PARTIAL NITRITATION/ANAMMOX AND CANON – NITROGEN REMOVAL SYSTEMS FOLLOWED BY CONDUCTIVITY MEASUREMENTS

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ABSTRACT
The deammonification process is a new biological promising method for a separate treatment of ammonium-rich digester supernatant. Its application can significantly reduce the nitrogen load in Wastewater Treatment Plants (WWTPs). The method is a two-step process and it can be accomplished in two separate stages (partial nitritation and Anammox) or in a singe one (CANON). Both these systems were tested at pilot plants: the CANON process in a laboratory-scale plant while partial nitritation/Anammox in a technical-scale one. The pilot plants were filled with Kaldnes rings as biofilm carriers and supplied with supernatant, coming from digested sludge dewatering at the Bromma and Himmerfjärden WWTPs, Stockholm, Sweden. The supernatant main ions - ammonium and hydrogen carbonate - were converted during the processes to carbon dioxide and nitrogen gas molecules and therefore the process performance could be followed by conductivity measurements. The experiments proved that conductivity was an easy and simple method to monitor the nitrogen removal processes. Moreover, the data from on-line conductivity instruments, installed in the Anammox reactor of the technical-scale pilot plant, showed great similarity with the manual measurements.

KEYWORDS
Anammox; CANON; conductivity; partial nitritation/Anammox; supernatant

INTRODUCTION

Sludge digestion and centrifugation processes are one of the sources of highly concentrated ammonium streams. During this process a protein breakdown occurs and about 50% of the sludge bound nitrogen is released to a wastewater stream in the form of ammonium (Siegrist, 1996). Streams with an ammonium concentration up to even 2 kg m^{-3} (Strous et al., 1997) can be obtained after dewatering of the digested sludge. Recycling of such a stream to the head of a WWTP contributes to the average increase in the total nitrogen load by about 15–20%. Application of the Anammox (ANaerobic AMMonium Oxidation) process for a separate treatment of supernatant coming from dewatering of digested sludge can significantly decrease a nitrogen load at WWTPs.

In the Anammox process, ammonia together with nitrite (electron acceptor) is converted under completely anoxic conditions to dinitrogen gas and small amounts of nitrate (Jetten et al., 1999) according to reaction 1:

$$NH_3 + 1.32NO_2^- + H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 2H_2O \qquad \text{reaction 1}$$

To remove ammonium nitrogen from wastewater using the Anammox bacteria, a proper nitrite-to-ammonium ratio is needed. Nitrite can be produced by aerobic autotrophic ammonia oxidizers, according to reaction 2.

$2NH_4^+ + 1.5O_2 + 2HCO_3^- \rightarrow NH_4^+ + NO_2^- + 2CO_2 + 3H_2O$ reaction 2

In practice, to perform successfully the Anammox process a preceding aerobic step is obligatory. In the first step ammonium is partially oxidized to nitrite (partial nitritation), which next, as an electron acceptor, reacts with the remaining ammonium to form nitrogen gas (Anammox step). The overall process is called "partial nitritation/Anammox" and can be operated in two stages; Ammonia oxidation is performed under oxic condition in the first stage, while the Anammox step takes place under anoxic conditions in the second one. In the CANON (Completely Autotrophic Nitrogen removal Over Nitrite) system both types of bacteria can co-exist in one reactor due to oxygen and oxygen-free zones within the biofilm depth (Hao et al., 2002; Sliekers et al., 2002, 2003; Third et al., 2001). Ammonia is partially oxidized under oxygen-limited conditions to nitrite and next nitrite together with remaining ammonia is converted to dinitrogen gas by the Anammox bacteria. The combination of these two processes can be expressed by the following reaction:

$NH_4^+ + 0.85O_2 \rightarrow 0.435N_2 + 0.13NO_3^- + 1.3H_2O + 1.4H^+$ reaction 3

The technology based on presented above processes can be applied for treatment of an ammonium-rich supernatant coming from dewatering of the digested sludge. As ammonium and hydrogen carbonate are the main ions (on a molar basis) affecting ionic charge in a supernatant and they both undergo transformations during partial nitritation and Anammox, it was possible to use conductivity measurements as a parameter to follow the nitrogen removal processes (Szatkowska et al., 2004a,b; Trela et al., 2004).

The objective of this paper was to evaluate application of conductivity, as an easy and simple parameter, to monitor the partial nitritation/Anammox process in a one or two-stage system.

