REMOVAL OF NITROGEN FROM THE MAIN STREAM OF MUNICIPAL WASTEWATER TREATMENT PLANT WITH COMBINATION OF ION EXCHANGE AND CANON PROCESS (IE-CANON) – EFFECT OF NACL CONCENTRATION

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Abstract

Completely Autotrophic Nitrogen Removal Over Nitrite (CANON) is a combination of partial nitritation and Anammox process that is currently used for treatment of wastewater streams with high ammonium concentration and low C:N ratio. Removal of nitrogen from the main stream of municipal wastewater which has relatively low ammonium concentration with CANON process is challenging because of low biomass production rates of Anammox bacteria. One of the possible solutions for overcoming this limitation is concentration of ammonium from the mainstream before biological treatment.

The technology that is being studied implies concentration of ammonium from mainstream municipal wastewater with ion exchange on strong acid cation exchange resin with further removal of ammonium by CANON process and is referred to as Ion Exchange assisted CANON (IE-CANON) process.

This paper presents results of evaluation of NaCl concentration on the two parts of the technology performance – ammonium concentration with ion exchange and CANON process. The results showed that higher NaCl concentrations give possibility to reach higher concentration of ammonium in regenerate in ion exchange process. However, these concentrations lead to partial inhibition of bacteria responsible for nitritation process and almost complete inhibition of anammox bacteria in CANON process. Therefore it is concluded that the optimal concentration of NaCl in regenerant is 10 g/L. At this concentration both the concentration of ammonium to the required level is possible and bacteria responsible for the biological removal are not getting inhibited. These results prove that it is possible to remove ammonium from the main stream of wastewater without any need of external carbon.

Introduction

The most widely used method of nitrogen removal from municipal wastewater is the combination of biological processes of nitrification and denitrification. The Anammox process, together with the nitritation process, offers the possibility to efficiently remove ammonium from a wastewater with lower oxygen supply and does not require external carbon addition (Gut 2006). Currently it is mainly used to treat highly concentrated ammonium streams, such as anaerobic digestion reject water.

Nowadays there is more attention put for improving energy retrieval from a wastewater. The highest biogas production from municipal wastewater can be reached in the system where suspended organics are processed in anaerobic bioreactors and dissolved organics are removed in upflow anaerobic sludge blanket (UASB) reactor (Tandukar *et al.* 2007, Urban *et al.* 2007). Anaerobic wastewater treatment in UASB reactor can efficiently remove dissolved organics with high biogas production, but ammonium concentration in the effluent from the reactor remains on the same level as in the inflow. Ammonium removal from such a wastewater with traditional nitrification/denitrification process or reverse osmosis brings high chemicals or electricity consumption respectively (Kieniewicz 2006).

Application of partial nitritation/Anammox process for ammonium removal from the main stream of municipal wastewater, especially when combined with dissolved organics removal in UASB reactors, can benefit in better economy of wastewater treatment. However, direct application of partial nitritation/Anammox process for treatment of wastewater streams with such low ammonium content (around 25-50 mg NH_4-N/L) is not possible due to the limitation of low Anammox bacteria yield (Strous *et al.* 1998). The other reason is the presence in untreated municipal wastewater of organic substances with low molecular weight, which were proven to irreversibly inhibit the Anammox process (Güven *et al.* 2004).

Possible solution for overcoming the above stated limitations is a two step process with first concentration of ammonium from the wastewater with ion exchange followed by removal of ammonium by Completely Autotrophic Nitrogen emoval Over Nitrite (CANON) and is referred to as Ion Exchange assisted CANON (IE-CANON) process.

Study on concentration of ammonium from synthetic wastewater using ion exchange (Malovanyy *et al.*, 2011) showed that strong acid cation (SAC) exchange resin is the most appropriate material for the purpose of ammonium concentration due to its high capacity and fast regeneration process. In this study NaCl solution with concentration 30 g/L was used as a regenerant. However, it is known, that this high concentration of NaCl can inhibit both nitrification and Anammox processes (Windey *et al.* 2005, Dapena Mora *et al.* 2010). Furthermore it is unknown if ammonium concentration from real wastewater will proceed the same as when synthetic wastewater is used since content of other ions and wastewater pH can influence the process. Also, since not only ammonium but also other cations are concentrated, it is unknown if these ion will not inhibit biological processes.

