Systems for ammonium concentration for further removal in the partial nitritation/anammox technology

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SUMMARY IN SWEDISH

Anammox är en av de viktigaste processer för att avlägsna ammonium från avloppsvatten som upptäckts ganska nyligen. Anammoxprocessen är kostnadseffektiv med lågt energibehov och inget behov av kolkälla. Partiell nitritation är en förutsättning för avloppsrening med anammox för avlägsnande av kväve och tekniken med partiell nitritation/Anammox studeras och tillämpas i full skala. Men tekniken kan för närvarande endast användas för att behandla strömmar med höga ammoniumhalter. Tillämpning av Anammox för behandling av avloppsvatten med låg ammoniumhalt är inte möjligt på grund av låg tillväxt av Anammoxbakterier. Studien syftar till att utforma strategier för att använda Anammoxtekniken för att behandla avloppsvattenströmmar med låg koncentration av ammoniumkväve. Målet var att få system som kan koncentrera ammonium från strömmar med låg ammoniumhalt, för att kunna behandla den med partiell nitritation/Anammoxprocess.

I studien har två metoder använts för att koncentrera ammonium: jonbyte och omvänd osmos. I jonbytesexperiment gick UASB-utflödet genom en starkt surt katjon-hartskolonn, som regenererades med 10 g / l NaCI för att utvinna koncentraten. Tre olika cykler av jonbytesexperimentet utfördes med initiala koncentrationer av ammoniumkväve på 40, 38 och 22 mg / liter. Tre koncentrat med olika NH_4-N koncentrationer erhölls från jonbytescyklerna. Enheten för omvänd osmos drevs med en volymreduktionsfaktor på upp till 5. Det erhållna RO-koncentratet delades in i tre olika satser för kväverening. Koncentraten från både IE och RO försöken kväverenades med ensteg partiell nitritation / anammoxteknik

Jonbytesmetod användes för att koncentrera UASB utflöden av 24 – 40 mg NH_4-N / l till 188 till 367 mg NH_4-N / l respektive, vilket är ca 9 gånger. Med RO erhölls vid VRF 5 ett koncentrat på 163 mg NH_4-N / l från 42 mg NH_4-N / l. Resultaten visade också att koncentrat från bägge metoderna kan behandlas med partiell nitritation / Anammoxteknik. Men det tog mer än 32 timmar att behandla jonbyteskoncentrat medan det tog mindre än 24 timmar att slutföra partiell nitritation / Anammoxprocess RO-koncentrat. Den längre tiden kan bero på hög salthaltkoncentration som är ett resultat av att NaCl användes för regenerering i jonbytesprocessen. Både jonbyte och omvänd osmos är användbara metoder för att koncentrera ammonium från UASB-utflödet. Löst syre var en mycket viktig faktor som påverkade den biologiska processen eftersom både anaeroba och aeroba processer sker i samma reaktor. DO på ~ 1 mg / l är optimalt för den ensteg partiella nitritation / Anammoxprocessen.

SUMMARY IN ENGLISH

Anammox is one of the main processes discovered quite recently for removal of ammonium from wastewater. Anammox process is cost effective in that low energy and no carbon source is needed. Partial nitritation is a perquisite for anammox in wastewater treatment for removal of nitrogen and therefore partial nitritation/Anammox technology is studied substantially and applied in full-scale. However the technology at present can only be used to treat high rich ammonium streams. Application of Anammox for treatment of low ammonium wastewater is not possible because of low yield of Anammox bacteria. The study aimed at devising strategies for using the Anammox technology to treat wastewater streams with low concentration of ammonium nitrogen. The objective was to design systems that could concentrate ammonium from low ammonium waste streams, so as to be able to treat it with partial nitritation/Anammox process.

In the study, two methods were used to concentrate ammonium: ion exchange and reverse osmosis. In the ion exchange experiment, strong acid cation resin column was exhausted with UASB effluent after which it was regenerated with 10 g/l NaCl to get the concentrates. Three different cycles of the ion exchange experiment were carried out with initial ammonium nitrogen concentrations of 40, 38 and 22 mg/l. Three concentrates with different NH_4-N concentrations were obtained from each of the ion exchange cycles. The reverse osmosis unit was operated up to a volume reduction factor 5. The RO concentrate obtained was divided into three different batches for nitrogen removal treatment. The concentrates from both the IE and RO experiments were treated for nitrogen removal using a single stage partial nitritation/ anammox technology

Ion exchange method was used to concentrate UASB effluents of 24 - 40 mg NH_4-N/l to 188 – 367 mg NH_4-N/l respectively which is about 9 times. At VRF 5 163 mg NH_4-N/l concentrate was attained from 42 mg NH_4-N/l RO feed. Results also showed that concentrates from both methods are able to be treated with partial nitritation/Anammox technology. However it took more than 32 hours to complete treatment of ion exchange concentrates while it took less than 24 hours to finish the partial nitritation/Anammox process of RO concentrates. The longer time taken can be attributed to high salinity of the concentrates which is as a result of NaCl which was used for regeneration in ion exchange process. Both ion exchange and reverse osmosis are viable methods for concentrating ammonium from UASB effluents Dissolved oxygen was very important factor that influenced the biological process since both anaerobic and aerobic processes were taken place in the same reactor. DO of ~1 mg/l is optimal for a single stage partial nitritation anammox process.

ACKNOWLEDGEMENTS

ACRONYMS AND ABBREVIATIONS

Anammox	Anaerobic ammonium oxidation
AOB	Ammonium-oxidizing bacteria
BV	Bed volume
B1	Batch one
B2	Batch two
B3	Batch three
COD	Chemical oxygen demand
C1	Cycle one
C2	Cycle two
C3	Cycle three
DO	Dissolved oxygen
F : M	Food to microorganism ratio
FIA	Flow injection analysis
IAEA	International atomic energy agency
IE	Ion exchange
IVL	Swedish Environmental Research Institute
MBBR	Moving bed bioreactor
N_2	Nitrogen gas
NaCl	Sodium chloride
NH_4-N	Ammonium nitrogen
NO_2-N	Nitrogen in nitrite form
NO_3-N	Nitrogen in nitrate form
RO	Reverse osmosis
SAC	Strong acid cation
UASB	Upflow anaerobic sludge blanket
VRF	volume reduction factor
WWTP	Municipal wastewater treatment plant

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ABSTRACT

Anammox is one of the main processes discovered quite recently for removal of ammonium from wastewater. Anammox process is cost effective, in that low energy and carbon source is needed. Partial nitritation is a perquisite for anammox in wastewater treatment for removal nitrogen and therefore partial nitritation/Anammox technology is studied substantially and applied in full-scale. However, the technology at present can only be used to treat high rich ammonium streams. Application of Anammox for treatment of low ammonium wastewater is not possible because of low yield of Anammox bacteria. The study aimed at devising strategies for using the Anammox technology to treat wastewater streams with low concentration of ammonium nitrogen. The objective was to get systems that could concentrate ammonium from low ammonium waste streams, so as to be able to treat it with partial nitritation/Anammox process. Two methods were used to concentrate ammonium: ion exchange and reverse osmosis. Ion exchange method was used to concentrate UASB effluents of about 24 - 40 mg NH_4-N/l to 188 - 367 mg NH_4-N/l respectively which is about 9 times the initial concentrations. At VRF 5, 163 mg NH_4-N/l concentrate was attained from 41.8 mg NH_4-N/l RO feed. Results also showed that concentrates from both methods are able to be treated with partial nitritation/Anammox technology. However it took more than 32 hours to complete treatment of ion exchange concentrates while it took less than 24 hours to finish the partial nitritation/Anammox process of RO concentrates. The longer time taken can be attributed to high salinity of the concentrates which is as a result of NaCl which was used for regeneration in ion exchange process. Both ion exchange and reverse osmosis are viable methods for concentrating ammonium from UASB effluents. Dissolved oxygen was very important factor that influenced the biological process.

Key words: Ammonium, Anammox, conductivity, dissolved oxygen, ion-exchange, nitrogen, partial nitritation, regeneration, reverse osmosis.

1. INTRODUCTION

Nitrogen is one of the major nutrients that can pose danger to the natural environment if not dispose properly. Nitrogen compounds can adversely affect human health and may also affect quality lakes and other water bodies. Nitrogen and phosphorus are the main causes of eutrophication of surface waters and marine systems. In view of this, strict environmental regulations are instituted to regulate the amount release into the environment by industries and municipal wastewater treatment plants. Several physiochemical and biological methods used to remove nitrogen from wastewater before discharge into the environment. In the conventional nitrification/dentrification process for instance, there is requirement of external carbon source and high energy for aeration in order to complete the nitrogen removal process. This makes such a biological process less cost-effective (Seyfried et al., 2001). Research has been underway since 1960s and 70s until recent discovery of the cost effective ANaerobic AMMonium OXidation (Anammox) process (van der Star, 2008). Ammonium is a major component of influent nitrogen in the wastewater stream. Anammox is one of the main biotechnologies discovered quite recently for removal of ammonium

from wastewater. In the anammox process, nitrite and ammonium are converted directly into dinitrogen gas. Nitritation of ammonium is prerequisite for an anammox process (Seyfried et al., 2001). Anammox process is cost effective in that low energy and carbon source is needed.

Anammox process coupled with partial nitritation has been studied extensively and applied in several applications. Anammox process has been successful for the treatment of ammonium-rich wastewaters such as sludge reject water and animal wastewaters (Fux & Siegrist, 2004; Joss et al, 2009; Yamamoto et al, 2006). However, at the present this process is limited to few types of wastewaters with high concentration of ammonium (Zhang et al., 2008). Several studies indicate that anammox process is restricted to high ammonium-rich effluents with low carbon-nitrogen ratio. The traditional nitrification/denitrification and methods other than anammox are used for nitrogen removal in treating influent from primary sedimentation of a municipal wastewater treatment plant (WWTP) with low ammonium concentration. The use of anammox technology for the treatment of low ammonium wastewater has not been successful because of biomass washout. In literatures, nitritation/anammox technology is not feasible for treating wastewater with NH_4-N concentration below 100mg/l (Mulder 2003). There is therefore a need for strategy to overcome this limitation so in order to be able to use anammox for the treatment of wastewater with low ammonium concentration.

Concentrating ammonium in a wastewater stream before nitrogen removal stage could be a good approach to use partial nitritation/anammox process to treat low ammonium influent. Ion exchange and reverse osmosis are among the few methods that are used to concentrate nutrients (Ek et al., 2006; Kieniewicz 2006; Bergström et al., 2006). With either of these systems, it is possible to concentrate ammonium in low ammonium wastewater streams such as effluents from primary sedimentation stage and upflow anaerobic sludge blanket reactor (UASB) reactor treating municipal wastewater. The concentrated effluent can further be treated for nitrogen removal through partial nitritation/Anammox process. The perspective technology gives possibility of efficient ammonium removal with lower energy consumption and without external carbon addition.

1.1. Biological nitrogen removal

In recent years, a number of innovative approaches to biological treatment of wastewater stream for nitrogen removal have been developed. Biological methods of removing nitrogen from wastewater are the preferred option to chemical methods due to its minimal impact on the environment and its less cost. Biological nitrogen removal is the most efficient way to eliminate nitrogen from the wastewater (Ekström, 2010). The main components of influent nitrogen into WWTP include ammonia (Ammonium), nitrate, particulate organic nitrogen, and soluble organic nitrogen.

1.1.1. *Nitrification/Denitrification*

The conventional biological way of primarily removing nitrogen from wastewater is nitrification/denitrification process. This process has long been applied in municipal wastewater treatment (Breisha & Winter, 2010). Ammonium nitrogen is the major form of nitrogen in a wastewater stream because most of the nitrogen components aforementioned are hydrolysed from organic nitrogen to ammonia /ammonium through the process of ammonification.

Nitrification process is conversion of ammonium to nitrate. This process is an aerobic and therefore requires oxygen. Nitrification is a two-step process that requires microorganisms at each stage. The first stage is nitritation stage where ammonium in the wastewater stream is converted to nitrite.