MATERIALS AND METHODS

Laboratory-scale pilot plant

Description The laboratory-scale pilot plant consisted of two reactors operated in series and filled with Kaldnes rings, as carrier material for biofilm growth. Each reactor was equipped with a mixer, to assure proper mixing and oxygen conditions, and with heaters to keep temperature at a stable level of 31^oC. The pH level was corrected with a continuous dosage of Na_2CO_3 solution to the first reactor (to keep pH around 8.2). Since 23rd July the amount of Na_2CO_3 solution was being gradually reduced until 23rd August when a correction was no longer necessary. The pilot plant was continuously fed with a supernatant from digested sludge dewatering at the Bromma WWTP; the plant receives municipal wastewater from central and western parts of the Stockholm region. To obtain the required influent concentration, the supernatant was diluted with tap water. A detailed description of the installation can be found in earlier publications (Plaza et al., 2003; Gut and Plaza 2003; Szatkowska et al., 2003).

Measurements and sampling The samples were collected twice or once a week, from both the inlet and outlet of each reactor of the pilot plant. They were analysed for the ammonium nitrogen (NH_4-N), the nitrite nitrogen (NO_2-N) and the nitrate nitrogen (NO_3-N) with TECATOR–AQUATEC 5400 ANALYZER (flow-injection system based on VIS spectrophotometry). Other parameters such as: dissolved oxygen, temperature and pH were measured every day. Moreover, simultaneously to the regular sampling the conductivity measurements were performed. To analyse a variable characteristic of the influent (supernatant) analyses of COD, PO_4-P tot; alkalinity and organic acid were performed (see Table 1).

Technical-scale pilot plant

Description Two pilot plant reactors (each of a 2.1 m^3 volume) were filled with Kaldnes rings (50% of volume) as biofilm carriers. The pilot plant was continuously fed with supernatant from dewatering of the digested sludge at the Himmerfjärden WWTP. The first reactor (R1) was divided into three zones, where partial nitritation took place and half of the ammonia was oxidised to nitrite. The nitritation step was followed by the Anammox process (R2) during which half of ammonia reacted directly with nitrite to produce nitrogen gas.

Measurements and sampling The processes were monitored by on-line measurements of pH, temperature, and conductivity (during the latest part of the experimental period). Additionally, analyses of such parameters as: N-fractions, COD, organic acids, alkalinity and Tot-P were performed in both supernatant and effluent from the reactors. Other manually done measurements included flow, oxygen, temperature, pH and conductivity in all reactor zones. A characteristic of supernatant is presented in Table 1.

Table 1. Characteristics of supernatant

	Bromma WWTP*					Himmerfjärdsverket WWTP *				
parameter	**NH_4-N** [mg N/l]	**COD** [mg O_2/l]	**PO_4-P_{tot}** [mg P/l]	**Alkalinity** [mmol HCO_3/l]	**Org. Acids** [mg/l]	**NH_4-N** [mg N/l]	**COD** [mg O_2/l]	**PO_4-P_{tot}** [mg P/l]	**Alkalinity** [mmol HCO_3/l]	**Org. Acids** [mg/l]
average	878	446	1.8	77	66	720	370	19.1	82	101
min	663	308	1.2	28	42	532	203	2.3	16	24
max	1000	711	3.8	107	109	918	691	46.4	189	259
st. dev.	108	109	0.8	27	25	98	136	17.4	42	79
n	13	13	10	13	6	52	24	18	49	8

* Period from 6th January 2004 to 30th December 2004

RESULTS AND DISCUSSION

Laboratory-scale pilot plant

A laboratory-scale pilot plant has been in operation at the Kungliga Tekniska Högskolan (KTH) for over 3 years. In this paper, a one-year operational period is presented. At that time the process proceeded at temperature and pH values of 31°C and 8.1, respectively. Dissolved oxygen in the reactor 1 was 0.34±0.20 mg O_2/l while its value in reactor 2 amounted to 0.31±0.23 mg O_2/l. Results from the experimental period showed that at nitrogen concentrations of around 300 mg NH_4-N/l the average nitrogen removal was 67% (varying from 36 to 91%). As it can be seen from Figures 1a and 1b, reactor 1 played a dominant role in the nitrogen removal. The average nitrogen removals were 38% and 29 % for reactor 1 and 2, respectively. They corresponded to the average nitrogen removal of 112 mg N/l in rector 1 and 84 mg/l N in reactor 2. In the laboratory-scale pilot plant, ammonium oxidation proceeded along with a nitrogen removal in both reactors. It meant that a partial nitritation took place parallel to the Anammox process and indicated the presence of the CANON process in both reactors. Low values of nitrite showed its rapid consumption during the Anammox process after its earlier production by ammonium oxidants. The formation of nitrate was very small, according to the Anammox reaction where nitrates production makes up about 13% of the incoming nitrogen.