The aim of this work is to find the optimal concentration of NaCl used in IE-CANON technology and its impact on the two parts of the technology performance and to test the technology using real municipal wastewater and CANON biological culture.

Methodology

Biomass

Biomass of CANON culture was taken from pilot-scale MBBR reactor located at Hammarby Sjöstadsverk research station in Stockholm. The reactor is fed with anaerobic digestion reject water and showed stable performance during 1.5 years. Reactor is filled with Kaldnes rings (K1) that are used as carriers for biofilm of nitritation and Anammox bacteria.

Oxygen uptake rate (OUR)

Oxygen uptake rate (OUR) tests were done using methodology adapted from the one described by Surmacz-Gorska (1995). Bottle with volume 1.56 L was used for the tests. Bottle was filled with anaerobic digestion reject water diluted with tap water to concentration of ammonium nitrogen equal 100 mg/L. Bottle content was thermostated at 25 °C and aerated to dissolved oxygen (DO) concentration above 6 mg/L. When test was started aeration was turned off, 0.1 L of biomass carriers was added and bottle was filled to the top and hermetically closed to avoid any oxygen leakage from the air inside the bottle. DO concentration was continuously measured with DO probe and data was transferred to computer. When stable decrease of DO concentration was observed (5-20 min depending on activity) $NaClO_3$ was added to concentration 17 mM. Addition of $NaClO_3$ results in inhibition of nitrite oxidizing bacteria (NOB) and leads to decrease of oxygen uptake rate. After another 5-20 min allilthiourea (ATU) was added to concentration 12 mg/L. ATU inhibits ammonium oxidizing bacteria (AOB) and after addition of it activity of hetherotrophic bacteria can be measured. Slopes of DO concentration decrease before and after inhibitors addition was transformed to rates of oxygen uptake by AOBs, NOBs and heterotrophic bacteria.

Specific Anammox activity (SAA)

Methodology used for determination of specific Anammox activity (SAA) using measurement of gas pressure is well known and is adapted from the one explained by Dapena-Mora (2007). The principle of methodology is based on the fact that with transformation of nitrogen from different forms into nitrogen gas the pressure inside gas volume of close system should increase proportional to amount of nitrogen, converted to nitrogen gas.

The tests were performed in glass bottles of total volume of 38 ml with 13 ml of gas phase. In order to keep pH at the same level during the tests, substrate was prepared using phosphate buffer (0.14 g/L KH_2PO_4 and 0.75 g/L K_2HPO_4). Salt content of buffer was adjusted to required salinity by addition of NaCl. For each test 15 ml of biomass carriers were used. Gas volume of bottles was deairated with purging nitrogen gas and substrate in form of NH_4Cl and $NaNO_2$ was added to concentrations of NH_4-N and NO_2-N equal 70 mg/L. Bottles were thermostated at 25 °C and pressure inside the bottles was measured regularly. From the slopes of stable pressure increase SAA was calculated.

Ion exchange batch tests

Ion exchange batch tests were performed using glass column of total volume 30 ml filled with SAC exchange resin (type KU-2-8). The column was exhausted by application of synthetic or real wastewater and concentration of ammonium was analyzed regularly in the outflow from the column. When concentration of ammonium exceeded 10 mg/L column was regenerated counter currently by application of NaCl with concentrations 10-30 g/L or HCl with concentration 6.24 g/L.

Synthetic wastewater with content close to municipal wastewater was used (Table 1) and it is the same as the one used in Malovanyy *et al.* (2011).

Table 1. Composition of synthetic wastewater solutions.

NH_4-N (mg/L)	Na^+, (mg/L)	K^+, (mg/L)	Mg^{2+}, (mg/L)	Ca^{2+} (mg/L)	Theoretical alkalinity, mmol/L	Total cation content, meq/L	pH
40	95	6.5	18	21	0	9.7	6.2

Real wastewater used in this work was taken after treatment in UASB reactor step of Hammarby Sjöstadsverk pilot-scale research wastewater treatment line.

