PRELIMINARY STUDIES ON DEAMMONIFICATION PROCESS KINETICS

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ABSTRACT
During one year period laboratory-scale pilot plant studies with the aim to better understand mechanisms controlling the deammonification process have been performed. Due to low growth rates of microorganisms responsible for anaerobic ammonia oxidation the process favours systems with long sludge retention times (biofilm systems), which continuously receive wastewater rich in ammonium and nitrites. In the experiments, the Kaldnes rings were used as biofilm carriers. In order to estimate reaction rates in the pilot plant, batch tests were carried out with the medium taken from two reactors of the pilot plant. In the paper five batch tests from both reactors are described and discussed. Based on achieved data ammonium and nitrite removal rates were calculated. An average removal rate of ammonium was 1.2 g NH_4-N/m^2·d and nitrite nitrogen removal occurred at about the same rate and the average was 1.1 g NO_2-N/ m^2·d. The increasing tendency in nitrogen removal rate was observed in the succeeding batch tests, what indicates the increase in the bacterial activity in the reactor. Due to introducing conductivity measurements, relationship between inorganic nitrogen and conductivity was found.

KEYWORDS
ammonium removal rate; Anammox; batch test; conductivity; deammonification

INTRODUCTION

The application of deamonification process for treatment of ammonium rich wastes streams, which includes leachates from landfills and supernatants from dewatering of digested sludge at wastewater treatment plants, can reduce the costs of plant operation and make the management more sustainable. The deammonification can be defined as a two steps reaction: one part is a nitritation, the other an anaerobic ammonium oxidation (Anammox). During the Anammox process equal amounts of ammonium and nitrite nitrogen react to produce nitrogen gas without additional supply of organic material. This new technical solution for handling of nitrogen rich wastewaters have been developed and studied by research groups in many countries (Plaza et al., 2002; Trela et al., 2001; Van Dongen et al., 2001; Mulder et al., 2000; Helmer et al., 2000; Hellinga et al., 1998; Siegrist et al., 1998; Hippen et al., 1997). Parallel to development of deammonification process, kinetics studies have been carried out for the better process understanding (Seyfried et al., 2001; Helmer et al., 2000; Hippen et al., 2000; Johansson et al., 1998; Siegrist et al., 1998).

To study the process performance and mechanisms of reactions between ammonium and nitrite a laboratory-scale pilot plant was designed and constructed. The plant has been running for more than one year at the Department of Land and Water Resources Engineering, Royal Institute of

Technology (KTH). Through the successful operation of the pilot plant it was possible to further characterise the reactions of the aerobic/anaerobic deammonification and bacterial culture behaviour. In order to focus more on the kinetics of the deammonification process five batch tests were run.

The main objective of the batch tests was to find out the nature of reactions inside the reactors and to determine the ammonium removal rate for the deammonification process in the pilot plant. Parameters like concentration of dissolved oxygen, pH and temperature affect the deamonification process, and therefore the second goal was to determine the most sensitive parameter in regard to proper operation of the pilot plant and batch tests performance.

MATERIAL AND METHODS

Pilot plant description

The laboratory-scale pilot plant consisted of two reactors and was operated over one year period to study the deammonification process. The reactors were filled with Kaldnes rings as carrier material for fixed film growth. Each reactor was equipped with mixer and thermostat (for keeping temperature constant at 31°C). The pH level was corrected with a continuous dosage of Na_2CO_3 solution to the first reactor (to keep a pH at the level about 8.2). The pilot plant was continuously fed with supernatant produced during dewatering of the digested sludge at the Bromma Waste Water Treatment Plant (WWTP). The plant receives municipal wastewater from central and western part of the Stockholm region. To obtain required concentration supernatant was diluted with tap water.

Batch test description

In a batch test a closed reaction system was developed in which the important process parameters were maintained at the optimal level. The equipment used in the batch test is shown in the Figure 1.