A lower nitrogen loss, which was recorded later on in the first reactor, was probably due to a lack of pH correction. Correction of pH was slowly abandoned to find out if system can work without addition of chemicals. A consequence of a gradual decrease of Na_2CO_3 solution dosage to the first reactor was especially noticeable in the first reactor, where a decrease of process efficiency was observed (see Figure 1a). Higher values of effluent nitrogen concentrations in the first reactor resulted in a higher influent load to the second reactor. In the last period, effluent ammonium concentrations from the second reactor exceeded 100 mg/l. However, the second reactor maintained a stable efficiency during the whole experimental period (see Figure 1b).

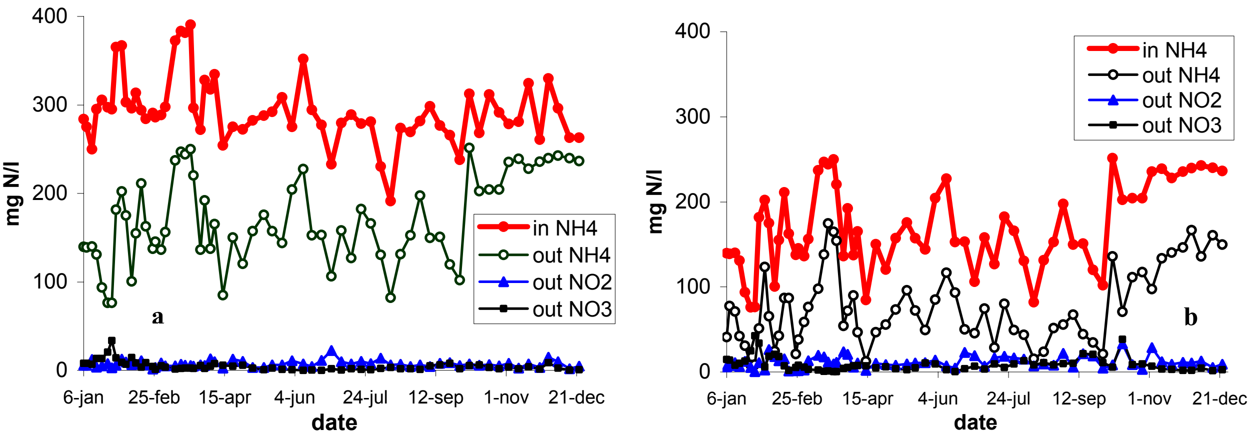

Figure 1. Nitrogen conversions in a laboratory-scale pilot plant: **a.** reactor 1, **b.** reactor 2

To evaluate whether the CANON process performance can be followed by conductivity, these measurements were introduced into daily routines. Figure 2 presents the results of manual conductivity measurements, performed together with sampling and nitrogen forms analyses in the influent and effluent from the laboratory-scale plant. The plots showed that the trends of conductivity curves could be compared with the courses of matching nitrogen curves. In the influent, higher ammonium concentrations corresponded to higher conductivity values, while drops in nitrogen concentrations were in agreement with a lower conductivity. It could be seen (Figure 2b) that deterioration of efficiency and higher values of effluent inorganic nitrogen concentrations were reflected in higher conductivity values.

