Estimation of denitrification potential with respiration based techniques

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Propositions

Belonging to the thesis entitled: "Estimation of denitrification potential with respiration based techniques" by Katarzyna Kujawa-Roeleveld

1. The statement of RANDALL ET AL., (1992) that "...fortunately biological nitrogen removal systems can be *acceptably* designed without an extensive wastewater characterisation as required for accurate modelling..." is misleading. Based on such a credo, an optimal design will be pure accidental.

Randall, C.W., Barnard, J.L. and Stensel, H.D. (1992) Design and retrofit of wastewater treatment plants for biological nutrient removal. Water Quality Management Library. Volume 5.

2. The denitrification potential of wastewater and activated sludge determines the nitrate effluent quality of a correctly configured activated sludge system. Control strategies aiming to optimise the denitrification process, cannot compensate a shortage in denitrification potential.

This thesis

3. There exists no *typical* composition of municipal wastewater.

4. The COD/N-ratio of wastewater is certainly not a universal indication of the denitrification potential of any activated sludge system.

This thesis

5. The conclusion of ANDERSSON AND ROSEN (1990) that pre-precipitation is not supposed to affect denitrification as only suspended organics are removed, neglects undeserved the biodegradability of particulate organic substrate.

Andersson, B. and Rosen, B. (1990). Upgrading for biological nitrogen removal – some full-scale experiences from Sweden. Wat. Sci. Tech. Vol. 22, No. 7/8, 93-104.

6. Via the combined process of nitrification and denitrification, nitrogen is not wasted as resource. It is only a pity that so much energy is required to prolong this N-cycle.

7. In centralised sanitation systems, high quality water is mixed with a potentially fine fertiliser, making both useless. Then a lot of money has to be spent to recover both resources.

8. Response for solving environmental problems generally occurs when they become too urgent to ignore.

9. The variety of spelling possibilities of a relatively simple foreign name results mainly from common laziness and hastiness.

(examples: Kasha, Kasja, Katharazin, Katarazyna, Katharzinia, Cataryna, van Jawa, Kujwa, Kujuwa, etc, etc.)

10. Implementation of the word *conventional* before any phenomenon or object should always be preceded by a detailed historical and geographical analysis.

Moim rodzicom

Aan Paul

ABSTRACT

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Denitrification with its prerequisite process nitrification, is a common practice to remove nitrogen from wastewater in activated sludge systems. Although the key factors detrimental to its performance are well recognised, not all links are implemented for optimal design and operation performance. The relation between detailed wastewater characterisation and denitrification potential (DP) is the most crucial example of information that should be better incorporated in design and optimisation procedures. The lumped parameters COD/N and BOD_5/N (nowadays used in many design approaches) or empirical values of denitrification rates do not allow to predict precisely the denitrification potential due to a unique character of each activated sludge and wastewater. Advanced activated sludge models require the input of a significant number of parameters. Since the estimation of each parameter is difficult and time consuming, the choice of default values is an option but this can lead to erroneous predictions of reality. Far-simplified models, usually based on on-line measurement of process state variables, describe processes with the simplest kinetics what in turn restricts seriously their implementation.

In this thesis a methodology is presented to estimate the DP in relation to wastewater and activated sludge characteristics. Two respiration techniques form the basis for two different approaches: the anoxic nitrate utilisation rate (NUR-) test and the aerobic oxygen utilisation rate (OUR-) test. The approach based on the NUR-test is a direct method for the assessment of the DP. The approach based on the OUR-test is an indirect method because a simplified model is necessary to transform oxygen utilisation rate to nitrate utilisation rate. The NUR-test, except of serving as a tool to estimate directly the DP, enables to acquire simplified denitrification kinetics and a relevant wastewater characterisation, leading consequently to a prediction of the denitrification capacity and nitrate effluent quality. Knowledge about actual activated sludge kinetics and wastewater (or other substrate) characteristics allows to establish relations between sludge loading rate and achievable denitrification rate.

The OUR-test was the base to formulate the simplified nitrification-denitrification model, where estimated substrate conversion rates are used without biomass population dynamics. Moreover, the aerobic and anoxic organic biodegradable substrate conversions are modelled with the same relations with the only difference that for anoxic conditions appropriate reduction factors are incorporated in conversion kinetics to reflect a slower activity of activated sludge under denitrifying conditions. A novel methodology based on aerobic and anoxic respiration tests is proposed to estimate the reduction factors. The proposed model approach constitutes an alternative for both complex and far-simplified model approaches. It enables to predict the overall N-removal potential and N-effluent quality of a system, based on an actual detailed wastewater and activated sludge characterisation. Good results from dynamic and static testing of the model implicates its possible implementation in control strategies, like e.g. a feed-back control of the denitrification by a nitrate-rich recycle rate, anoxic volume or the addition of an external carbon source.

The effect of a decrease in the biodegradable COD-fraction by pre-treatment (pre-precipitation) on the DP was examined. For an evaluation the developed respiration based methodologies were used to estimate the DP in relation to wastewater and activated sludge characteristics. Implemented optimisation procedures revealed that the original denitrification potential of the wastewater determines the process capacity and efficiency. Optimisation steps by the manipulation of technological parameters in the existing process configuration or control strategies may therefore improve process performance only to small extent.

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First of all I would like to thank Bram Klapwijk, my 'daily' guide and co-promotor, for enabling my 'attachment' to Wageningen University and sewing up all pieces of fellowships to create a reasonable PhD program and searching for a 'rode draad' in these denitrification considerations.

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Henk Rensink who supported friendly my first steps in the Netherlands. The work in that period was then not yet related to this thesis. However, the first assessment of denitrification aspects provided finally the results for chapter 6.

Undoubtfully Harry Brouwer, the creator of RESCUE, who introduced me into the meanders of aerobic respiration and provided some data to test the nitrification-denitrification model. A part of his work became a starting point for the developments in this study, hopefully worth to be implemented and further improved.

Henry Spanjers for his time and valuable comments on a part of this work.

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The Bennekom crew created a friendly and free sphere, contributing in acquiring my Dutch skill. Especially I would like to name Grietje, Hardy, Wendy, Michiel, Adriaan and many students and foreign visitors.

My parents, a perfect combination of charm and strength, stimulating me the most by just asking from time to time a little tiny question: 'when you will finish?' They are the best example of how much can be achieved in life.

Paul, a strong base of trust, love and friendship that makes life easy and simple, and quite funny too. Be sure that I will never underestimate your significant scientific contribution to this work.

Finally I want to express my thanks to my family and friends: Polish, giving me the feeling that I have never left them and Dutch who made the adaptation process practically manageable.

ESTIMATION OF DENITRIFICATION POTENTIAL

WITH RESPIRATION BASED TECHNIQUES

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1

General introduction

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1.1 NITROGEN IN DOMESTIC WASTEWATER

Various nitrogen (N) forms in municipal wastewater originate primarily from protein metabolisms in human bodies (VAN DER WIJST AND GROOT-MARCUS, 1998). The main fraction of nitrogen in municipal wastewater constitutes Kjeldahl-N (N_{Kj}), which is the sum of ammonia-N (S_{NH}) and organic-N (N_{org}) (e.g. RAUCH, 1994). The fraction S_{NH} is in general the prevailing fraction of the influent-N (HENZE ET AL., 1987, 1996). According to the IAWQ Activated Sludge Models (ASM) (HENZE ET AL., 1987, 1996) four sub-fractions can be distinguished within N_{org}: inert soluble and inert particulate (S_{NI} and X_{NI}), soluble readily biodegradable (S_{ND}) and particulate slowly biodegradable (X_{ND}). In the sewer system and activated sludge system, biodegradable N_{org} will be decomposed to S_{NH} as a consequence of hydrolysis and ammonification, and this normally takes place at a high rate. Nitrate (S_{NO3}) and nitrite (S_{NO2}) concentrations are usually negligible, but can occur in cases where some types of industrial wastewater are discharged to the sewer system. When nitrogen is not removed, municipal wastewater forms a significant source of the external nitrogen load to surface waters (CUWVO, 1991).

Since the early 70's a dynamic development in advanced activated sludge wastewater treatment methods has been noticed and the primary function of activated sludge for carbonaceous material removal has been subsequently extended to biological nitrogen removal with the processes nitrification and denitrification. Besides nitrogen removal, also phosphorus removal was introduced via chemical and/or biological processes.

1.2 CONVENTIONAL NITROGEN REMOVAL

Nitrogen compounds from wastewater can undergo numerous biological conversions in wastewater treatment plants. In conventional biological treatment plants, assimilation and conversion to nitrogen gas via nitrification and denitrification are the dominant activated sludge processes for nitrogen removal.