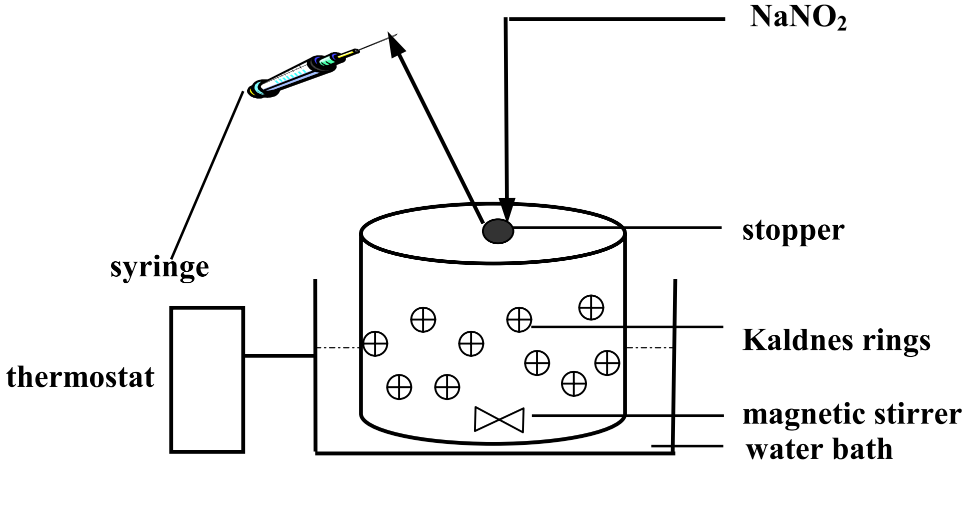


Figure 1. Batch test equipment scheme.

The batch test was run in two parallel bottles of 1 litre working volume. On test days, the carriers were taken from both reactors of the continuously working pilot plant (described above) and put into the bottles to fill 50% of their volume. Then, the liquid from the reactors was poured over the Kaldnes rings up to 1 litre volume. Medium from the first reactor was placed in bottle 1, while medium from the second one in bottle 2. The liquid and the Kaldnes rings were handled with a great care. Obviously, the rings were taken out right before the test and returned immediately after the test completion; otherwise the deammonification process could have been disturbed. The temperature in each test was kept stable through a water bath.

The initial concentrations of ammonium, nitrite and nitrate were set for each test. To obtain the required concentrations, $NaNO_2$ and NH_4Cl solutions were used (2 mg/ml NO_2-N or NH_4-N). Test 1 was run at 30°C while during tests 2, 3, 4 and 5 temperature was set at 31°C. The solution of 1M sodium hydroxide was prepared for pH correction.

To shorten the reaction time it was decided that the Kaldnes rings level was increased up to 50% of the volume, instead of 20% used in the pilot plant. Magnetic stirrers were placed in the bottles to assure an adequate mixing of medium throughout the test. The batch bottles had holes in the middle of the lid for samples taking. The openings were shut with the stoppers to prevent air from getting into the bottles.

Measurement and sampling procedure

Each of the batch tests lasted 8 hours. The proposed sampling strategy enabled very accurate control during the test - every hour or every two hours 15 ml sample was taken from the bottle by syringe. The samples were filtrated with a pre-filter and a 0.45 μm filter and then stored at -10°C. The number of samples was different for each batch test depending on the test performance and changes in process parameters. Samples were analysed for NH_4-N, NO_2-N and NO_3-N with TECATOR – AQUATEC 5400 ANALYZER (flow-injection system based on VIS spectrophotometry).

Moreover, pH, dissolved oxygen concentration and conductivity were measured. The samples were analysed for COD as well.

RESULTS

Depending on the results from the pilot plant obtained on the previous day the ammonia and nitrite concentration was calculated. The requirement for the initial concentrations of ammonia and nitrite was 150 mg NH_4-N/l and 75 mg NO_2-N/l, respectively. Ammonia concentrations always extended this value and it was no need to increase it. To achieve necessary nitrite concentration, $NaNO_2$ solution (2 mg NO_2-N/ml) was added to the medium. The material had to be taken in a way as to avoid aeration. To thoroughly evaluate conversion of nitrogen compounds samples were taken every one or two hours.

