground water treatment systems is vast, with the strength of unnecessary disposal of concentrated waste solutions (Jensen et al., 2012). Metals such as zero-valent iron (ZVI), copper, zinc, platinum and palladium can transform nitrate to other nitrogen compounds (Westerhoff et al., 2009). However, the weaknesses of these materials restrict the chemical denitrification process used for water treatment due to the use of low pH levels, heat addition and requirement of strong reductant medium (nitrogen gas).

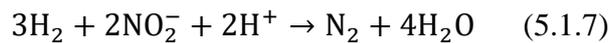
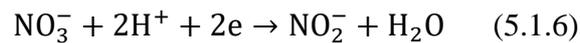
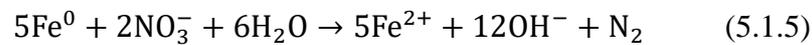
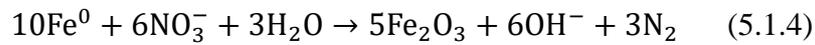
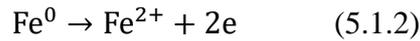
The chemical denitrification is performed by two steps: nitrate is converted into nitrite; nitrite is reduced into molecular nitrogen. Since nitrate is very stable, the transformation of nitrate into nitrite is sufficient to produce ammonia subsequently.

Moreover, the chemical reduction processes used for nitrate removal is not only purely a chemical process, but also synergistically associated with other processes, such as catalytic reduction processes and electrochemical processes (Ferro et al. 2003).

The process occurs with very active metals in the metallic form. The indirect nitrate reduction process happens with the help of nascent (H) or molecular hydrogen (H₂). In aerobic conditions, the dissolved oxygen, as the preferred electron acceptor (equation 5.1.1), captures electron from zero-valence metal and results in the production of hydroxide ions (OH⁻).



The indirect nitrate reduction process occurs by the means of activity of the zero valent metal. Under anoxic conditions, ZVI is available to reduce nitrate directly and hydrogen can be used for reducing them indirectly. Performed reactions are shown as below in equation 5.1.2—5.1.7. The reduction process may proceed further to the synthesis of ammonia, however the performance of Fe^{2+} , Fe^{3+} , Fe_2O_3 , Fe_3O_4 restricts to reaction conditions.

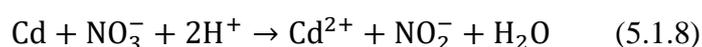


Many studies discovered that it is necessary to inject acid constantly to guarantee an available reduction environment where be buffered to keep in a low pH conditions (Ferro et al.,2003). In addition, the concomitant corrosion on the surface of zero-valent iron is generated by nitrate reduction process, which refers to a

passivation layer containing oxides iron and hydroxides iron, decreasing reaction efficiency. The removal of the passivation layer can be commonly performed by acid washing or acidity treatment of the solution, as well as cracking such films by means of ultrasound (Hwang et al., 2011).

The use of ZVI for nitrate reduction has been demonstrated and brings out the formation of ammonium (Crane et al., 2012). For enhance the production of molecular nitrogen (N_2), iron particles are modified by the deposition of copper, lead and precious metals to improve the catalytic activity. In terms of modified zero-valent iron application, it can alter the stability of adsorbed intermediate and contribute the recombination to molecular nitrogen.

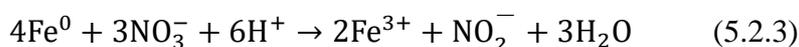
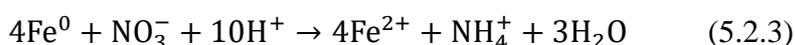
Another chemical reduction method is conducted by treating nitrate concentrated solution with cadmium or zinc associated with silver, copper or mercury as catalysts. The preliminary pathway is the conversion of nitrate to nitrite in where the solution passes through a cadmium-contained column (equation 5.1.8). Subsequently, the aqueous solution with nitrite produces nitrogen and carbon dioxide facilitated by an amide (H_2NA) (equation 5.1.9), such as urea (Ferro et al. 2003). The combination of zinc and sulfamic acid (H_2NSO_3H) has been indicated by many scientists for chemical reduction of nitrate as well.



5.2. Nitrate reduction by zero-valent iron (ZVI)

Zero-valent iron (ZVI) has been used for denitrification of water since it is easy to use, it is environmentally safe and the costs are low (Fu et al., 2014). ZVI is very reactive in water, where the oxidation reaction of iron releases electrons, which can be used for further nitrate reduction as an electron donor (Hiroyuki et al., 2014). In aqueous

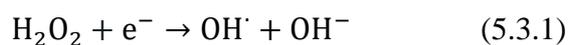
solutions, zero-valent iron (Fe^0) is readily oxidized into ferrous ion (Fe^{2+}) and two electrons are released in the solution (equation 5.2.1) due to ZVI metal corrosion. Nitrate, the electron acceptor, proceed to the reductive decomposition with the electrons released from the oxidization of ZVI (Guo et al., 2015). The final products of this electrochemical corrosion reactions could be ammonium or nitrogen (equations 5.2.2 and 5.2.3). The whole process is an oxidation-reduction (redox) reaction.



A lower pH condition is more favorable for this reaction, since acid can dissolve the passivation layer (magnetite or green rust) covered on the surface of iron particles, guaranteeing a fresh ZVI surface (Gordon et al., 2005).

5.3. ZVI/ H_2O_2 system in Fenton's peroxidation

ZVI is commonly combined with hydrogen peroxide (H_2O_2), a strong oxidant, in Fenton's reaction in oxidation processes for organic matter degradation in wastewater treatment (Neyens et al., 2003). In Fenton oxidation process, hydroxyl radicals (OH^\bullet) are generated from the degradation of hydrogen peroxide with iron ions in the acid conditions (equation 5.3.1), while iron, usually in Fe^{2+} form, is oxidized to Fe^{3+} (equation 5.3.2) (Behrooz et al., 2013). Ferric ions (Fe^{3+}) are obtained in this process, which has low capability to catalyze hydroxyl radicals due to the production of hydroperoxyl (HO_2^\bullet) radicals which are weaker than OH^\bullet , decreasing the efficiency of the reaction (Samarghandi et al., 2013). Usually Fenton's oxidation starts with a catalyst in Fe^{2+} form but it is possible to have a catalyst in Fe^{3+} or Fe^0 (ZVI) and in these cases the reaction is called Fenton-like reaction (equation 5.3.3).



Despite not being a Fenton's reaction, hydrogen peroxide has been demonstrated to improve the reactivity of ZVI surface that contribute to remove passivation layer and enhance the capacity of nitrate removal (Guo et al., 2015; Karimi et al. 2014). Despite the literature seems to be really scarce on this topic and the mechanism of surface activation is not very well described, it seems that H_2O_2 can oxidize and corrode ZVI surface with high rate of reaction driving the nitrate reduction. No studies were performed with real waters, which can bring scientific value to this thesis.

5.4. Other additive materials (oxidants) associated with ZVI

Due to the formation of surface passivation by oxides iron and hydroxides iron, the reactivity of ZVI becomes lower than before seriously restricting the potential of nitrate reduction (Dong-Wan et al., 2011). The performance of ZVI deactivation limits the mass transmission of targeted contaminants through passive oxide layer for water remediation (Xu et al., 2012). Therefore, several additive materials have been investigated to activate the ZVI surface for facilitating nitrate reduction, such as: red mud, magnetite (Fe_3O_4), potassium permanganate (KMnO_4), chromium ion (Cr_4^{2-}), oxygen (O_2) as well as CO_2 gas bubbling and ultraviolet (UV) light (Dong-Wan et al., 2015).

Dong-Wan et al. (2011) indicated that red mud, as a waste residue of alumina production containing aluminum, iron, titanium, silicon hydroxides and oxides, is able to promote ZVI activity maintaining a fresh surface for nitrate reduction in solution. Magnetite nanoparticles were used in another study performed by Dong-Wan and his co-workers (2015) to add with a ZVI system to improve the ZVI surface.

Regarding to their magnetic characteristic, magnetite particles are evenly distributed and attached on ZVI surface, generating localized electron intermediaries helping electron transference from ZVI into adsorbed nitrate ions (Huang et al., 2003). The presence of magnetite significantly contributes to ZVI corrosion for a long period of time improving the performance of ZVI systems for nitrate reduction. Guo et al., (2015) observed that some oxidants like O_2 , $KMnO_4$ and Cr_4^{2-} were used to improve the surface reactivity of ZVI, which contributes to the enhancement of targeted nitrate removal rate. These combined systems prevented the formation of ZVI surface passivation layers and ultimately achieved 97% of nitrate reduction (Figure 10). Moreover, Jiang et al. (2012) demonstrated that the addition of Fe^{2+} and Fe_3O_4 in ZVI system can promote the reductive denitrification rate to 98.1%. As good conductor, Fe^{2+} and Fe_3O_4 facilitate the transference of electrons on the iron surface through the redox reaction and accelerate the reductive efficiency of nitrate.

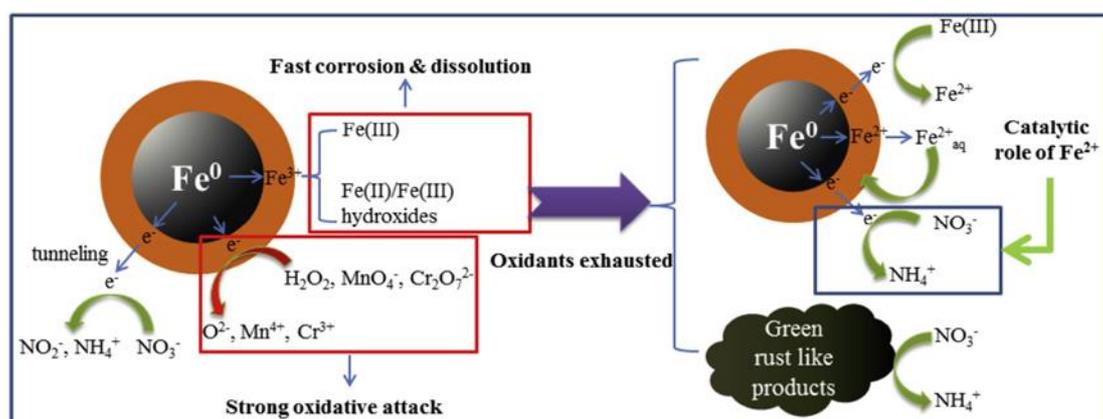


Figure 10. Schematic model of oxidants (H_2O_2 , $KMnO_4$, Cr_4^{2-}) in nitrate reduction by ZVI (Guo et al., 2015)

EXPERIMENT PART

6. MATERIALS AND METHODS

In this chapter, all used materials, experimental setups and procedures as well as analytical techniques used during the experiments will be introduced.

6.1. Materials

Mine water samples were taken from an open pit in Siilinjärvi mine, operated by Yara Oy. pH, electric conductivity (EC) and oxidation reduction potential (ORP) were measure on site. Water was kept in the freezer for further analysis, performed by Ramboll Analytics. The analysis performed can be seen in Table 2. The main ions present in the water are 180 mg/L of NO_3^- , 0.55 mg/L of NH_4^+ , 0.65 mg/L of NO_2^- and 200 mg/L of SO_4^{2-} , 65mg/l K^+ , 100mg/l Ca^{2+} , 19mg/l Mg^{2+} , 76mg/l Na^+ .



Figure 11. Mine water from Siilinjärvi Mine.

Table 1. Chemical analysis of the mine water samples from Yara Siilinjärvi.

pH	NO ₃ ⁻ (mg/L)	NH ₄ ⁺ (mg/L)	NO ₂ ⁻ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	Ca ²⁺ (mg/L)	K ⁺ (mg/L)	SO ₄ ²⁻ (mg/L)
8.15	180	0.55	0.65	19	76	100	65	200
O ₂ (mg/L)	PO ₄ ⁻ (mg/L)	Cl (mg/L)	F (mg/L)	Ba (mg/L)	Mn (mg/L)	Mo (mg/L)	Si (mg/L)	U (mg/L)
10.20	0.030	30	1.10	0.091	0.015	0.0058	5.6	0.0068

Iron powder (-325 mesh, 97%) and hydrogen peroxide ($\geq 30\%$ RT) were purchased from Sigma-Aldrich, without further pretreatment. Synthetic nitrate solution was prepared by dissolving $CaSO_4 \cdot 2H_2O$ and KNO_3 (Merck) in deionized water. Iron oxides powder (Fe_2O_3), a by-product from Yara Oy in Kokkola site, as a side product of pyrite roasting unit. The chemical characterization of iron oxides is shown in Table 3.