1.2.1 ASSIMILATION OF NITROGEN

Since N constitutes an essential nutrient for activated sludge micro-organisms, a part of the influent S_{NH} will be assimilated for the synthesis of cellular material. If S_{NH} is limiting, S_{NO3} or S_{NO2} can be used for the assimilative requirement, after being reduced to S_{NH} (METCALF&EDDY, 1991). Assimilatory N-removal occurs under aerobic, anoxic and anaerobic conditions (CASEY ET AL., 1994).

The overall removal of N via assimilation depends on the daily sludge production, which on itself is generally proportional to the organic sludge loading rate and inversely proportional to the activated sludge retention time (SRT). In high loaded systems, the nitrogen assimilation may attain a significant rate, especially when treating concentrated wastewater in terms of COD and N. In the treatment of municipal wastewater the percentage of N removal via assimilation may range from 8 to 30% (V. HAANDEL ET AL. 1981b, SDA, 1989). However, if the treatment plant involves sludge handling processes, a portion of the assimilated N will return in the form of S_{NH} to the activated sludge tank via reject waters. For design purposes, the N-load from reject waters has to be included in the total N-load.

1.2.2 NITRIFICATION

The nitrification process is a prerequisite for a dissimilatory N-removal. The S_{NH} from the influent and formed from hydrolysis and ammonification of biodegradable N_{org}, is oxidised in a two-step reaction to S_{NO3} by many species of autotrophic nitrifying bacteria which derive energy from inorganic compounds. The oxidation of S_{NH} is generally attributed to *Nitrosomonas europaea* and the oxidation of S_{NO2} to *Nitrobacter agilis.*

$$NH_4^+ + 1\frac{1}{2}O_2 \xrightarrow{Nitrosomonas} NO_2^- + 2H^+ + H_2O + 352kJ\ /\ mol$$

$$NO_2^- + \frac{1}{2}O_2 \xrightarrow{Nitrobacter} NO_3^- + 73kJ\ /\ mol \qquad (1.1, 1.2)$$

There is no organism described which is able to perform the overall nitrification process (V. LOOSDRECHT AND JETTEN, 1998). Due to a low yield and substrate (S_{NH}) level, compared with COD, nitrifiers constitute only 2-5% of the total activated sludge population (RANDALL ET AL., 1992). The autotrophic nitrifiers are considered to be more susceptible to pH, temperature and toxic chemicals than heterotrophs.

1.2.3 DENITRIFICATION

In the dissimilatory N-removal, denitrification is the reduction of S_{NO3} or S_{NO2} via a chain of intermediates to the end product nitrogen gas (N_2), as a consequence of redox reactions to obtain energy from organic material. The pathway of denitrification consists of a number of steps by which electrons are passed from the electron transport pathway to one of the N-oxides to produce a more reduced N-oxide. The generally accepted entire denitrification pathway can be described as (PAYNE, 1973):

$$NO^-_{3(aq)}{}^{(+5)} \rightarrow NO^-_{2(aq)}{}^{(+3)} \rightarrow NO_{(g)}{}^{(+2)} \rightarrow N_2O_{(g)}{}^{(+1)} \rightarrow N_{2(g)} \qquad (1.3)$$

Each N-oxide (NO_3^-, NO_2^-, NO and N_2O) can serve thus as electron acceptor (e.g. HADJIPETROU AND STOUTHAMER, 1965, MCCARTHY ET AL., 1981).

1.3 CONDITIONS FOR DENITRIFICATION

In order to perform a satisfactory denitrification, a number of conditions is necessary to be accomplished (e.g.KLAPWIJK, 1978, VAN HAANDEL, 1981a,b, EKAMA ET AL., 1984):

- presence of N-oxides;
- presence of facultative heterotrophic biomass;
- absence or low level of dissolved oxygen;
- and presence of a suitable electron donor.

1.3.1 PRESENCE OF N-OXIDES

To assure the nitrate and/or nitrite level, denitrification has to be proceeded (in time or place) by nitrification or N-oxides have to be available in the wastewater.

1.3.2 PRESENCE OF FACULTATIVE HETEROTROPHIC BIOMASS.

In the respiratory metabolism of heterotrophic organisms, organic substrate is oxidised to the end products CO_2 and H_2O. During oxidation, organisms are able to capture energy for substrate utilisation, maintenance and growth. The energy becomes available via a serie of internally mediated redox reactions, involving electron and proton transport from an electron donor (organic substrate) to the final electron acceptor (oxygen or N-oxides) through a number of intermediate enzyme complexes. A large fraction of heterotrophic organisms - facultative heterotrophs - in biological treatment plants is capable for dissimilative denitrification. When dissolved oxygen (DO) becomes limiting, they can metabolise organic substrate with nitrate and/or nitrite as terminal electron acceptor.

Not the entire active biomass fraction that respires aerobically, is expected to use N-oxides as terminal electron acceptor (e.g. KLAPWIJK, 1978, HENZE, 1986, ORHON ET AL., 1996). Also not all denitrifying organisms can execute the entire pathway of denitrification (CASEY ET AL., 1994) but only part of it, i.e. from one ionic N-compound (NO_3^- or NO_2^-) to one of the gaseous N compounds (NO, N_2O or N_2). Such organisms are referred as partial denitrifiers. Other organisms reduce nitrate only to nitrite and they are called nitrate reducers. The electron transport pathways for aerobic and anoxic respiration have common enzyme complexes for a substantial part, which are utilised under both conditions. Other enzyme complexes are specific to only aerobic or anoxic respiration. Reduction of each N-oxide is catalysed by the corresponding N-oxide reductase (CHONG AND MORRIS, 1962, WPCF, 1983, CASEY ET AL., 1994).

1.3.3 ABSENCE OR LOW LEVEL OF DISSOLVED OXYGEN

When oxygen is absent or present at very low concentrations, nitrate/nitrite will act as electron acceptor. Such conditions are termed anoxic in the field of wastewater treatment in contrast to microbiology and biochemistry (CASEY ET AL., 1994).

The synthesis of N-oxide reductases can be executed at the absence or low levels of DO and the presence of the specific N-oxide, the reactant for a reductase. When the environment for facultative organisms is changed from aerobic to anoxic conditions, the synthesis of some oxidases - enzymes specific for aerobic respiration - is inhibited and the synthesis of reductases is initiated. When the facultative organisms are transferred to aerobic conditions the formation of reductases is inhibited (CHONG AND MORRIS, 1962, WPCF, 1983, WILD ET AL., 1994). According to PAYNE (1981), reductases of some facultative organisms are inactivated by DO, whereas of others the synthesis of reductases is repressed but the existing enzymes disappear gradually.

Different electron transport pathways have a significant influence on the energy conservation. It can be deduced or proved experimentally (e.g., DELWICHE, 1970, VAN VERSEVELD ET AL., 1981, EKAMA ET AL., 1984, CASEY ET AL., 1994) that free energy released in presence of organic material and oxygen is higher than in the presence of N-oxides. It means, that if both are present, the more energy yielding process will take place preferentially. An example of the oxidation-reduction reaction with glucose and nitrate or oxygen shows this difference:

$$\begin{aligned} &5C_6H_{12}O_6 + 24NO_3^- \rightarrow 30CO_2 + 18H_2O + 24OH^- + 12N_2 + 2394kJ\ /\ mol \\ &C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 2881kJ\ /\ mol \end{aligned} \qquad (1.4,\ 1.5)$$

The inhibitory effect of DO on denitrification has been extensively reported in literature and a high variety in reported DO levels can be found. SKERMAN AND MACRAE (1957) and WUHRMANN (1960) reported that denitrification can proceed at a DO concentration of 0.2 - 0.5 $mgO_2.\ell^{-1}$ while CARLSSON (1971) found that at 0.2 $mgO_2.\ell^{-1}$ no significant denitrification was obtained. CHRISTENSEN AND HARREMOËS (1977) define a critical DO concentration of lower than $0.5mgO_2.\ell^{-1}$, where facultative heterotrophs are able to switch from oxygen to N-oxides as electron acceptor. For practical purposes the SDA (1989) states that denitrification can be ignored when DO is greater than 1.0 $mgO_2.\ell^{-1}$. The high variety in reported DO levels can be explained by the existence of a DO gradient in bacterial flocs, where despite of aerobic conditions in the environment outside the floc, anoxic conditions prevail in its centre (KRUL, 1976). The structure of activated sludge flocs, their size as well as mixing conditions may play an important role in the process performance and different results can be found on the limiting DO level.

