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NITRIFICATION PROCESS CONTROL IN ACTIVATED SLUDGE USING OXYGEN UPTAKE RATE MEASUREMENTS

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ABSTRACT

A method, based on oxygen uptake rate measurements combined with the application of selective nitrification inhibitors, is presented which allows monitoring nitrifying activities of activated sludge samples. Nitrification activity measurements, only requiring a dissolved oxygen probe, can yield information on NH_4^+ and NO_2^- concentrations in mixed liquor samples. In this way, oxygen uptake rate measurements are a helpful tool to monitor the completion of the oxidation of NH_4^+ and NO_2^- in activated sludge processes. Some examples, demonstrating the value of alternate oxic and anoxic periods for nitrogen removal during sequencing batch reactor processes, also indicate the value of activity measurements for nitrification control purposes. The presented method offers a possibility to optimise the length of oxic-anoxic sequences in sequencing batch reactors which results in a better effluent quality of the treatment plant.

Keywords: activity monitoring, fed batch respirometer, inhibition, nutrient removal, sequencing batch reactor

INTRODUCTION

Nutrient removal becomes more and more important in aerobic wastewater treatment due to the more stringent effluent criteria that have to be met. In the last years, different reactor configurations, continuous and discontinuous, were developed for biological N and P removal from wastewaters. An overview of existing biological nutrient removal process configurations can be found elsewhere (1). One of the techniques is a sequencing batch reactor, a discontinuous system that cycles through oxic and anoxic stages (2,3). Table 1 gives an example of a typical sequencing batch reactor time schedule.

Nitrification and denitrification are the key processes in biological N removal. Nitrification is a two step reaction : *Nitrosomonas* bacteria oxidise NH_4^+ to NO_2^-, *Nitrobacter* bacteria convert NO_2^- to NO_3^-. During denitrification, nitrate acts as the terminal acceptor of electrons. An external source of organic carbon is often needed as additional electron source for the reduction of nitrate to nitrogen gas, since most biodegradable organics are oxidised earlier in the aerobic stage (4,5). Supplying a reactor with extra organic carbon increases costs of the wastewater treatment process but improves reliability. It is profitable to divide a sequencing batch reactor cycle into alternating short oxic (nitrification) and anoxic (denitrification) phases. This offers the possibility to denitrify at least a part of the nitrate formed during nitrification with organic carbon present in the wastewater itself.

The nitrification process is generally recognised as the process that is most sensitive to toxic substances (6). Selective inhibitors of the two nitrification phases have been described in literature and can be used to determine the nitrifying activities of the activated sludge. Two commonly used inhibitors are $NaClO_3$ and allylthiourea (7). $NaClO_3$ is an inhibitor of

nitrite oxidation by *Nitrobacter* at a concentration of 20 mM (7,8,9). $NaClO_3$ can be used without exerting immediate inhibitory effects on ammonium oxidation by *Nitrosomonas* (9). Allylthiourea is a selective inhibitor of ammonium oxidation by *Nitrosomonas* at a concentration of 5 mg l^{-1} (7,10).

The aim of the experiments carried out was to evaluate the usefulness of a nitrification activity test based on oxygen uptake rate measurements as method for the control of biological nitrification in sequencing batch reactor plants.

MATERIALS AND METHODS

Respiration measurements were done with a conventional fed batch respirometer (Figure 1). Mixed liquor samples were taken from the sequencing batch reactor, saturated with oxygen by shaking the sample and transferred to the respirometer (V = 100 ml). The respirometer vessel was carefully closed, with no air bubbles remaining in it. Samples were stirred during measurements by means of a magnetic stirrer at 150 rpm. The selective inhibitors were freshly prepared stock solutions of allylthiourea (125 mg l^{-1}) and $NaClO_3$ (0.5 M).

As first step in the procedure the total oxygen uptake rate is determined without addition of inhibitors. Subsequently, the oxygen uptake rate is determined after addition of 20 mM $NaClO_3$ (2.13 g l^{-1}) to the mixed liquor sample. The decrease of the oxygen uptake rate after addition of $NaClO_3$ is considered as the oxygen uptake rate of the nitrite oxidisers (activity of nitrification phase II). Finally, 5 mg l^{-1} allylthiourea is added to the mixed liquor sample and the remaining oxygen uptake rate is quantified. The difference between the oxygen uptake rates with $NaClO_3$ and both inhibitors, $NaClO_3$ and allylthiourea, represents the ammonium oxidising activity (activity of nitrification phase I). The oxygen uptake rate measured in the presence of both inhibitors reflects the organic carbon respiration activity. Nitrification activity measurements result in oxygen uptake profiles as illustrated in Figure 2.