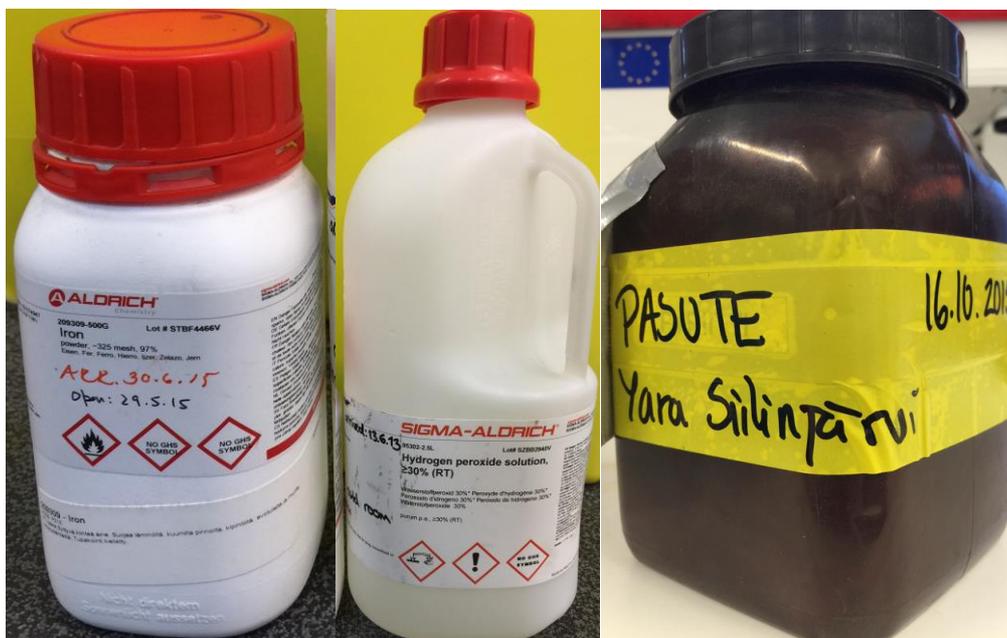


Figure 12. Used chemicals (Iron powder, Iron oxides powder, hydrogen peroxide)

Table 2. Characterization of iron oxides

	H ₂ O	Fe	S	Zn	SiO ₂	TiO ₂	Al ₂ O ₃	MnO	MgO	CaO	BaO
mg/L	20.2	60.5	0.85	0.2	6.04	0.02	1.29	0.01	0.35	0.5	0.31

6.2. Experimental setups and procedures

Before apply ZVI/H₂O₂ system to nitrate reduction in real mine water, some preliminary tests were performed according to paper from (Xuejun et al. 2015). The purpose was to preliminarily estimate the feasibility of ZVI/ H₂O₂ system for nitrate reduction. This group of experiments were carried out by diluted mine water and synthetic nitrate-containing solution with 14 mg/L of nitrate, prepared with by HNO₃. The reduction was performed in a round bottom flask with a volume of 200 mL of nitrate solution whereas added to 1 g of iron powder was added. The reaction was stirred by a magnetically mixer at speed of 400 rpm at room temperature (24 ± 1 °C). A small droplet of 20.4 μl H₂O₂ (1 mM) was injected into reaction solution after 2 hours. The pH of solution was adjusted continuously by adding NaOH and HCl in order to maintain pH 7. Throughout the six hours reaction period, the ORP were detected constantly by HACH redox electrode.

Moreover, because of too many interferential components in real mine water, a group of synthetic water test was carried out to further predict the potential feasibility of ZVI/H₂O₂ system in real mine water. As shown in Table 1, besides 180 mg/l NO₃⁻, other principal components in real mine water were 200 mg/l SO₄²⁻, 65 mg/l K⁺, 100 mg/l Ca²⁺. Thus, suitable chemicals for preparation of synthetic nitrate-concentrated solution were CaSO₄ * 2H₂O and KNO₃. The nitrate-concentrated solution was synthesized by dissolving calculated amount of 160 mg/l KNO₃ (104.37 mg) and 100 mg/l CaSO₄ * 2H₂O (171.84 mg) in the deionized water. A 500 ml two-necked flask filled with 400 ml synthetic water was used for conducting experiment. The

reaction solution was mixed by magnetite stirrer and simultaneously purged nitrogen gas bubbling. The reaction was performed in 5 hours, where 5.16 g iron powder (ZVI) was added in synthetic water in the very beginning of reaction, then 105 μl hydrogen peroxide ($2.58\text{mM H}_2\text{O}_2$) was injected into system after one hour reaction. The initial pH values were adjusted to 5, 7, 9 by adding drops of *NaOH* or *HCl* and maintained constantly within the five hours reaction duration.

The group of normal nitrate reduction experiment by ZVI/ H_2O_2 system was conducted in a 500 mL two-necked round bottom flask with 400 mL of mine water (180 mg/L NO_3^-), where a certain amount of iron powder was added in a range of 1g/L to 13 g/L, for 5 h, under a continuous N_2 bubbling. The reaction was stirred at a speed of 700 rpm with a magnetic stirrer, at room temperature around $24\pm 1^\circ\text{C}$. After one hour of reaction, a range of H_2O_2 between 1 mM to 100 mM was quickly injected into the reactor. The initial pH of the water was adjusted for a range between 5 to 9 during the experiments and it was kept constant by adding NaOH and HCl during the reaction. Simultaneously, around 12 mL of sample were taken every 20 minutes and it was passed through a 0.20 μm cellulose acetate membrane filter. Experiments were repeated three times for the calibration of process. The experimental setup for nitrate reduction is shown in Figure 13.

In the last section of experiments, iron oxide was used for nitrate reduction in iron/ H_2O_2 system and ZVI to investigate the feasibility of iron waste for nitrate reduction in mine water. These group of experiments were separated into two parts: the one is using iron oxide waste and ZVI; the other one only iron oxide waste. Experimental setups were exactly the same as before, except the dosage of reducing agent. The dosage of 26.1 mg iron oxide waste and 5.16 g Fe^0 were used at first part, meanwhile, the dosage of 7.384 g iron oxide waste was added into second part. Both of them were calculated as proportion as previous work.



Figure 13. Experimental set up for nitrate reduction reaction.

6.3. Analytical techniques

A DR 2800 HACH device was used with nitrate kit tests for the preliminary results. Due to the maximum measured value of nitrate in DR 2800M spectrophotometer is 35 mg/L, the original mine water was diluted by deionized water for the measurement of nitrate concentration. . In order to accelerate experiments proceeding, all samples were sent to Ramboll Analytics (Lahti, Finland) for chemical analysis of NO_3^- , NH_4^+ and NO_2^- concentrations. The pH value, oxidation-reduction potential (ORP) and electric conductivity (EC) were measured by using a Hach HQ40d portable device with an IntelliCAL™ pHC101 pH probe, an IntelliCAL™ REDOX MTC101 redox probe and an IntelliCAL™ CDC401 conductivity probe.

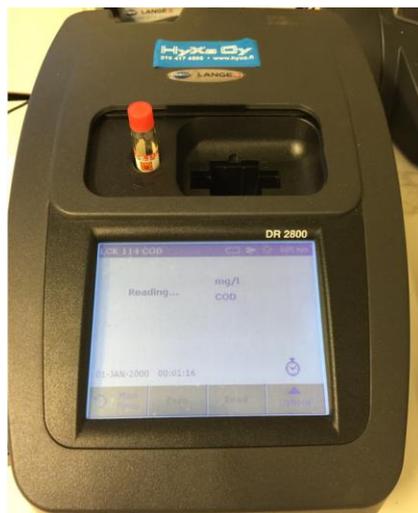


Figure 14. DR 2800 Spectrophotometer

Characterization of iron powder and iron oxide waste from Yara Oy were performed by X-ray diffraction (XRD), BET (Brunauer-Emmett-Teller) surface area before nitrate reduction reaction and scanning electron microscopy (SEM) after nitrate reduction reaction. The iron samples taken after the nitrate reduction reaction were dried in vacuum for 24 hours and sent immediately for analysis. The characterization of iron sources, iron powder and waste (Fe_2O_3) were carried out by BET surface area which results showed to be $0.257 \text{ m}^2/\text{g}$ and $1.508 \text{ m}^2/\text{g}$, respectively, at a 101.3250 kPa pressure. BET adsorption isotherm diagram is shown in Appendices 1 and 2. XRD pattern of zero-valent iron and iron oxide waste are presented in Appendices 3 and 4. The surface micro-structures of zero-valent iron and iron oxide waste were analyzed by SEM Hitachi SU3500, where acceleration voltage was 5 kV and detectors SE or BSE was used in the images.

7. RESULTS AND DISCUSSION.

7.1. Preliminary tests

Preliminary studies were performed in order to estimate the feasibility of ZVI/H₂O₂ system for nitrate reduction, taking into account the research conducted by Xuejun et al. (2015). This group of experiments were carried out by diluted mine water and Synthetic nitrate-contained solution with 14 mg/L NO₃⁻. Throughout 6 hours reaction of synthetic nitrate-contained solution, ORP was followed continuously. The potential gradually decreased from 298 mV to -218 mV, after the addition of iron powder, indicating that a reducing medium was settled, allowing the reduction of nitrate. After spiking H₂O₂, the potential immediately increased to 120 mV, since H₂O₂ is a strong oxidant. However, within 2 min the potential was dropped down to -178 mV, achieving -312 mV at the end of 6 h, leading to a new reduction medium. This phenomenon was observed by Guo et al. (2015) after spiking oxidants to synthetic waters with NO₃⁻. It demonstrates that nitrate alone with ZVI before the oxidant addition had no effect on the increase of ORP and this parameter only changed after the addition of H₂O₂. The ORP dropped to -312 mV after H₂O₂ reduction and elimination, creating a reducing medium suitable for NO₃⁻ reduction. This mechanism was studied later by investigating the iron surface after reaction.

As the consequence of experiments, the nitrate removal efficiency of synthetic nitrate-contained solution was 83.6% (2.3 mg/L of NO₃⁻), overtaking diluted mine water with 29.3% (9.9 mg/L of NO₃⁻). The results have demonstrated the preliminary feasibility of ZVI/H₂O₂ system application for nitrate reduction. Some dilution and analytical errors might be associated with these determinations since the Hach kits used for the quantification had a limit on the nitrate presence in the water, which was 35mg/L, and iron is one of the interferences with the Hach method. Thus, the next nitrate, nitrite and ammonium species were quantified by a certified laboratory.

7.2. Synthetic water test

Furthermore, as too many interferential components in real mine water, synthetic nitrate-concentrated solution was particularly needed to further predict the potential feasibility of ZVI/H_2O_2 system in real mine water. The chemicals $CaSO_4 \cdot 2H_2O$ and KNO_3 were used for preparing synthetic nitrate-concentrated water. The initial pH values were adjusted to 5, 7, 9 by adding drops of $NaOH$ or HCl and maintained constantly within the five hours reaction duration. Three different pH values including acidic (5), neutral (7) and alkaline (9) were tested in this group of experiments to investigate the feasibility of ZVI/H_2O_2 system. Figure 15 shows that the nitrate removal efficiencies were 99.44% at pH 5 and pH 7, whereas approximately close to zero at pH 9. After two hours reaction, the nitrate reduction rate of pH 5 achieves 99.44%, overtaking pH 7, only 30%. This results demonstrate that acidic condition could be favorable in the nitrate reduction process by ZVI/H_2O_2 system (Shima et al.2013).

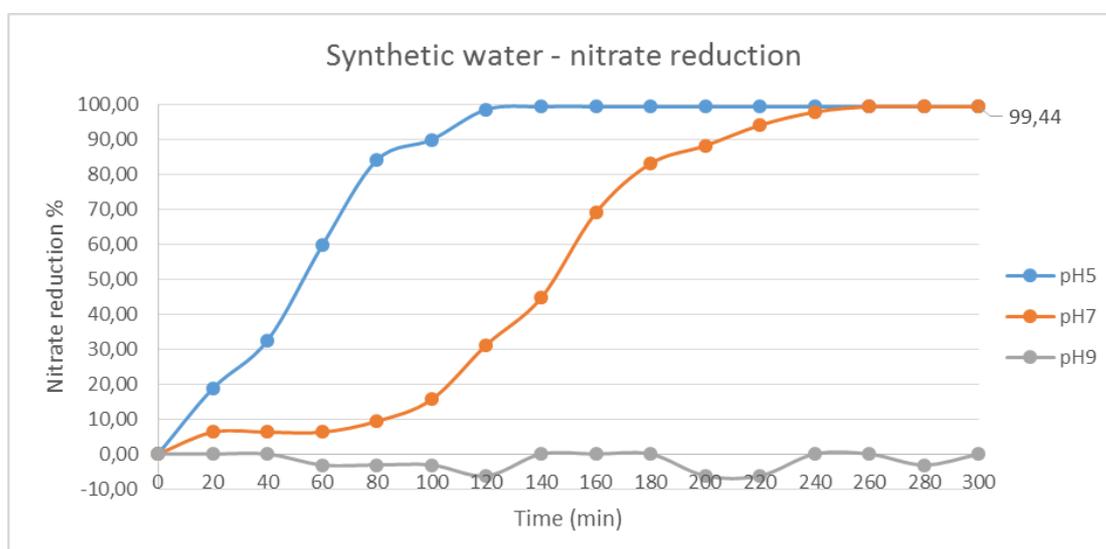


Figure 15. Nitrate reduction rate of synthetic water at pH 5, 7 and 9.

7.3. Optimization of the ZVI reactivity activation with H₂O₂

In order to optimize the ZVI/H₂O₂ reactivity methodology for nitrate reduction, a set of operating variables such as the effect of pH, dosage of ZVI and concentration of H₂O₂ were investigated.

7.3.1. Effect of pH on nitrate reduction

The natural pH value of mine water (pH=8) was tested and it was adjusted to five different values 5, 6, 7, 8 and 9, while it was kept constant. ZVI load and H₂O₂ concentrations used for testing the effect of pH were 13 g/L of iron powder and 2.58 mM of H₂O₂.

The addition of H₂O₂ was made at 60 min of reaction, indicating that there was no removal of NO₃⁻ without the spiking of H₂O₂ for pH 8 and 9 (Figure 16 a) and b)). However, it seems that for pH 5, 6 and 7, some removal was achieved with 65.4%, 35.5%, 12.9%, respectively. Guo et al. (2015) achieved around 5% of NO₃⁻ reduction before the addition of the oxidants. In general, when pH is not controlled during the experiment, the pH increases during the reaction due to the formation of OH⁻ ions, which stops the reduction. In this particular case, some reduction was possible since the pH was kept constant, allowing the entrance of H⁺ into the system needed for surface washing (Choe et al., 2004). It is noticeable from Figure 16 that nitrate reduction rates achieved 99.5% of NO₃⁻ reduction at pH 5 and pH 6 after 180 minutes reaction, overtaking 82.2% at pH 7, 17.7% at pH 8 and 5.9% at pH 9. When reactions were accomplished by 5 hours, the final nitrate removal efficiency were approximately 99.1% at pH 7, compared with 59.1% at pH 8 and 5.6% at pH 9.