Process parameters

During batch test temperature in both bottles was kept constant (30 or 31°C) to make the results more comparable. In this way the process conditions were similar to those at the pilot plant. The pH level was not corrected. The minimum vale of pH was 8.14 and maximum was 8.43. The average value of pH in bottle 1 amounted to 8.28 and in second to 8.23. In the batch tests the pH -value was considerably constant which also indicates that there was no significant change in alkalinity, for instance due to heterotrophic denitrification. The DO concentration in both bottles was kept consistently below 0.5 mg O_2/l. Only once DO exceed this level during batch test 5 and amounted to 0.52. The average value of DO for bottle 1 during all five batch tests amounted to 0.34 and for second to 0.38. Table 1 present average values of DO, temperature and pH during five batch tests.

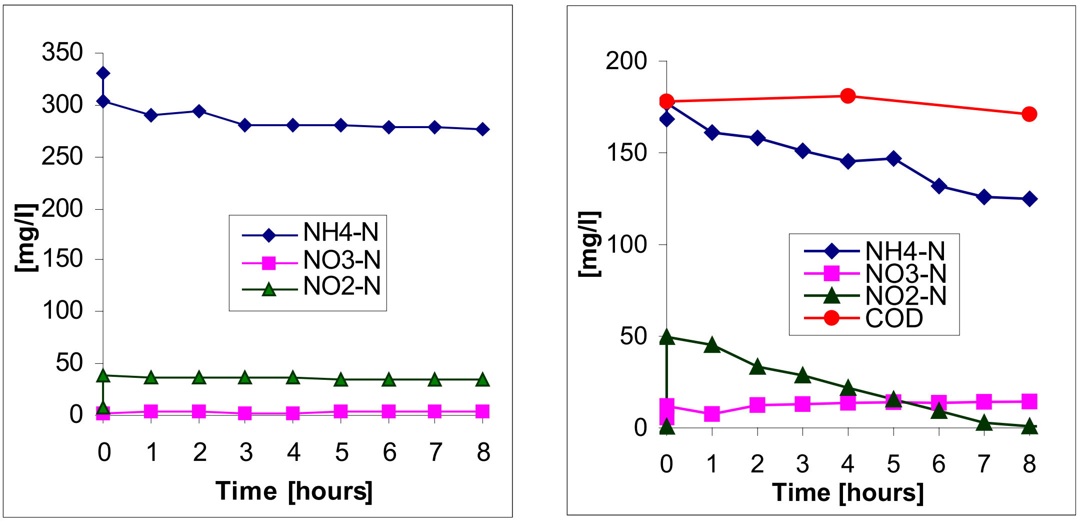
Table 1. Average values of DO, temperature and pH during batch tests.

Test No	Average DO		Average T		Average pH	
	Bottle 1	Bottle 2	Bottle 1	Bottle 2	Bottle 1	Bottle 2
1	-	0.29	-	30	-	8.20
2	0.28	0.26	31	31	8.29	8.26
3	0.24	0.22	31	31	8.36	8.41
4	0.45	0.37	31	31	8.26	8.30
5	0.41	0.38	31	31	8.20	8.21

One of the goals of batch tests was to identify which parameter is the most sensitive for the process performance. Optimal temperature and pH was easy to maintain at the required level. Even if some fluctuations in pH and temperature occurred, it did not have much influence on process performance. Opposite to temperature and pH, dissolved oxygen was a much more sensitive parameter. Sometimes it was difficult to stabilize it at a certain desired value.

Nitrogen conversion

Analysing results of nitrogen variation from all batch tests the differences between first and second bottle in nitrite utilization can be observed. As the example from the performed tests the comparison of the results obtained for the medium from reactor 1 (bottle 1) and reactor 2 (bottle 2) is presented in Figure 2.



A) B)

Figure 2. Comparison of the nitrogen forms variation in bottle 1 (reactor 1) (A) and bottle 2 (reactor 2) (B) - batch test 2.

Differences in nitrite utilization indicate diverse processes occurring in the reactors. In the first bottle, ammonium was removed without a simultaneous reduction of nitrite and at a constant nitrate concentration. When the medium from reactor 2 was investigated a different path of nitrogen compounds conversions was observed. It became obvious that nitrite and ammonium were converted simultaneously. After complete utilization of nitrite, ammonium was reduced only to a small degree. Results from the performed batch tests for the medium from reactor 2 (bottle 2) are presented in the Figure 3.