To evaluate the developed activated sludge nitrification activity monitoring method, experiments were performed on a 500 l pilot scale sequencing batch reactor for nutrient removal. A precise description of the pilot plant can be found elsewhere (11). During operation of the pilot plant, dissolved oxygen (CONDUCTA 905-S) and oxidation-reduction potential (CONDUCTA PPY-DR-532) of the mixed liquor are continuously measured. Dissolved oxygen and oxidation-reduction potential electrodes are placed in a flow-through cell to avoid fouling. The sewage that is treated consists mainly of domestic wastewater but at regular intervals also contains inputs (up to 20 % of the COD load) of textile industry wastewater.

Nitrogen removal was achieved via different oxic-anoxic time sequences. Normal operation of the sequencing batch reactor plant, which includes one long oxic nitrification period and one long anoxic denitrification period, is illustrated in Table 1. The normal operation of the sequencing batch reactor treatment plant was compared with schedules consisting of different alternating short oxic and anoxic phases.

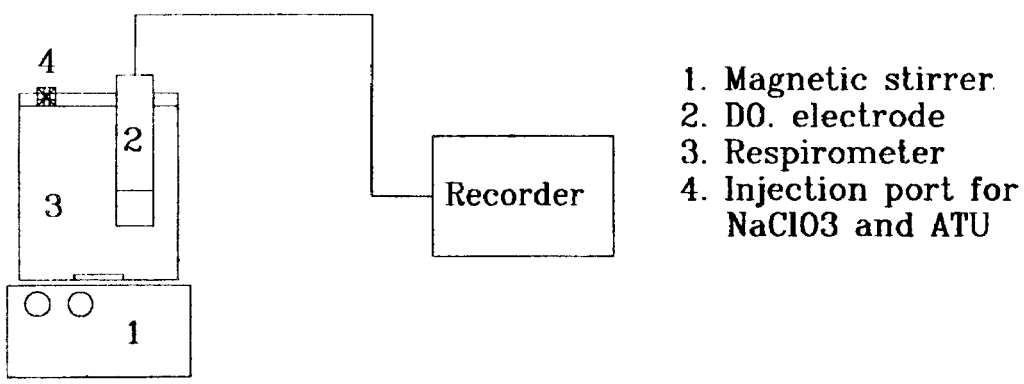

Figure 1. Fed batch respirometer used for recording oxygen uptake profiles (ATU = allylthiourea)

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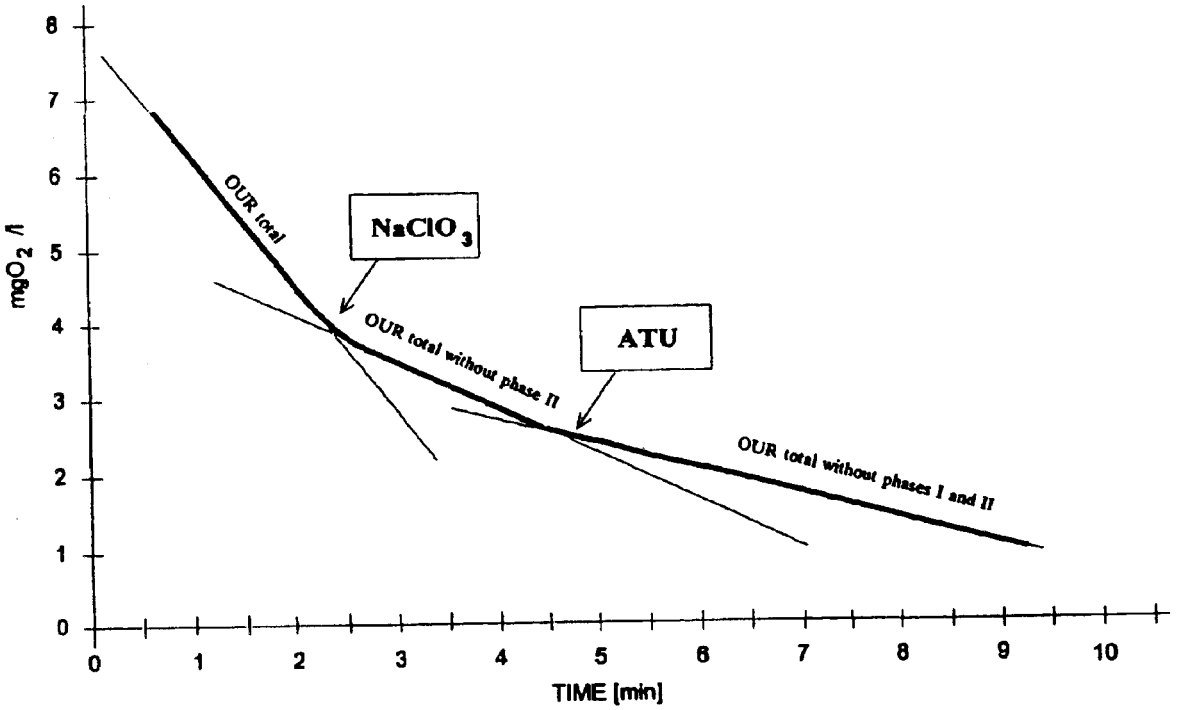