The most efficient NO₃⁻ reduction occurred at pH 5, where the nitrate concentration reduced from initial value of 180 mg/L NO₃⁻ to residual value less than 0.9 mg/l. However, in alkaline conditions, the NO₃⁻ concentration only decreased up to 69.5 mg/L at pH 8, while pH 9 remained unchanged. The efficiency of NO₃⁻ reduction by ZVI/H₂O₂ system increases with the decrease in the pH from 9 to 5. These results illustrate that the reaction of nitrate reduction by ZVI/H₂O₂ system, as a process of acid consumption and alkaline production, is favorable when maintaining the solution

under acidic conditions.

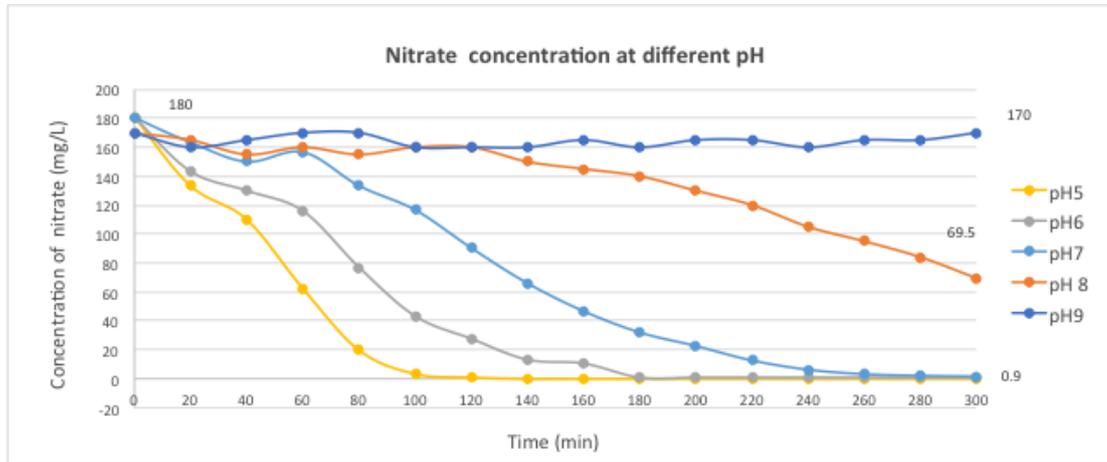


Figure 16 a). Effect of pH on nitrate reduction in real mine water at pH 5-9

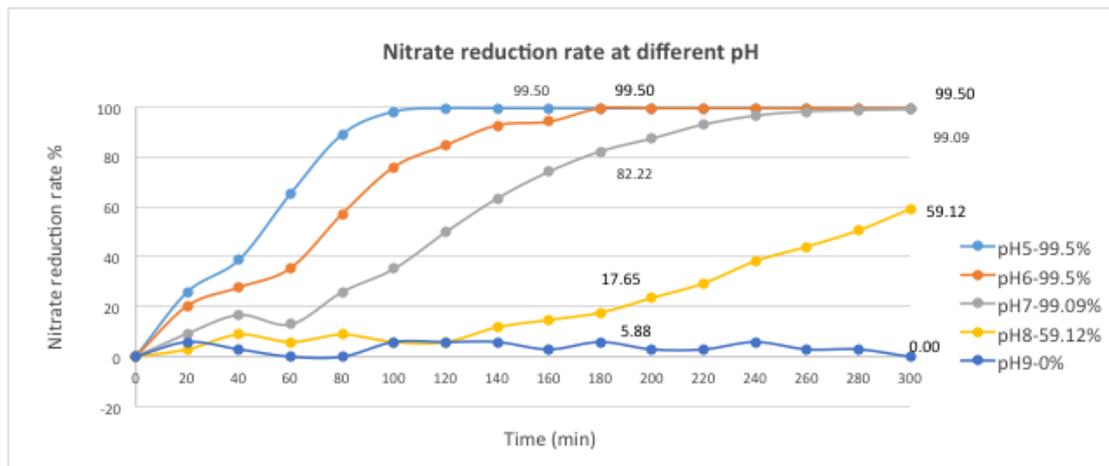
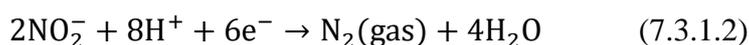
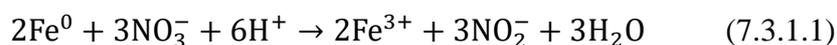


Figure 16 b). Nitrate reduction rate of real mine water at pH 5-9.

In fact, strong acids may facilitate the process of ZVI corrosion, which results in the continuous exposure of ZVI surface and contribute to the free transfer of electrons from the surface of iron to the nitrate acceptor. Behrooz et al. (2013), studied the iron oxide and hydroxyl passivation layer which was deposited on the surface of ZVI during reaction. The oxide layer would dissolve away at lower pH, that acquire more fresh active sites for nitrate reduction. This phenomenon shows that the thickness of passivation layer increases as pH increases, explaining the advantages of keeping the pH constant during the reduction reaction

On the other hand, hydrogen peroxide is stable in acidic conditions, since it dissolves a proton to form an oxonium ion (H_3O^+). Furthermore, the oxonium ion makes hydrogen peroxide electrophilic, where hydroxyl radicals (OH^\cdot) are generated during the reaction, significantly reducing the reactivity with ferrous ion. At lower pH, the amount of hydroxyl radicals would reduce in the reaction solution, where hydroxide are generated immediately after addition of hydroxyl radicals (OH^\cdot).

Nitrite and ammonium can be the products of nitrate reduction (Xuejun et al., 2015), according to the equations 7.3.1.1 to 7.3.1.3.



As shown in Figure 17, the concentration of nitrite, NO_2^- , at pH 5, 6, 7, 9 remained without significant changes besides pH 8 that showed a pick at 160 min with a concentration below 6 mg/L. Figure 18 indicated that ammonium, NH_4^+ , concentration gradually rose from 0.55 mg/L up to 29.5 mg/L, 33 mg/L, 42.33 mg/L, 16 mg/L at pH 5, 6, 7 and 8, respectively. Based on these results, NH_4^+ was recognized as the final product in the nitrate reduction process.

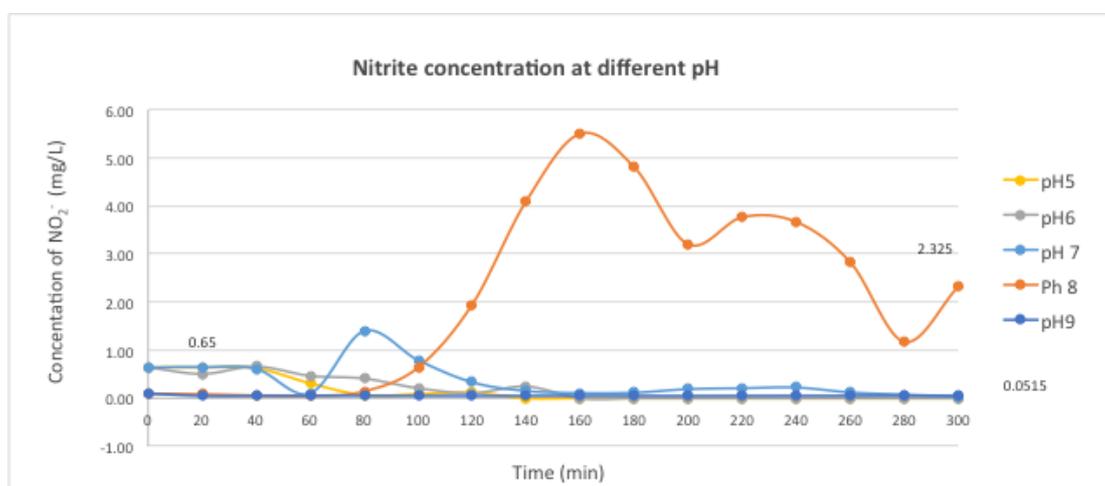


Figure 17. Effect of pH in nitrite production in real mine water at pH 5-9

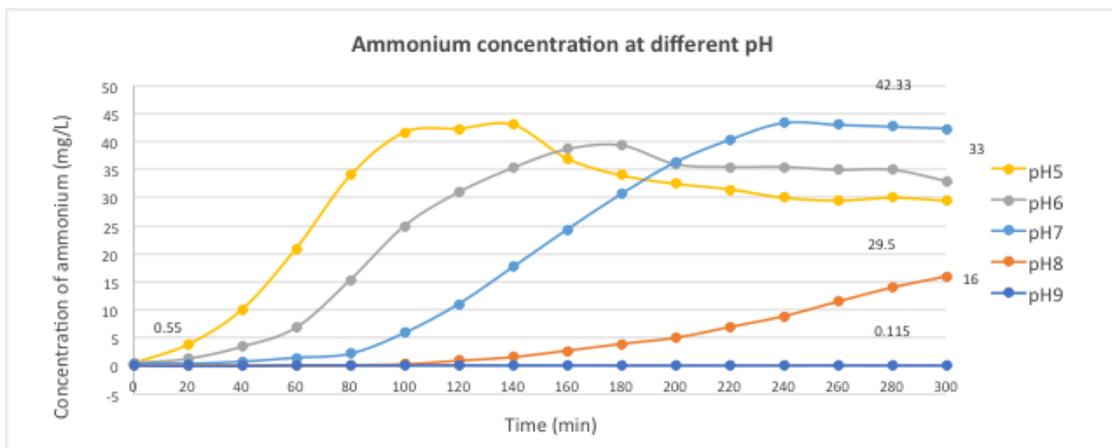


Figure 18. Effect of pH in ammonium production in real mine water at pH 5-9

The pH optimization indicated that nitrate reduction efficiency at pH 5 and pH 6 reached 99.5%. However, pH 6 was selected as the optimal option for further studies, due to the fact that pH 6 it is nearer to neutral pH, thus less HCl to decrease the pH from the natural of the effluent is needed.

7.3.2. Effect of Fe⁰ concentration on nitrate reduction

In order to investigate the effect of Fe⁰ concentration on nitrate reduction process in ZVI/H₂O₂ system, five different dosages of Fe⁰, such as 13, 6.5, 3 and 1 g/L were tested at pH 6 and with 2.58 mM of oxidant concentration. As shown in Figure 20, the kinetics of chemical denitrification process was strongly influenced by the concentration of Fe⁰. First of all, before the H₂O₂ addition at 60 min, there was 35.6% and 19.38% of nitrate reduction at the higher loads of ZVI, 13 g/L and 6.5 g/L, respectively. No reduction was observed by using lower dosages of ZVI. The highest nitrate reduction rate achieved 99.5% at a concentration of 13 g/L of Fe⁰ after 180 minutes of reaction. Meanwhile, 86.8%, 51.4% and 7.0%, were reached with the dosage of 6.5, 3 and 1 g/L, respectively. These results indicate that the nitrate reduction process is more efficient with higher loads of Fe⁰, which agrees with the studies reported in literature (Liao et al., 2003; Rodríguez-Maroto et al., 2009).

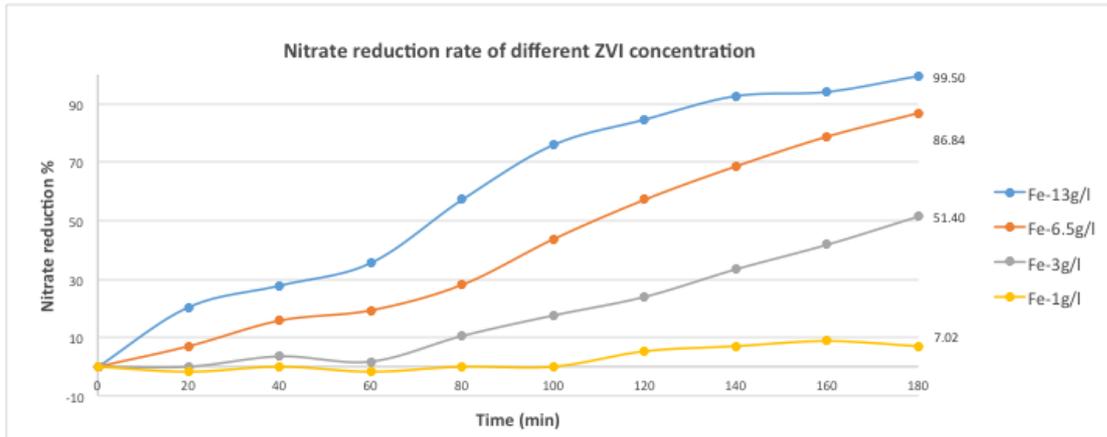


Figure 19 a). Effect of ZVI dosage on nitrate reduction at pH 6

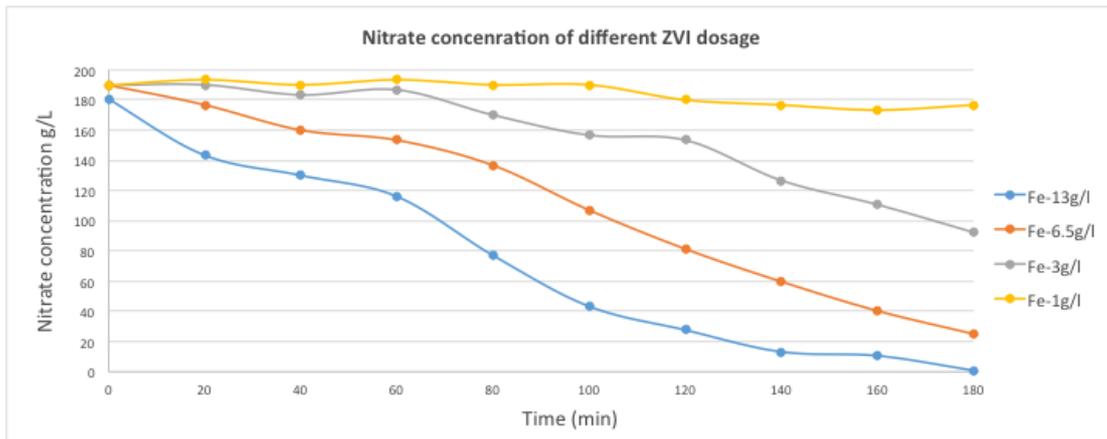


Figure 19 b). Nitrate reduction rate of different ZVI dosage

Since the reduction of nitrate by ZVI is performed at the surface of the particles, it seems that the quantity of iron particles significantly influence the nitrate reduction efficiency because there is more iron available to be corroded to Fe^{2+} and then Fe^{3+} with the help of H_2O_2 , while more nitrate is able to be reduced. In summary, the dosage of 13g/L of Fe^0 , as the maximum of tested dosage, was recommended for the optimization.