1.3.4 PRESENCE OF A SUITABLE ELECTRON DONOR

The oxidation of biodegradable organic compounds provides energy for facultative heterotrophs for the synthesis of new biomass and endogenous respiration. The energy for denitrification from organic compounds can be categorised as follows:

- **internal** present in the influent wastewater;
- **self-generated** in the system from decay and lysis of biomass;
- **external** carbon source as e.g. methanol, ethanol, acetic acid, starch, etc.

The composition and concentration of organic compounds (HENZE, 1986, GRABINSKA-LONIEWSKA, 1991) determine the denitrification rate. When wastewater forms the only source of organic substrate the availability of biodegradable COD can be a shortcoming.

1.3.5 REQUIREMENT FOR BIODEGRADABLE COD

When nitrate serves as electron acceptor, the stoichiometrically equivalent mass of oxygen is used: 1 mg $N\text{-}NO_3$ (S_{NO3}) ≡ 2.86 mg O_2 (S_{O2}) (e.g. KLAPWIJK, 1978, V. HAANDEL ET AL., 1981, EKAMA ET AL., 1984). COD is required for two purposes during denitrification. One portion ($1\text{-}Y_{HD}$) is oxidised by denitrifying heterotrophs to CO_2 and H_2O, from which process energy is released and this energy is utilised for the assimilation of a second portion of COD (Y_{HD}). The anoxic heterotrophic yield (Y_{HD}) is equal to the efficiency of the cell to convert organic substrate into biomass (Copp and Dold, 1998). The total COD consumption to reduce 1 mg S_{NO3} will be $2.86/(1-Y_{HD})$ (UCT, 1984). When assuming according to ASM1 (Henze et al., 1987) $Y_{HD} = 0.67$, a theoretical demand of organic biodegradable substrate of 8.67 mg COD is required to reduce 1 mg S_{NO3}. In practice the theoretical COD-requirement for heterotrophic denitrification will be determined by the net biomass yield of activated sludge (including biomass decay).

The amount of COD for biomass synthesis will depend on the chemical structure of the COD compounds in the influent (McCarty et al., 1969, Chudoba et al., 1989, Grabińska-Łoniewska, 1991, Her and Huang (1995) and within one group of organic compounds on the number of C-atoms (Grabińska-Łoniewska, 1991).

1.4 DENITRIFICATION IN RELATION TO WASTEWATER CHARACTERISTICS

1.4.1 PARAMETERS DESCRIBING DENITRIFICATION PERFORMANCE

To describe the denitrification performance in an activated sludge system, different parameters are used: denitrification rate, denitrification potential, denitrification capacity and denitrification efficiency. To avoid any confusion they will be first generally defined while in the course of the thesis the definitions will get extended and relations between them will be established.

To characterise the denitrifying sludge activity, the **specific denitrification rate** (k_D) can be used. Most commonly, k_D is defined as a mass of S_{NO3} removed per time unit (t) per mass of volatile suspended solids (MLVSS, X_V) (WPCF, 1983):

$$k_D = -\frac{dS_{NO_3}}{dt}\cdot\frac{1}{X_V};\ \mathrm{mgN.gVSS^{-1}}.h^{-1} \tag{1.6}$$

For an on-going process, the denitrification rate is calculated from the nitrate balance over the anoxic reactor (Purtschert et al., 1996).

$$k_D = \frac{\Sigma(Q_{i,e}\cdot S_{NO3i,e})}{V_D}\cdot\frac{1}{X_V};\ \mathrm{mgN.gVSS^{-1}}.h^{-1} \tag{1.7}$$

where $Q_{i,e}$ refers to any flows (wastewater, sludge recycle, nitrate-rich recycle) entering and leaving the denitrification volume (V_D) and $S_{NO3i,e}$ is the nitrate concentration assigned to a given flow.

The **denitrification potential** (DP, $\mathrm{mgN}.\ell^{-1}$) is the maximal mass of nitrate that **can** be denitrified in the anoxic volume(s) of a considered system per unit of influent flow (van Haandel et al., 1982, Ekama et al., 1983). The DP depends on the concentration of biodegradable COD in the influent and the sludge activity.

The **denitrification capacity** (DC, $\mathrm{mgN}.\ell^{-1}$) is related to the DP and system configuration. It is the concentration of nitrate per influent flow that **is** denitrified in the system. In the most beneficial conditions the DC is equal to the DP. When, for instance, DO is present in the recycle streams entering the anoxic reactor the availability of biodegradable COD for denitrification is decreased and the DC is lower than the DP. Anoxic volumes determine how much of biodegradable COD is utilised for the denitrification process and this affects the denitrification capacity. The DC is also affected by environmental factors as temperature, pH (HENZE AND BUNDGAARD, 1982) and toxic components (RANDALL ET AL., 1992).

Another indication of denitrification performance is the **denitrification efficiency** that can be defined as the reduction rate of 'denitrifiable N', the amount of S_{NO3} that can be denitrified in a given system. This can be assessed from a N-balance that can attain different rates of complexity concerning the number of defined N-fractions and the number of involved N-conversions.

1.4.2 WASTEWATER CHARACTERISTICS

In the field of activated sludge modelling it has been established that, with respect to the response of activated sludge, organic matter of wastewater is generally divided into soluble readily biodegradable COD (S_S), particulate slowly biodegradable COD (X_S) and inert soluble and particulate COD (S_I and X_I respectively) (e.g. MARAIS AND EKAMA, 1976, DOLD ET AL., 1980, HENZE ET AL., 1987). Several approaches were developed to characterise wastewater, generally divided into physical-chemical and biological methods (STOWA, 1996a). Indirect determination of S_S and X_S can be obtained with the oxygen utilisation rate (OUR) test (EKAMA ET AL., 1986, SOLLFRANK AND GUJER, 1991, KAPPELER AND GUJER, 1992) or with the nitrate utilisation rate (NUR) test (EKAMA ET AL., 1986, KRISTENSEN ET AL., 1992, SCHEER AND SEYFRIED, 1994). Both techniques are considered to be rather complex in their performance and interpretation (SCHEER AND SEYFRIED, 1994).

The S_S-fraction constitutes usually a small fraction in domestic wastewater (7-20%) (HENZE, 1992, SCHEER, 1995, NAIDOO ET AL., 1998). Higher values can be found in cases were the fraction of industrial wastewater is high and in case of sewer systems with long pressure mains. The X_S-fraction forms usually a major part of the total biodegradable COD (40-60%) (HENZE, 1992) and is assumed to consist of relatively complex molecules. They will adsorb to activated sludge flocs and hydrolysed to simple molecules by extracellular enzymes. According to the IAWQ ASM's (HENZE ET AL., 1987, 1996), S_S is the product of the X_S-hydrolysis.

The fractions S_S and X_S have different consequences upon achievable denitrification rates. This can be easily observed in a so-called nitrate utilisation rate (NUR) batch test where a wastewater sample is added to an anoxic denitrifying sludge. Three volumetric denitrification rates are distinguished (Figure 1.1). The high rate (r_{D1}) is associated with the direct utilisation of S_S from the influent and the lower rate (r_{D2}) is associated with the utilisation of S_S, produced by the hydrolysis of X_S. The lowest denitrification rate (r_{D3}) is the basic or endogenous denitrification rate. The endogenous denitrification rate is determined, among the others, by storage, decay and lysis processes and hydrolysis rates of their products (HENZE ET AL., 1987).

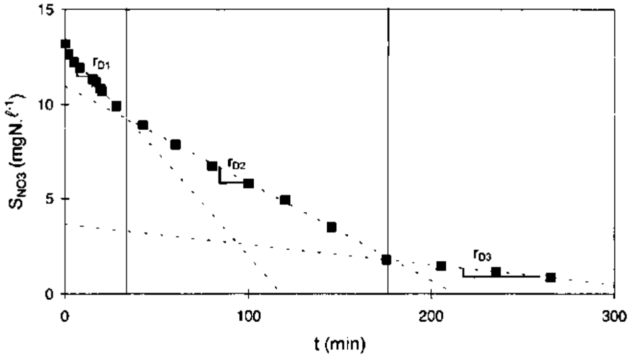

Figure 1.1 The NUR-course that can be observed after pulse addition of a domestic wastewater sample to an activated sludge sample in an anoxic batch experiment (see also v. HAANDEL ET AL., 1981a, EKAMA ET AL., 1984)

Process conditions and wastewater composition have an effect on the endogenous denitrification rate. Under conditions where both biodegradable organic wastewater fractions, S_S and X_S, are present, the overall denitrification rate is a resultant of the three rates. At prevailing concentrations of X_S in the wastewater, the hydrolysis rate determines the overall denitrification rate.