CANON batch test

Removal of ammonium from regenerate of ion exchange was done in a reactor of 1 L total volume equipped with magnetic stirrer and air supply. Reactor was filled with 550 ml of regenerant (initial concentration of NH_4-N equal 367 mg/L) and 250 ml of biomass carriers were added. In order to supply enough alkalinity source 1.1 g of NaHCO3 was added in the beginning of the test, which corresponds to 75 % of theoretical alkalinity needed for removal of ammonium through CANON pathway. Another 1.1 g of NaHCO3 was added after 26 h of batch test start. Temperature inside the reactor was not control and was in the range of 23-25 °C. DO was controlled on the level of 1.5 mg/L. Samples were taken regularly and were analyzed for ammonium, nitrite and nitrate. pH and conductivity of samples was measured also.

Results and discussions

Influence of NaCl concentration on CANON process performance

Influence of NaCl concentration on CANON process was evaluated separately for the two biological steps – nitrification and Anammox - by performing batch tests with determination of activities of functional organisms under salinities of medium in the range 0-30 g/L.

Results of OUR tests (Fig. 1) showed that the main aerobic organisms in the biological community were AOB. Second biggest group is heterotrophic bacteria and NOB were always on the limit of detection. It is clearly seen that with increase of salinity activity of both AOB and heterotrophs decreases. Since activity of NOB is on the very low level, it is hard to make conclusions about impact of salinity on these microorganisms. However, it was shown in Liu et al. (2008) that NOB are more sensitive to increased salinity then AOB.

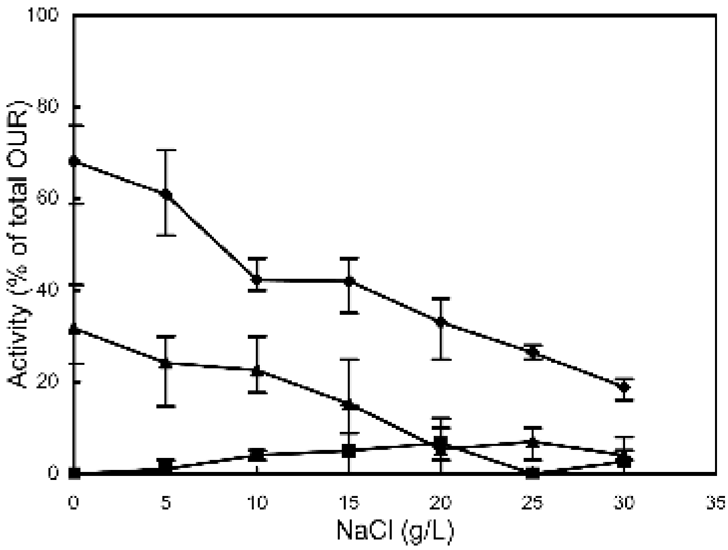

Fig. 1. Influence of NaCl concentration on activity of aerobic bacteria in CANON biomass: ♦ – AOB, ■ – NOB, ▲ – heterotrophs.

Among aerobic microorganisms only activity of AOB is crucial for performance of CANON process. The other groups are not desired in biological culture but anyway exist due to favorable conditions for their activity. Looking only on impact of salinity on AOB activity (Fig. 2) it may be concluded that increase of NaCl concentration to 10 g/L leads to decrease of activity by 20-40% and increase further to 30 g/L cause loss of activity only to 20-30% of activity without NaCl stress.

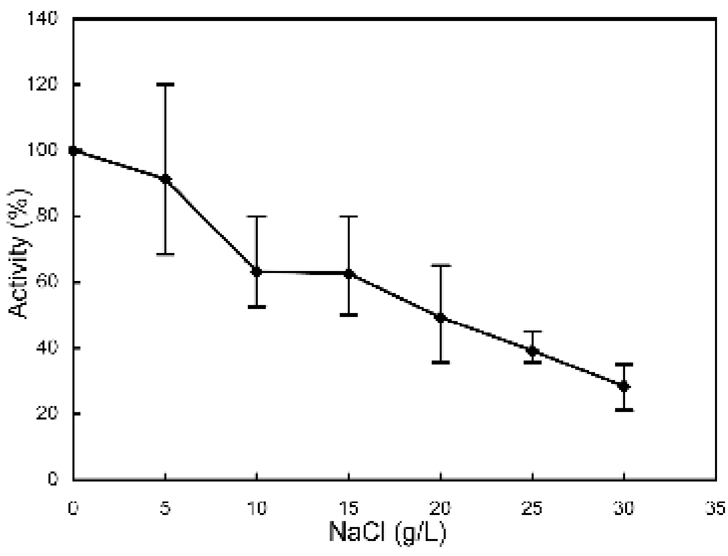

Fig. 2. Influence of NaCl concentration on activity of aerobic ammonium oxidizing bacteria.