The addition of ZVI to the reaction solution leads to two oxidation stages: the pathway from Fe^0 to Fe^{2+} and from Fe^{2+} to Fe^{3+} . Fe^0 is oxidized into ferrous ion (Fe^{2+}) by releasing two electrons to hydroxyl radical (OH^\cdot), that mainly contribute to iron corrosion. The by-product of iron corrosion, such as Fe^{2+} and $\text{Fe}(\text{OH})_2$, leads to the

generation of ferrous accumulation for reducing nitrate to ammonium. Furthermore, magnetite (Fe_2O_3) is the major corrosion product of oxidation reaction produced from ferrous ion under near-neutral pH.

Figure 20 shows that the concentration of nitrite with dosage of 1g/L and 3g/L ZVI increased to 7.6 g/L and 5.5 g/L after 3 hours reaction, while the dosage of 3g/L and 13g/L almost remained the same value as before. As indicated in Figure 21, ammonium concentration significantly increased to 39.3 g/L and 36.3 g/L with dosage of 13 g/L and 6.5 g/L ZVI, overtaking 7.9 g/L and 1.93 g/L with 3 g/L and 1 g/L ZVI. According to these results, NH_4^+ was recognized as the main product in the nitrate reduction process.

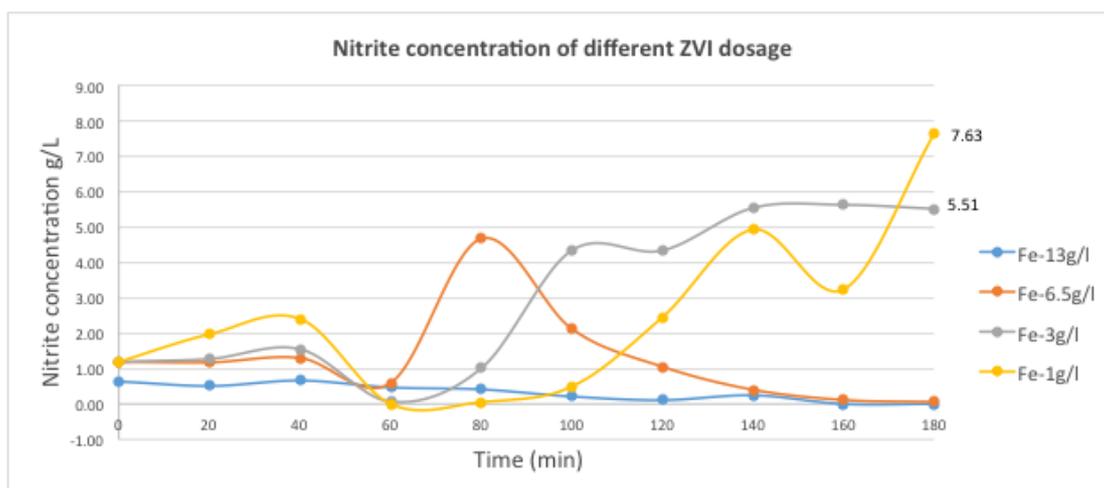


Figure 20. Effect of ZVI dosage on nitrite production at pH 6

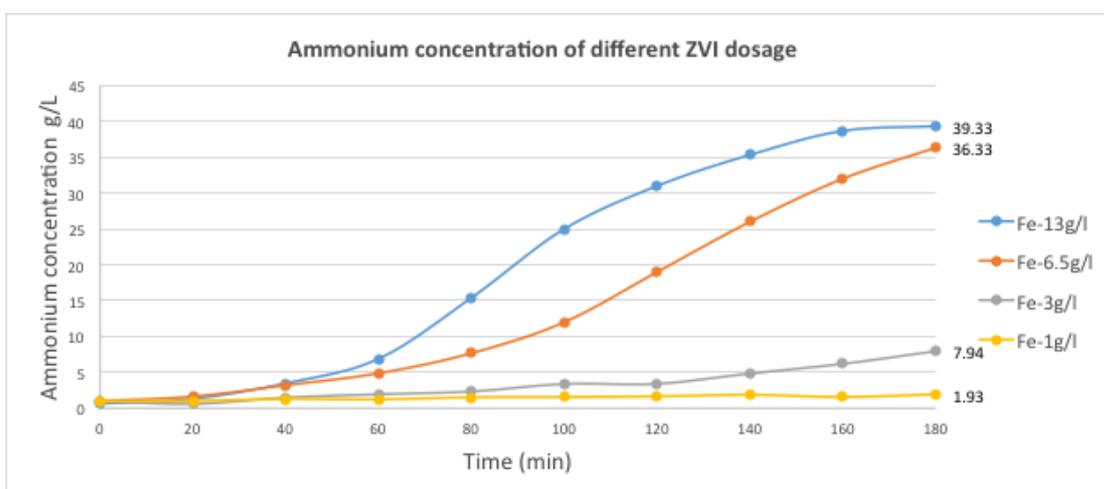


Figure 21. Effect of ZVI dosage on ammonium production at pH 6.

7.3.3. Effect of H₂O₂ concentration on nitrate reduction

Five different dosages of H₂O₂ were tested to study the impact of the oxidant concentration on the nitrate reduction efficiency. As it can be seen from Figure 21, by testing the concentrations of 1, 2.58, 19, 50 and 100 mM H₂O₂, the nitrate was removed by 99.0%, 99.5%, 99.5%, 97.0% and 99.5%, respectively, within 180 minutes of reaction, indicating that there is not a significant difference of H₂O₂ concentration at the end of the reaction. Only the curves of highest H₂O₂ concentration (50 and 100 mM) showed to have a different behavior from 60 to 160 min, where the nitrate reductions rate was kept relatively constant for 40 min, until it reached the 100 min. Thus, after 100 min, the nitrate reduction rate started to increase again until the end of the reaction. This may suggest that higher oxidant dosages might corrode the surface of the iron at a higher rate of corrosion, but it needs more time for the complete H₂O₂ consumption when compared with smaller H₂O₂ dosages because after the consumption of the oxidant, nitrate reduction capacity started to increase through time for all the concentration tested. Based on these results, the concentration of 2.58 mM H₂O₂ was considered as the optimal selection, with 99.5% of nitrate removal efficiency, despite the other concentrations tested had similar results because it seems that at the end of 5 h, spiking the water with smaller dosages of oxidant has similar results with higher dosages, so it is more economical to choose smaller dosages.

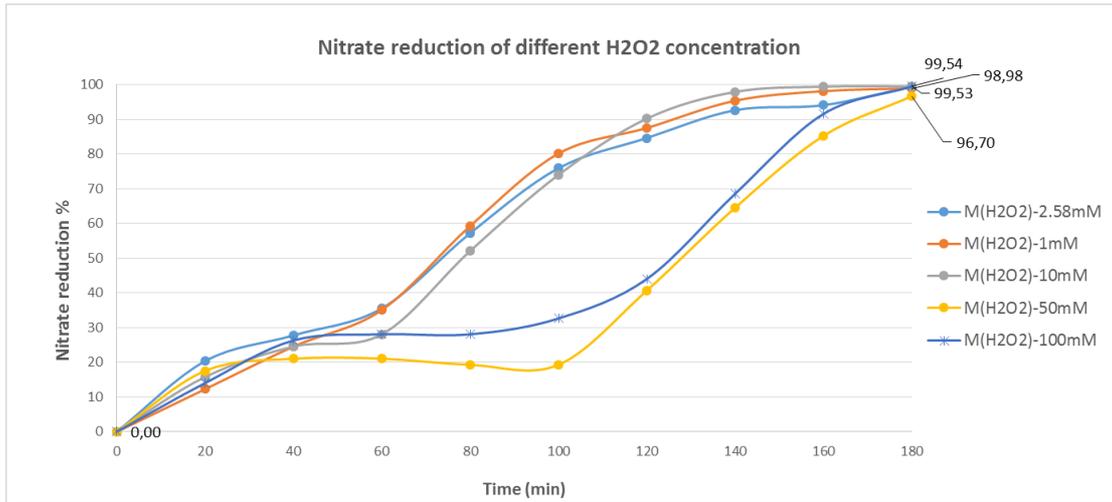


Figure 22 a). Effect on the nitrate reduction rate at different H₂O₂ concentrations.

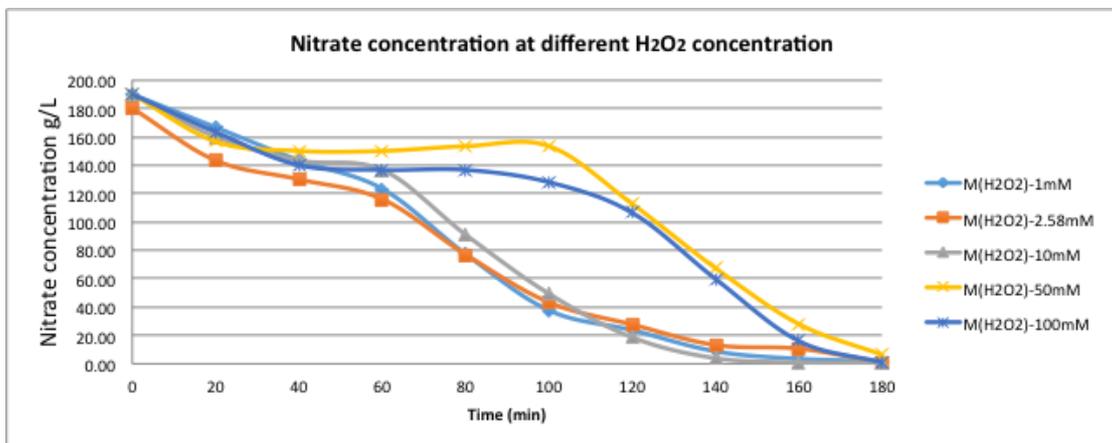


Figure 22 b) Effect on the nitrate concentration at different H₂O₂ concentrations

Hydrogen peroxide seemed to improve the reactivity of ZVI surface. Nitrate reduction is only possible when iron is corroded (Fe^0 is corroded to Fe^{2+} and/or Fe^{3+}), however if the rate of corrosion is high, higher will be the possibility of reducing nitrate. Since H_2O_2 is a strong oxidant, it will act fast for iron surface corrosion, leading to higher rates of nitrate reduction.

Besides this, the formation of the intensive corrosion layer of iron have a large specific surface area, creating highly reactive sites for electron tunneling allowing the inner Fe^0 to react with green rusts and other iron hydroxides formed. This combination of iron and iron hydroxides will lead to nitrate reduction. This mechanism was described for the first time by Guo et al. (2015), however, there is no proof of electron tunneling. Adsorption can be a good explanation for nitrate

reduction, since iron oxides and green rusts act as adsorbents of contaminants at near neutral pH (Fan et al., 2009a; Fan et al., 2009b). As shown in SEM image (Figure 23), the appearance of ZVI surface is rutted and uneven in an irregular shape. It illustrates that an intensive corrosion process was performed in the presence of H_2O_2 , therefore, the ZVI surface occurs a very rough texture.

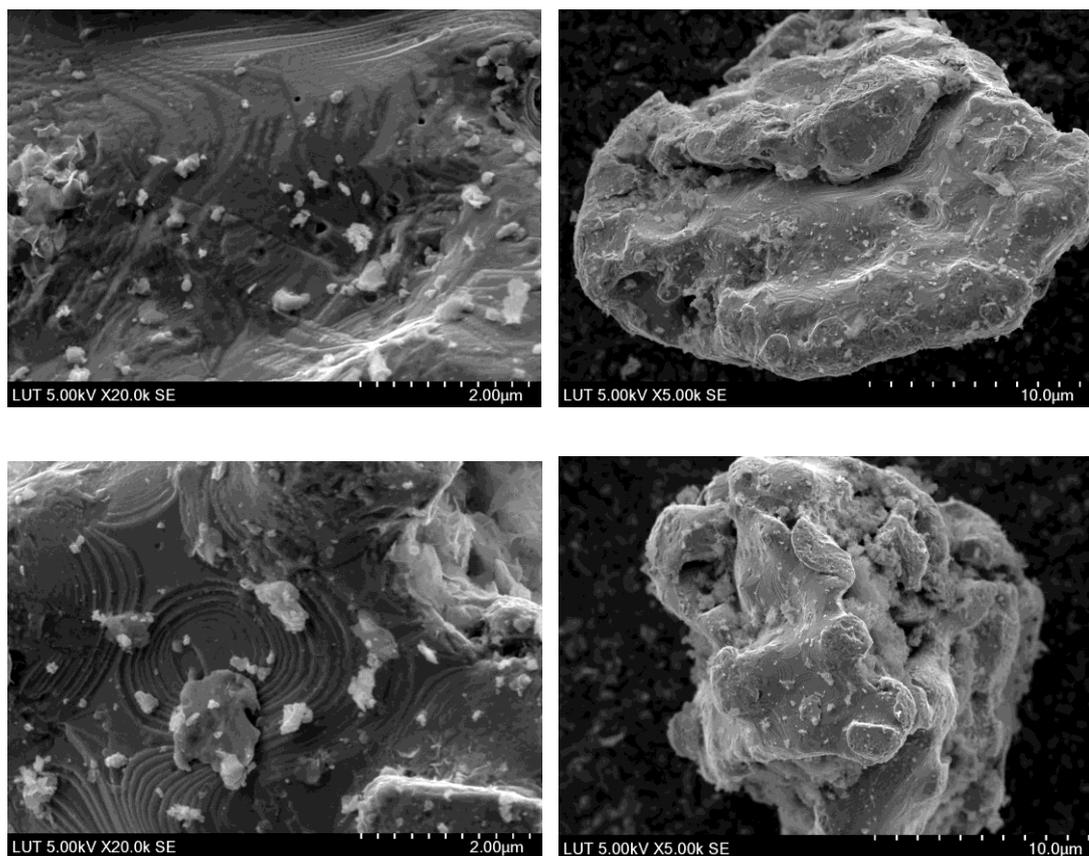


Figure 23. SEM images of ZVI surface after H_2O_2 addition

7.4. Effect of iron oxide waste for nitrate reduction in iron/ H_2O_2 system

In this section, the feasibility of iron oxide waste combined with H_2O_2 as a spiking oxidant was investigated for nitrate reduction in mine water. The tested iron oxide waste came from Yara Oy.