The results showed that as long as an excess of nitrite was present in the batch, the reaction proceeded. When the whole amount of nitrite was consumed the reaction was suppressed. Without presence of nitrite the bacterial culture cannot follow the Anammox path. The fact that in bottle 2 ammonium was eliminated together with removal of nitrite allows for the assumption that this reaction also occurred in the pilot plant operated at KTH. To go further, the reaction observed in the bottle 1 (medium from reactor 1) during batch tests showed removal of ammonium without utilisation of additional nitrite supply.

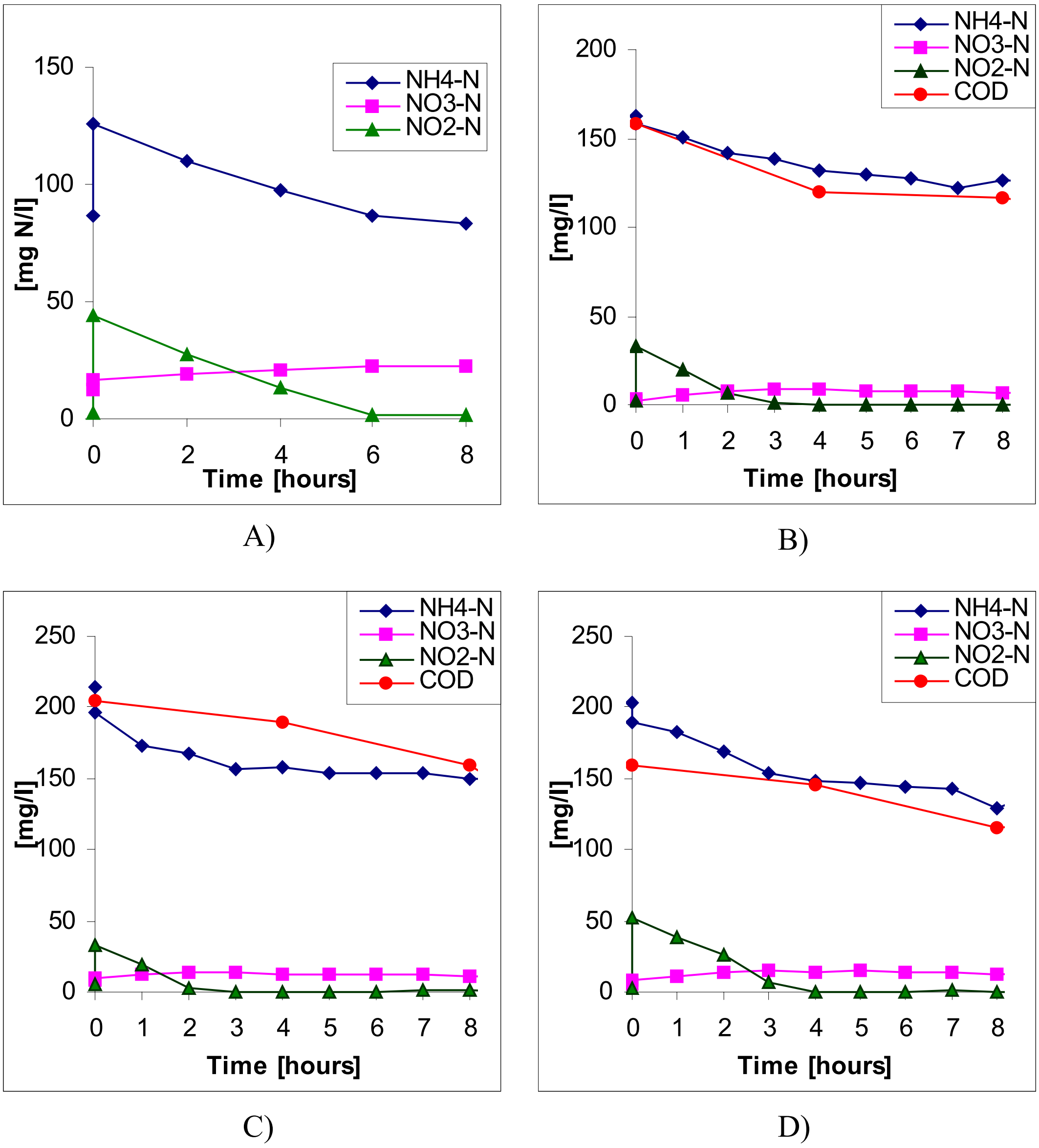


Figure 3. Analytical results from bottle 2 (reactor 2) for batch test 1(A); batch test 3(B); batch test 4(C); batch test 5(D).

It can be assumed that bacterial culture in the first reactor is able to perform nitritation process as both ammonium and nitrite removal rates were at low levels. On the contrary, the bacteria culture from reactor 2 was utilising ammonium at required level only with a surplus of nitrite. At low level of nitrite the deammonification process is much slower. It indicates a demand for providing an additional nitrite supply from reactor 1, necessary for the Anammox reaction.