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad\quad (1)$$
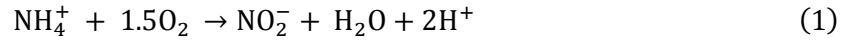
This stage is carried out mainly by ammonia oxidizing bacteria known as Nitrosomonas. Nevertheless, other bacteria like Nitrosococcus, Nitrosopira, Nitrosovibrio and Nitrosolobus are also capable of oxidizing ammonium to nitrite. These are found in the beta subdivision of Proteobacteria (Breisha & Winter 2010). The nitrite form is then oxidised to nitrate in a process called nitratation.

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \quad\quad (2)$$

Nitrobacters are the common group of autotrophic bacteria that is involved in the second stage of the nitrification process. Several other genera such as Nitrospira, Nitrospina, Nitrococcus, and Nitrocystis are also known to be involved in the nitrite oxidation process. The complete nitrification that may occur during wastewater treatment for nitrogen removal can be expressed as:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad\quad (3)$$

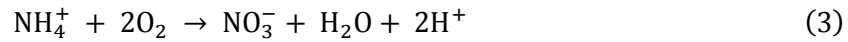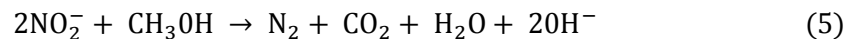As it can be noticed from equation (3), during nitrification process alkalinity is consumed which lowers the pH of the wastewater. The lower pH in the stream can affect the biological nitrogen removal process by causing reduction in growth of the nitrifying bacteria. The optimum pH for Nitrisomonas and Nitrobacter is between 7.5 and 8.5 (Breisha & Winter, 2010). Alkalinity is therefore required for the nitrification reaction to ensure adequate buffering. The Nitrification process also requires a low food to microorganism ratio (F : M), a long retention time, and a high mean cell residence time or Sludge Age.

There is subsequent process of denitrification after the nitrification process that occurs when no oxygen is available and nitrate becomes the primary oxygen source for microorganisms. The oxidized nitrogen compounds (NO_2^- and NO_3^-) are reduced to gaseous nitrogen by microorganisms. Denitrification occurs in the absence of oxygen. Organic matter is also used as a carbon and energy source. In the denitrification process, both heterotrophic and autotrophic bacteria are involved. The most common and widely distributed denitrifying bacteria are Gram-negative bacteria *Pseudomonas, Alcaligenes*, *Paracoccus*, and *Thiobacillus* (Breisha and Winter, 2010). The denitrifying bacteria usually need a carbon source as food for survival. The bacteria break apart the nitrate to gain oxygen, nitrate (NO_3^-) is reduced to nitrite (NO_2^-) and eventually to nitrogen gas which escapes to the atmosphere.

$$3NO_3^- + CH_3OH \rightarrow 3NO_2^- + CO_2 + 2H_2O \quad\quad (4)$$

$$2NO_2^- + CH_3OH \rightarrow N_2 + CO_2 + H_2O + 2OH^- \quad\quad (5)$$
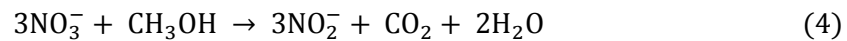
The overall denitrification reaction with methanol as carbon source is given as follows:

$$6NO_3^- + 5CH_3OH \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^- \quad\quad (6)$$
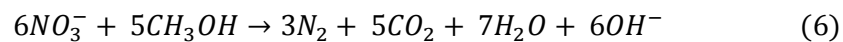
1.1.2. *Partial Nitritation/Anammox*

Since its discovery in the 1990s, anaerobic ammonium oxidation process has been used in many applications for the treatment of wastewater of high ammonium concentration. Ammonium is a predominant

Figure 1: Metabolic pathway of the anammox process (Breisha & Winter, 2010).

component of influent nitrogen. However, in order to remove nitrogen from wastewater by anammox process, there suppose to be proper nitrite-ammonium ratio. Partial aerobic oxidation of ammonium to nitrite is therefore strictly required to precede an anammox process (Szatkowska et al., 2007). In the partial nitritation/anammox process, about half of ammonium is therefore oxidised to nitrite by autotrophic bacteria. At the partial nitritation stage only about 50 % of th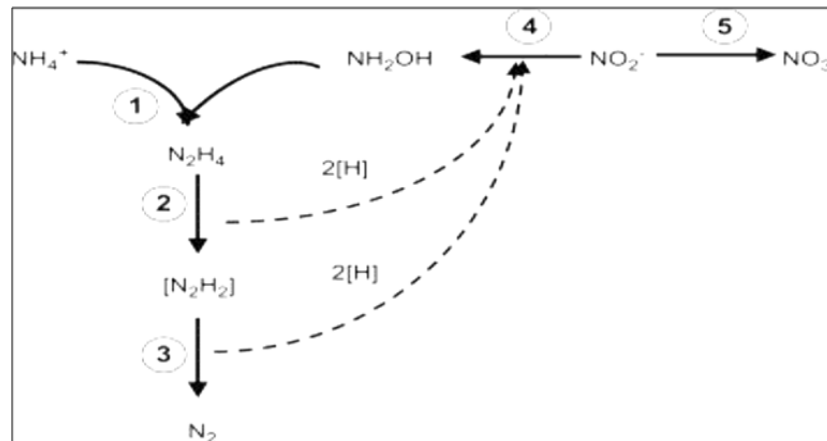e ammonium is oxidised. The partial nitritation is possible because in the middle way through the process the alkalinity in the system is already consumed leading to a drop in pH which prevent any further nitrification (Jetten et al., 2001). *Nitrosomonas*-like aerobic ammonium-oxidizing bacteria (AOB) are responsible for the partial nitritation process. The reaction for the partial nitritation stage of the process is as follows:

$$2NH_4^+ + 1.5O_2 + 2HCO_3^- \rightarrow NH_4^+ + NO_2^- + 2CO_2 + 3H_2O \quad (7)$$
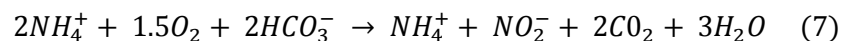
The nitrite that is formed together with the remaining ammonium is then converted by anammox bacteria to dinitrogen and small amount of nitrate. Breisha & Winter (2010) indicated that the nitrite is temporarily reduced to hydroxylamine and the hydroxylamine then reacts with the electron donor ammonium to form hydrazine. The hydrazine is later converted to dinitrogen gas (Fig. 1). According to Jetten et al. (2001), the oxidation of hydrazine to dinitrogen gas produces the electrons for the initial reduction of nitrite to hydroxylamine. The formation of hydrazine is as intermediate to the final reaction (Kartal et al., 2010).

The process occurs under anaerobic condition with nitrite as an electron acceptor. The overall reaction involved is as follows:

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 2.03H_2O + 0.26NO_3^- + 0.066CH_2O_{0.5}N_{0.15} \qquad (8)$$
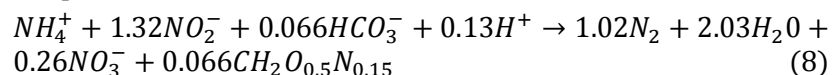
The bacteria species responsible for the anammox process are gram-negative which belong to the group of the *Planctomycetales*. The anammox bacteria contain anammoxosome, a membrane-bound organelle in which ammonium and nitrite are converted to nitrogen gas (Jetten et al., 1999. There are many species of Anammox bacteria. Generally, there are 3 main Anammox genera: *Brocadia*, *Kuenenia* and *Scalindua*. Other species such as *Candidatus Anammoxoglobus propionicus* also exist (van Hulle et al., 2010).

Factors affecting partial nitration/Anammox process

Like all biological processes, certain conditions need to prevail in order for the partial nitration/anammox process to occur. Microorganisms responsible for the process can work only under certain conditions which favour their growth are appropriate for the process. Parameters such as dissolved oxygen, pH and temperature are critical to the survival of AOBs and anammox bacteria.

- *Dissolved Oxygen*: The amount of oxygen that is dissolved in a nitration/anammox system is very crucial since two different kinds of bacteria are involved in the process. One kind of bacteria- AOB strictly requires oxygen for metabolic activities and the other-anammox bacteria work under anaerobic conditions. In this case, lack of oxygen in the system inhibits the activities of AOBs whereas too much oxygen may undermine the survival of anammox bacteria. AOBs utilize oxygen at the partial nitration stage to oxidise part of ammonium to nitrite (equation (7)). According to Liang & Liu (2007), DO concentration of 0.8–2.3 mg/L is suitable for maintaining the growth of nitrifying bacteria at the partial nitration stage of the process. Meanwhile, study by Kimura et al. (2011) showed that DO concentration more than 2.5 mg/L can inhibit the activities of Anammox bacteria. Bertino (2011) concluded that dissolved oxygen is a key parameter for ensuring optimal performance of a nitration/anammox process, and indicated again that DO concentration of 1.5-1.6 mg/L is optimum for such system. In partial nitration/anammox system, both lower and higher DO's can inhibit the process. It is therefore very important to monitor and control the amount of dissolved oxygen continuously.

- *Temperature;* like dissolved oxygen, is an important parameter in every biological process. Temperature affects the metabolic activities of microorganisms. As shown by Liang and Lui (2006), partial nitration process rate increases with the increase of temperature (20–30 °C), but started to decrease at a temperature of 35 °C. However, a review by Breisha & Winter (2010) reported that high temperature of 28–38 °C is favourable for nitrogen removal via nitrite. They reported that it is favourable to start nitration with high temperatures and a gradually decline to room temperatures.

- *pH;* is also an important parameter that affects the partial nitration/Anammox process. In the partial nitration stage, pH has an influence on the NH_4^+/NH_3^{-1} and HNO_2/NO^{-1} equilibria (van Hulle et al., 2010). pH also have direct effect on activities of bacteria responsible for the process. pH between 7 and 8 is optimum for partial nitration process, however the Anammox process has optimal pH interval of 6.7–8.3 with an optimum of 8.0 (Strous et al., 1999).

Anammox configurations

Basically, there are two main configuration of partial nitration/anammox process:

- *A two-stage configuration-* with this type of configuration, the partial nitration stage where about fifty percent of ammonium in the wastewater is oxidised to nitrite (NO_2^-) occurs in an aerated reactor, after which the anammox process take place in a

second bioreactor where the remaining NH₄-N and the nitrite are converted to N₂ under anaerobic conditions.

- *A single-stage configuration* - here, both the partial nitritation and anammox take place in the same reactor. In this configuration, the nitritation takes place on the outer layer of granular on moving beds within the reactor while the anammox process takes place in the anaerobic zone deeper within the beds. Intermittent supply of oxygen to the reactor is also a possible way achieving both nitritation and anammox process in a single reactor.

1.2. Systems for Concentrating Ammonium

Ammonium has been concentrated in various instances in wastewater treatment process. Nutrients are concentrated in wastewater treatment process mainly for agricultural use. In some few instances, efforts are been made to pre-concentrate compounds before further removal from the wastewater stream. Bergström et al., (2006) investigated various methods for concentrating of nutrients from urine and reject from digestion of sludge. In their work they compare various methods including reverse osmosis, evaporation, precipitation and distillation. Moreover other methods have been used to remove ammonium directly from wastewater. These systems can therefore serve as a way of concentrating ammonium for biological nitrogen removal.

1.2.1. *Ion exchange*

Ion exchange (IE) is one of the well known chemical-physical method of nitrogen removal from wastewater. The ion exchange technology has been studied detailed in many researches for removing ammonium from wastewater (Thornton et al., 2007; Zhang et al., 2011; Demir et al., 2002). Ion-exchange has been used as an alternative method to biological method for the removal of NH₄-N from wastewater in many instances (Rahmani & Mahvi, 2006) in a case of low organic concentration to avoid the use of external carbon source.