The iron waste was tested by XRD analysis (Figure 23 a), b.) where a peak of Fe_2O_3 was identified. The experiments were carried by using combination of iron oxide waste and ZVI and iron oxide waste separately for nitrate reduction, in order to investigate the experimental results of nitrate reduction compared with ZVI. Using only iron waste, Fe_2O_3 , showed to have no impact on nitrate reduction (Figure 22). However, nitrate removal efficiency reached 99.5% when the waste was combined with ZVI ($\text{ZVI} + \text{Fe}_2\text{O}_3$) within 180 min of reaction. The same results was observed by using ZVI only in 180 min. Figure 22 also indicate that the use of $\text{ZVI} + \text{Fe}_2\text{O}_3$ obtained 98.3% denitrification rate after 120 minutes of reaction, overtaking 13.6% by using ZVI alone. According to these results, the use of $\text{ZVI} + \text{Fe}_2\text{O}_3$ seems to have a great potential for nitrate reduction, being able to reduce the amount of ZVI added to the chemical reaction by adding a wastes.

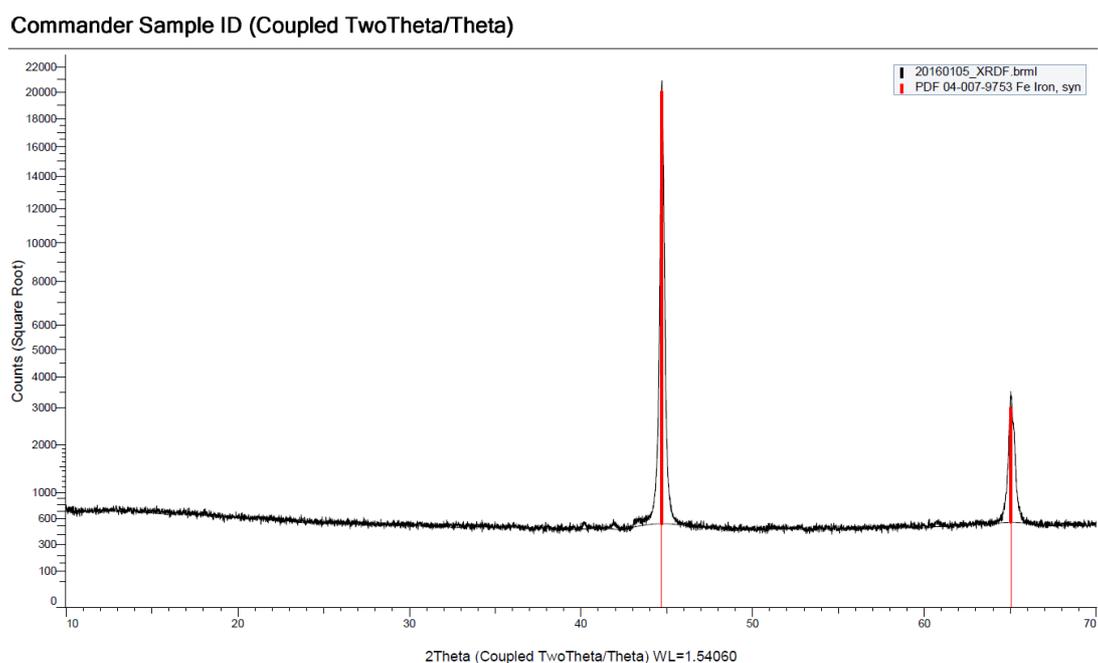


Figure 24 a) XRD pattern of zero-valent iron

Commander Sample ID (Coupled TwoTheta/Theta)

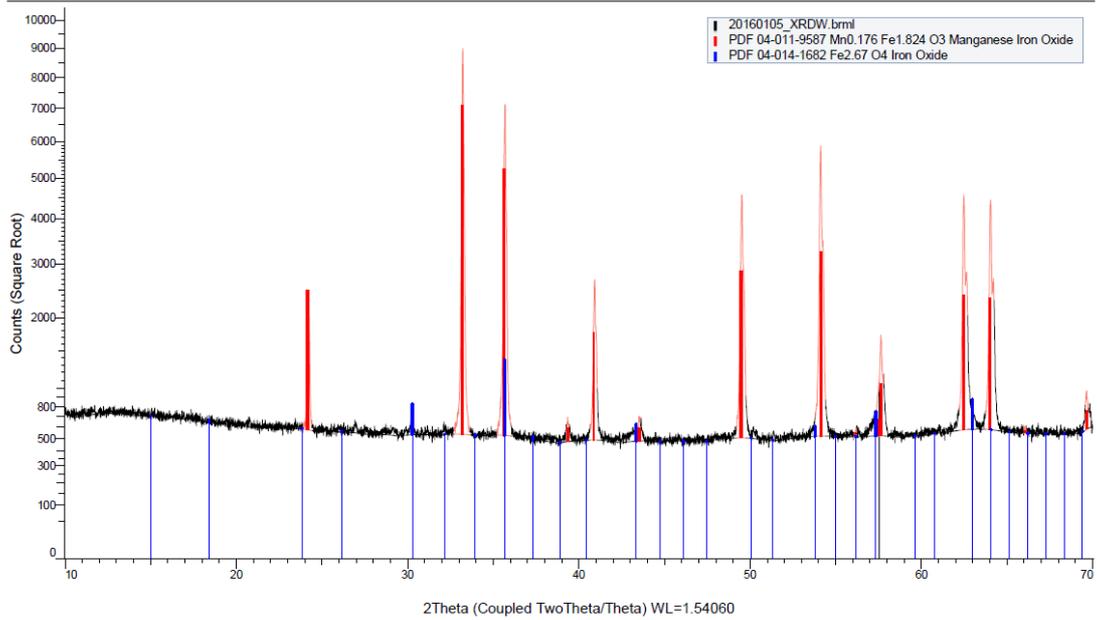


Figure 24 b) XRD pattern of iron oxide waste

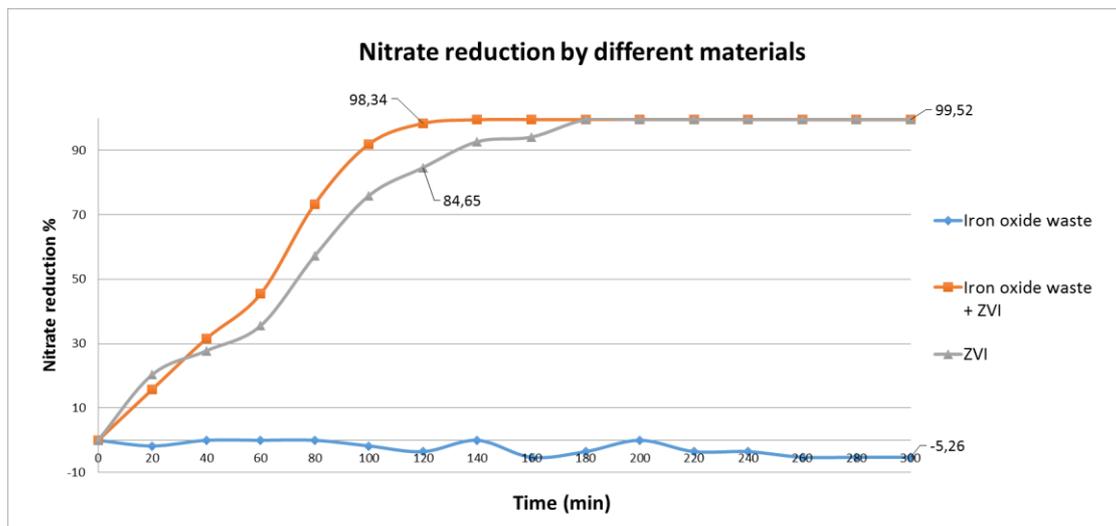


Figure 25. Nitrate reduction rate with different iron sources

8. CONCLUSIONS

One of the problematic issues in using blasting agents in mining activities containing nitrate, is the contamination of the mine water with high levels of nitrate, which constitutes an environmental concern. ZVI methodology has been used for the reduction of nitrate from water, however, it seems this approach requires acidic mediums in order to achieve relevant nitrate reduction efficiencies. Therefore, the main objective of the present thesis was to improve the ZVI surface in order to use it in a near neutral pH. This study investigated the reactivity activation of ZVI surface with the addition of a strong oxidant, H_2O_2 , which according to Guo et al. (2015) would speed the corrosion of Fe^0 , allowing a faster rate of nitrate reduction, as well as will be able to create a larger oxide surface area with edges, allowing the electron tunneling to the water. Thus, Fe^0 from the inner core will bond with iron hydroxides.

First of all, preliminary tests were carried out to prove the feasibility of the ZVI/ H_2O_2 system for nitrate reduction in mine water. This group of experiments were performed by using diluted mine water and synthetic nitrate-contained solution of HNO_3 , which acquired results of 28.9% nitrate reduction efficiency in diluted mine water and 83.6% in the synthetic solution. In the next batch experiments, synthetic water prepared by $CaSO_4 * 2H_2O$ and KNO_3 were tested at different pH levels, such as acidic, neutral and alkaline. The mission of these tests was to demonstrate the further feasibility of ZVI/ H_2O_2 system at different pH conditions. The result indicates that nitrate was reduced by 99.44% at pH 5 and pH 7, whereas approximately unchanged at pH 9. The acidic condition could be favorable in the nitrate reduction process by ZVI/ H_2O_2 system.

In order to optimize the ZVI/ H_2O_2 system for nitrate reduction, several variables were investigated to improve the efficiency. Five different pH levels with the range from 5 to 9 were tested in real mine water. After five hours experiments, the nitrate reduction rate achieved 99.5% at pH 5 and 6, 99.1% at pH 7, overtaking 59.1% at pH 8 and 5.6% at pH 9. Since the rate of nitrate reduction increases with the decrease of pH, it was shown that ZVI/ H_2O_2 system works efficiently under acidic conditions, but due to the addition of the oxidant, it was possible to obtain similar results for

neutral pH. The optimal pH value chosen is pH 6, since it is near to neutral pH, not having to decrease the natural pH of the water to 5. To investigate the optimal load of ZVI on nitrate reduction process, five different dosages of ZVI (13, 6.5, 3 and 1 g/L) were tested. The highest nitrate reduction rate achieved was 99.5% with a concentration of 13 g/L of Fe^0 after 180 minutes reaction. Around 86.8%, 51.4% and 7.0% were reached with the dosage of 6.5, 3 and 1 g/L of Fe^0 , respectively. Consequently, 13 g/L of ZVI was the result of the optimization. From the five H_2O_2 concentrations tested, 1, 2.58, 19, 50 and 100 mM, the nitrate was reduced by 99.0%, 99.5%, 99.5%, 97.0% and 99.5% after 180 minutes of reaction, suggesting that the spiked oxidant dosage is not a relevant parameter within the range tested. However, from an economic point of view, 2.58 mM of H_2O_2 was considered as the optimal dosage.

Iron oxide waste from Yara Oy (pyrite roasting unit) was used as an alternative to ZVI for nitrate reduction in mine water. A X-Ray diffraction (XRD) analysis confirmed that the waste was mainly constituted by Fe_2O_3 . When the iron oxide waste was combined with ZVI and with 2.58 mM of H_2O_2 at pH 6, 99.5% of nitrate reduction was achieved, On the other hand, iron oxide waste alone at the same operational conditions showed to have no influence on nitrate reduction.

In conclusion, the study on this thesis demonstrated that the use of ZVI/ H_2O_2 system at near neutral pH value (pH 6) achieved a satisfactory nitrate reduction efficiency in mine water but the mechanism described by Guo et al. (2015) could be more than electron tunneling. In fact, once hydroxides or green rust are formed at near pH neutral conditions, these iron phases can adsorb pollutants such as nitrate. The addition of iron oxide waste with ZVI/ H_2O_2 system had great potential for nitrate removal, being able to reduce the amount of ZVI used. Once again, the iron waste, an iron oxide, could act as an adsorbent for nitrate reduction. It can be summarized that the objectives of this thesis were accomplished and this methodology improved the previous studies of nitrate reduction in acidic mediums by ZVI.

9. FUTURE RESEARCH WORK

This present work demonstrated that nitrate can be reduced to generate ammonium, NH_4^+ , at near neutral pH. Despite the best pH chosen was 6, pH 7 and 8 showed to have high efficiencies as well, allowing the production of NH_4^+ at similar operational conditions as the natural pH of the effluent by using the iron waste from Yara mixed with ZVI, which decreases the operational costs. Thus, further studies may focus on investigations of a fertilizer production, struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) from the NH_4^+ ions produced. Mg^{2+} and PO_4^{3-} ions will have to be added in excess to the NH_4^+ . Those ions can be obtained from wastes or by-products from Yara Oy, decreasing the experimental costs and bringing scientific innovation to the struvite production from mine water.