When besides the composition, the concentration of organic compounds is considered, several denitrification rates can be distinguished, analogously to respiration rates with oxygen as electron acceptor (SPANJERS, 1993):

- **maximum** in the presence of S_S in excess (saturated conditions);
- **actual** in the presence of biodegradable COD (S_S, X_S) in the anoxic reactor at non-saturated concentrations;
- **minimal** (basic or endogenous) - the least efficient (ABUFAYED AND SCHROEDER, 1986) in the sole presence of (internal) COD released by biomass (AVCIOUGLOU ET AL., 1998).

The range and variety of reported denitrification rates for different carbon sources and process conditions is impressive (Table 1.1). For wastewater the minimum k_D was found to be 0.1 while the maximum 20 mgN.gVSS^{-1}.h^{-1}. The variations in the reported values are the results of different process conditions (sludge loading rate, SRT, temperature, pH), configurations (pre-, post- or simultaneous denitrification), implemented carbon source, its characteristics and concentration, rate definition (e.g. maximum, actual, in relation to the total anoxic reactor volume, etc.) and definition of biomass concentrations (e.g. total, volatile, active) (MARAIS AND EKAMA, 1976, ARGAMAN, 1986).

1.4.3 COD/N- OR BOD$_5$/N-RATIO AND EFFECT OF PRE-TREATMENT ON DENITRIFICATION

For the prediction of the denitrification potential of a certain activated sludge system, the COD/N- or BOD$_5$/N-ratio is often used (EKAMA ET AL., 1984, KAYSER, 1983, 1991, HOFFMAN, 1986, PÖPEL, 1987). The definition of this parameter differs in literature. Some references use the ratio between the total COD (or BOD$_5$) and total nitrogen concentration in the influent, usually N_{Kj}

(e.g. EKAMA ET AL., 1984, KAYSER, 1983). Others describe it as the ratio between total COD (or BOD_5) and nitrate entering the anoxic zone (e.g. WPCF, 1983, STOWA, 1992a,b, RAUCH, 1994) or as the ratio between total COD (or BOD_5) and nitrate that exclusively are participating in the denitrification process (e.g. MCCARTY ET AL., 1969, HENZE AND HARREMOËS, 1992, HENZE ET AL., 1994).

Detailed wastewater characteristics, regarding COD- and N-fractions as defined in § 1.1 and § 1.4.2, can carry valuable information for a prediction of the denitrification potential. However, in the COD/N- or BOD_5/N-ratio's these characteristics are hidden. Next to a variation in process conditions and configurations, the variety in reported practical requirements for COD/N-ratio (Table 1.2) result from wastewater characteristics that can vary meaningfully for different locations.

With the BOD_5/N-ratio, the biodegradability of COD is considered but a shortcoming of the BOD_5-value is that it does not represent the total amount of biodegradable COD for activated sludge systems (METCALF&EDDY, 1991). Depending on wastewater characteristics concerning S_S and X_S, the ratio of BOD_5 to total biodegradable COD can vary from 0.5 to 0.8 (ROELEVELD AND KRUIT, 1998). In a report about pre-denitrification (STOWA, 1992a) it is claimed that the BOD_5/N-ratio is not a universal term to characterise wastewater for denitrification. The high variations in COD/N- and BOD_5/N-ratio's (Table 1.2) suggest that these parameters can be only a very rough indication for a prediction of the denitrification capabilities.

For municipal wastewater a few factors will effect the COD/N- or BOD_5/N-ratio (MAIER, 1993): high fractions of industrial wastewater, removal of organics in the sewer system, a shift of peaks in concentrations for organic material and nitrogen, the recycle of nitrogen from reject waters and the introduction of biological phosphorus removal. In the course of this thesis COD will be used as a general parameter characterising the organic wastewater fraction. This is dictated mainly by the fact that in many model approaches COD is used also because its analytical determination is far simpler than of BOD_5.

The implementation of various pre-treatment methods (e.g. pre-aeration, sedimentation, pre-precipitation) will change the COD- and N-profile of the wastewater (COD/N-ratio) and will influence biological treatment processes (KRISTENSEN ET AL., 1992) including denitrification (HENZE AND HAREMOËS, 1992, GIESEN AND PEETERS, 1994). Regarding the often-implemented pre-precipitation, conflictive opinions exist on its effect on the denitrification potential. According to some authors a significantly reduced denitrification potential is already observed when pre-settling is introduced ahead of an activated sludge reactor (EKAMA ET AL., 1984, HENZE AND HARREMOËS 1992) while the others state that the settleable COD-fraction of wastewater has a negligible contribution in the denitrification potential of a plant (UITERLINDE AND V.D. ROEST, 1994). ANDERSSON AND ROSEN (1990) and KARLSSON AND SMITH (1991) state that pre-precipitation decreases the COD/N-ratio, but that denitrification is hardly affected because the remaining fraction of organics shows the highest denitrification rate. An extremely different point of view is represented by NYBERG ET AL. (1996) who states that all particulate organic material is removed by pre-precipitation and that required COD has to be provided in an external form.

1.4.4 NECESSITY FOR EXTERNAL CARBON SOURCE ADDITION

On plants where wastewater is characterised generally by low COD/N-ratio or low availability of S_S and X_S, insufficient denitrification potential and capacity can be increased by the addition of an external carbon source (HASSELBLAD AND HALLIN, (1994), KRISTENSEN AND JØRGENSEN, (1994), ØDEGAARD ET AL., 1995). Possible carbon sources are methanol, ethanol, acetic acid, industrial waste products and products from sludge hydrolysis (RABINOWITZ AND OLDHAM, 1986, HENZE AND HAREMOËS, 1992, ISAACS ET AL., 1994a, HALLIN ET AL., 1996a,b, PURTSCHERT ET AL., 1996, 1998, NYBERG ET AL., 1996). Some, mainly experimental, attempts to enhance denitrification were made with raw primary sludge (ANDERSSON AND ROSEN, 1990), surplus activated sludge (SEKOULOV ET AL., 1990) and biogas (WERNER AND KAYSER, 1991).

Sometimes there is a need to elevate denitrification potential only in stress situations like at winter conditions (HENZE, 1991) or at peak nitrogen loads (ISAACS ET AL., 1994a). In these cases it is important that conditions, with regard to the necessity of an adaptation of activated sludge to several substrates, are taken into account (NYBERG ET AL., 1992, 1996, HER AND HUANG, 1995, LEE ET AL., 1995, HALLIN ET AL., 1996 a,b, PURTSCHERT ET AL., 1996).

1.5 DESIGN APPROACHES FOR N-REMOVAL

The objective of design is to ensure upper limits for effluent standards with given wastewater characteristics and environmental conditions. When both do not allow satisfying those limits an optimal (or highest possible) removal of required wastewater compounds is aimed (EKAMA ET AL., 1984). In nitrogen removal systems the most essential is to find the optimal volumes and division between aerated and un-aerated (anoxic) biomass fractions to ensure optimal nitrification and denitrification efficiencies and a required effluent quality concerning COD. The optimal aeration and mixing as well as effect of temperature and pH on process performance have to be considered (RANDAL ET AL., 1992) and prevention against oxygen input to the anoxic zones has to be taken into account. The introduction of biological phosphorus removal can interact with denitrification and this makes the design for N-removal more complex.

One of the first design approaches for N-removing activated sludge systems was a static model, developed at the University of Cape Town (EKAMA ET AL., 1984). Based on wastewater characterisation (N_{Kj}, total and biodegradable COD) the maximum unaerated (anoxic) sludge mass fraction and nitrification capacity for a selected sludge age is calculated. The anoxic fraction is further divided into primary and secondary anoxic sludge mass fraction and this division fixes denitrification potential. A proper choice of recycle ratios aims to utilise completely the present denitrification potential. With the UCT-model, information can be gained about the feasibility of a complete denitrification. Apart from South Africa and partially the United States (RANDALL ET AL., 1992), no broader acceptance was noted till now for the advanced UCT-model.