The term ion exchange describes a reversible process whereby ions from solution are exchanged for similarly charged ions that are electrostatically bound to the functional group contained within immobile solid particles (IAEA, 2002). When the functional groups are negatively charged the exchange will involve cations and vice versa. In nitrogen removal process in wastewater treatment the ion-exchange process normally involves the replacement of the Na^+ ion in an ion exchanger by the NH_4^+ ion. The Na^+ ion concentration in the system therefore increases in the liquid phase during the processes. The equation involve in such a reaction is as follows:

$$R - Na + NH_4^+ \rightarrow R - NH_4 + Na^+ \qquad (9)$$

where R represents the insoluble matrix of the ion exchange resin.

Ion exchangers are categorised depending on the type of functional group. This then gives the names of ion exchangers as: strong acid, strong base, weak acid and weak base. Strong acidic ion exchangers are those that contain sulpho- and phospho-acidic functional groups. Meanwhile exchangers that have tetra-ammonium basic group are strong basic exchangers. Weak acidic and weak basic exchangers contain phenolic and primary amino groups respectively. In a more complex way ion exchangers with carboxyl groups take a medium position between strong and weak acidic. Exchangers with tertiary amino groups also take a medium position between strong and weak basic exchangers. Cation exchangers have acidic functional groups whereas anion exchangers have

basic functional groups (IAEA, 2002). Usually, the materials that are practically used for ion exchange processes for ammonium removal from water and wastewater include natural zeolite, synthetic zeolite and strong acid cation resin. Previous study on materials for ion exchange revealed that strong acid cation resin has the highest ammonium exchange capacity compared to both natural and synthetic zeolites (Malovanyy et al, 2011).

Regeneration is very important step in the ion exchange process. Upflow or downflow regeneration method is applied to the set up after the ion-exchanger has reached breakthrough, thus when the ions are replaced and equilibrium state is reached. In a study involving column studies by Demir et al. (2002), solution of 20 mg/L NH_4 concentration prepared synthetically with only NH_4Cl and deionized water, was fed to ion exchange column of 0.125-1 mm natural zeolite. Having reached a breakthrough after applying about 500 BV, the IE resin was regenerated with 20 g/L NaCl solution and a concentration of about 650 mg NH_4/L was obtained. However, it should be noted that in the study the pH of the regenerate was adjusted with NaOH. The pH of the regenerate was then 12.3 and therefore to be used for biological removal it needs to be neutralized, making it very costly.

1.2.2. *Reverse Osmosis*

Reverse Osmosis (RO) is a membrane filtration process where solvent moves from a solution of greater concentration through a semi-permeable membrane to a solution of lower concentration. It is called 'reverse' because in normal osmosis phenomenon solvent passes through a membrane into a more concentrated solution. Normal osmosis process is a passive process, and therefore there is natural tendency for solvent with a low concentration of dissolved particles to move across a semi-permeable membrane to an area of solvent with a high concentration of dissolved particles. This movement of solvent (usually water) will continue until equilibrium is reached where the concentrations at both sides of the membrane are the same. The osmosis phenomenon in natural membranes was first observed by French clergyman and physicist, Jean-Antoine Nollet in 1748. Osmosis process occurs often in many natural systems. Several living cells take in water and nutrients through osmosis process. The roots of plants take up nutrients from the soil through osmosis process.

Reverse osmosis is a membrane separation technique which was discovered by University of California Los Angeles (UCLA) and the University of Florida initially for desalination of seawater using semi-permeable membranes to produced fresh water from seawater in the mid-1950s (Glater, 1998). In the process of reverse osmosis, water is forced through a semi-permeable membrane in the opposite direction of the natural osmotic flow by applying pressure to the high concentrated side of the system; leaving the dissolved particles and salt in the more highly concentrated solution. Thus reverse osmosis process can only occur when the pressure applied exceed the normal osmotic pressure. As illustrated, RO operate on a principle known as cross flow filtration (Fig. 2). Unlike the conventional filtration where entire water solution to be filtered is pumped through the filter media and all contaminants too large to pass through the pores of the membrane are trapped or retained on the surface, in cross flow filtration, two exit streams are generated – a concentrate stream containing those material which do not pass through the membrane, and the permeate stream which has been pumped through the membrane.
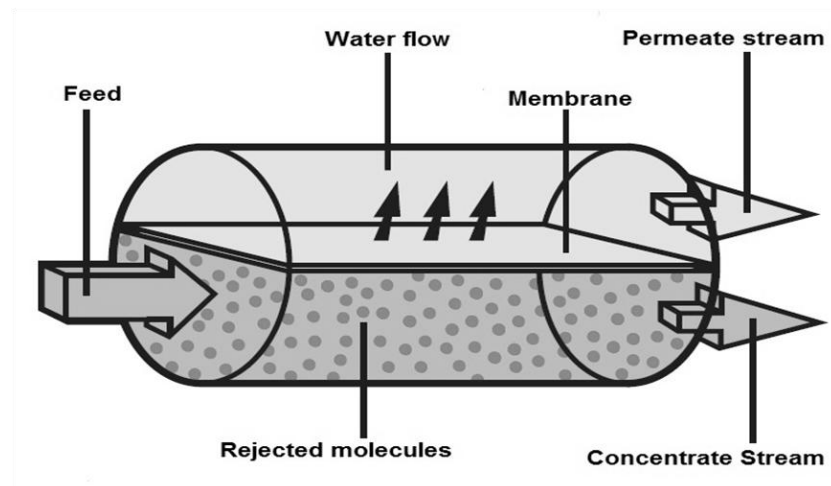
Figure 2: Schematic diagram of reverse osmosis based on the principle of cross flow filtration.

Since its inception reverse osmosis technology has been used in many applications including drinking water purification, food industry, and hydrogen production. Quite recently, reverse osmosis is been used in wastewater treatment plant for various applications. In wastewater treatment application, RO membrane process can be used to remove both inorganic and organic pollutants. RO has been used to remove contaminants such as pesticides, chemical oxygen demand (COD), heavy metals, ammonium and nitrate from wastewater (Williams, 2003). Literature on concentrating ammonia from wastewater using RO process is very scarce. Few papers are found on this topic. Reverse osmosis process has been applied in recovery of nutrients from wastewater. Ek et al. (2006) used reverse osmosis together with other process such as precipitation of phosphorus, distillation of ammonia and evaporation and drying to concentrate nutrients (nitrogen and phosphorus) from urine and reject water. They concluded that concentration with reverse of osmosis was the most cost effective process among the aforementioned methods. Even though it is general idea that RO is expensive process, they made argument from the fact that great amount of nutrient was recovered from urine. One typical work that has been used for concentrating ammonium from wastewater for further removal was done on mine wastewater with relatively low ammonium concentration. Häyrynen et al. (2009) conducted the research on actual mine water from Pahtavaara gold mine. In their research RO technology was used to concentrate ammonium and nitrate from the mine water in order to be further removed by biological nitrogen removal process. Feed of NH_4-N concentration of 9.48 mg/l was able to produce a concentrate of 104 mg NH_4-N /l. Such great performance indicates that biological nitrogen process could be applied to further remove the nitrogen.

2. AIMS AND OBJECTIVES OF THE STUDY

Anammox technology, as discussed before, will be a boom to wastewater treatment industry when applied in large scale because of it low energy and no external carbon requirements. However, as of now, there is no application of it in the mainstream of wastewater. The ultimate aim of this project was to devise strategies for using the partial

nitritation/Anammox technology to treat wastewater with low concentration of ammonium nitrogen.

This thesis work aimed at developing systems that could concentrate ammonium from low ammonium waste streams and then treated it with partial nitritation/Anammox technology to remove nitrogen. Therefore, the project sought to use ion exchange and reverse osmosis methods to concentrate ammonium from municipal wastewater after being treated in UASB reactor before applying partial nitritation/Anammox process to treat the concentrate.

The specific objectives of the work were:

- To use ion exchange method to concentrate ammonium from municipal wastewater
- To determine how the concentration of ammonium in inflow into ion exchange column affect the exchange of ammonium and operation of the system.
- To monitor the effect of initial concentration of ammonium in wastewater on the effective operation of the ion exchange system.
- To determine the possibility of applying partial nitritation/Anammox for treating regenerate from ion exchange column.
- To use reverse osmosis technology to concentrate the ammonium from low concentration wastewater and
- To further treat the RO concentrate with partial nitritation/Anammox process.
- To find out which of the two methods: IE and RO, is efficient in concentrating ammonium.
- To find out among the two methods: IE and RO, produces concentrate that can be treated conveniently for nitrogen removal using partial nitritation/Anammox process.

3. MATERIALS AND METHODS

The experiment was divided into two main parts: the concentration part and the biological part. The concentration part involves the use of ion exchange (IE) and reverse osmosis (RO) to concentrate ammonium nitrogen of effluent from UASB to make the wastewater suitable for partial nitritation/Anammox process.

3.1. IE Experiment

3.1.1. *Description of IE set-up*

In this study, concentration of ammonium nitrogen was achieved by using ion exchange column which was composed of a glass tube with an inner diameter and volume of 1cm and 28.6 cm^3 respectively. The ion exchange material used in the experiment was a synthetic strong acid cation (SAC) resin that has sulfonic acid (SO_3H) functional group fixed on cross-linked styrene-divinylbenzene matrix and therefore has a chemical behaviour similar to that of a strong acid and exhibit high cation exchange capacities. The SAC resin was of KU-2-8 type in acid form with particle size of 0.6-1.2 mm. The bed height and the weight of the resin which was filled in the column were 37 cm and 22 g respectively. Furthermore, a conductivity meter was inserted in collecting bottle to ensure continuous measurement during the exhaustion (Fig. 3).
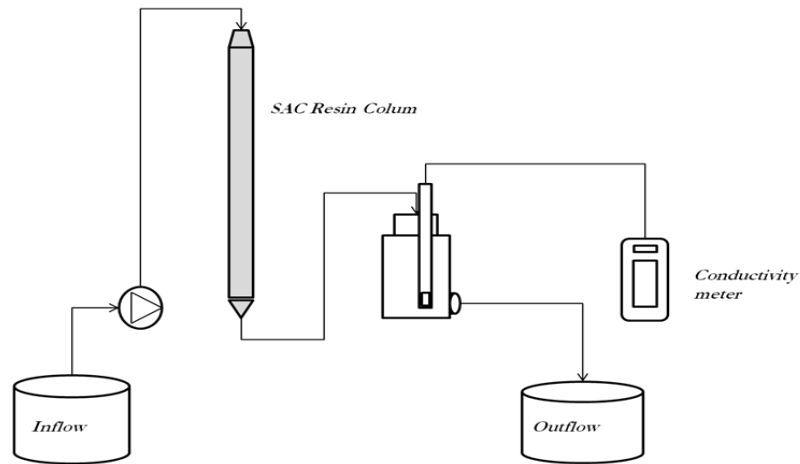
Figure 3: Schematic diagram of ion exchange set up for adsorption of ammonium from wastewater.

3.1.2. *Operation of IE system*

Initially, 12 litres of 40 mg/l NH_4-N solution was pumped through the SAC resin column. The column was later regenerated with 1 litre of 10 g/l NaCl which therefore left the resin in sodium form. Thus Na^+ would be exchange with the NH_4^+ in the wastewater during the exchange process. The reactions that were involved in the preparation stage could be envisaged as:

$SOOOH + NH_4^+ \leftrightarrow SOOONH_4 + H^+$ - Operation Stage

$SOOONH_4 + NaCl \leftrightarrow SOOONa + NH_4Cl$ - Regeneration

The SAC ion exchange resin was therefore change to sodium form and used in the experiment since NaCl solution was intended to be used for the regeneration.

The wastewater that was used in the experiment was filtered through paper filters to remove any suspended particles in order to prevent clogging of the resin column.