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APPENDICES

Appendix 1. BET surface area report of iron oxide waste



Surface Area

Gemini V1.00 Unit 1 Serial #: 5002 Page 1

Sample: BETW
 Operator: Jaana Ruokonen
 Submitter: MIC
 File: C:\GEMINI\RUOKONEN\001-203.SMP

Started: 20.1.2016 10:13:59 Analysis Adsorptive: N2
 Completed: 20.1.2016 10:51:12 Equilibration Time: 5 s
 Report Time: 20.1.2016 10:51:12 Sat. Pressure: 101.3250 kPa
 Free Space Diff.: 0.2491 cm³ Sample Mass: 0.1632 g
 Free Space Type: Measured Sample Density: 1.000 g/cm³
 Gemini Model: 2380

BET Surface Area Report

BET Surface Area: 1.5080 ± 0.0041 m²/g
 Slope: 64.008913 ± 0.170408 g/mmol
 Y-Intercept: 0.693912 ± 0.036136 g/mmol
 C: 93.243553
 Qm: 0.01546 mmol/g
 Correlation Coefficient: 0.9999894
 Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ^o)	Quantity Adsorbed (mmol/g)	1/[Q(p ^o /p - 1)]
0.099874998	0.01560	7.11227
0.149861838	0.01716	10.27389
0.199874998	0.01856	13.45707
0.249921056	0.01997	16.68807
0.299993415	0.02152	19.91686

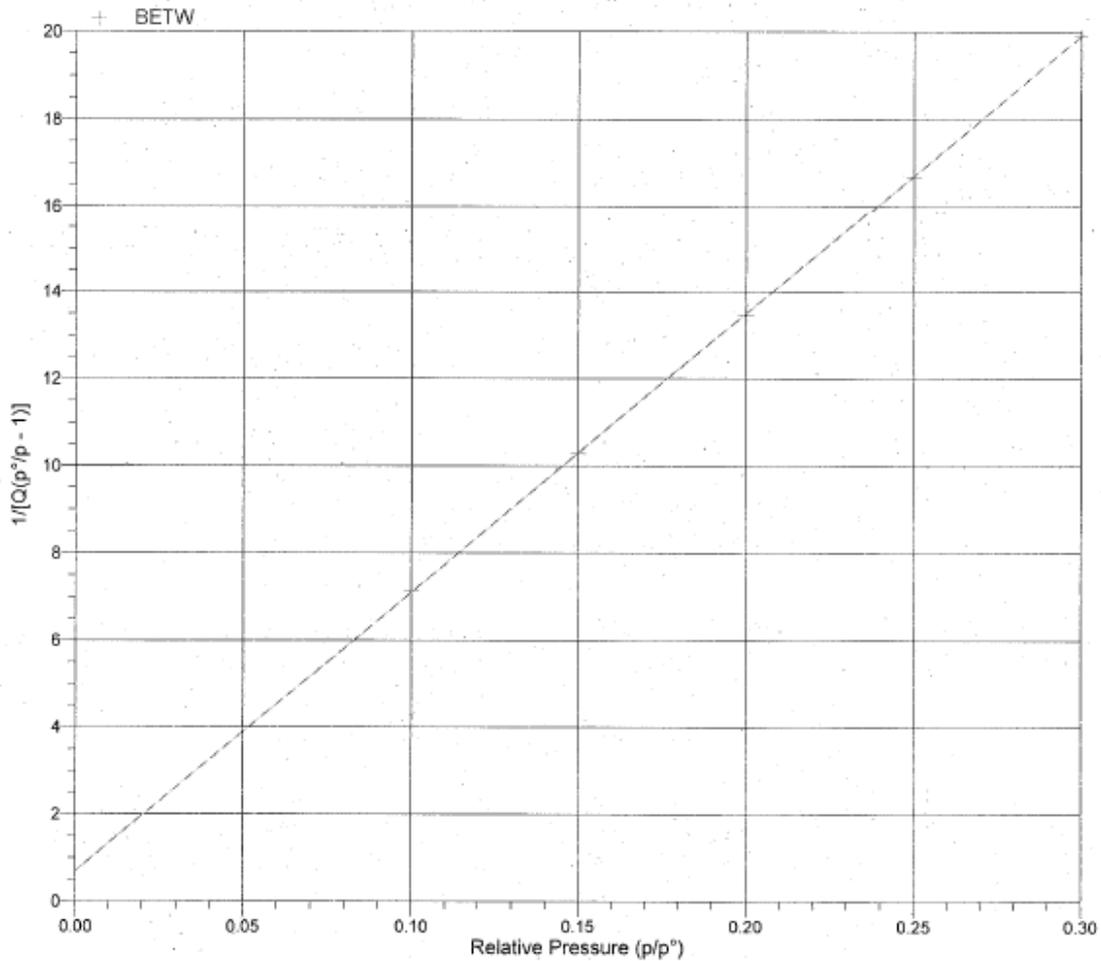
Appendix 2. BET adsorption isotherm of iron oxide waste

Sample: BETW
Operator: Jaana Ruukonen
Submitter: MIC
File: C:\GEMINI\RUUKONEN\001-203.SMP

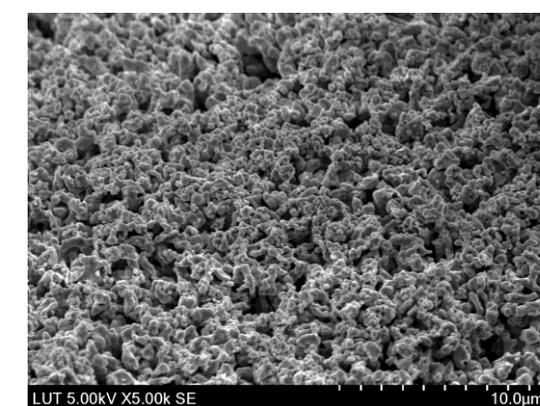
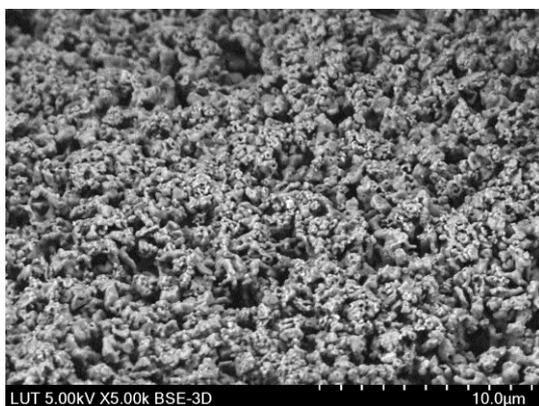
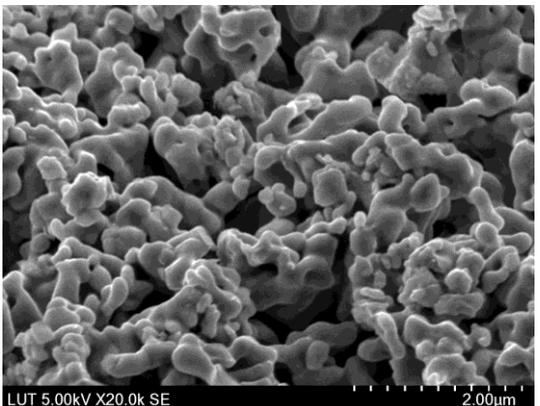
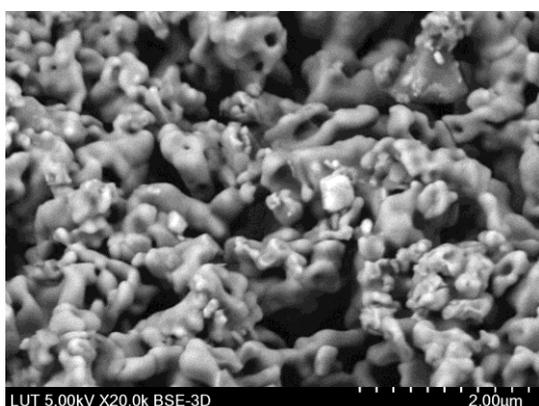
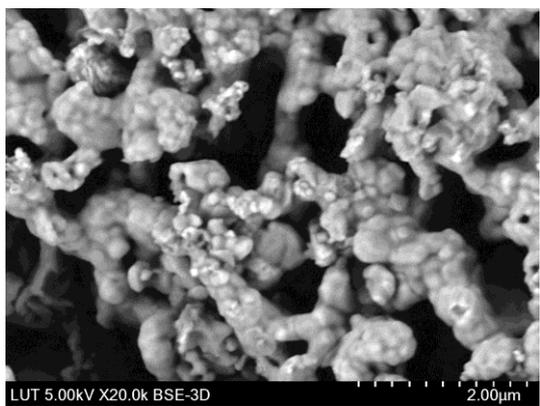
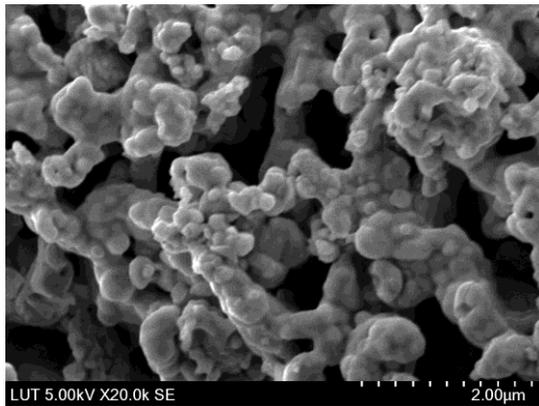
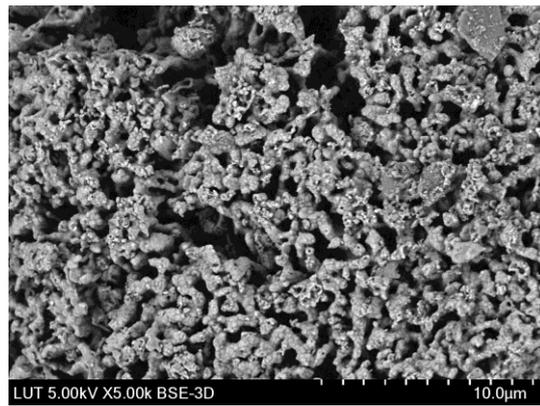
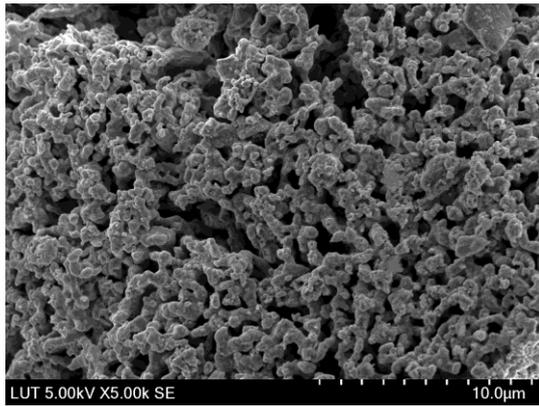
Started: 20.1.2016 10:13:59
Completed: 20.1.2016 10:51:12
Report Time: 20.1.2016 10:51:12
Free Space Diff.: 0.2491 cm³
Free Space Type: Measured
Gemini Model: 2380

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 101.3250 kPa
Sample Mass: 0.1632 g
Sample Density: 1.000 g/cm³