Figure 2. Example of a typical oxygen uptake profile recorded with the nitrification activity determination method (ATU = allylthiourea)

Table 1. Normal sequencing batch reactor time schedule used for biological N and P removal in the pilot plant (11)

Time sequence (min)	Processes occurring	Label
0 - 60	filling + anaerobic P release	Anaerobic
61 - 210	P uptake, nitrification, COD removal	Aerobic 1
211 - 270	denitrification	Anoxic
271 - 300	excess COD removal, N_2 stripping	Aerobic 2
301 - 345	sedimentation	Settling
346 - 360	decantation	Decanting

During the experiments, filtered samples were taken from the mixed liquor at regular times. Changes of nitrogen compounds were analysed according to Standard Methods (12). Immediately after sampling, nitrite was determined colorimetrically according to the method of Montgomery and Dymock (13). Samples for ammonium and nitrate determination were acidified with sulfuric acid before storage. Ammonium and nitrate were determined afterwards in the laboratory (12). Samples for nitrification activity measurements were taken at regular times during oxic periods. The activity measurements were performed immediately after sampling. No activity measurements were performed during the anoxic periods because the nitrifying population is not active under anoxic conditions.

RESULTS

In a separate experiment, the short-term effect of dosing 20 mM $NaClO_3$ was investigated. Endogenous activated sludge (no nitrifying activity by lack of NH_4^+) was mixed with CH_3COONa to give a final concentration of 100 mg BOD/l. The sample was saturated with oxygen and the oxygen uptake rate was monitored. After 250 seconds, 20 mM $NaClO_3$ was added to the sludge. The oxygen uptake rate before and after $NaClO_3$ dosage were calculated. The experiment was repeated 4 times. The oxygen uptake rate

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before $NaClO_3$ dosage (24.0 ± 0.64 mg O_2/l.h) was slightly higher than the oxygen uptake rate after $NaClO_3$ dosage (22.6 ± 0.48 mg O_2/l.h). The difference between the calculated oxygen uptake rates can be explained by the dilution effect due to the dosage of the nitrification inhibitor. It can be concluded that the dosage of $NaClO_3$ exerts no immediate negative effects on the activity of the heterotrophic activated sludge bacteria. $NaClO_3$ can thus be used as a nitrification inhibitor for short-term activity measurements.

Experiments were performed to compare the effect of one single long nitrification phase followed by a long denitrification phase with a sequence of alternate short nitrification and denitrification phases. Besides DO and oxidation-reduction potential, nitrification activity measurements were used to follow the sequencing batch reactor processes. The DO and oxidation-reduction potential measurements for a normal sequencing batch reactor cycle are presented in Figure 3. During aerobic phases, the DO concentration was controlled between 2.0 and 3.0 mg l^{-1}. DO measurements corresponded well with the on-line nitrification activity measurements (Figure 4B) and the NH_4^+ removal (Figure 4A). After 100 minutes (aerobic 1), nitrification was finished, which was observed in the DO profile by a slower DO decrease (= lower oxygen uptake rate) each time the 3.0 mg l^{-1} setpoint was reached. Indeed, according to Figure 4, the activity of nitrification phase I became zero after 100 minutes indicating the end of the NH_4^+ oxidation.