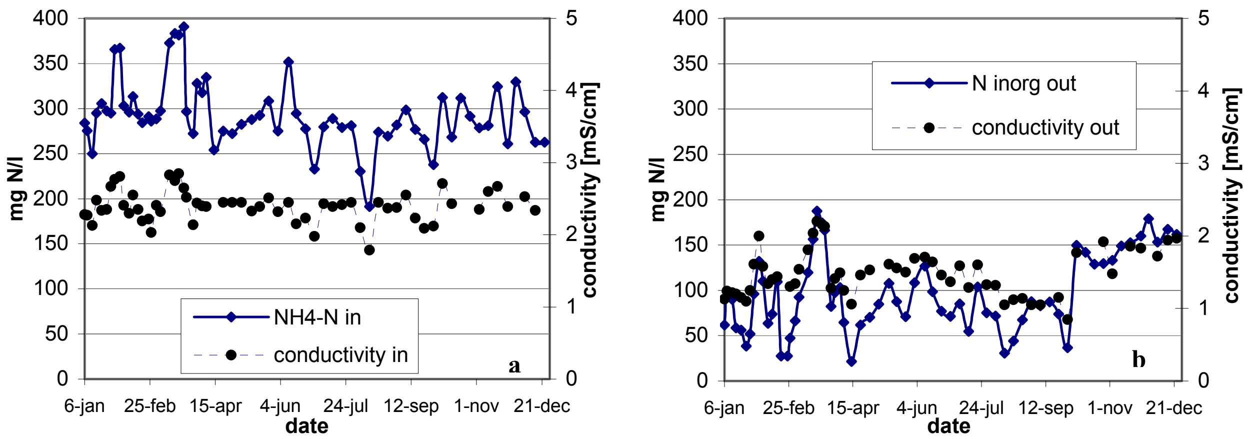

Figure 2. Inorganic nitrogen and conductivity measurements in a laboratory-scale pilot plant **a.** influent, **b.** effluent

Observations of nitrogen conversions and conductivity measurements allowed presuming that there was a correlation between these parameters. Partial nitritation and the Anammox process occurred in both reactors simultaneously resulted in nitrogen removal and an accompanying conductivity decrease. As it was shown in Figure 3, it was possible to plot curves outlining a relationship between inorganic nitrogen and conductivity for influent and both effluents.

Good relationships were demonstrated with quite high correlation coefficients for all three cases examined. Especially the both effluents curves indicated similar slops and abscissas.

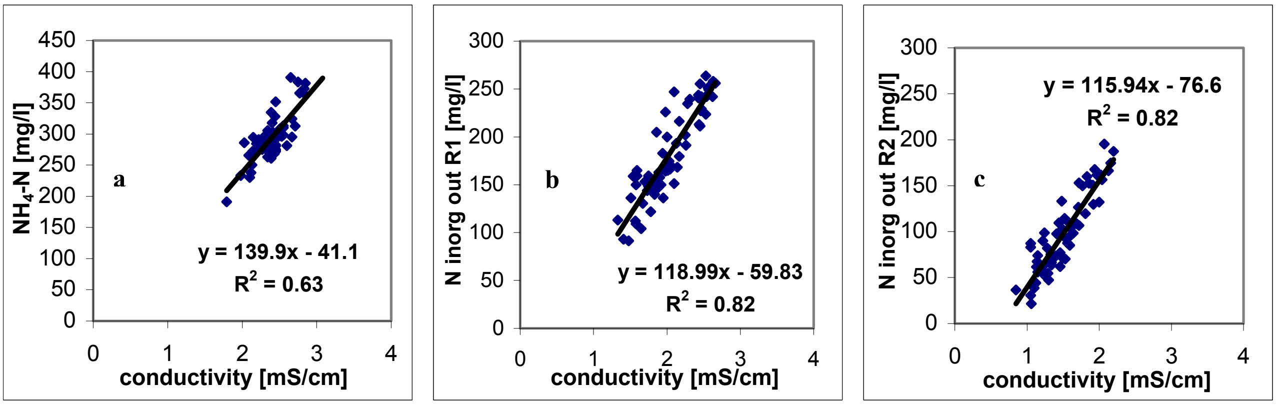

Figure 3. a. Correlation between influent ammonium and conductivity (R1); **b.** Correlation between effluent inorganic nitrogen and conductivity (R1); **c.** Correlation between effluent inorganic nitrogen and conductivity (R2).

Technical-scale pilot plant

Partial nitritation and the Anammox process were also successfully tested at a technical-scale pilot plant. At this plant, two processes were run separately in two different reactors. The partial nitritation was run at the average dissolved oxygen concentration of 1.1±0.94 mg O_2/l and temperature of 31.5±2.1 ^oC. The first reactor (R1) was supplied with ammonium-rich supernatant with concentrations varying from 530 to 920 mg/l (see Figure 4a). In this reactor, about a half of ammonium was oxidised to nitrite, without further oxidation of nitrite to nitrate due to a proper adjustment of aerobic conditions and a pH control. The average nitrite-to-ammonium ratio recorded in the first reactor effluent was 1.2 (for the Anammox process is should be 1.3, according to the stoichiometry of reaction 1).