In many European Countries the Kayser- or HSA-approach (e.g. KAYSER, 1983, 1991, BÖHNKE AND PINNENKAMP, 1986, PÖPEL, 1987, HOFMANN, 1986, ATV, 1991) is used for design of N-removal activated sludge systems. In contrast to the UCT model, the wastewater is described in less detail because BOD_5, N_{Kj} and suspended solids form the main parameters. In the HSA-approach for design of the nitrification volume, two safety factors are encountered for any inhibition factors and peak loadings of influent nitrogen. Denitrification design is primarily based on influent BOD_5 and kinetics of heterotrophic biomass. The difference between the anoxic and aerobic respiration rate is expressed by a reduction factor (constant value). The N-fraction used for biomass assimilation is calculated in a very detailed way. Since the original approach uses a number of empirical values for biomass kinetics it is the responsibility of user to adjust the parameters values to local conditions. Kayser gives a number of relations in form of nomograms where the empirical relations between several system and process parameters leading to calculation of nitrification and denitrification volumes. Limited information about the wastewater characteristics is quoted as one of the shortcomings of the Kayser- and HSA-approach (STOWA, 1995).

American design approaches of combined nitrification-denitrification systems, dedicate more attention to nitrification than to denitrification process. Some use an empirical value for the specific denitrification rate as the only design parameter to calculate the anoxic residence time (METCALF&EDDY, 1991). Others use correlations between denitrification rates and other operating parameters, like the correlation between the BOD_5 sludge loading rate and the denitrification rate (BURDICK ET AL., 1982).

1.6 N-REMOVAL PROCESS CONFIGURATIONS

An important aspect in system design is to make a selection of the process configuration that will consider the optimal utilisation of the denitrification potential of the wastewater the most efficiently. For N-removal a variety of process configurations was developed in the 60's and early 70's. Around 1970 the first N-removing plants, usually retrofitted from existing nitrifying plants, were already in operation (HENZE, 1991).

A single sludge system with **post-denitrification** (Figure 1.2A) was proposed by WUHRMANN (1964). In this configuration the energy for nitrate reduction was derived from biomass decay and lysis (endogenous). To obtain a meaningful efficiency of the denitrification process, the anoxic fraction of a reactor had to be large what interacted with the demands of the nitrification.

In the process of Ludzack and Ettinger (LE-process) organic material from the influent (Q_i) was utilised as energy source for denitrification in a primary anoxic zone (LUDZACK AND ETTINGER, 1962). This configuration is referred generally as **pre-denitrification** system. Due to an indistinct separation of both zones and no nitrate rich recirculation from the nitrification zone (Q_{ir}) to the anoxic zone (only sludge recycle Q_{ir} was provided), denitrification results in the LE-process were variable. A significant improvement in the control of the performance of the LE-process was obtained with a clear separation between the anoxic and aerobic reactors

and the introduction of recycle streams to the anoxic reactor (BARNARD, 1973) (Figure 1.2B). Since with pre-denitrification a part of the flow will be discharged with the effluent, complete denitrification could not be obtained with the modified LE-process (MLE). To produce a relatively nitrate-free effluent, BARNARD (1973) combined the Wuhrmann process with the MLE process and named it Bardenpho. Experience has shown that also oxidation ditches can be easily retrofitted to accomplish biological N-removal (e.g. RANDALL ET AL., 1992, SEN ET AL., 1990, VAN'T OEVER, 1991). Because of a high recycle ratio, distinct zones do not exist in oxidation ditches and **simultaneous nitrification-denitrification** (Figure 1.2C) occurs. The efficiency of the total N-removal is partly determined by the oxygen profile over the reactor. A more controlled effluent quality can be achieved by putting two oxidation ditches in series. An **alternating nitrification-denitrification** (Figure 1.2D) concept with multiple oxidation ditches was developed and firstly put in operation in Denmark (Biodenitro process). This concept employs an alternating mode of operation (CHRISTENSEN, 1974, KLAPWIJK, 1974, ARVIN, 1985, EINFELDT, 1992, BUNGAARD, 1988) where nitrification and denitrification are performed in a semi-batch manner by periodically changing the wastewater flow through parallel tanks, aerated according to a fixed or controlled strategy (ISAACS ET AL., 1994a).
The **intermittent nitrification-denitrification** (KLAPWIJK, 1974, 1978) uses the alternating nitrification-denitrification concept but is executed in one reactor. In the intermittent concept aerated and non-aerated (anoxic) zones are separated in time (phases) and not in space. To obtain a high N-removal efficiency, pre-denitrification has the preference. At the end of the denitrification phase the aeration is switched on and the accumulated S_{NH} (and additionally from influent if this is provided during nitrification phase) is nitrified (KLAPWIJK ET AL., 1998) (Figure 1.2E). In this concept it is important to know when nitrification and denitrification processes are completed (ZHAO ET AL., 1994a,b, KLAPWIJK ET AL., 1998).
Sequencing batch reactors (SBR) are systems that can also make use of an intermittent nitrification-denitrification concept. Different operational conditions appear within one cycle (Figure 1.2F): filling (FILL) with wastewater, mixing (REACT), aerating (REACT), settling (SETTLE) and withdrawing (DRAW) (IRVINE ET AL., 1983). The SBR reactors are often used as reference for research on activated sludge processes (e.g. ARGAMAN, 1986, WILDERER, ET AL., 1987, BERNARDES, 1996, ZHAO ET AL., 1999).

The choice of a process configuration for N-removal depends on many factors such as: wastewater characteristics, effluent requirements, traditions, geographical conditions, selection of aeration system, type of secondary settler, maximal and minimal operation temperature, wastewater alkalinity, etc. Concerning denitrification, a concept based on pre-denitrification is more reasonable when biodegradable COD is available in the incoming wastewater. In the opposite case, post-denitrification with an external carbon source can be considered. To make an optimal use of biodegradable COD from the influent, the anoxic volume should be divided into two parts according to NYBERG ET AL. (1996): a small pre-denitrification and a big post-denitrification reactor.

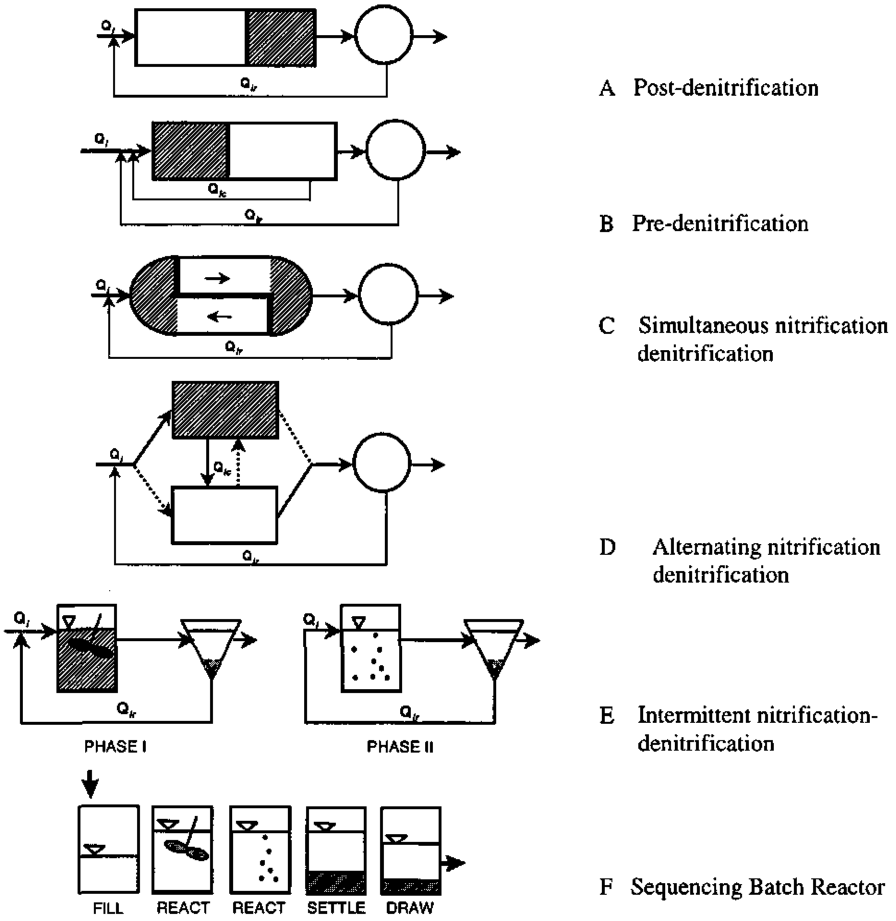

Figure 1.2 Schematic representation of the main concepts for activated single sludge N-removal

1.7 CONTROL ASPECTS FOR N-REMOVAL

Conventional N-removal with nitrification and denitrification processes became an integral, well-established part of the majority of wastewater treatment plants (WWTP) all over the world (Isaacs et al., 1995). However, its optimisation and control (usually based on on-line measurement of process variables) are still subject to intensive investigations, testing, evaluation and discussions.