Batch tests performed for the medium from the reactor 1 showed a very low ammonium removal rate, what support the hypothesis that Anammox process took place mostly in the reactor 2. Removal of ammonium in reactor 2 was at the average rate of 1.2 g NH_4-N/m^2·d (as average from the performed tests varying from 0.7 to 2.3 g NH_4-N/m·^{2}·d). Figure 4 shows that nitrite nitrogen removal occurred at about the similar rate (except one batch test) and the average value was 1.1 g NO_2-N/m^2·d (varying from 0.6 to 1.5 NO_2-N/m^2·d).

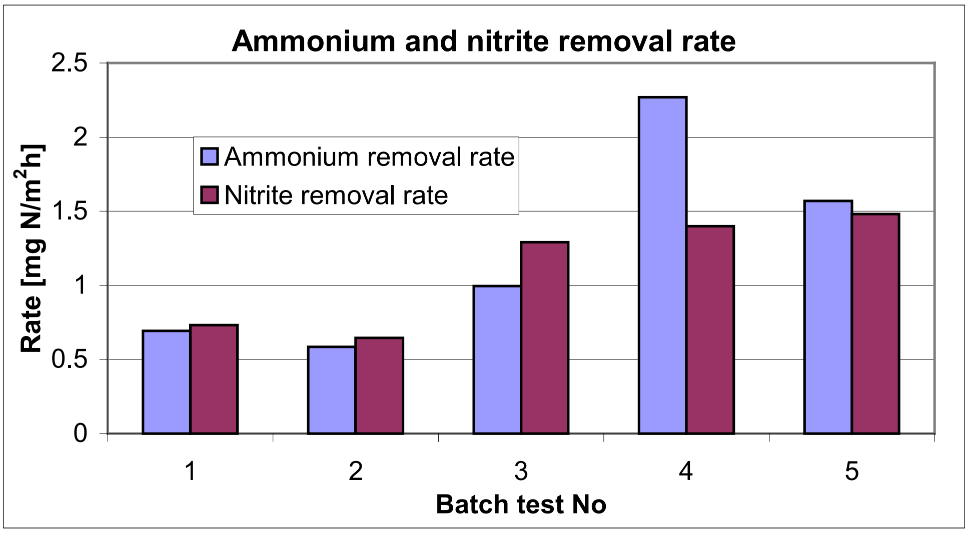


Figure 4. Ammonium and nitrite removal rate for bottle 2.

Approximately the same rates for ammonium and nitrite nitrogen removal are an indication of deammonification process. The fact that the ratio of NO_2-N removed / NH_4-N removed was around 1 signifies the high efficiency of the Anammox process. The increasing tendency in nitrite nitrogen removal rate (which can be observed in Figure 4) was observed in the succeeding batch tests, what indicates the increase in the bacterial activity in the reactor. Curves representing NH_4-N and NO_2-N conversions run almost parallel, what can be observed in Figure 3. Ammonium and nitrite were removed simultaneously. The concentration of nitrate, after a slight preliminary increase, was kept constant.