A continuous nitrification period of 150 minutes (being part of the sequencing batch reactor cycle shown in Figure 3 and Table 1) under normal nitrogen loading conditions (approximately 13 mg N l^{-1} reactor $cycle^{-1}$) is presented in Figure 4. The evolution of the nitrogen species (Figure 4A) shows a typical pattern. There is an initial increase of NH_4^+ due to ammonification. The increase of the NO_3^- is well correlated with the decrease of the NH_4^+. NO_2^- build-up is limited to low concentrations (maximum 2.3 mg NO_2^--N l^{-1}). After the NH_4^+ was removed, all NO_2^- that was still remaining in the reactor liquid is also converted to NO_3^-. The results of the nitrification activity measurements are presented in Figure 4B. Changes in the activities of both nitrification steps correspond well to changes of the inorganic nitrogen species concentrations presented in Figure 4A.

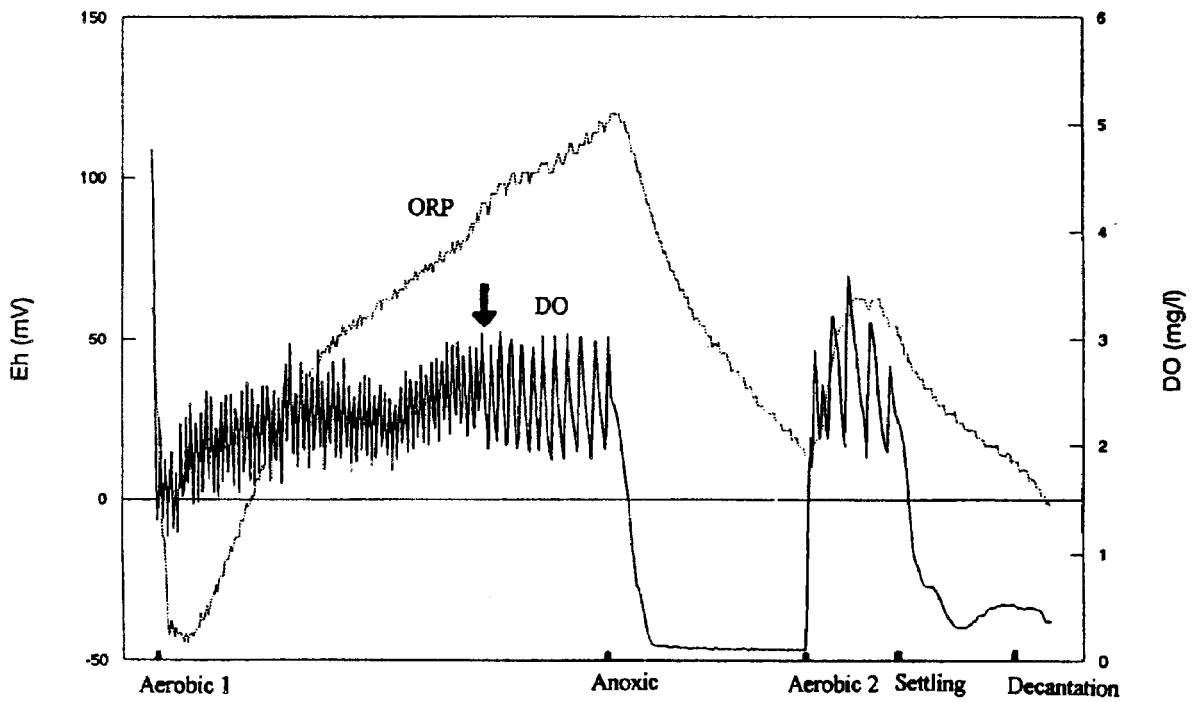

Figure 3. Dissolved oxygen (DO) and oxidation-reduction potential (ORP) profiles recorded during a normal sequencing batch reactor cycle. The arrow indicates the end of the oxidation processes during the aerobic 1 period of the reactor cycle