If not used at the moment, the filtered wastewater was refrigerated at 4 °C to prevent any biochemical process that could change the composition. Moreover filters were place at both ends of the ion exchange resin column to further remove any suspended material that could clog the resin. These extra filters supported the resin and prevented any wash away of the resin from the column. In the experiment three different cycles were carried out with different initial concentration ammonium in the wastewater. The characteristics of each of the UASB effluent used for three cycles were measured (Table 1). Having made the set-up, the pre-treated wastewater sample was pumped

Table 1: Characteristics of initial wastewater used for exhaustion of ion exchange resin.

Cycles	NH_4-N (mg/l)	pH	Temperature (^{o}C)	Conductivity (µS/cm)
C1	40.4	7.44	22.8	869
C2	37.9	7.46	21.5	828
C3	21.8	7.16	16.1	730

Figure 4: Ion exchange set-up.

through the column at rate of 10 ml/minute. The wastewater was pumped from the top to the bottom of the resin column, i.e. downward flow (Fig. 4). The electrical conductivity of the outflow (treated wastewater) was recorded regularly and samples were taken after pumping every 500 ml for analysis of NH_4-N. The conductivity was recorded in order to know when the effluent standard was reached. The electrical conductivity corresponds to the total ions content in the sample.

When the resin column was exhausted, it was then regenerated using NaCl solution. Previous study indicates that higher concentration of NaCl regenerant gives faster regeneration (Malovanyy et al., 2011b). However, in this study NaCl concentration of only 10 g/l was used because the ammonium concentrates were further treated for nitrogen removal using partial nitritation/anammox process. Unlike the saturation stage, the regeneration was done in an upward flow at flow rate of 3 ml/minute (Fig. 5). Samples were taken after every 50-100 ml pumped for analysis.
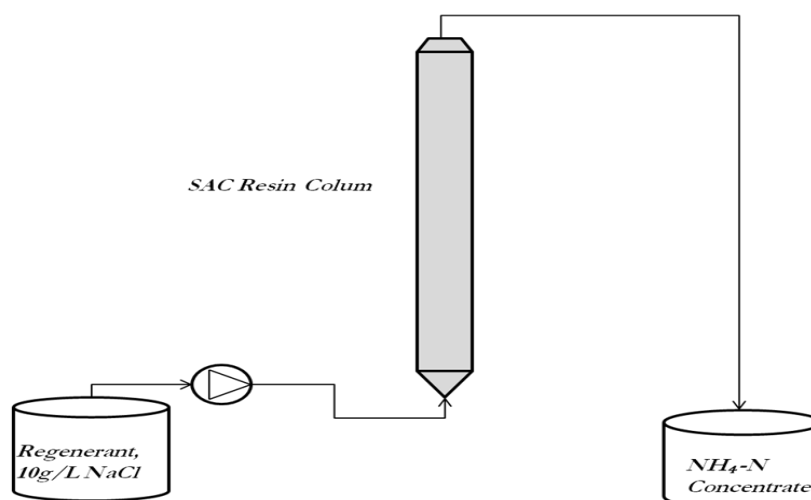

Figure 5: Regeneration of exhausted ion exchange column with 10 g/l NaCl solution.

Figure 6: The RO plant at IVL.

3.2. **RO experiment**

3.2.1. *Description of RO unit*

The RO plant used in the operation was a single stage high performance plant at the IVL-Swedish Environmental Institute, Stockholm (Fig. 6). The RO unit constitute a feed/concentrate tank, high power pump, RO membrane module, permeate tank for collecting stream passing through the membrane (Fig. 7). The unit also has a heat exchanger for regulating the temperature of the stream. There is also a built in thermometer for monitoring the temperature. Moreover, two pressure meters at each side of the membrane for measuring the pressures of the concentrate and permeate streams are put in place. There is a valve located on the concentrate line for regulating the pressure. A metre for monitoring the flux of concentrates and permeates can also be found. The membrane used in the research was a FilmTec SW 30-2540F spiral wound membrane module type manufactured by DOW water & process solution (Fig. 8). The membrane has surface area of 2.8 m², permeate flow rate of 2.6 m³/day with a stabilized salt rejection of 99.4 %.

3.2.2. *Operation of RO system*

The wastewater used in the study was an effluent from a UASB plant. The wastewater had a concentration of 41.8 mg NH_4-N/L. The
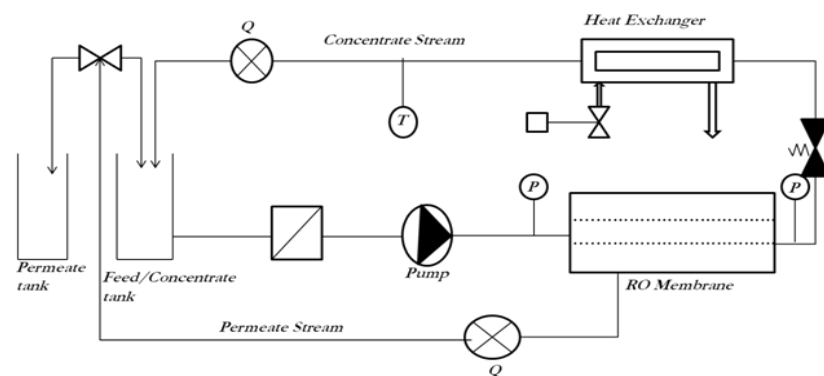

Figure 7: Schematic diagram of reverse osmosis plant and process.

Figure 8: DOW FilmTec SW 30-2540F spiral wound membrane module.

wastewater was pre-treated by filtering with 10 μm cartridge filter to remove any suspended particles which might cause the membrane fouling (Kieniewicz, 2006) and affected the operation. Moreover, the membrane was cleaned by the used of alkaline sodium hydroxide solution (pH~11) for several times at a pressure of 7.5 bars.

The membrane was then rinsed with water for several times until the base was seen to be completely removed. To check that the membrane was completely clean and ready for use, tap water was pumped through at the working pressure of 40 bars and then the flux as well as conductivity of concentrate and permeate were measured.

Initially, the feed tank was filled with the pre-treated wastewater. The pH of the wastewater was 7.2 but was reduce to about 6.5 with concentrated sulphuric acid. The pH was reduced to prevent precipitation of carbonates and solute charge effect (Hongyan, 2010). The feed water was pumped by the high performance pump at a pressure of 40 bars through the membrane. The concentrate line is fixed with a heat exchanger to regulate the temperature. The temperature of the flow in the RO unit was maintained at room temperature (~25 °C). The concentrate returns to the feed tank where as permeate was collected at different tank. The system was run for volume reduction factor (VRF) 2 and 5. The start volume of feed was 105 litres. The volume of concentrate for VRF 1, 2 and 5 were therefore 105, 52.5 and 21 L respectively. At each of the VRFs, samples of both concentrate and permeate were taken and analysed. The end of the process, VRF 5, the volume of the concentrate left was 21 L.

3.3. Biological removal of Nitrogen with partial nitritation/Anammox

3.3.1. Operation of moving bed bioreactor (MBBR)

The biological removal of concentrated ammonium nitrogen was accomplished by the use of single-stage MBBR configuration of partial nitritation/anammox process. A reactor which consisted of a plastic container of volume 2 liters with a magnetic stirrer was used in the experiment. Kaldnes rings of volume 250 ml were used as moving bed with biomass in the reactor. Specific amount of $NaHCO_3$ was added depending on the NH_4-N concentration of the regenerate batches (Table 2) according to equation (9). The $NaHCO_3$ was divided into two

Table 2: Amount of NaHCO₃ used for biological treatment based on NH₄-N concentration.

Concentrate		NH$_4$-N (mg/l)	Mass of NaHCO$_3$ used (g)
IE	C1	367.20	2.22
	C2	329.50	2.00
	C3	187.50	1.13
RO		163.00	0.99

in each cycle; half was added at beginning and the rest at middle way through the experiment.

An aerator and a DO meter were connected to the set-up to supply oxygen and measure the dissolved oxygen respectively (Fig. 9). In the first cycle C1, the DO was maintained at a concentration of around 1.5 mg/l. However, with the high NO$_3$-N concentration in previous cycle, DO was reduced to about 1.0 in both C2 and C3. Each cycle was run for 3 days and samples were taken at two hour interval. The samples volume was only 5 ml, so that the volume in the reactor will not reduce significantly along the process. The concentration of NH$_4$-N in RO concentrate obtained at VRF 5 was 163 mg/l.

3.3.2. *Experimental strategy*

Three different partial nitritation/Anammox experiments were run using 750 ml of concentrate each time. NaHCO$_3$ was added in the same proportion as C1-C3. Process of each of the three RO batches B1-B3 last in about 24 hours.

3.4. **Physical and Chemical Analysis**

The parameters; electrical conductivity, temperature, pH and dissolved oxygen were measured using:

- Conductivity- WTW Cond 330i together with electrode WTW Tetra Con 325
- Temperature- WTW Cond 330i together with electrode WTW Tetra Con 325
- pH- WTW pH 330 together with electrode WTW SenTix 41
- Dissolved oxygen - Hach Lange HQ30d together with electrode Hach Lange LDO 101

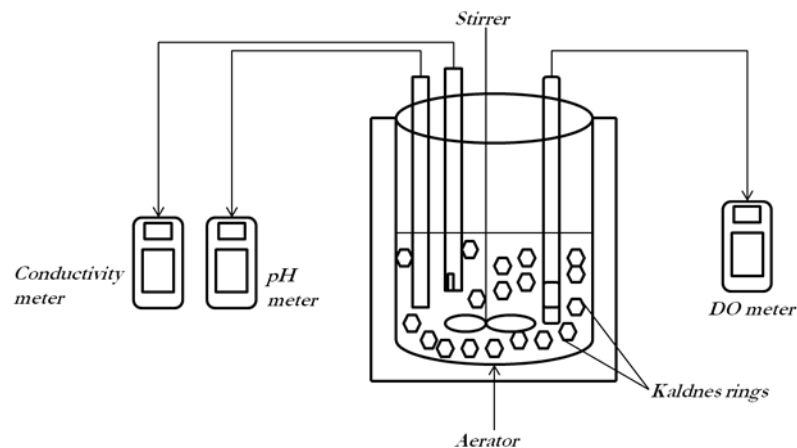Ammonium, nitrite and nitrate were analyzed by either curvette or flow

Figure 9: Partial nitritation/Anammox experimental set-up.

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injection analysis (FIA) technique. For the curvette method, Dr Lange XION 500 spectrophotometer was used to analyse the concentration of nitrogen compounds. Samples were pre-treated by filtering with 0.45 μm pore size filters. In analysis of NH_4-N, NO_2-N and NO_3-N, the standard cuvettes produced by Hach Lange GMBH were used:

- NH_4-N – LCK 303, 2-47 mg/L
- NO_2-N – LCK 342, 0.6-6 mg/L
- NO_3-N – LCK 340, 5-35 mg/L

When using FIA samples were frozen. Tecator Aquatec FIA system for analysis of ammonium, phosphate and nitrite/nitrate in water solution was the instrument employed in this analysis. The instrument is composed of a sampling unit 5027 sampler, and analyzing unit Aquatec-5400 analyzer, and a connected control computer. When samples are injected into a transplant flow and gets into the analyzer, they react with reagents in the replaceable cassettes which were fixed depending on the substance being analysed (ammonium, nitrite or nitrate). Light absorbance through product formed as result of the reactions between sample and reagent is measured at specific wavelengths (Karlberg & Pacey, 1989). In the case of ammonium analysis for instance, the sample is mixed with a sodium hydroxide stream resulting in formation of ammonia gas which diffuses through a gas permeable membrane into an indicator stream. The mixture of acid-base indicators reacts with the ammonia gas and result in a colour which can be measured photometrically at wavelength of 590 nm.

In the experiment, standard concentrations of 0, 50, 100, 200, 500, 1000 μg/l were prepared from stock standard for each of the substances analysed for calibration before the start of the main analysis. The stock standard solutions used were 1000 mg/l NH_4-N, 200 mg/l NO_2-N and 200 mg/l NO_3-N for analysis of ammonium, nitrite and nitrate respectively.