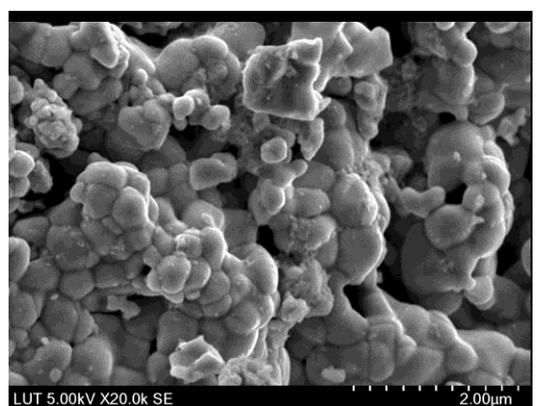
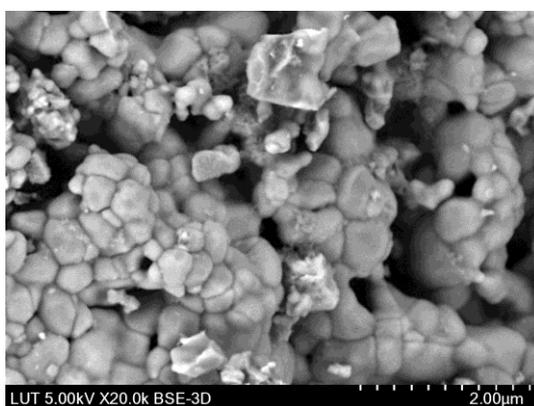
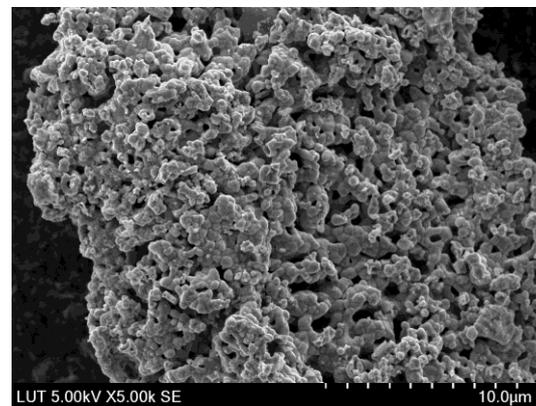
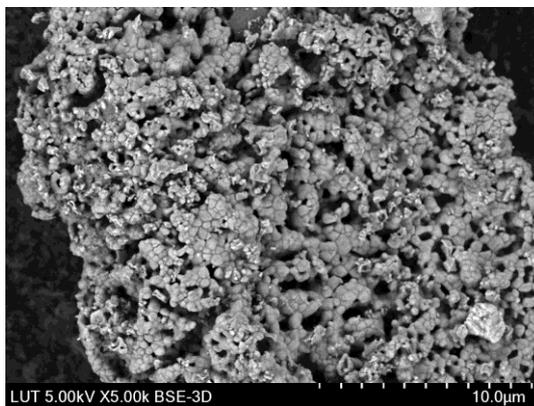
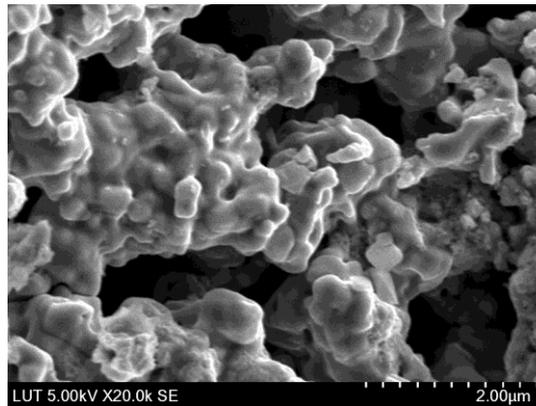
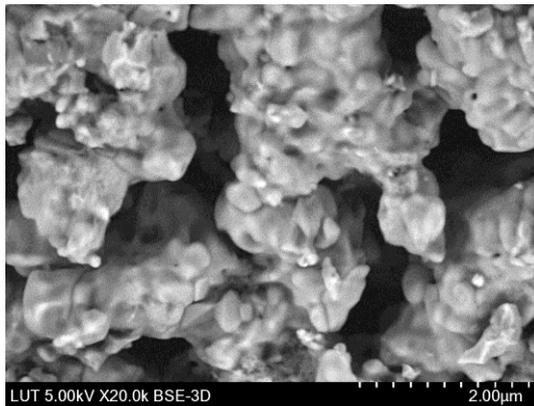
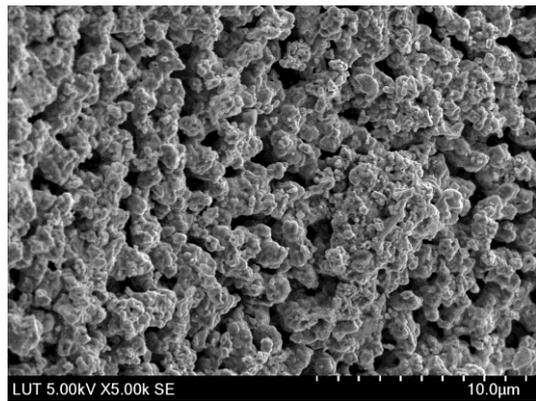
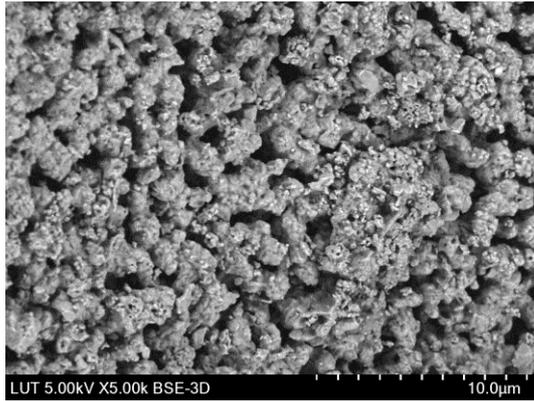
BET Surface Area Plot



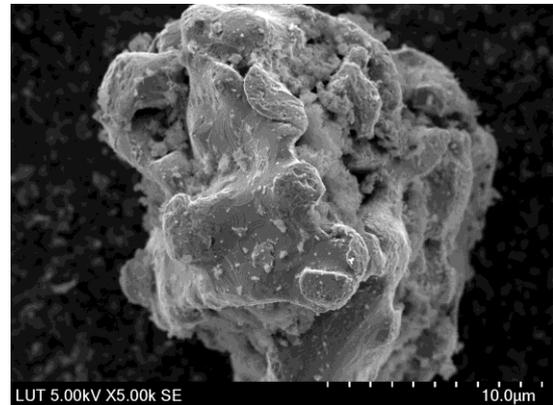
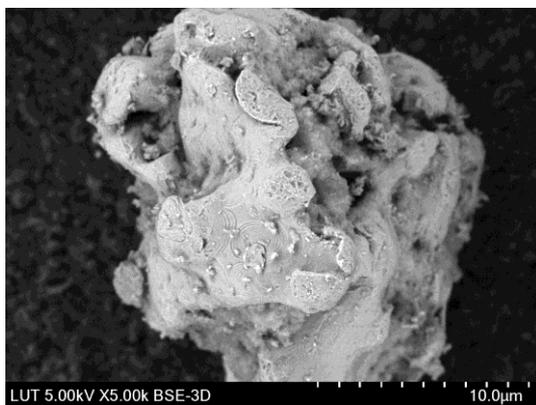
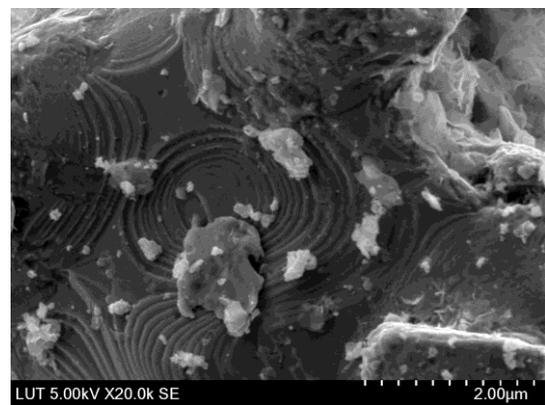
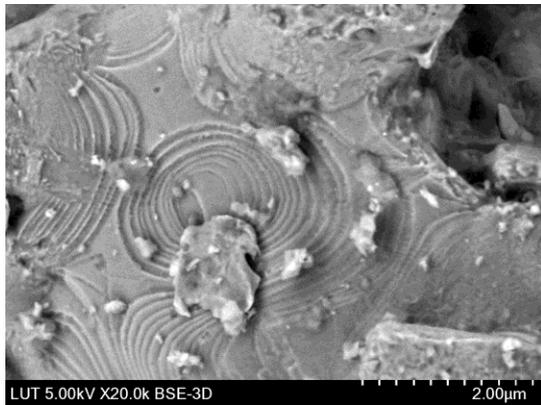
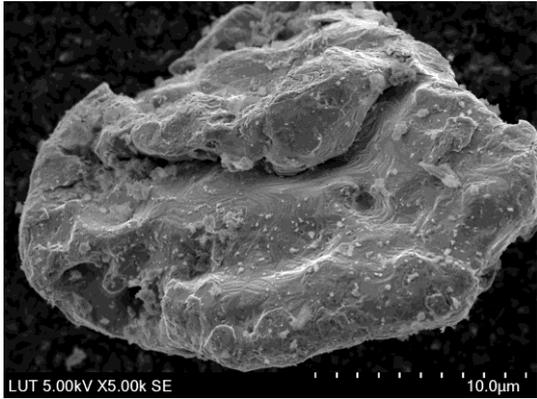
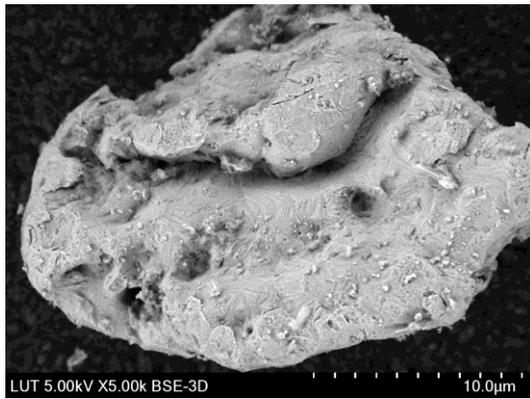
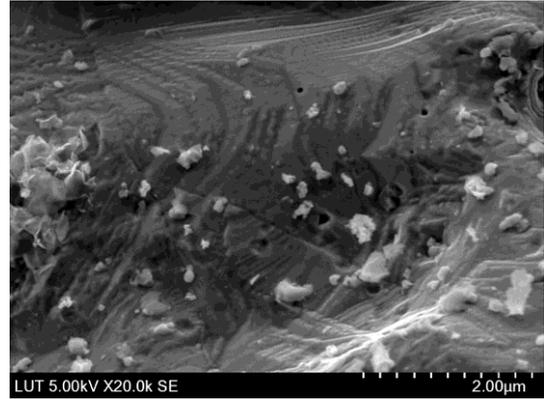
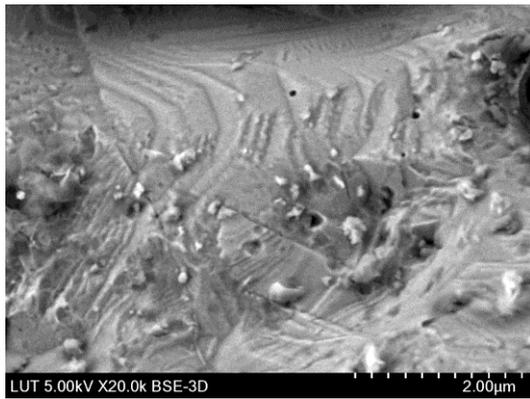
Appendix 3. SEM images of iron oxide waste particles before reaction



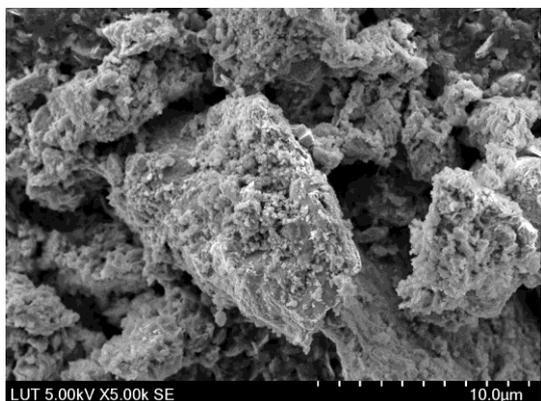
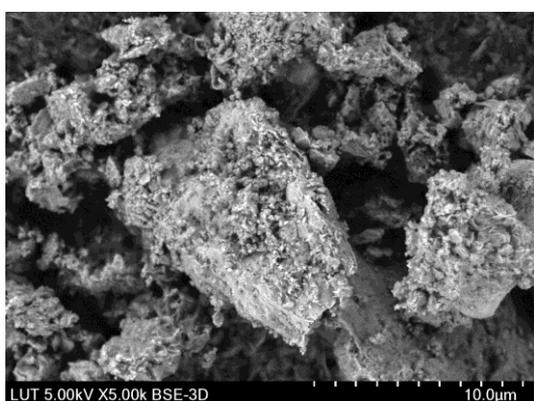
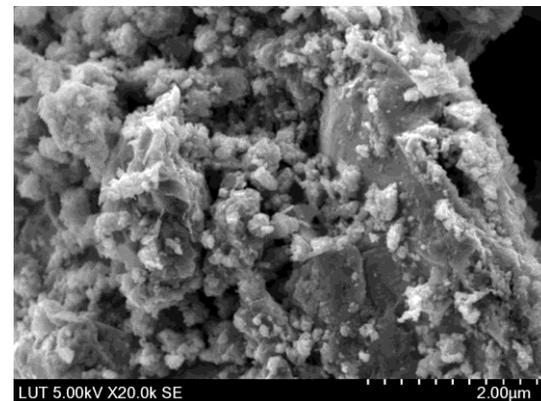
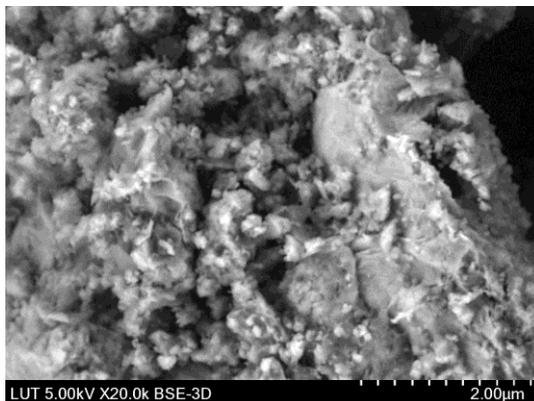
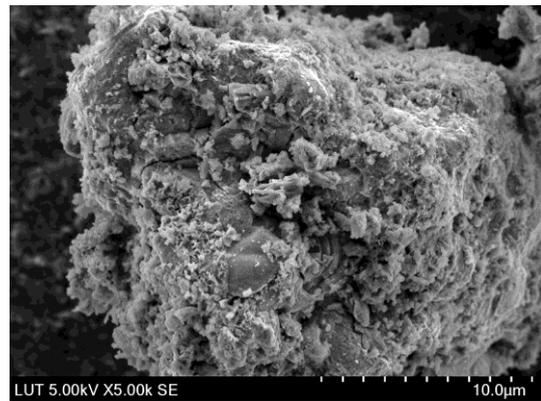
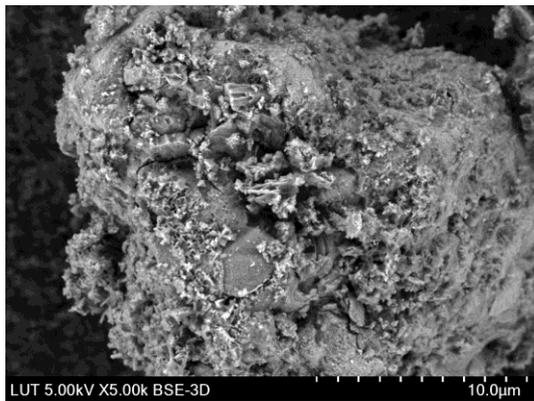
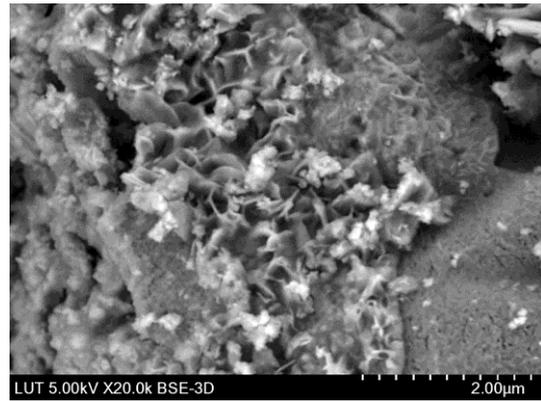
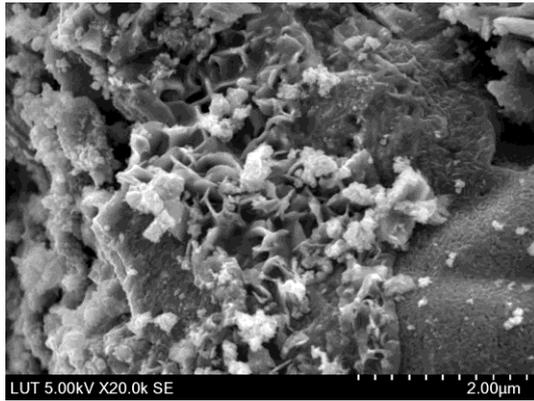
Appendix 4. SEM images of iron oxide waste particles after 5 hours reaction