Objective of control strategies is to maintain a relatively constant effluent quality at maximum process flexibility and the required process efficiency should be linked to minimum costs. In activated sludge systems a small number of process variables which could be manipulated, has been a major obstacle in developing control strategies (Andrews, 1992, Isaacs et al., 1994). Traditional control strategies comprised: aeration intensity, the rate of excess sludge wastage and recirculation rates (Olsson, 1985, Stephenson, 1985, Schlegel, 1990). They served basically to ensure an appropriate DO-level, a constant biomass concentration or a certain SRT in the activated sludge basin. However, they did not provide a sufficient degree of freedom in the nutrient removal processes. These processes require control actions that also compensate for variations in the wastewater composition and flow and nitrogen in the influent wastewater, while maintaining a proper balance between classes of organisms in the activated sludge (ZHAO ET AL., 1994A,B). Recently, addition of an external carbon source to enhance denitrification (ISAACS AND HENZE, 1995, BARROS AND CARLSSON, 1997) enriched the list of control variables, allowing in some cases for compensation of a poor denitrification performance. Another inhibition factor in developing control strategies was a lack of reliable on-line techniques. Nowadays control approaches involve the use of on-line (or side-stream) measurement techniques, like:

- S_{NH}, S_{NO3} (or S_{NO2}) measurements (BARROS AND CARLSSON, 1998, PEDERSEN ET AL., 1990) characterised often to be expensive and requiring extensive maintenance and sample pre-treatment;
- Respiration measurement for the oxygen consumption for nitrification, organic matter and cell maintenance. Properly designed experiments and estimation procedures allow among the others for a characterisation of the wastewater, biomass and oxidation kinetics (e.g. VANROLLEGHEM AND VERSTRAETE, 1993, 1998, SPANJERS AND VANROLLEGHEM, 1995, BROUWER ET AL., 1999, SPANJERS ET AL., 1998). The method is generally considered to be complex in interpretation.
- Redox potential provides information about the transition between anaerobic, anoxic and aerobic conditions (e.g. KOCH AND OLDHAM, 1985, WAREHAM ET AL., 1991, ISAACS ET AL., 1998).

Recently also in-situ pH-meters yielding an information about both nitrification and denitrification processes (HAO AND HUANG, 1996, GERNAEY ET AL., 1997) and NAD(P)H meters indicating the transition from anoxic to anaerobic conditions (ISAACS ET AL., 1998) have been used to control alternating and intermittent processes.

1.8 MODEL ASPECTS FOR DENITRIFICATION

The complexity of existing wastewater treatment systems and a lack of methods to predict the overall process efficiency, focused attention on the development of models which can identify and describe the kinetic behaviour of biological processes in activated sludge systems (WENTZEL ET AL., 1991). Starting from the 80's the development of activated sludge models became accelerated. The IAWQ Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment Processes formulated a series of models (ASM1, ASM2 and recently ASM2d and ASM3) (HENZE ET AL., 1987, 1996, 1999, GUJER ET AL., 1999 respectively). The main goal of the Task Group was to introduce a simple approach having the capability of a realistic prediction of the performance of single sludge systems for COD-oxidation, nitrification, denitrification and phosphorus removal. The authors of the subsequent models emphasise that dynamic models are tools serving research, full-scale process optimisation, troubleshooting, teaching and design assistance (HENZE ET AL., 1996). Full design of required nitrification and denitrification volumes is not recommended. With an accurate calibration of ASM's a wide range of operational decisions can be evaluated. Especially ASM1 became a major reference for many scientific and practical applications (e.g. SIEGRIST AND TSCHUI, 1992, LESOUEF ET AL., 1992, OTTERPOHL ET AL., 1994, NOVÁK, 1995).

For an estimation of the denitrification potential with ASM1, ASM2 and ASM2d, the knowledge about the difference between anoxic and aerobic population behaviour is essential. The growth rate of heterotrophs (μ_H) and hydrolysis rate of X_S (k_H) are slower at anoxic conditions in comparison with aerobic conditions what is expressed by the reduction factors η_1 and η_2 respectively (also symbols η_g and η_H are used). In ASM3 the introduced anoxic endogenous respiration rate is lower than the corresponding aerobic rate and this is expressed with the reduction factor η_3.

Although the reduction factors in ASM's are certainly essential for an assessment of the denitrification potential, no fundamental and practical consensus has been reached till now regarding their choice, and the nature of this fact is still not explained. Most researchers agreed that the utilisation rate of X_S is lower under anoxic conditions (e.g. VAN HAANDEL ET AL., 1981a, HENZE ET AL., 1987, WENTZEL ET AL., 1991, 1992, HENZE AND MLADENOWSKI, 1991, KAYSER, 1997) but others found that anoxic conditions do not cause a reduced anoxic hydrolysis rate (e.g. KRISTENSEN ET AL., 1992, GOEL ET AL., 1998, 1999). A reduced growth of heterotrophs under anoxic conditions is supported by experimental results (e.g. SÖZEN ET AL., 1998, SPERANDIO ET AL., 1999), calibration of ASM's (e.g. HENZE ET AL., 1987, 1996, 1999, GUJER ET AL., 1999, KAYSER, 1997) but it can also be explained based on energetic aspects (e.g. CASEY ET AL., 1994). In contrast the same growth rate was observed in anoxic and aerobic conditions by e.g. WUHRMANN (1964), VAN HAANDEL ET AL. (1981a,b) and STILL ET AL. (1986).

Introduction of endogenous respiration in ASM3 started a discussion on its magnitude in the presence of oxygen and nitrate. Reduced anoxic, endogenous respiration rates are postulated by MCCLINTOCK ET AL. (1988), KAYSER (1997), GUJER ET AL. (1999) and AVCIOUGLU ET AL. (1998).

Another question for a reliable description of the denitrification process using activated sludge models is a proper choice of the value for the anoxic heterotrophic yield coefficient (Y_{HD}), which is suspected to be lower than the corresponding aerobic value (KLAPWIJK, 1978, SCHEER AND SEYFRIED, 1994, ORHON ET AL., 1996, ÇOKGHÖR ET AL., 1998, COPP AND DOLD, 1998, SPERANDIO ET AL., 1999).

Advanced mathematical models such as ASM's, although simplified with respect to the complexity of the activated sludge process itself, are still substantially complex for the user. Estimation of a significant number of model parameters is complex and time consuming. On the other hand, use of default values for parameters may lead to an erroneous estimation of the process performance. For practical implementation such as process control, simplified models have been successfully used (e.g. ZHAO ET AL., 1994 a,b, 1995, 1999, ISAACS AND HENZE, 1995, BERNARDES, 1996, BROUWER ET AL., 1999). Simplified models of the chosen activated sludge processes are characterised by a reduced number of model components and biomass population dynamics are not explicitly modelled. For a successful implementation of simplified models usually on-line measurement of some process variables is necessary. Limited information on process performance can be attained by their implementation.

1.9 NON-CONVENTIONAL N-CONVERSIONS

For the removal of nitrogen from wastewater, the conventional N-conversion through nitrification and denitrification (via nitrate) is a wide implemented technology. Nevertheless, several authors (e.g. POTH, 1986, REMDE AND CONRAD, 1990, ABELIOVICH AND VONSHAK, 1992, BOCK ET AL., 1995, PATUREAU ET AL., 1997, LOOSDRECHT AND JETTEN, 1998) reported 'new' microbial nitrogen conversions that will be referred here as non-conventional N-conversions.

- **heterotrophic nitrification and aerobic denitrification**

Aerobic denitrification is carried out by bacteria that can co-respire nitrate and oxygen, like *Thiosphaera pantotropha, Alcaligenes faecalis* and *Comamonas Sp. strain SGLY2* (ROBERTSON AND KUENEN, 1984, 1990, BONIN AND GILEWICZ, 1991, PATUREAU ET AL., 1997). The same micro-organisms were found to be capable of heterotrophic nitrification (ROBERTSON AND KUENEN, 1987, ROBERTSON ET AL., 1988). Conflictive opinions categorise the rate of these processes as negligible (V.LOOSDRECHT AND JETTEN, 1998) or substantial (MÜNCH ET AL., 1996, PATUREAU ET AL., 1997).
According to ROBERTSON AND KUENEN *(1990)* only *at a high* wastewater COD/N-*ratio* (>*10*) a portion of N can be denitrified aerobically. Aerobic denitrification can be confused with conventional denitrification in aerobic reactors subjected to oxygen diffusion limitation and formation of anoxic zones inside flocs or biofilms (KRUL, 1976).