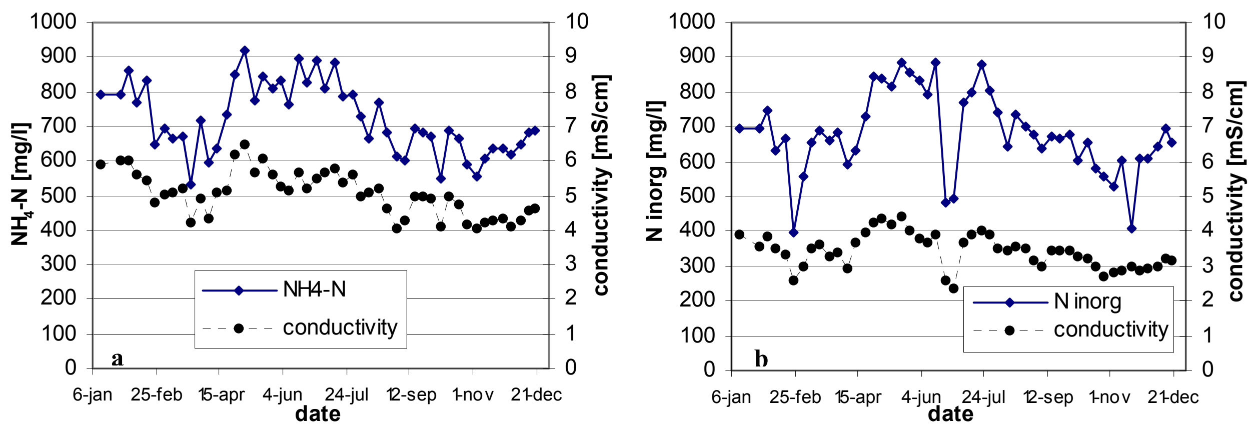

Figure 4. Nitrogen and conductivity in the partial nitritation reactor (R1); **a.** influent, **b.** effluent.

The first reactor effluent was diluted with tap water (to slowly build-up the process) before being supplied the second Anammox reactor (R2). A dilution rate decreased gradually to increase the nitrogen load. An influent inorganic nitrogen concentration varied within the range of 98-420 mg/l, while the effluent contained mainly nitrates formed during the Anammox process, and the concentration was below 50 mg/l (see Figure 5b). The average dissolved oxygen in R2 amounted to 0.13±0.06 mg O_2/l.

The partial nitritation is a transformation of ammonium and hydrogen carbonate, as they are the main ions present in the supernatant. Hydrogen carbonate is almost completely utilised while half of ammonium is transfer to the nitrite. Then, ionic charge of reduced ammonium is compensated by the produced nitrite ions. Therefore, the conductivity values measured in the effluent from the partial nitritation were lowered down by conductivity values of hydrogen carbonate (see Figure 4a and b). The average value of alkalinity in the influent was 82 mmol $HCO3^-$/l, while in the effluent it was 8.7 mmol HCO_3^-/l. A satisfactory performance of partial nitritation, resulting in oxidation of about half of ammonium to nitrite, corresponded to a stable conductivity difference between the influent and effluent from the first reactor (average difference was 1.63 mS/cm) (Figure 4a and b). It could be seen that both influent and effluent conductivity curves could be compared with the corresponded nitrogen curves. The peaks of ammonium concentrations in the first reactor (R1) corresponded to higher values of conductivity, while the minimums in nitrogen concentrations were accompanied with a lower conductivity.