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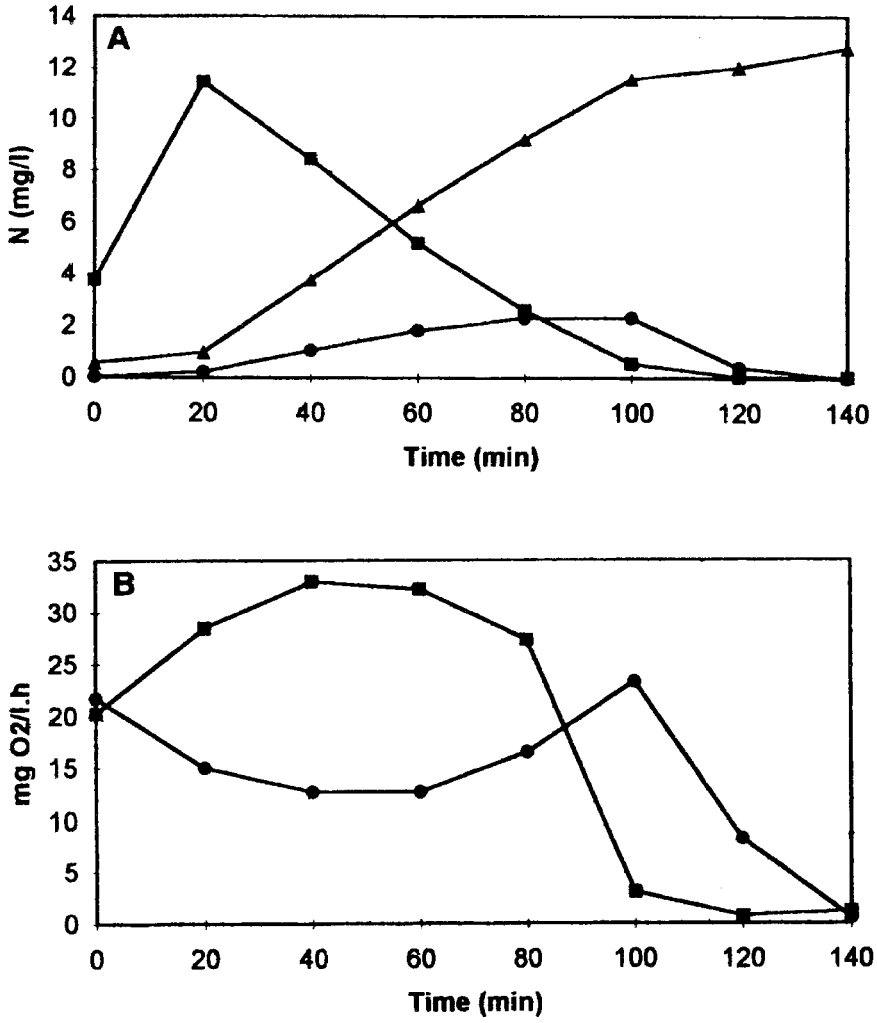

Figure 4. Aerobic 1 phase of a normal sequencing batch reactor cycle. (A); Evolution of NH_4^+ (■), NO_2^- (●) and NO_3^--N(▲) concentrations with time. (B); Evolution of the activity of nitrification phase I (■) and nitrification phase II (●) with time

When the concentration of NH_4^+ was high, the activity of nitrification phase I was also high. The activity of nitrification phase I decreased to zero with decreasing NH_4^+ concentrations. The same patterns were observed for the relationship between nitrification phase II activities and NO_2^- concentrations. The curve representing the activity of nitrification phase II (Figure 4B) corresponds well with NO_2^- concentrations. The highest activity of nitrification phase II (23.25 mg O_2 $l^{-1}h^{-1}$) could be observed after 100 minutes, when NO_2^- reached its highest concentration (2.3 mg NO_2^--N l^{-1}). Activity of nitrification phase II became zero with decreasing NO_2^- concentrations.

The effect of alternate short oxic and anoxic periods, each with a constant length of 21 minutes, is shown in Figure 5. Figure 5A shows the evolution of nitrogen species during the sequencing batch reactor cycle. Nitrification was finished after 150 minutes. The maximum NO_2^- level (1.3 mg NO_2^--N l^{-1}) was lower than in the control experiment with the single oxic phase (Figure 4). The evolution of the nitrogen species correlated with the oxic and anoxic periods. During the oxic periods, NH_4^+ was oxidised and NO_3^- was formed, as evidenced by the increasing NO_3^- concentrations. NH_4^+ concentrations remained constant during the anoxic periods, while denitrification took place as can be seen from the decrease in the NO_3^- concentrations. The final NO_3^- concentrations (6 mg NO_3^--N l^{-1}) obtained without using an external organic carbon source for denitrification were quite low compared to normal operation of the sequencing batch reactor (Figure 4 ; 12.8 mg NO_3^--N l^{-1}

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remaining in the reactor liquid at the end of the long oxic nitrification period). Organic carbon from the wastewater was more efficiently used as carbon source for denitrification. Denitrification was slow during the last anoxic period, probably because all rapid biodegradable carbon source had been removed from the reactor liquid before.