Results of SAA tests (Fig. 3) showed that Anammox bacteria are also inhibited by NaCl and the inhibition for them is stronger then for aerobic oxidizing bacteria. Under concentration of NaCl 10 g/L activity of 25-60% of activity in unstressed conditions can be expected. Further increase of salinities of 20 g/L and higher leads to loss of activity to the detection limit of the method.

These results are in agreement with previous studies (Dapena Mora *et al.* 2010, Windey *et al.* 2005) where similar inhibitory effects were evaluated. In these studies it was shown also that under step-wise increase of salinity both Anammox and AOB can be adapted to NaCl concentration of 30 g/L.

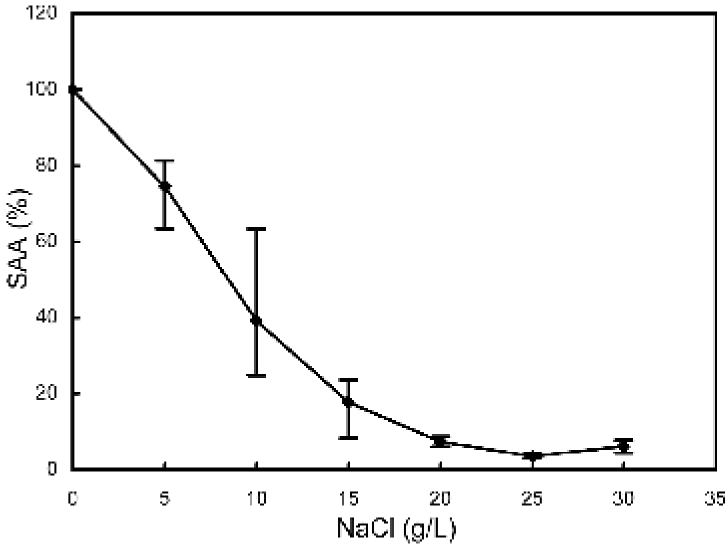

Fig. 3. Influence of NaCl concentration on activity of Anammox bacteria.

Influence of regenerant content on ammonium concentration with ion exchange

After ion exchange material is exhausted and ammonium is detected in the outflow from ion exchange column, it has to be regenerated in order to be able to use it for the next time. Regeneration of SAC resin can be made either by NaCl or by HCl. In first case SAC resin in sodium form is used during exhaustion and in latter case in hydrogen form. If HCl is used for regeneration, regenerate has low pH and has to be neutralized (for example with NaOH) before ammonium can be removed biologically. Therefore, in either of the cases, regenerate that comes to biological ammonium removal step mainly comprise of NH_4Cl and NaCl. So, in batch test with HCl solution as regenerant, HCl concentration of 6.24 g/L was chosen, which corresponds to 10 g/L NaCl if regenerant is neutralized with NaOH.

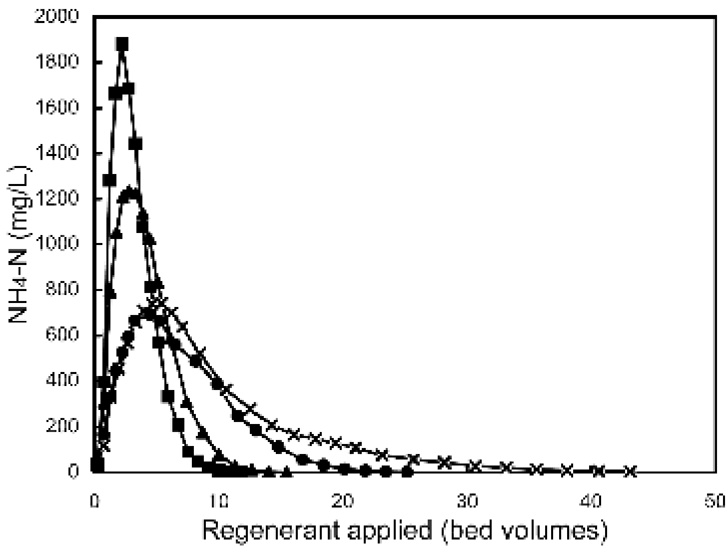

Fig. 4. Influence of regenerant content on regeneration rate: ■ – 30 g/L NaCl; ▲ – 20 g/L NaCl; ● – 10 g/L NaCl; x – 6.24 g/L HCl.