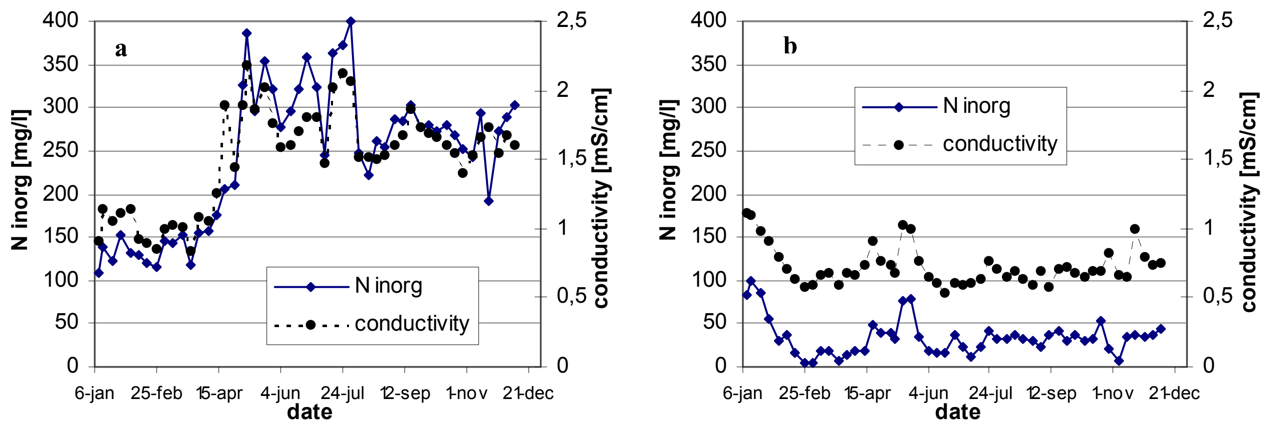

Figure 5. Nitrogen and conductivity in the Anammox reactor (R2); **a.** influent, **b.** effluent.

The higher values of inorganic nitrogen run parallel to the measured conductivity values in the Anammox reactor (R2), as it could be seen in Figure 5a. During the Anammox process about equal amounts of ammonium and nitrite ions were transferred to the molecules causing a decrease in conductivity. The respond to small effluent inorganic nitrogen concentrations were low conductivity values.

Similar to the laboratory-scale pilot plant, a linear relationship with relatively high correlation coefficients was found for nitrogen and conductivity in the partial nitritation process of the technical-scale pilot plant (Figure 6a and b). Influent ammonium was correlated there with the measured conductivity values in supernatant (see Figure 6a), while oxidised ammonium was correlated with a conductivity drop (see Figure 6b) due to alkalinity consumption and oxidation of half of ammonium.

In the Anammox process alkalinity changes were insignificant, and conductivity was mainly governed by conversions of ammonium and nitrite ions to dinitrogen gas molecules. Therefore, it was possible to plot a curve showing a strong relationship between inorganic nitrogen and conductivity; they both were removed in the second reactor where the Anammox process took place (Figure 6c). The presence of other ions and sub-processes could contribute to lower values of the correlation coefficient.

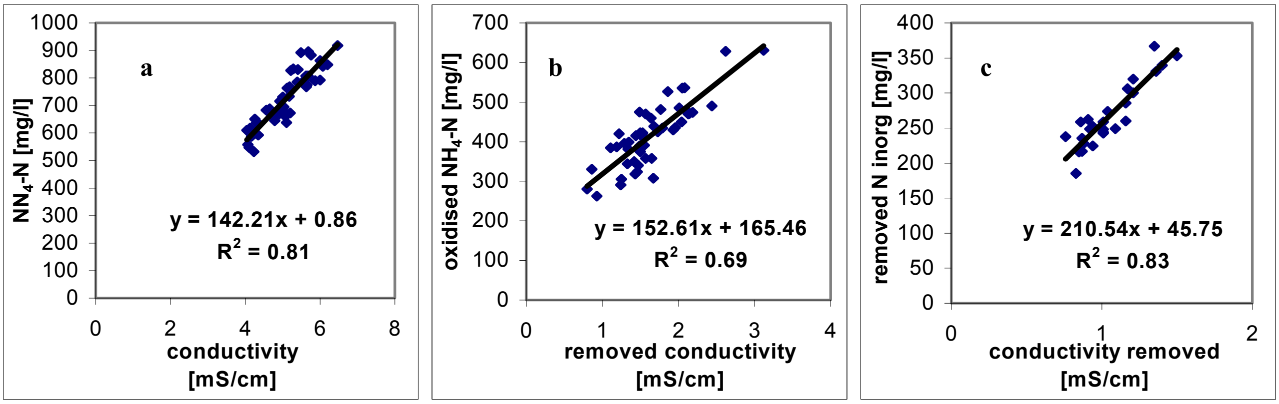

Figure 6. a. Correlation between influent ammonium and conductivity (R1); **b.** Correlation between oxidised ammonium and removed conductivity (R1); **c.** Correlation between removed inorganic nitrogen and removed conductivity (R2).