Nitrification activity measurements (Figure 5B) confirm the data from Figure 5A. Activity measurements were only performed during oxic periods. The first three oxic periods were characterised by a high activity of nitrification phase I, resulting in a fast decrease of NH_4^+ concentrations. After 150 minutes, when all NH_4^+ was oxidised, activity of nitrification phase I became zero. Activities of nitrification phase II corresponded in the same way with NO_2^- concentrations in the mixed liquor. The conditions at the beginning of the oxic periods were far from ideal for the aerobic nitrifying bacteria. This explains why the activity of nitrification phase II sometimes increased during oxic periods with quite constant NO_2^- concentrations. As can be expected, activity of nitrification phase II became zero when all NO_2^- was removed.

A sequence of alternate oxic and anoxic periods with different length gave similar results (Figure 6). The cycle was started with long oxic periods and finished with short oxic periods. The evolution of the length of the anoxic phases was just the opposite : short periods at the beginning and longer periods at the end. The aim of the experiment was to keep the NO_3^- removal per anoxic phase more or less constant. This

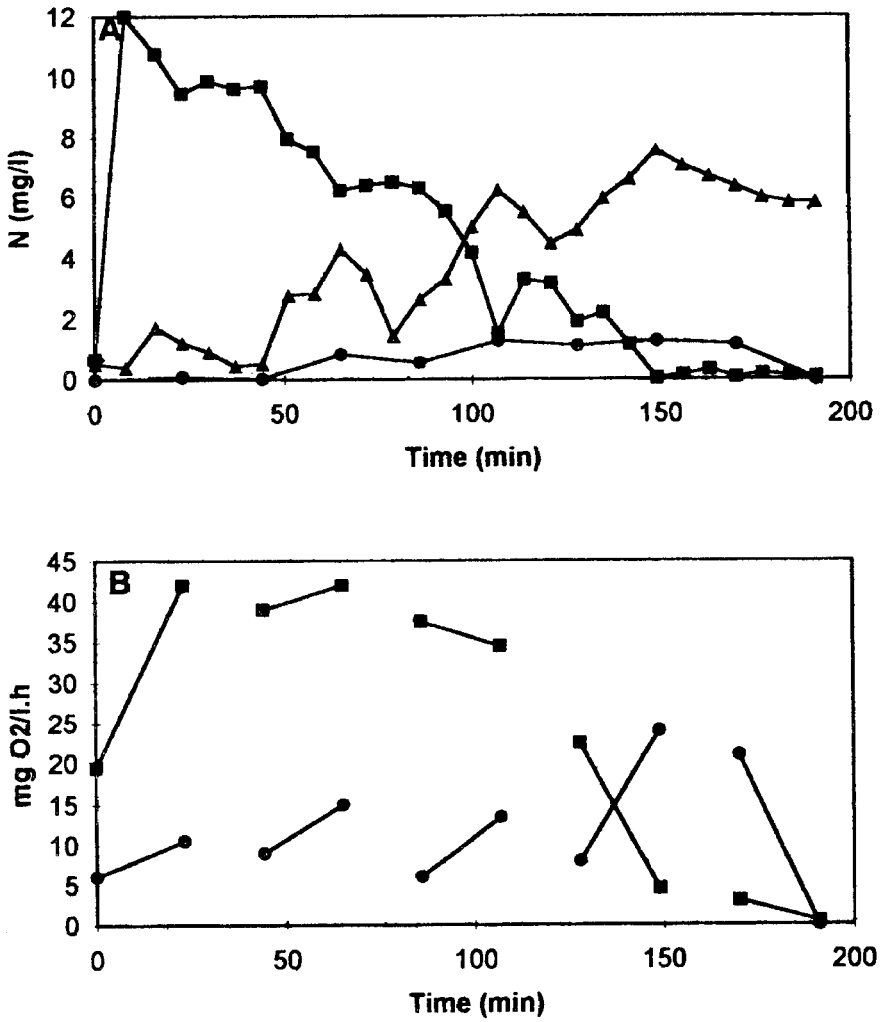

Figure 5. Alternate short oxic and anoxic periods with constant length. (A); Evolution of NH_4^+ (■), NO_2^- (●) and NO_3^--N(▲) concentrations with time. (B); Evolution of the activity of nitrification phase I (■) and nitrification phase II (●) with time. A solid line between 2 nitrification activity data points indicates an oxic period

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could be achieved by changing length of the anoxic phases because it was found before that denitrification is fast at the beginning of a cycle and slows down at the end of the cycle (11). The length of the oxic phases was decreased to keep the length of each oxic/anoxic combination constant.