Saturation of SAC resin with ammonium from synthetic wastewater followed the same pattern for resin in sodium and hydrogen form with the difference that 13% more ammonium was uptaken from wastewater when resin in hydrogen form was used.

Regeneration of resin (Fig. 4) with NaCl solutions of different concentrations showed that the fastest regeneration can be done with regenerant of the highest concentration. When comparing regeneration of resin with NaCl and HCl of the same molar concentration it can be concluded that complete regeneration with HCl is much slower process than regeneration with NaCl. It may be explained by the fact that SAC resin has higher affinity for sodium ion than for hydrogen ion (Packer et al. 1998). Results of four cycles of exhaustion and regeneration are summarized in Table 2.

Table 2. Results of SAC resin exhaustion and regeneration.

Volume of wastewater until exhaust-tion (BV*)	Dynamic exchange capacity (mg NH_4-N /ml of resin)	Regenerant	Volume of regenerant used (BV*)	Average concentration in regenerate (mg NH_4-N/L)	Volume reduction factor
		30 g/L NaCl	10.1	706	18.4
186	7.1	20 g/L NaCl	15.5	460	12
		10 g/L NaCl	25.2	283	7.4
205	8.0	6.24 g/L HCl	43.2	165	4.7

* BV – bed volumes

IE-CANON batch test

Based on results of ammonium concentration with ion exchange and determination of activities of aerobic and anaerobic ammonium oxidizing bacteria under different levels of salinities, it was decided to make 1 cycle of ammonium concentration using real wastewater as a source of ammonium and 10 g/L of NaCl as a regeneration solution followed by removal of ammonium from concentrate with CANON process.

Exhaustion of SAC resin was done with applying wastewater after treatment in UASB reactor with ammonium concentration 39.8 mg NH_4-N/L (Fig. 5). The first traces of ammonium in the outflow were detected after application 122 bed volumes (BV) of wastewater and reached 10 mg NH_4-N/L after application 178 BV of wastewater. Conductivity of treated wastewater showed good correlation with concentration of ammonium in it.

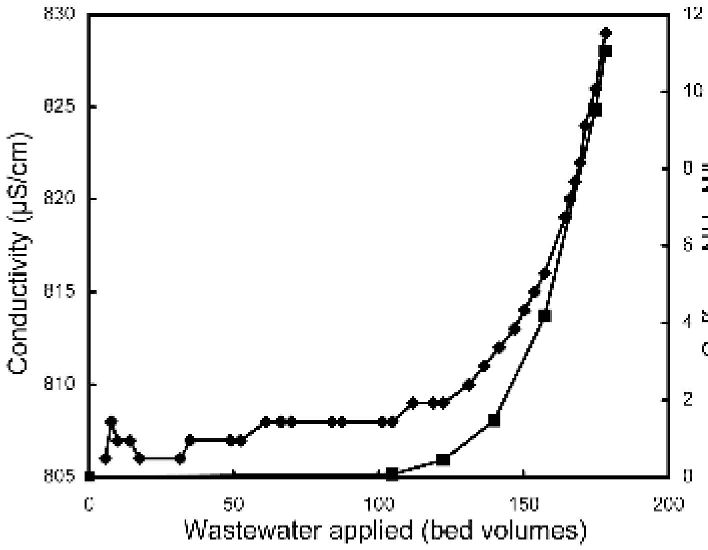

Fig. 5. Ion exchange column exhaustion with real wastewater: ■ – C_{eff}, ♦ - Conductivity.