4. RESULTS AND DISCUSSION

This section gives the results and discussion of the experiments carried out in the study

4.1. Ion Exchange

The results for the IE experiment are presented for both the exhaustion and regeneration stages.

4.1.1. Exhaustion of Ion Exchange Resin

In order to monitor the exhaustion of the SAC ion exchange resin, the conductivity of the outflow was measured. Increase in the conductivity of ouflow means the ion-exchange column is being exhausted (Fig. 10). The increase in conductivity is an indication of higher concentration of ions. There was perfect correlation between the conductivity of the outflow and the NH_4-N concentration in it (Fig. 10 - 12). The result follows a similar trend in a previous study by Malovanyy et al. (2011b) where there was similar correlation between conductivity and NH_4-N concentration. In each of the cycles different volume of wastewater was used to reach the end point of the exhaustion of resin. The volumes of wastewater used in the exhaustion process were related to the concentration of ammonium. In C1 which had the highest ammonium concentration, 5000 ml was used whiles in C3 with the lowest concentration 5800 ml was used (Table 3). This is because, with low ammonium concentration, more of the wastewater is used before the ion
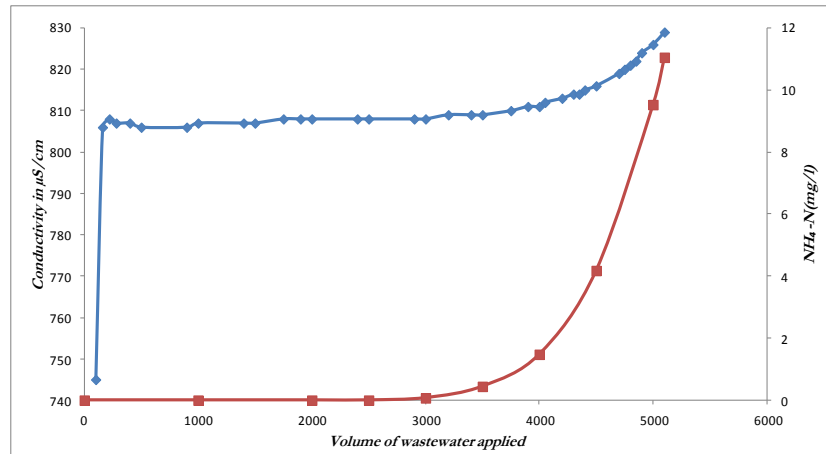
Figure 10: ———— *Conductivity of outflow from the SAC resin column (C1);* ——■— *Concentration of NH₄-N measured in the ion-exchange column ouflow (C1).*

exchange capacity of the resin is exhausted. It is therefore an indication when the concentration of ammonium inflow in wastewater is low, then more wastewater is pumped to the column before the resin material is exhausted.

From the ammonium concentration graphs, during the initial stages of the exhaustion process, eventually all of the ammonium in the wastewater was exchanged into the resin and there is therefore zero concentration of NH_4-N in the ouflow. As the process continues, the concentration in the ouflow increases due to the fact that exchange sites for ions get used. If the system is not monitored carefully and appropriate end point is not chosen there will be higher concentration of ammonium in the 'treated' wastewater. In all the cycles, ammonium could only be observed in the ouflow after pumping more than 2000 ml of wastewater (Fig. 10-12).

The efficiency of the resin could have decrease through the cycles; however there was no observable evidence of change in efficiency. In order to show how efficiency of the SAC resin deteriorates, the same concentration of initial ammonium could have been used. However, in this study, wastewaters with different initial concentrations of ammonium were used and therefore it will be hard to determine how efficiency of SAC resin declines. It could also be noticed from the results that ammonium concentration in the inflow corresponds well with conductivity. However, the conductivity were very low at the beginning of pumping but rises quickly after pumping some small amount of wastewater. The initial conductivity (Fig. 10-12) was very low because of distilled water used to wash resin before starting the experiment.

Table 3: Volume of wastewater used for exhaustion of ion exchange resin.

Cycle	Volume used for exhaustion of resin (ml)
C1	5000
C2	5300
C3	5800

Figure 11: ——— *Conductivity of outflow from the SAC resin column (C2);* —■— *Concentration of NH$_4$-N measured in the ion-exchange column ouflow (C2).*

4.1.2. Regeneration of Ion exchange column

After the ion exchange material is exhausted with ammonium in the wastewater, it was regenerated to get the ammonium concentrate. In all the cycles after applying about 600-700 ml of regenerant of 10 g NaCl/l, the system was almost completely regenerated (Fig. 13). After 700 ml only traces of ammonium could be measured in the outflow. From the regeneration curve (Fig. 13), the concentration of NH$_4$-N in the concentrate rises sharply just at the start of the process and begins to drop. The peak is not at the very beginning of the regeneration because of wastewater that is left in the column. After the peak concentration of ammonium,
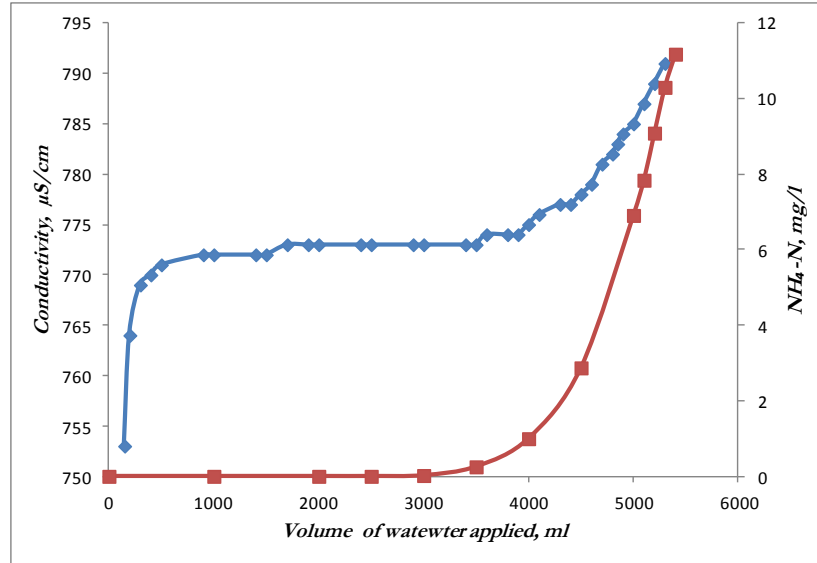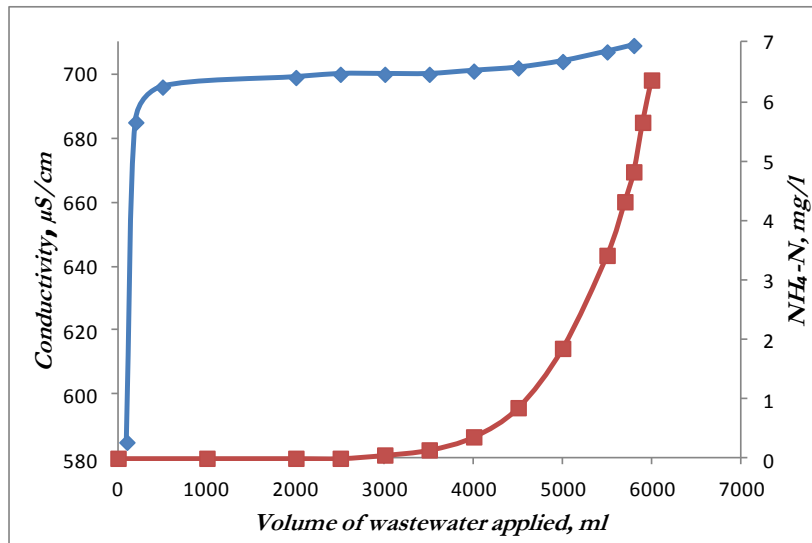

Figure 12: ——— *Conductivity of outflow from the SAC resin column (C3);* —■— *Concentration of NH$_4$-N measured in the ion-exchange column ouflow (C3)*
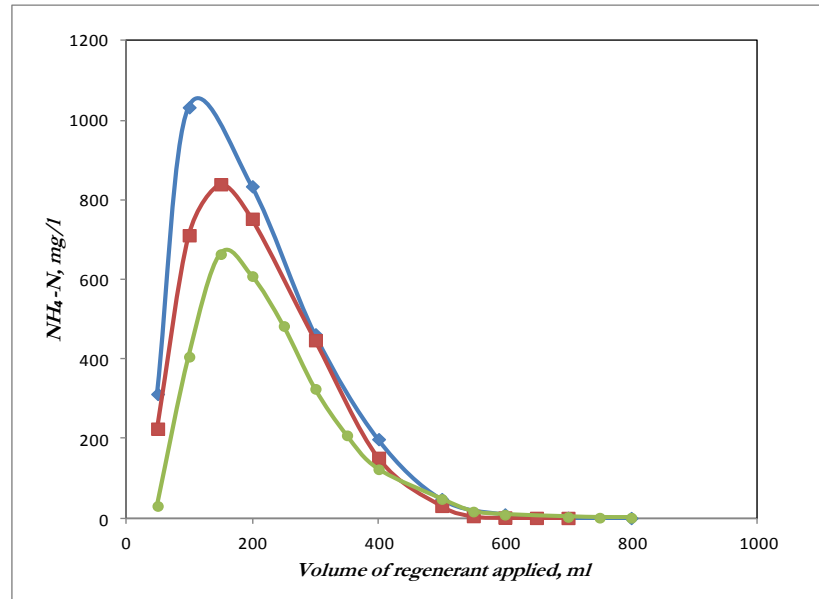
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Figure 13: Regeneration curve showing NH$_4$-N in the concentrates; ──── C 1, ──■── C 2 and ──── C 3.

the regeneration continues until ammonium is fully exchange with sodium. Moreover, it makes sense that C1 has the highest NH$_4$-N (Fig. 13) in concentrate compared with C2 and C3, since the initial ammonium concentration was the highest among the three.

4.2. **Reverse Osmosis**

The physical operation parameters for each other VRFs were measured by the use of the already built in various measuring devices. The physical parameters like the pressure, flux and temperature were then recorded in the course of the process. Samples of permeate and concentrated were also taken to the laboratory for analysis of NH$_4$-N concentration.

The pressure of the RO unit was maintained at 40 bars and temperature was set at between 25-27 ^{o}C. With this pressure, permeate fluxes of 25, 22.9 and 22.5 L/m²h were obtained for VRF 1, 2 and 5 respectively (Table 4).

It is obvious from the permeate fluxes that the rate of flow across the membrane decreases with time. Particles may be stacked in the pores of the membrane causing membrane fouling and scaling which reduce the flow rate. It could be seen from results (Table 5) that the conductivity of the VRF2 was more than double of the VRF1 which is expected for 100 % efficiency. This higher conductivity could be attributed of H$_2$SO$_4$ added to reduce the pH of the feed to about 6.5. However, after VRF 5 a

Table 4: Results recorded from operation RO unit.