Appendix 5. SEM images of ZVI particles after H₂O₂ addition (1 hour)



Appendix 6. SEM images of ZVI surface after 5 hour reaction



Appendix 7. Sample results of synthetic water tests at pH 5

Certificate

1/2

Project: 1510021208/32

Lappeenranta University of Technology
LUT Chemtech, Laboratory of Green Chemistry

Sammonkatu 12
50130 MIKKELI

Sample information:	LUT Chemtech, Laboratory of Green Chemistry, samples		
Reference:	Sixing Cao	Date of sampling:	
		Date of arrival:	23.10.2015
Sampling by:		Research started:	23.10.2015

Water analyce

	SS520	SM540	SM560	SM580	SM5100	Unit	Method	
Sampling point	15SL	15SL	15SL	15SL	15SL			
Sample ID	08134	08135	08136	08137	08138			
ANALYSIS								
Nitrate (NO3)					31	mg/l	RA2035*	L
Nitrate (NO3)	140	120	82	45		mg/l	RA2087*	L
Nitrite (NO2)	0,16	0,090	<0,050	<0,050	<0,050	mg/l	RA2035*	L
Ammonium (NH4)	2,5	4,8	14	22	33	mg/l	RA2046*	L

Water analyce

	SM5120	SM5140	SM5160	SM5180	SM5200	Unit	Method	
Sampling point	15SL	15SL	15SL	15SL	15SL			
Sample ID	08139	08140	08141	08142	08143			
ANALYSIS								
Nitrate (NO3)	3,5	<0,90	<0,90	<0,90	<0,90	mg/l	RA2035*	L
Nitrate (NO3)						mg/l	RA2087*	L
Nitrite (NO2)	0,087	<0,050	<0,050	<0,050	<0,050	mg/l	RA2035*	L
Ammonium (NH4)	43	44	43	44	43	mg/l	RA2046*	L

Water analyce

	SM5220	SM5240	SM5260	SM5280	SM5300	Unit	Method	
Sampling point	15SL	15SL	15SL	15SL	15SL			
Sample ID	08144	08145	08146	08147	08148			
ANALYSIS								
Nitrate (NO3)	<0,90	<0,90	<0,90	<0,90	<0,90	mg/l	RA2035*	L
Nitrate (NO3)						mg/l	RA2087*	L
Nitrite (NO2)	<0,050	<0,050	<0,050	<0,050	<0,050	mg/l	RA2035*	L
Ammonium (NH4)	43	35	34	33	33	mg/l	RA2046*	L

The results apply solely to the samples analyzed. The certificate may only be copied as whole.

Certificate

Project: 1510021208/20

Lappeenranta University of Technology
LUT Chemtech, Laboratory of Green Chemistry

Sammonkatu 12
50130 MIKKELI

Sample information:	LUT Chemtech, Laboratory of Green Chemistry, samples		
	Date of sampling:		
	Date of arrival:	5.10.2015	
Sampling by:	Research started:	5.10.2015	

Water analyce

	SM620	SM640	SM660	SM680	SM6100	Unit	Method	
Sampling point	SM620	SM640	SM660	SM680	SM6100			
Sample ID	15SL 07314	15SL 07315	15SL 07316	15SL 07317	15SL 07318			
ANALYSIS								
Nitrate (NO3)						mg/l	RA2035*	L
Nitrate (NO3)	130	130	120	90	50	mg/l	RA2087*	L
Nitrite (NO2)	0,51	1,4	0,69	0,98	0,34	mg/l	RA2035*	L
Ammonium (NH4)	0,32	1,4	3,7	8,2	19	mg/l	RA2046*	L

Water analyce

	SM6120	SM6140	SM6160	SM6180	SM6200	Unit	Method	
Sampling point	SM6120	SM6140	SM6160	SM6180	SM6200			
Sample ID	15SL 07319	15SL 07320	15SL 07321	15SL 07322	15SL 07323			
ANALYSIS								
Nitrate (NO3)	30	4,7	<0,90	<0,90	<0,90	mg/l	RA2035*	L
Nitrate (NO3)						mg/l	RA2087*	L
Nitrite (NO2)	0,22	0,44	<0,050	<0,050	<0,050	mg/l	RA2035*	L
Ammonium (NH4)	29	36	39	38	37	mg/l	RA2046*	L

Water analyce

	SM6220	SM6240	SM6260	SM6280	SM6300	Unit	Method	
Sampling point	SM6220	SM6240	SM6260	SM6280	SM6300			
Sample ID	15SL 07324	15SL 07325	15SL 07326	15SL 07327	15SL 07328			
ANALYSIS								
Nitrate (NO3)	<0,90	<0,90	<0,90	<0,90	<0,90	mg/l	RA2035*	L
Nitrate (NO3)						mg/l	RA2087*	L
Nitrite (NO2)	<0,050	<0,050	<0,050	<0,050	<0,050	mg/l	RA2035*	L
Ammonium (NH4)	37	37	37	36	37	mg/l	RA2046*	L

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Certificate

Project: 1510021208/38

Lappeenranta University of Technology
LUT Chemtech, Laboratory of Green Chemistry

Sammonkatu 12
50130 MIKKELI

Sample information:	LUT Chemtech, Laboratory of Green Chemistry, samples		
Reference:	Sixing Cao	Date of sampling:	
		Date of arrival:	5.11.2015
Sampling by:		Research started:	5.11.2015

Water analyce

	FA620	FA640	FA660	FA680	FA6100	Unit	Method	
Sampling point	15SL	15SL	15SL	15SL	15SL			
Sample ID	08745	08746	08747	08748	08749			
ANALYSIS								
Nitrate (NO3)	180	160	160	150	120	mg/l	RA2087*	L
Nitrite (NO2)	1,4	1,9	0,45	1,5	2,6	mg/l	RA2035*	L
Ammonium (NH4)	1,5	2,6	4,1	5,6	8,0	mg/l	RA2046*	L

Water analyce

	FA6120	FA6140	FA6160	FA6180	Unit	Method	
Sampling point	15SL	15SL	15SL	15SL			
Sample ID	08750	08751	08752	08753			
ANALYSIS							
Nitrate (NO3)	100	84	63	44	mg/l	RA2087*	L
Nitrite (NO2)	2,4	0,56	0,18	0,065	mg/l	RA2035*	L
Ammonium (NH4)	13	17	24	26	mg/l	RA2046*	L

* Method is accredited by the FINAS. Uncertainty of measurement is reported if requested.

Ramboll Analytics



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www.ramboll-analytics.fi
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FINAS
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T038 (EN ISO/IEC 17025)

Certificate

Project: 1510021208/60

Lappeenranta University of Technology
LUT Chemtech, Laboratory of Green Chemistry

Sammonkatu 12
50130 MIKKELI

Sample information:	LUT Chemtech, Laboratory of Green Chemistry, samples		
	Date of sampling:		
	Date of arrival:	18.11.2015	
Sampling by:	Research started:	18.11.2015	

Water analyce

	HA620	HA640	HA660	HA680	HA6100	Unit	Method	
Sampling point								
Sample ID	15SL 09404	15SL 09405	15SL 09406	15SL 09407	15SL 09408			
ANALYSIS								
Nitrate (NO ₃)						mg/l	RA2035*	L
Nitrate (NO ₃)	160	150	130	78	42	mg/l	RA2087*	L
Nitrite (NO ₂)	2,0	2,6	0,60	0,071	<0,050	mg/l	RA2035*	L
Ammonium (NH ₄)	2,9	5,1	9,9	20	33	mg/l	RA2046*	L

Water analyce

	HA6120	HA6140	HA6160	HA6180	Unit	Method	
Sampling point							
Sample ID	15SL 09409	15SL 09410	15SL 09411	15SL 09412			
ANALYSIS							
Nitrate (NO ₃)	12	1,1	<0,90	<0,90	mg/l	RA2035*	L
Nitrate (NO ₃)					mg/l	RA2087*	L
Nitrite (NO ₂)	0,080	<0,050	<0,050	<0,050	mg/l	RA2035*	L
Ammonium (NH ₄)	45	51	51	51	mg/l	RA2046*	L

* Method is accredited by the FINAS. Uncertainty of measurement is reported if requested.

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Certificate

Project: 1510021208/70

Water analyce

	WF620	WFT640	WF660	WF680	WF6100	Unit	Method	
Sampling point	WF620	WFT640	WF660	WF680	WF6100			
Sample ID	15SL 10458	15SL 10459	15SL 10460	15SL 10461	15SL 10462			
ANALYSIS								
Nitrate (NO3)					16	mg/l	RA2035*	L
Nitrate (NO3)	160	130	100	50		mg/l	RA2087*	L
Nitrite (NO2)	1,2	0,11	<0,050	<0,050	<0,050	mg/l	RA2035*	L
Ammonium (NH4)	2,5	6,6	14	26	45	mg/l	RA2046*	L

Water analyce

	WF6120	WF6140	WF6160	WF6180	WF6200	Unit	Method	
Sampling point	WF6120	WF6140	WF6160	WF6180	WF6200			
Sample ID	15SL 10463	15SL 10464	15SL 10465	15SL 10466	15SL 10467			
ANALYSIS								
Nitrate (NO3)	1,1	0,95	<0,90	<0,90	<0,90	mg/l	RA2035*	L
Nitrate (NO3)						mg/l	RA2087*	L
Nitrite (NO2)	<0,050	<0,050	<0,050	<0,050	<0,050	mg/l	RA2035*	L
Ammonium (NH4)	42	48	37	48	35	mg/l	RA2046*	L

Water analyce

	WF6220	WF6240	WF6260	WF6280	WF6300	Unit	Method	
Sampling point	WF6220	WF6240	WF6260	WF6280	WF6300			
Sample ID	15SL 10468	15SL 10469	15SL 10470	15SL 10471	15SL 10472			
ANALYSIS								
Nitrate (NO3)	<0,90	<0,90	<0,90	<0,90	<0,90	mg/l	RA2035*	L
Nitrate (NO3)						mg/l	RA2087*	L
Nitrite (NO2)	<0,050	<0,050	<0,050	<0,050	<0,050	mg/l	RA2035*	L
Ammonium (NH4)	49	48	48	47	46	mg/l	RA2046*	L

* Method is accredited by the FINAS. Uncertainty of measurement is reported if requested.

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FINAS
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Certificate

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Project: 1510021208/68

Water analyce

	W620	W640	W660	W680	W6100	Unit	Method	
Sampling point	15SL	15SL	15SL	15SL	15SL			
Sample ID	10402	10403	10404	10405	10406			
ANALYSIS								
Nitrate (NO3)						mg/l	RA2035*	L
Nitrate (NO3)	190	190	190	190	200	mg/l	RA2087*	L
Nitrite (NO2)	0,50	0,77	1,3	1,3	1,3	mg/l	RA2035*	L
Ammonium (NH4)	0,57	0,54	0,45	0,48	0,41	mg/l	RA2046*	L

Water analyce

	W6120	W6140	W6160	W6180	W6200	Unit	Method	
Sampling point	15SL	15SL	15SL	15SL	15SL			
Sample ID	10407	10408	10409	10410	10411			
ANALYSIS								
Nitrate (NO3)		180				mg/l	RA2035*	L
Nitrate (NO3)	200		200	200	200	mg/l	RA2087*	L
Nitrite (NO2)	0,97	0,97	0,97	0,92	0,99	mg/l	RA2035*	L
Ammonium (NH4)	0,48	0,49	0,48	0,48	0,49	mg/l	RA2046*	L

Water analyce

	W6220	W6240	W6260	W6280	W6300	Unit	Method	
Sampling point	15SL	15SL	15SL	15SL	15SL			
Sample ID	10412	10413	10414	10415	10416			
ANALYSIS								
Nitrate (NO3)						mg/l	RA2035*	L
Nitrate (NO3)	200	200	200	200	200	mg/l	RA2087*	L
Nitrite (NO2)	1,0	1,1	0,97	1,0	0,98	mg/l	RA2035*	L
Ammonium (NH4)	0,49	0,48	0,46	0,51	0,47	mg/l	RA2046*	L

* Method is accredited by the FINAS. Uncertainty of measurement is reported if requested.

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