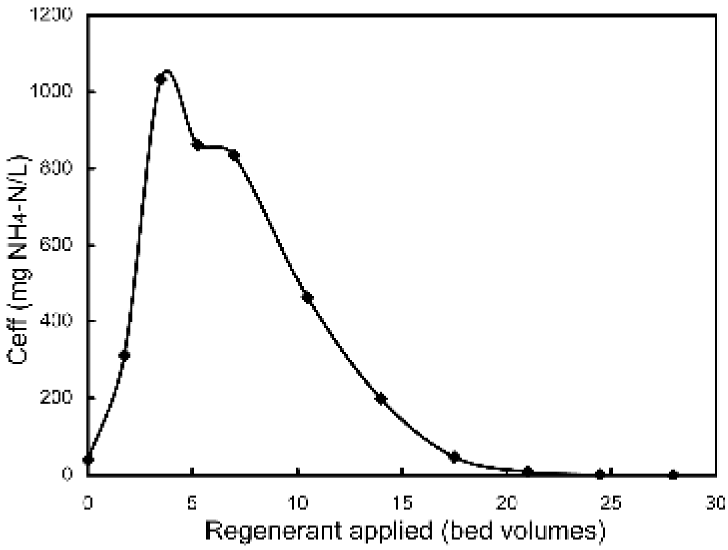

Fig. 6. Ion exchange column regeneration with 10 g/L NaCl solution.

Complete regeneration of SAC resin was reached after application of 22 BV of regenerant meaning that volume reduction factor of 8.1 was reached. This is comparable with the results of ammonium concentration from synthetic wastewater presented above.

Removal of ammonium from produced regenerate (Fig. 7) with CANON process was proved to be possible with biomass not adapted to increased salinity. However, in the end of the test relatively high amounts of nitrite (concentration 29.0 mg NO_2-N/L) and nitrate (concentration 21.2 mg NO3-N/L) accumulated. This can be explained by the fact that aerobic ammonium oxidizers are inhibited less with NaCl than Anammox bacteria which was shown above. In order to avoid nitrite and nitrate accumulation CANON process can be performed under lower DO concentration.

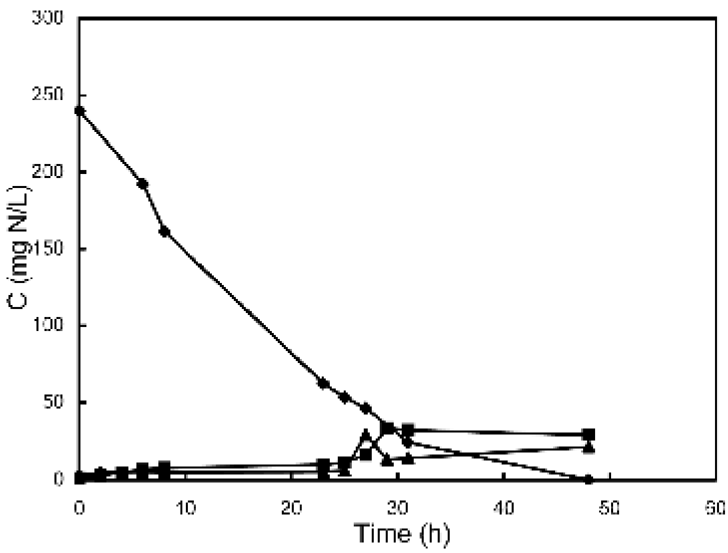

Fig. 7. Biological nitrogen removal from regenerate of ion exchange batch test with CANON process: ♦ - NH_4-N ■ – NO_2-N; ▲ – NO_3-N.

Conclusions

Based on the present results such conclusions can be made:

- Increase of salinity leads to decrease of activity of both AOB and heterotrophic bacteria.
- Anammox bacteria are inhibited by NaCl more then aerobic ammonium oxidizing bacteria.

- Optimal concentration of NaCl in regenerant is 10 g/L if unadapted biomass culture is used for further removal of ammonium with CANON process. At this concentration both the concentration of ammonium to the required level is possible and bacteria responsible for the biological removal are not getting inhibited.

- The fastest regeneration can be done with regenerant of the highest NaCl concentration. Regeneration with NaCl performs faster than with HCl, even though use of HCl as regenerant leads to slightly increased exchange capacity of resin.

- IE-CANON is a promising technology for ammonium removal from the main stream of wastewater with low aeration requirements and without need of external carbon.

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