- **autotrophic denitrification**

Autotrophic nitrifiers (e.g. *Nitrosomonas europaea*) were observed to be responsible for a substantial production of N-gases (N_2O, NO or N_2) that may indicate that they can carry denitrification of nitrite with ammonium or hydrogen as electron donor - autotrophic denitrification (ANDERSON AND LEVINE, 1986, BOCK ET AL., 1995). The conversion rates are however an order of magnitude slower than these for conventional nitrification and denitrification reactions.

- **anaerobic ammonia oxidation (Anammox)**

In 1995, MULDER ET AL. observed the removal of ammonium in a fluidised denitrification bed reactor. This brought them to a hypothesis of microbial catalysis of two autotrophic conversions: anaerobic oxidation of ammonia to N-gas (Anammox) and anaerobic oxidation of nitrite to nitrate (VAN DE GRAAF ET AL., 1996). The Anammox process, when once established, may be characterised by high conversion rates (MULDER ET AL., 1995). When the Anammox process is combined with a process in which nitrite is produced a nitrogen removal process can be developed which requires less oxygen and no COD (V.LOOSDRECHT AND JETTEN, 1998).

- **nitrogen removal via the nitrite-route**

Another promising non-conventional technology in activated sludge systems, operating especially at low COD/N-ratio's, is the N-removal via the nitrite-route (STOWA, 1997). The process consists of two sub-processes (1) the oxidation of S_{NH} by ammonium oxidisers to

S_{NO2} and (2) the reduction of S_{NO2} by denitrifiers to N_2. In comparison with the conventional N-removal process, nitrite forms the intermediate between nitrification and denitrification instead of nitrate. The absence of nitrite-oxidisers is controlled by the maintenance of a low aerobic SRT while ammonium-oxidisers have to be regularly supplemented. This technology causes the (theoretical) decrease of the COD demand for denitrification up to 40%. The additional stimulation of denitrification via the nitrite-route is ensured by low-DO conditions in the reactor. This causes that a bigger part of the bacterial floc is anoxic which contributes in a lower nitrification- and higher denitrification rate. It is essential to find an optimal DO concentration that will ensure a proper balance between both conversion rates and an optimal N-removal.

Summarising, all described N-conversion pathways, both conventional and non-conventional are presented schematically in Figure 1.3.

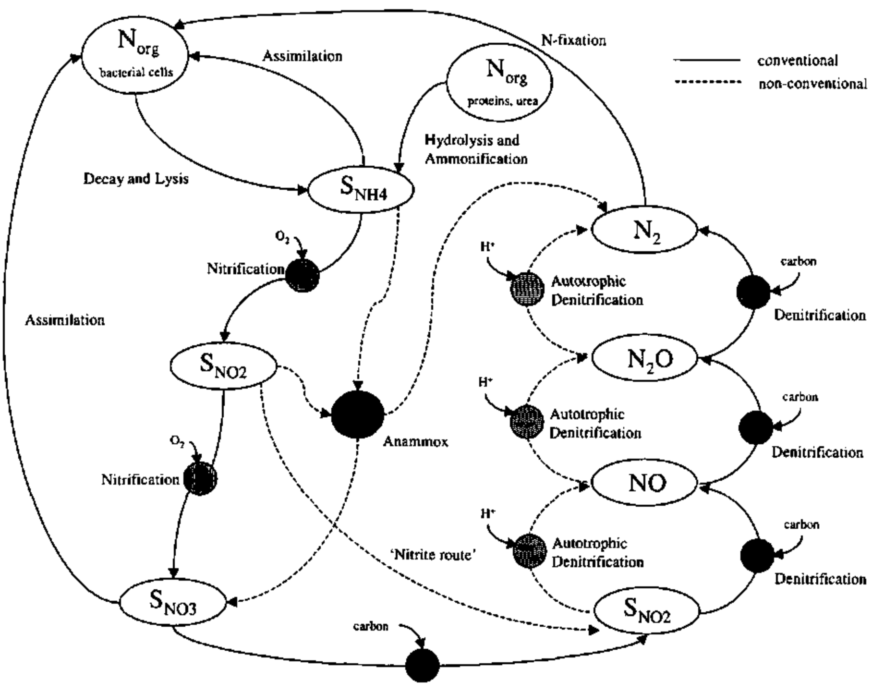

Figure 1.3 Possible microbial N-conversions

1.10 OBJECTIVES OF THE THESIS

Denitrification is a well established process for biological N-removal in activated sludge wastewater treatment plants and it is generally agreed that the availability of organic biodegradable matter, process configuration and activated sludge characteristics determine predominantly the denitrification potential and capacity. Nevertheless, regarding the estimation of denitrification potential in relation to a detailed wastewater and sludge characterisation, there is still requirement to establish a reliable estimation method.

Many design approaches use empirical values of denitrification kinetic parameters and/or use general COD/N- or BOD_5/N-ratios, which are characterised by a high rate of 'hidden information'. More detailed models exist (ASM) but despite their additional value they are complex and require a significant effort to choose or estimate properly a large number of parameters. Incompetent use of ASM's may bring erroneous prediction and interpretations of the process capabilities. A simplification of models will result in a decrease of number of parameters but the use of simplified models is usually restricted to the necessity of measurement techniques and provides limited information on process capabilities.

The main goal of this thesis was to develop and validate a methodology to predict the denitrification potential for activated sludge systems. Aerobic and anoxic respiration techniques formed the basis of the methodology. They enabled to estimate wastewater- and activated sludge characteristics. Attention was paid on the relation between the respiration of activated sludge under aerobic and anoxic conditions and its relevance to the mathematical description of denitrification processes. This formed a basis for the development of a simplified denitrification model, which was integrated with an existing nitrification/aerobic COD-oxidation model (BROUWER AND KLAPWIJK, 1995). The simplicity of the presented approach resulted from the modelling of substrate conversion rates, while activated sludge population dynamics were not explicitly described. Testing and validation of developed methodologies to estimate the denitrification potential and overall N-removal potential were performed using several case studies (batch tests, pilot plants) where the characteristics of activated sludge and wastewater varied.

Regardless how the denitrification potential can be estimated, interacting opinions are traced in literature on the effect of pre-treatment (pre-precipitation) on the denitrification potential. Statements about a change in wastewater characteristics by pre-precipitation are evident, but in literature the connection between this fact and denitrification potential is somehow unclear. To evaluate the effect of changed wastewater characteristics on the denitrification potential two experiments were performed. Two reactors, lab- and pilot-scale, characterised by different influent characteristics and process conditions, were fed with pre-precipitated influent. Using the developed methodology to estimate the denitrification potential, an attempt was undertaken to formulate more precise statements about the denitrification behaviour in systems fed with low-strength wastewater. Several optimisation steps, including the implementation of an advanced respiration based control strategy and modelling with the developed simplified denitrification model, supported the considerations.

1.11 STRUCTURE OF THE THESIS

In chapter 1 (this chapter) a literature survey on N-removal aspects is given with a special impact on denitrification. Process fundamentals are followed by a description of conditions and factors determining the denitrification performance. Attention is paid on the relation between the requirement for biodegradable COD and the denitrification potential. The denitrification rate, potential and capacity are, as important operational parameters, defined in relation to wastewater and activated sludge characteristics. It is emphasised that both the magnitude of denitrification rate and COD requirement for denitrification (expressed by COD/N or BOD_5/N) are very specific for different conditions (Table 1.1 and Table 1.2). The effect of pre-precipitation on a change of wastewater characteristics and denitrification efficiency is briefly reviewed. The survey of the variety of N-removal configuration concepts is given and existing control strategies for N-removal processes are briefly described. Furthermore, model approaches for design, optimisation and control of denitrification are mentioned.

In chapter 2 the nitrate utilisation rate (NUR) test is presented as a simple anoxic respiration method to estimate the denitrification potential of existing activated sludge systems. A methodology to estimate the denitrification potential and capacity in relation to wastewater characteristics, process configuration and activated sludge characteristics is given. The procedure to extract maximum information from a NUR-test, like wastewater characterisation and kinetic and stoichiometric parameters is worked out. The implementation of a simple model, based on estimated parameters, allows for the prediction of a relation between the organic anoxic sludge loading rate and the denitrification rate. A NUR-test with acetate allows estimating an anoxic heterotrophic yield in a simplified way. Using the developed approach also a relational model between the attainable denitrification rate and the required amount of external carbon source can be easily formulated.

Modelling of the denitrification process uses often currently aerobic kinetics, multiplied with reduction factors, reflecting the decreased activated sludge activity under anoxic conditions. A methodology to obtain reduction factors for S_S-oxidation, X_S-hydrolysis and endogenous respiration is proposed in chapter 3. It is based on a respiration response of activated sludge under aerobic and anoxic conditions. Other aspects are briefly discussed, like the choice of a heterotrophic yield coefficient and wastewater characterisation under aerobic and anoxic conditions. The dependency of reduction factors on activated sludge characteristics and process conditions is supported by some results with several activated sludge samples, originating from different pilot-plant configurations.