VRF	Pressure (bar)	Flux L/m²h	Feed Volume (L)	pH	Temp (°C)
1	40	25.0	105	6.6	26
2	40	22.9	52.5	6.6	25
5	40	22.5	21	6.7	27

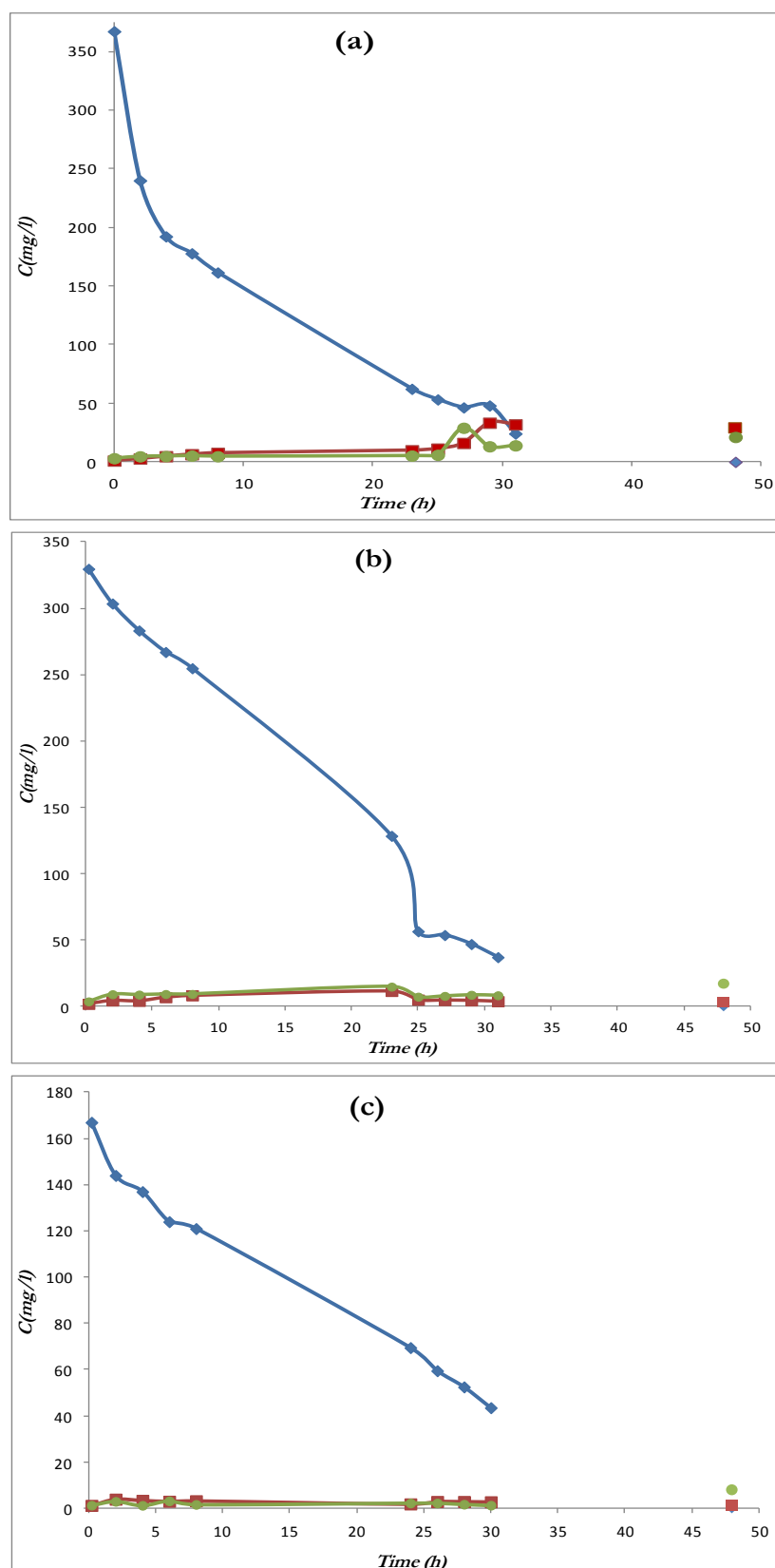*Figure 14: Partial nitritation / anammox treatment of the ion exchange concentrate (a) C 1 (b) C 2 (c) C 3.* ——— NH_4-N; —■— NO_2-N; ——— NO_3-N.

Table 5: Characteristics of RO concentrates and permeate.

VRF	Conductivity (µS/cm)		NH₄ N (mg/L)	
	Concentrate	Permeate	Concentrate	Permeate
1	857	13	41.8	0.693
2	1800	19	78.5	1.05
5	3460	26	163	1.56

conductivity of 3460 µS/cm was obtained which is reasonable. Having an initial concentration of 41.8 mg NH_4-N/L, a removal efficiency of 96.27 % was achieved after VRF 5 since only 1.56mg/L was left in the permeate (Table 5). However, the concentration of NH_4-N was in the concentrate after VRF 5 was 163 mg/L. If the membrane was 100 % efficient, then one would have expected NH_4-N amount of 5*41.8 mg/L in the concentrate. From the initial concentration of 41.8 mg/L used and the concentration of 163 mg/L obtained at the end of the process, then 19 % of NH_4-N was lost in the process. It might be that $MgNH_4PO_4$ was precipitated on the membrane. Meanwhile, the concentration of NH_4-N achieved was enough for the biological process.

4.3. Partial nitritation/Anammox Processes

In the biological treatment process, the use of partial nitritation/anammox technology for the removal of NH_4-N worked perfectly. From the graph the concentration of NH_4-N decrease until it eventually got to zero in all the cycles (Fig. 14). In C1, the concentration of NH_4-N decreases drastically from 367.18 mg/l at start of the process to about 46 after 27 hours of operation.

The concentration then increase slightly to 48 mg/l after addition of the second half of the 2.22 g $NaHCO_3$ that was used as a carbon source. This is could be as result of an error in the measuring procedure. On the other hand, in all the other cycles, the concentration of NH_4-N kept on decreases even after the addition of the second half of the $NaHCO_3$. The decrease in the NH_4-N is attributed to both equations (7) and (8). In the case of NO_2-N and NO_3-N were both very high in C1 (Fig. 14a). The concentrations of NO_2-N and NO_3-N were between 1.1 and 33.4 mg/l, and 3.1 and 29.1 mg/l respectively from the start to the end of the process. The highest concentration was recorded just after the addition of the second half of $NaHCO_3$. This is because, when the $NaHCO_3$ was added, AOBs had enough substrates and therefore their metabolic activities increase thereby converting NH_4-N to NO_2-N (equation (7)). However, the concentration of NH_4-N did not decrease that much after adding the second batch of the carbon source.

The concentration of NO_2-N and NO_3-N was very high in C1 than both C2 and C3. The high concentration of nitrate and nitrate recorded in C1 can be attributed to the high oxygen concentration in the system. In C1 the DO of the system was maintained around 1.5 mg/L. Generally, high amount of nitrite and nitrate were recorded at the end of the tests. After 31 hours, it was noticed that ammonium was almost consumed. Therefore, when the system was allowed to go on, nitrite was converted to nitrate hence high NO_3-N was recorded at the end of each of the test. Moreover the high amount of NO_2-N and NO_3-N recorded at the end of the test may be explained by the fact that aerobic ammonium oxidizers are inhibited less by NaCl than Anammox bacteria (Malovanyy
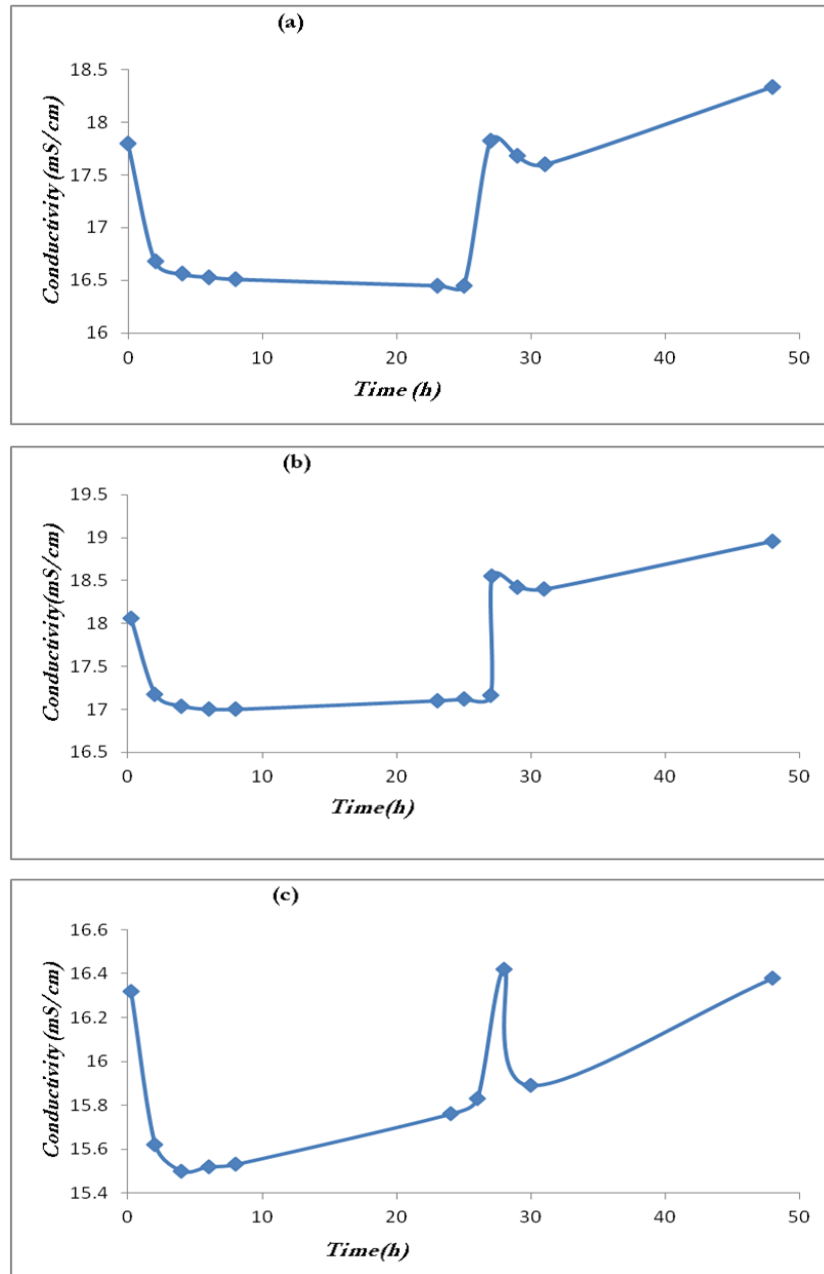
Figure 15: Conductivities of partial nitritation/Anammox process. (a) C 1 (b) C 2 (c) C 3.

et al., 2011b) and therefore all the ammonium where converted to nitrates but because of the inhibition anammox bacteria could not complete the process to convert it to N_2. The concentrate as known from the ion-exchange was regenerated with NaCl and had some amount in it.

Conductivity was monitored to check the progress of the process. The graphs of conductivities of the partial nitritation/Anammox process for all three cycles are presented in Figure 15. From the conductivities graphs, it can be noticed that the conductivity decreases drastically in the first two hours and continues to decrease gradually. The decrease in the conductivities can be no doubt attributed to removal of ammonium.