The correlation observed between manually measured conductivity and analysed nitrogen forms encouraged a hypothesis that replacement of manual measurements with on-line measurements could give the same or even better results. Therefore, on-line instruments were installed to monitor the second Anammox reactor in the technical-scale pilot plant. Data from a three-month readout period of on-line conductivity electrodes, at the inlet and the outlet of the Anammox reactor, are presented in Figure 7.

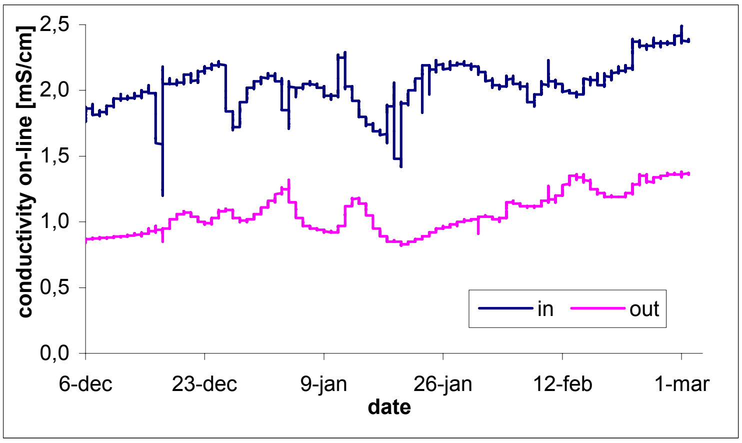

Figure 7. On-line readouts from conductivity electrodes, inlet and outlet of the Anammox process (R2).

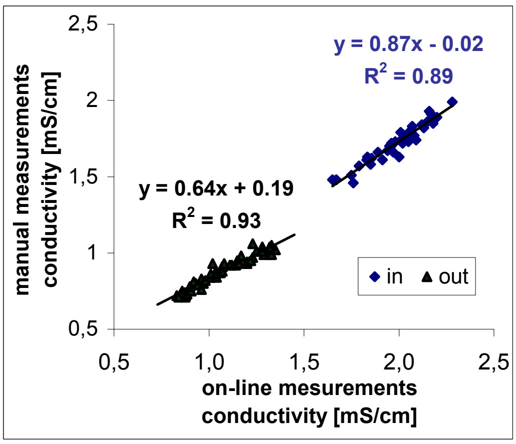

Figure 8. Correlation between on-line and manual measurements of conductivity for the Anammox reactor (R2).

To find out compatibility between manual and on-line electrodes a relationship between them was plotted, for the inlet and outlet of the reactor, separately (Figure 8). The curves with the same slopes and high correlation coefficients were obtained and they confirmed that manual and on-line measurements were in general agreement. It meant that on-line measurements were a reliable tool and they could replace manual measurements, if necessary.

CONCLUSIONS

Comparing a two-step deammonification process preformed in a one-stage (CANON) and in a two-stage (partial nitritation and Anammox in following reactors) system, it can be concluded that better results were obtained for the technical-scale pilot plant, were both processes were run separately. A separate performance of these two processes enables a better control the whole system. A proper adjustment of oxic conditions, resulting in a pH drop, led to oxidation of half of ammonium with only a minor oxidation of nitrite to nitrate. It was possible to obtain an appropriate value of nitrite-to-ammonium ratio (close to 1.3) in the nitritation step effluent; such ratio assured high nitrogen removal efficiency in the Anammox step (370 mg N/l as the maximum value).

Both CANON, operated at a laboratory-scale pilot plant, and partial nitritation/Anammox, run in separate reactors at a technical-scale pilot plant, were monitored by manual conductivity measurements. Experiments showed that the conductivity curves were parallel to the plots of analysed nitrogen forms. As a high correlation coefficient between conductivity and nitrogen was obtained for both influent and effluent, conductivity measurements could be helpful to evaluate the efficiency of the nitrogen removal systems. The performed investigations proved that the readouts from on-line conductivity instruments gave comparable results to the manual values. The curves plotted for both inlet and outlet of the Anammox reactor (technical-scale pilot plant) had high correlation coefficients and they confirmed that on-line conductivity measurements could be used as an easy and simple parameter to monitor the process.

The promising results obtained during these studies allowed for a conclusion that conductivity could be implemented as a process monitoring tool. It provides opportunity to save operational costs (lower chemicals demand) and time (no time-consuming nitrogen analyses) at the WWTPs.

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