The results presented in Figure 6 again show a good correlation between the evolution of the nitrogen species (Figure 6A) and the activity measurements (Figure 6B). Nitrification was finished after 110 minutes. The sharp decrease of the activity of nitrification phase I indicated that all NH_4^+ was oxidised. NO_2^- build-up was limited to a maximum of 1.19 mg NO_2^--N/l. The effect of the anoxic phases is illustrated by a decrease in NO_3^- concentrations due to denitrification. The results obtained were comparable with the previous experiment operated with periods of equal and constant length.

DISCUSSION

A method is presented for monitoring nitrifying activities of activated sludge. The method can distinguish between oxygen uptake rates due to carbon substrate and ammonium oxidation by simple oxygen uptake rate measurements in combination with the addition of two selective nitrification inhibitors ($NaClO_3$ and allylthiourea). This was illustrated with 3 cases, all with a normal nitrogen loading but different oxic-anoxic time sequences for nitrogen removal. In all 3 cases nitrification activity measurements clearly

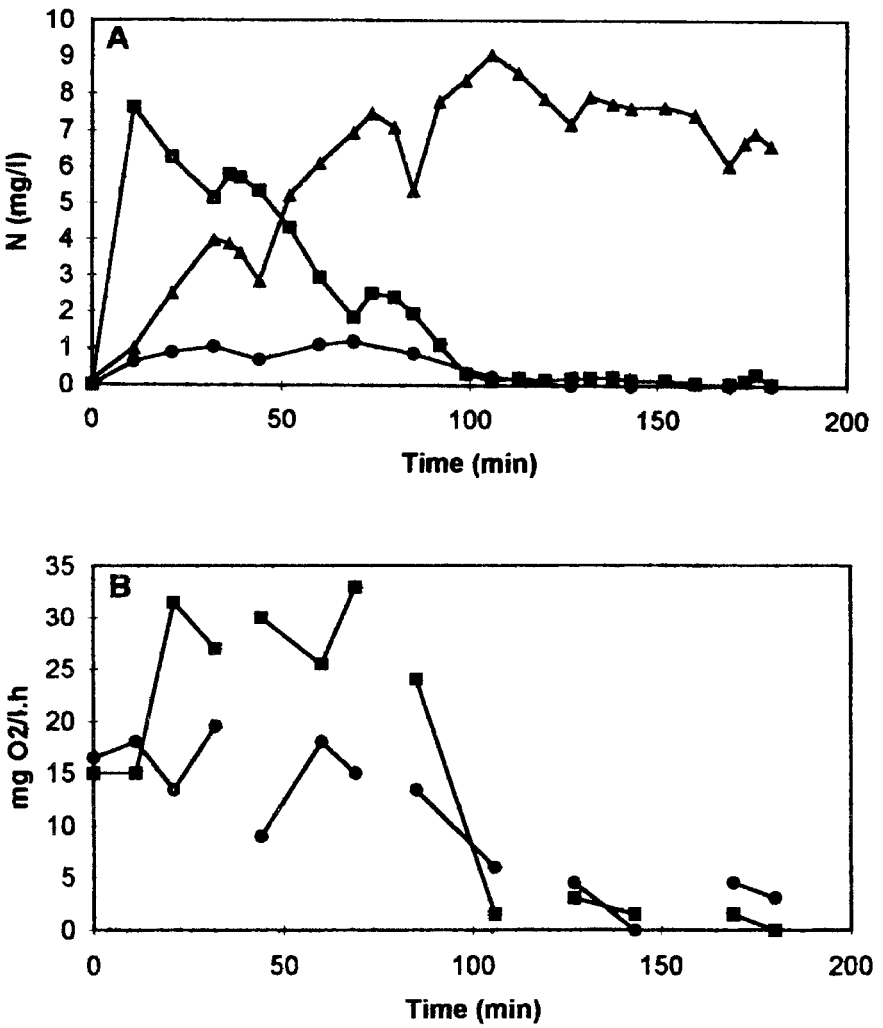

Figure 6. Alternate oxic and anoxic periods starting with a long oxic period. (A); Evolution of NH_4^+ (■), NO_2^- (●) and NO_3^--N(▲) concentrations with time. (B); Evolution of the activity of nitrification phase I (■) and nitrification phase II (●) with time. A solid line between 2 nitrification activity data points indicates an oxic period

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indicated the end of the ammonium oxidation process.