However, conductivity began to rise again even after ammonium removal was near completion (Fig. 15). Since there was NaCl salt which

did not remove in the process, evaporation of the wastewater could account for the rise in conductivity. This is evident from the ammonium of wastewater that was left after the process. In cycle 2 and 3, initial volume of wastewater were 590 and 740 ml respectively and therefore having taken in each case 10 different samples of volume 5 ml for analysis, it was expected that volumes of 540 and 690 ml will be left at the end of the process. Meanwhile, each of the cycles had end volume of
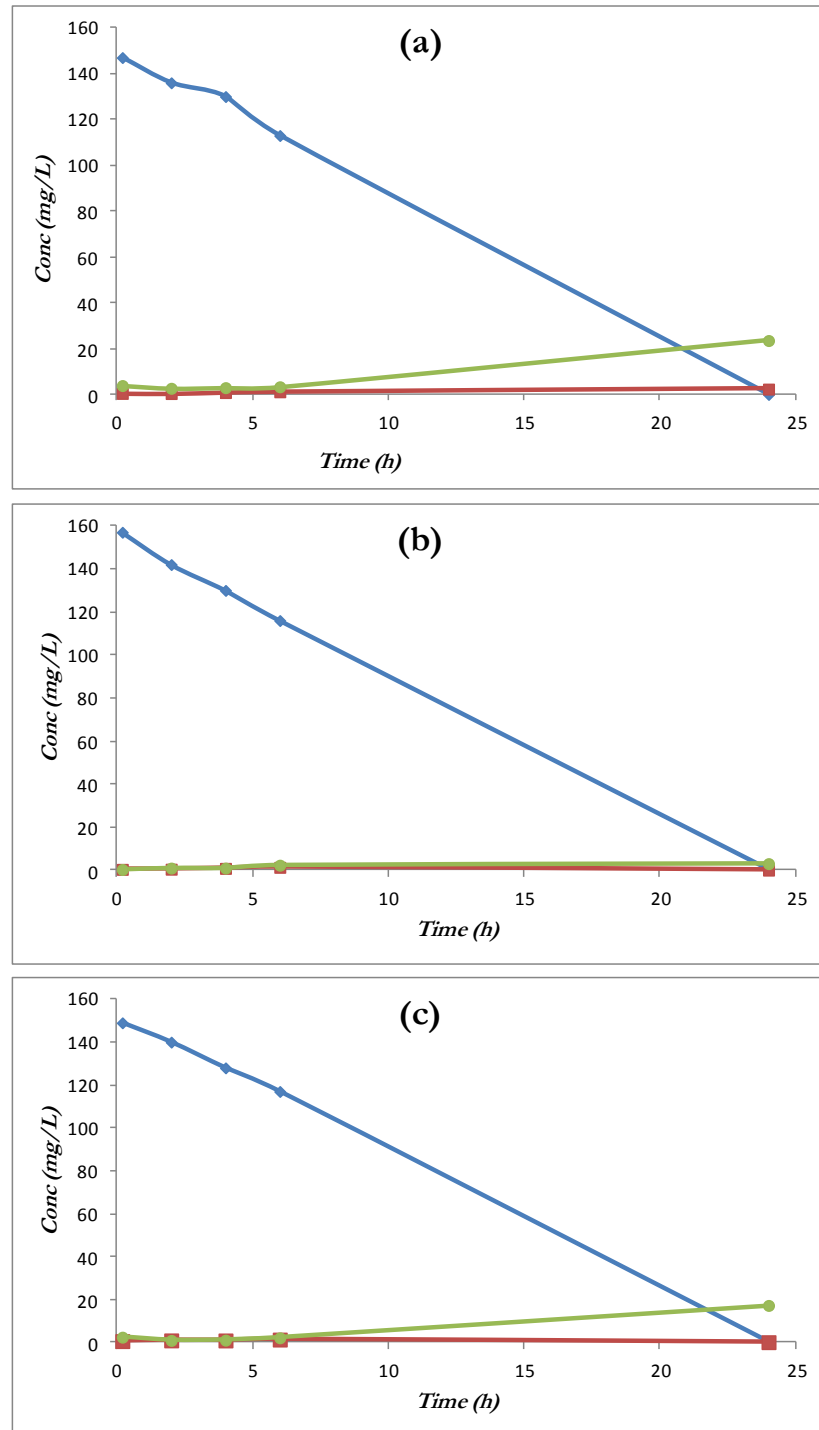

Figure 16: Biological treatment of RO concentrate with partial nitritation/anammox process. (a) B 1 (b) B 2 (c) B 3 —— NH₄-N; —■— NO₂-N; —— NO₃-N.

415 and 555 ml accounting for evaporation of 175 and 185 ml respectively. Evaporation obviously results in the rise in conductivities. In each of the conductivity curves (Fig. 15), a sharp rise in conductivity is noticed between 26-30 hours. This sharp rise could be as a result of the addition of $NaHCO_3$ as carbon source since it the ions it can influence the conductivity. Conductivity then gradually dropped again as the process progress owing to the removal of HCO_3 and NH_4 (Szatkowska, 2007).

Three different batches (B1–B3) of the RO concentrate were run for removal of ammonium using partial nitritation/Anammox process. The results for each batch are presented on a graph (Fig. 16). From the results of the biological treatment of nitrogen removal it could be observed in all the batches that after 24 hours ammonium nitrogen was completely removed from the wastewater. The NH_4-N curves (Fig. 16) show how ammonium decreased with time in the process. The process leading to the decrease can be attributed to the conversion of ammonium to nitrite AOBs and further transformation of the two to nitrogen gas and nitrate as it is illustrated in equation (8). In batch, 23.7 mg/L of NO_3-N was recorded at end of the partial nitritation/anammox process which is about 14 % of the initial nitrogen amount of 163mg NH_4-N/L in wastewater. This amount is a bit more than 11 % which should be according to stechiometry of Anammox process (Strous et al., 1998). The concentration of NO_3-N at the end of batches 2 and 3 were 3.1 and 17.3 mg/L which accounts for only 2 % and 10.6 % of the initial nitrogen concentration, which lower than the expected values according to equation (8). The high concentration of NO_3-N in the batch 1 effluent could only be linked to high amount of DO (~ 7 mg/L) recorded after the 24 hours of operation (Appendix 1). Meanwhile the DO concentration in the batch 2 effluent was equally high (~6 mg/L) and one would have expect high concentration of NO_3-N but it did not turn out to be so. Meanwhile, the difference between experimental value of 2 % and stoichiometry of 11 % in batch 2 could result from the presence of heterotrophic denitrifying bacteria (Szatkowska et al., 2007). Batch 3 recorded almost the same amount of NO_3-N (~11 %) as expected from the stoichiometry (equation 8).

Conductivity in the wastewater also decreases as the ammonium concentration decrease (Fig. 17). This is clearly indicates that ammonium influence conductivity of wastewater (Szatkowska et al., 2007). Comparing to IE experiments (Fig. 15), values of conductivity as a monitoring parameter is higher. The correlation of ammonium decrease with conductivity drop is better in the RO than IE because evaporation does not cause that big change of conductivity as ammonium removal. Thus, percentage of conductivity due to NH_4 presence is higher than that in IE experiments. In IE experiments conductivity was mainly attributed to NaCl presence. The pH of the process did not change much. The major change was observed at the start of the process when the $NaHCO_3$ was added to the process. This increases the pH from about 6.8 to about 7.2 and continues to increase to about 7.8 (Appendix 2). At the end of the process decrease in pH was observed, probably because of the HCO_3^- consumption in nitrification process.

4.4. General Discussion

If the partial nitritation/anammox technology becomes feasible in applying it the main stream of wastewater treatment, it is going to be a major breakthrough in the industry because of the expected reduction in
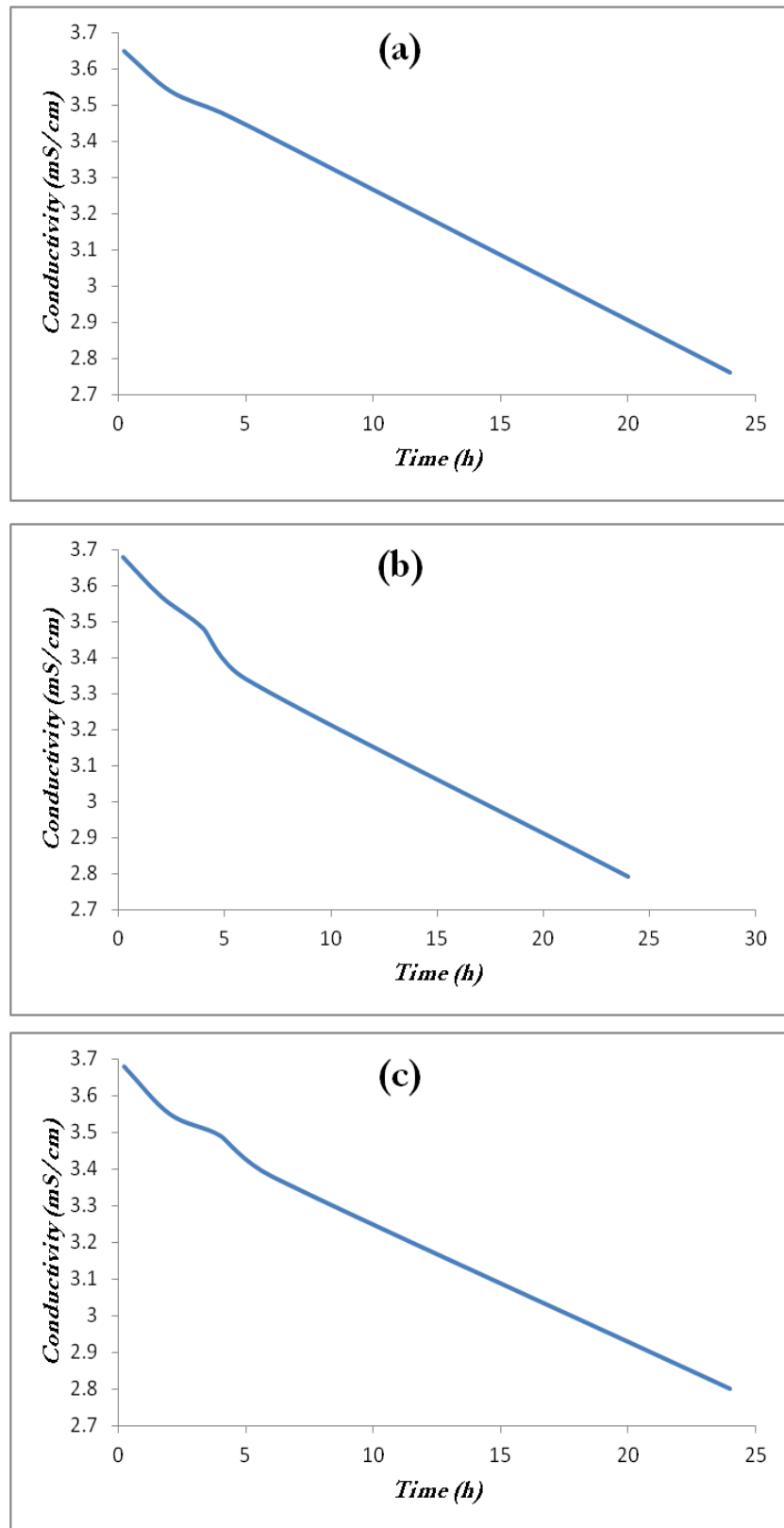
Figure 17: Conductivity curves of partial nitritation/Anammox process of RO concentrates. (a) B 1 (b) B 2 (c) B 3.

operation cost as a result of reduction in aeration and external carbon source. The two systems for ammonium concentration that were studied in this thesis work are very promising methods that could make it possible to apply the partial nitritation/Anammox technology in the main low ammonium stream of wastewater.

Malovanyy et al. (2011a) described the possible configurations for applying the ion exchange together with partial nitritation/Anammox in the main stream of wastewater treatment plants; this study deals with the option which suggest the use of anaerobic digestion of dissolved organics applying for example UASB reactors before ammonium removal step. Using UASB technology for the removal of organics still leaves the nitrogen in the wastewater not removed. The use of ion exchange together with partial nitritation/Anammox for the removing nitrogen from the stream before discharge is very feasible. The results of this study show clearly the process works very well. However using the ion-exchange as ammonium concentration method affects the partial nitritation/Anammox process and makes the rate of the process slower due to the high salinity in the wastewater. Even though the rate of the process was influenced largely by the initial NH_4-N concentration, the rate was influenced by the salt content of the wastewater. The rate was calculated from the nitrogen removal during steady state periods of the process (4 - 27 hours for IE and 0.2 – 6 hours for RO). IE C1 which had highest NH_4-N concentration did not have the fastest rate of N removal because of the very high NO_3-N and NO_2-N recorded in the system. C2 had highest rate of nitrogen removal. However, C3 had the least concentration (187.50 mg/L) among IE concentrates but gave lower rate (0.500 g N/m²day) than all RO batches with low initial NH_4-N of only 163 mg/L in each case (Table 6). Even though, this project did not do any studies on the financial cost of the process, a reduction of about half in aeration occurring from the partial nitritation/anammox process is very significant to make up to any cost resulting from high hydraulic retention time. A major challenge that can come about is the high salinity of the effluent that can affect the salinity of the receiving water.
This problem will not be seen if the receiving body is a sea or brackish water.