Low values of removed COD per removed nitrite proved that heterotrophic denitrification can not take place in the reactors as at least 3 g COD is needed per 1 g removed nitrite nitrogen.

Table 2 presents the comparison of the ammonium removal rate results obtained for different types of experiment and medium. As it can be observed, some of the experiments on the deammonification process were similar to the KTH experiment with the Kaldnes rings, as the biofilm carrier. Analysing the values of reaction rates reported in those studies, it could be stated that ammonium removal rates obtained in batch tests at the laboratory–scale pilot plant operated at KTH, are comparable. However, in the experiments conducted by Johansson et al. (1998) the values were much higher than those obtained in other experiments.

Table 2. Comparison of reaction rates obtained during deammonification studies.

Rate [g NH_4-N/m^2·d]	ASL [g NH_4-N/m^2·d]	Type of experiment	Type of medium	References
2	4 - 8	Pilot plant	Kaldnes	Seyfried C.F., Hippen A., Helmer C., Kunst S., Rosenwinkel K.-H. (2001).
1.9 2.6 2.0	11.9 9.9 7.8	Batch tests/moving-bed pilot plant	Kaldnes	Helmer C., Tromm C., Hippen A., Rosenwinkel K-H., Seyfried C. F. and Kunst S. (2000).
2	4 - 8	Laboratory-scale plant	Kaldnes	Hippen A., Johansson P., Beier M., Rosenwinkel K.-H., Seyfried C.F. (1999).
1.0 – 3.7	4 - 8	Pilot plant	Kaldnes	Johansson P., Nyberg A., Brier M., Seyfried C.F., Rosenwinkel K.-H. (1998).
0.5 – 3.0	1.4 – 3.2	Leachate treatment plant	Rotating biological contactor	Siegrist H., Reithaar S., Koch G. and Lais P. (1998).
0.6 – 2.3	0.5 – 2.3	Pilot plant	Kaldnes	Pilot plant at KTH

Conductivity

Parallel with parameter like DO, pH and temperature conductivity was measured. It could be observed in the second bottle that, the lower inorganic nitrogen concentration was, the smaller conductivity value. The study of relationship between inorganic nitrogen and conductivity, enabled to find a linear equation using the method of least squares. The linear equations and correlation coefficients were calculated and are presented in Table 3.

Table 3. Relation between inorganic nitrogen and conductivity measurements - results from batch tests for second bottle.

Batch test No.	Equation	Correlation coefficient
1	y = 59.522x–60.734	R^2= 0.765
2	y = 43x+35.264	R^2= 0.735
4	y = 157.39x–425.13	R^2= 0.868
5	y = 192.67x–309.99	R^2= 0.800

A high correlation coefficient obtained in the batch tests indicates that the conductivity measurement can be a reliable parameter for the observation of the deammonification process. The values of inorganic nitrogen and the values of conductivity decrease simultaneously as it can be observed in Figure 5. This leads to the conclusion, that conductivity measurements can be used as an easy and simple indicator of the deammonification process.