In the first experiment, the effect of short oxic and anoxic phases with constant length was compared to the normal operation conditions of the sequencing batch reactor. A second experiment was carried out with oxic and anoxic periods of different length. It was found previously (11) that a sequence of short oxic/anoxic phases is better than the usual sequence consisting of one long oxic nitrification phase in combination with one anoxic denitrification phase. We showed that in an alternating oxic/anoxic regime approximately half of the nitrate was denitrified with organic carbon originating from the wastewater, while during continuous processing (one long oxic phase followed by a long anoxic phase) all organic carbon was degraded during the long oxic phase. This means that the use of a sequencing batch reactor time sequence with alternating short oxic and anoxic phases results in an important external carbon source (usually methanol) cost saving.

Control of nutrient removal processes in sequencing batch reactor systems can be done in various ways. Dissolved oxygen and oxidation-reduction potential measurements are parameters that can be helpful for control purposes (14). Denitrification can be determined based on oxidation-reduction potential measurements. DO measurements are useful during aerobic periods. As illustrated by Figure 3, differences in oxygen uptake rates can be detected. It is nevertheless impossible to accurately interpret the signal coming from the DO electrode. The decrease in the oxygen uptake rate that was detected (Figure 3) could be caused either by a decrease of the carbon respiration or the nitrification activity. Based on DO measurements in the mixed liquor only, reliable detection of partial or even complete inhibition of nitrification is impossible. The presented new method using selective inhibitors, enables detection by the operator of irregularities in the nitrification rate e.g. by toxic substances.

Activity measurements can detect when the ammonium oxidation in the mixed liquor is finished and thus when aeration can be stopped. When activity of nitrification phase I becomes zero, all ammonium has been oxidised and denitrification can take place. A control strategy based on nitrification activity measurements can result in important aeration cost savings, since input of aeration energy taking place after the ammonium oxidation has been finished is superfluous. Nitrite oxidation doesn't have to be finished because denitrification can take place with both nitrate and nitrite as electron acceptors (15). Also, organic carbon that was remaining in the mixed liquor becomes oxidised and can thus no longer be used as carbon source for denitrification. Nitrification activity measurements can also be applied in plug-flow reactor systems. Activity measurements can indicate at which point in the reactor nitrification is completed. Starting from this point aeration should be stopped so that denitrification can take place.

In case of toxicity resulting in lower nitrification activities, the aerobic nitrification period of a sequencing batch reactor cycle can be extended until nitrification activity measurements detect that all ammonium has been oxidised. A variable length of the aerobic period results in a variable length of the total sequencing batch reactor time schedule. A flexible length of the total sequencing batch reactor time schedule based on nitrification activity measurements may not be achievable in practice, because an increasing length of the total cycle results in a lower flow of treated wastewater. A lower wastewater flow implies a lower nitrogen loading. It is useful, when keeping the normal nitrogen loading, to have a complete ammonium oxidation rather than denitrification because free ammonia is toxic in low concentrations to fish. In case of inhibition complete ammonium removal and a constant length of the total sequencing batch reactor cycle can be achieved by keeping the total time needed for nitrification and denitrification constant : an increase of the length of the aerobic nitrification period is followed by an equal decrease of the length of the anoxic denitrification period. This can be a valuable alternative for varying the total length of the sequencing batch reactor cycle.

CONCLUSIONS

Nitrification activity measurements can detect the presence of NH_4^+ and NO_2^- in activated sludge processes. Applied on a sequencing batch reactor, reduced aeration costs and optimal use of wastewater biodegradable organics as electron source for denitrification can be achieved, resulting in a cheaper wastewater treatment process. Activity measurements combined with flexible nitrification/denitrification time scheduling can give rise to a better effluent quality with a minimal amount of remaining ammonium.

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