Using reverse osmosis as method for concentrating ammonium and further removal raise much questions about the cost of the RO unit and operation. In the study, VRF 5 was enough to concentrate sufficient about of ammonium for the partial nitritation/anammox. Again studies on the cost of technology were not done in this project; however it was clear from the results that the use of RO gave concentrates with relatively low salinity and therefore the rate of nitrogen removal in the partial nitritation/Anammox process was faster. Further studies about the total cost all the systems will therefore give very clear picture about the feasibility of each of the process.

Looking at the conductivity curves of partial nitritation/ Anammox process of ion exchange concentrate (Fig. 11) and reverse osmosis

Table 6: Rate of nitrogen removal from wastewater during the partial nitritation/Anammox process.

Method	IE			RO		
ID	C1	C2	C3	B1	B2	B3
Rate of N removal (g N/m²day)	0.599	1.133	0.500	0.840	0.945	0.784

concentrate (Fig. 17), it can be noticed that the curves of RO concentrate decline with time throughout the biological process.

However, for that of the ion exchange, there was a decline in the conductivity due to removal of the ammonium from the system but with time there was an increase again which can be attributed to evaporation. It can be argued that, evaporation also occurred in treatment process of the RO concentrates and therefore a rise in conductivity could have been happened at the end of the process since ammonium is not the only substance that influences the conductivity. The reason for not seeing any rise in conductivity of the RO batches, unlike the ion exchange cycles is because the RO concentrate took less than 24 hours whereas the time taken to complete the partial nitritation/Anammox process of the ion exchange concentrate was more than 31 hours. Therefore ion exchange concentrates were much more exposed to evaporation than the RO concentrates in the biological process.

5. CONCLUSION

Looking at the results, the following conclusions can be drawn from the study:

- Ion exchange and reverse osmosis are viable methods for concentrating ammonium from UASB effluents.
- Ion exchange method was used to concentrate UASB effluents of about 24 - 40 mg NH_4-N/l to 188 - 367 mg NH_4-N/l respectively.
- At VRF. 5, 163 mg NH_4-N/l concentrate was attained from 41.8 mg NH_4-N/l RO feed.
- Concentrates from both ion exchange and reverse osmosis can further be treated for biological nitrogen using partial nitritation/anammox technology.
- Salinity affects the partial nitritation /Anammox technology due to inhibition of AOBs and anammox bacteria.
- It took more than 32 hours to complete treatment of ion exchange concentrates while it took less than 24 hours to finish the partial nitritation/Anammox process of RO concentrates.
- The rate of nitrogen removal by partial nitritation/Anammox technology was $0.5 - 1.1$ g N/m²day for IE concentrate, and $0.8 - 0.9$ g N/m²day
- IE Concentrate regenerated with salt takes longer time to be treated with partial nitritation/Anammox process than concentrates from RO due to high salinity of the former.
- Dissolved oxygen is very important parameter that greatly influences single stage partial nitritation/ Anammox process.
- Dissolved oxygen ~1 mg/l is optimal for the operation of partial nitritation/Anammox process when treating solution obtained from ion exchange column regeneration

REFERENCE

Bertino A. 2011. Study on one-stage partial nitritation/Anammox process in Moving Bed Biofilm Reactors: A sustainable nitrogen removal. TRITA-LWR Degree Project. 11-05: 85.

Breisha GZ, Winter J. 2010. Bio-removal of nitrogen from wastewaters-A review. Journal of American Science. 6(12): 508 – 528.

Demir A, Günay A, Debik E. 2002. Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite. Water SA. 28: 329-336.

Ek M, Bergström R, Bjurhem JE, Björlenius B, Hellström D. 2006. Concentration of nutrients from urine and reject water from anaerobically digested sludge. Water Science and Technology. 54: 437-444.

Ekström S. 2010. N$_2$O production in a single stage nitritation/anammox MBBR process. Lund University, Lund, Sweden. LTH. Master Project Degree. 2010-01: 61.

Fux C, Siegrist H. 2004. Nitrogen removal from sludge digester liquids by nitrification/denitrification or partial nitritation/anammox: environmental and economical considerations. Water Science & Technology. 50(10): 19-26.

Glater J. 1998. The early history of reverse osmosis membrane development. Desalination. 117:297-309.

Häyrynen K, Pongracz E, Väisänen V, Pap N, Mänttäri M, Langwaldt J, Keiskia RL. 2009. Concentration of ammonium and nitrate from mine water by reverse osmosis and nanofiltration. Desalination. 240: 280-289.

Hongyan Z. 2010. Influence of molecular properties of micro organic pollutants on the retention by nanofiltration (NF). TRITA-LWR Degree Project. 10-27: 23.

International Atomic Energy Agency (IAEA). 2002. Application of ion exchange processes for the treatment of radioactive waste and management of spent ion exchangers. Technical report series no. 408, Vienna.

Jetten MSM, Wagner M, Fuerst J, van Loosdrecht M, Kuenen G, Marc Strous M. 2001. Microbiology and application of the anaerobic ammonium oxidation ('anammox') process. Current Opinion in Biotechnology. 12:283-288.

Joss A, Salzgeber D, Eugster J, König R, Rottermann K, Burger S, Fabijan P, Leumann S, Mohn J, Siegrist H. 2009. Full-Scale Nitrogen Removal from Digester Liquid with Partial Nitration and Anammox in One SBR. Environment and Science Technology. 43 (14): 5301–5306.

Karlberg B, Pacey GE. 1989. Flow injection analysis: a practical guide. Amsterdam. Elsevier: 384p.

Kartal B, Kuenen JG, van Loosdrecht MCM. 2010. Sewage Treatment with Anammox. Science. 328: 702-703.

Kieniewicz A. 2006. A reverse osmosis (RO) plant for sewage treatment and nutrient recovery – the influence of pre-treatment methods. TRITA-LWR Degree Project. 06-08: 36.

Liang Z, Liu J. 2007. Control factors of partial nitritation for landfill leachate treatment. Journal of Environmental Sciences. 19: 523–529.

Malovanyy A, Plaza E, Yatchyshyn Y. 2011a. Concentration of ammonium from wastewater using ion exchange materials as a preceding step to partial nitritation/Anammox process. Proceedings of international conference Environmental (Bio)Technologies, Gdansk, 6-8 Sept. 2011, 1-17.

Mulder A.2003.The quest for sustainable nitrogen removal technologies. Water Science and Technology. 48 (1): 67-75.

Rahmani AR, Mahvi AH. 2006. Use of Ion Exchange for Removal of Ammonium: A Biological Regeneration of Zeolite. Global NEST Journal. 8: 146-150.

Seyfried CF, Hippen A, Helmer C, Kunst S, Rosenwinkel KH. 2001. One-stage deamonification: nitrogen elimination at low cost. Water Science and Technology.1(1): 71-80.

Strous M, Kuenen JG, Jetten MSM. 1999. Key physiology of anaerobic ammonium oxidation. Applied and Environmental Microbiology. 65: 3248–3250.

Strous M, Heijnen JJ, Kuenen JG, Jetten MS. 1998. The sequencing batch reactor as a powerful tool for the study of slowly growing anaerobic ammonium-oxidizing microorganisms. Applied Microbiology and Biotechnology. 50 (5): 589–596.

Szatkowska B. 2007.Performance and control of biofilm systems with partial nitritation and anammox for supernatant treatment. KTH-Royal Institute of Technology, Stockholm, Sweden. TRITA-LWR PhD Thesis 1035: 63p. .

Szatkowska B., Cema G., Plaza E., Trela J. & Hultman B. 2007. A one-stage system with partial nitritation and Anammox processes in the moving-bed biofilm reactor. Water Science and Technology. 55: 19-26.

Thornton A, Pearce P, Parsons SA. 2007. Ammonium removal from solution using ion exchange on to MesoLite, an equilibrium study. Journal of Hazardous Materials. 147: 883–889.

van der Star W. 2008. Growth and Metabolism of Anammox Bacteria. Wouter Van der Star.150p

van Hulle SWH, Vandeweyer HJP, Meesschaert BD, Vanrolleghema PA, Dejans P, Dumoulin A. 2010. Engineering aspects and practical application of autotrophic nitrogen removal from nitrogen rich streams. Chemical Engineering Journal.162: 1–20.

Williams ME. 2003. A Review of Wastewater Treatment by Reverse Osmosis. EET Corporation and Williams Engineering Services Company Inc.

Yamamoto T, Takaki K, Koyama T, Furukawa K.2006. Novel Partial Nitritation Treatment for Anaerobic Digestion Liquor of Swine Wastewater Using Swim-Bed Technology. Journal of Bioscience & Bioengineering. 102 (6): 497–503.

Zhang M, Zhang H, Xu D, Han L, Niu D, Zhang L, Wu W, Tian B. 2011. Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes. Desalination. 277: 46–53.

Other reference

Malovanyy A, Plaza E, Yatchyshyn Y, Trela J, Malovanyy M. 2011b. Removal of nitrogen from the mainstream of municipal wastewater treatment plant with combination of ion exchange and canon process (IE-canon) –effect of NaCl concentration. http://www.wis.pk.edu.pl/media/file/konferencje/Malovanyy_Plaza .pdf [Accessed on 17/01/2012]

APPENDIX 1. PH AND TEMPERATURE IN THE REACTOR OF PARTIA NITRITATION/ANAMMOX TREATMENT OF ION EXCHANGE CONCENTRATES.

Table 1A. Temperature and pH of partial nitritation
/Anammox process of Cycle 1 ion exchange concentrate

Time (hour)	pH	Temperature (°C)
Before Start	7.26	22.8
0.2	7.75	22.8
2	7.81	23.2
4	7.87	23.9
6	7.87	24.7
8	7.87	24.3
23	7.52	25.0
25	7.39	25.2
27	7.92	24.6
29	7.89	24.5
31	7.95	24.8
48	8.35	24.8

Table 2A. Temperature and pH of partial nitritation
/Anammox process of Cycle 2 ion exchange concentrate

Time (hour)	pH	Temperature (°C)
Before Start	6.98	19.3
0	7.61	19.1
2	7.66	21. 0
4	7.72	21.5
6	7.77	22.2
8	7.75	22.7
23	7.37	22.6
25	7.23	22.9
27	7.73	22.9
29	7.88	22.8
31	7.9	22.8
48	8.18	22.7

Table 3A. Temperature and pH of partial nitritation /Anammox process of Cycle 3 ion exchange concentrate

Time	pH	Temperature (°C)
Before Start	6.66	20.8
0.2	7.71	19.7
2	7.6	21.0
4	7.63	22.1
6	7.43	21.5
8	7.42	21.4
24	6.98	22.8
26	6.85	22.0
28	7.6	22.4
30	7.63	22.6
48	7.94	22.3

APPENDIX 2: PARAMETERS OF REACTORS PARTIAL NITRITATION/ANAMMOX TREATMENT OF REVERSE OSMOSIS CONCENTRATES

Table 4A: Reactor parameters of RO batch 1

Time (hour)	pH	T(°C)	DO(mg/l)
Before start	6.94	27.1	-
0.2	7.19	25.3	1.63
2	7.76	17.6	0.88
4	7.83	17.5	1
6	7.85	19.4	0.87
24	7.6	19.9	7.3

Table 5A: Reactor parameters of RO batch 2

Time (hour)	pH	T(^{o}C)	DO(mg/l)
Before start	6.87	29.3	-
0.2	7.22	29	0.67
2	7.8	23.2	0.96
4	7.9	23	0.85
6	7.89	22.8	1.11
24	7.83	21.7	6

Table 6A: Reactor parameters of RO batch 3

Time (hour)	pH	T(^{o}C)	DO(mg/l)
Before start	6.71	28.6	-
0.2	7.18	26.8	1.55
2	7.7	23.1	1.01
4	7.8	22.6	0.77
6	7.8	22.6	0.92
24	7.73	22.5	3.92