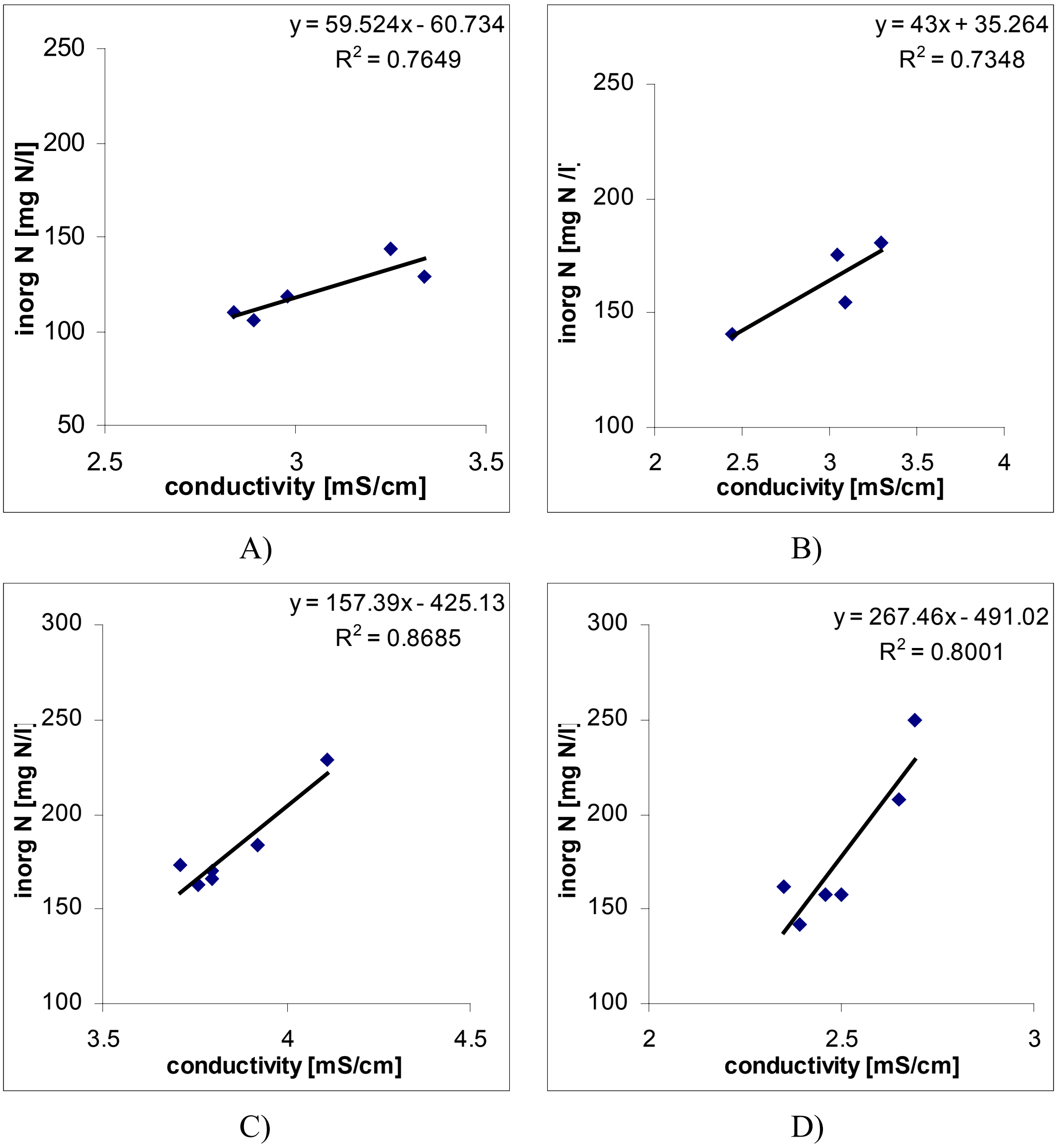


Figure 5. Relation between inorganic nitrogen and conductivity values during batch test 1(A); batch test 2(B); batch test 4(C); batch test 5(D).

CONCLUSIONS

Results from batch tests helped to gain more extent knowledge of reaction kinetics in deammonification process. Achieved ammonium removal rate was in the range 0.6 - 2.3, what is comparable with many different authors' results. The average value of ammonium removal rate in reactor 2 was 1.2 g NH_4-N/m^2·d, while the nitrite removal rate occurred at about the similar rate (except one batch test) and the average value was 1.1 g NO_2-N/m^2·d. Approximately the same rates for ammonium and nitrite nitrogen removals are an indication of deammonification process.

Batch tests performed for the medium from the reactor 1 showed a very low ammonium removal rate, what support the hypothesis that Anammox process took place mostly in the reactor 2. The increasing tendency in nitrogen removal rate was observed in the succeeding batch tests, what indicates the increase in the bacterial activity in the reactor.

Some fluctuations in pH and temperature did not have much influence on process performance. Dissolved oxygen turned out to be the most sensitive parameter. Relationship between conductivity measurements and inorganic nitrogen require more investigation. However, based on performed batch tests, it can be confirmed that conductivity measurements are very useful during deammonification process control.

The methodology developed for conducting batch test worked out successfully during the course of the study and can be applied in further batch tests.

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