A possible implementation of the information about activated sludge kinetics and wastewater characterisation acquired from respirometric measurements (both aerobic and anoxic) is presented in chapter 4. A simplified respiration based denitrification model is developed to estimate the denitrification potential. Its integration with an existing nitrification/aerobic COD-oxidation model (BROUWER AND KLAPWIJK, 1995) leads to the formulation of an overall simplified N-removal activated sludge model. The model is simplified because it is based on substrate conversion rates while activated sludge population dynamics are not explicitly modelled. For a frequent update of model parameters, one type of measurement is used: the aerobic respiration test. The simplified nitrification-denitrification model is validated for two pilot-scale N-removal plants (chapter 5), characterised by a significantly different wastewater composition and process parameters.

Denitrification potential and capacity in systems fed with low-strength, pre-precipitated wastewater is analysed in the chapters 6 and 7. The effect of pre-precipitation on wastewater composition, the overall removal efficiency and sludge activity in an ultra-low loaded lab-scale SBR-system, with fixed nitrification and denitrification phases, is described in chapter 6. With help of a simplified N-removal model, the denitrification potential of the system is examined when optimising the system performance. In chapter 7 it is studied to which extend process optimisation steps, such as an increase of the sludge loading rate and anoxic volume fraction, or implementing an effective control strategy, can increase the overall denitrification potential and capacity of the system. General considerations about possibilities to attain a satisfactory denitrification performance in systems fed with low-strength wastewater are carried out in light of literature statements.

In chapter 8 a general discussion is given, summarising the developed methodologies and indicating their possible applications and bottlenecks in practice.

Table 1.1 Reported denitrification rates obtained with different C-sources and process configurations

Denitrification rate	Unit	Carbon source	Author	System
23.75	mgN.gVSS^{-1}.h^{-1}	VFA from biologically hydrolysed sludge	Æsøy and Ødegaard (1994)	lab-scale biofilm rotating biological contactor
1-3 0.5 >3 4 5	mgN.gVSS^{-1}.h^{-1}	wastewater, good conditions wastewater, non-optimal conditions hydrolysed starch hydrolysed starch formate	Andersson and Rosén (1990)	pre-denitrification, full scale plant post-denitrification, full-scale pilot-scale tests
3-4	mgN.gVSS^{-1}.h^{-1}	methanol	Andersson et al. (1992)	post-denitrification full-scale reactor
0.6-1.5	mgN.gMLSS^{-1}.h^{-1}	internal (wastewater) and endogenous	Argaman (1986)	laboratory tests in continuously fed intermittently decanted process (CFID)
8.7-13.3 5.0-37.5 1.2-4.6 0.71-2 2.1-6.2	mgN.gVSS^{-1}.h^{-1}	methanol methanol wastewater endogenous metabolism wastewater	Beccari et al. (1983) EPA (1975) EPA (1975) Ekama et al. (1984) EPA (1975)	
1.44-1.75 2.4-6	mgN.gVSS^{-1}.h^{-1}	endogenous carbon wastewater	Carruci et al. (1996)	batch tests
$30(1.20)^{T-20}$ $4.2(1.08)^{T-20}$ $3.3(1.03)^{T-20}$	mgN.gX$_a^{-1}$.h^{-1}	all wastewater components +endogenous activity wastewater X_S + endogenous activity endogenous activity	Van Haandel et al. (1981a), Ekama et al. (1984), Clayton et al. (1991)	pilot plant studies with plug-flow pre-anoxic and post-anoxic reactor
3-25 2-6	mgN.mgVSS^{-1}.h^{-1}	acetate methanol	Hallin et al. (1996 a,b)	batch tests
0-16.7	mgN.gVSS^{-1}.h^{-1}	raw wastewater	Henze (1986)	batch tests with raw wastewater and activated sludge samples from different full scale WWTP
2.5-6.5	mgN.gVSS^{-1}.h^{-1}	raw wastewater	Henze (1989)	batch tests
7-20 1-5 0.2-0.5	mgN.gVSS^{-1}.h^{-1}	methanol, acetic acid, hydrolysed sludge, brewery wastewater, digester supernatant, hydrolysed starch, easily biodegradable COD ethanol, whey, raw wastewater, molasses endogenous, methane	Henze (1991)	full scale plants
10-20 2-4 0.2-0.5	mgN.gVSS^{-1}.h^{-1}	directly biodegradable COD of wastewater (T=20°C) easily biodegradable COD of wastewater (T=20°C) slowly biodegradable COD of wastewater (T=20°C)	Henze et al. (1994)	
5-18	mgN.gVSS^{-1}.h^{-1}	hydrolysate of primary sludge from various hydrolysis processes (biological, chemical or combination)	Henze and Harremoës, (1990)	
0.6-3 0.6-3 1-10	mgN.gVSS^{-1}.h^{-1}	raw wastewater (T=7-20°C) pre-precipitated wastewater (T=7-20°C) hydrolysed sludge (T=7-20°C)	Henze and Harremoës, (1990)	

2-10 2-10		acetic acid (T=7-20°C) methanol (T=7-20°C)		
2.1-3.2 0.6-0.7	mgN.gVSS^{-1}.h^{-1}	acetate (depending on dose) endogenous	Isaacs and Henze (1995)	pilot-plant study (Biodenipho)
0.4-2.2 1.1-7.4 1.4-7.9	mgN.gVSS^{-1}.h^{-1}	endogenous carbon acetate hydrolysate	Kristensen et al. (1992)	NUR-tests with activated sludge from a pilot plant and full from scale plants
0.1-0.72 1.56-4.86	mgN.gVSS^{-1}.h^{-1}	endogenous metabolism settled wastewater	Kujawa et al. (1997)	respiration tests with activated sludge and wastewater from WWTP Assen (Holland)
3-7.3 2-3 1-2	mgN.gVSS^{-1}.h^{-1}	centrifuged raw wastewater (initial rate) centrifuged, coagulated wastewater acetate X_S of wastewater endogenous (probably some X_S present)	Naidoo et al. (1998)	NUR tests with activated sludge samples from different European WWTP's
0.6 2.4 2.1	mgN.gVSS^{-1}.h^{-1}	endogenous methanol acetate	Nyberg et al. (1996)	batch tests
10 3		ethanol methanol	Nyberg et al. (1996)	full-scale system with pre-precipitation and post-denitrification
0.4-3.75	mgN.gVSS^{-1}.h^{-1}	domestic wastewater (strong dependancy on sludge loading rate is emphasized)	Schlegel (1987)	full-scale system with two step 'Kaskadendenitrifikation'
0.8-1	mgN.gMLSS^{-1}.h^{-1}	thickened activated sludge from the first step (C oxidation) to denitrify the effluent from trickling filter	Sekoulov et al. (1990)	pilot-plant studies
1.2-3.3	mgN.gMLSS^{-1}.h^{-1}	wastewater	Stensel, (1981), Burdick et al. (1982)	single-stage pre-anoxic zone in a pilot-plant study and in a full-scale Bardenpho plant
0.2-0.5 0.5-1.2 2.0-4.0 1.1-1.5 0.8-1.2	mgN.gMLSS^{-1}.h^{-1}	endogenous metabolism X_S in combination with endogenous S_S (or acetate) in combination with endogenous actual with wastewater (T=20°C) actual with wastewater (T=15°C)	STOWA (1992a,b)	pilot-plant installations characterised by rather low organic loading rate (B_{XBOD}=0.035-0.07 g.g^{-1}.d^{-1})
1.3-5.5 2.0-5.2 5.7-8 3.5	mgN.gMLSS^{-1}.h^{-1}	acetol ethanol methanol external carbon source (general)	Weber and Krauth (1998)	test in full-scale system with post-denitrification at B_{XCOD}=0.4-0.5 g.g^{-1}.d^{-1} universal value for design in the system with $B_{X,COD}$=0.4-0.5 g.g^{-1}.d^{-1}, T=12°C; no lost of substrate because of DO input
1.54	mgN.gMLSS^{-1}.h^{-1}	biogas (60% methane)	Werner and Kayser (1991)	lab-scale activated sludge reactor
1.7-13.8	mgN.gVSS^{-1}.h^{-1}	industrial wastes	WPCF (1983)	

Table 1.2 Reported carbon/nitrogen ratio's required for complete/satisfactory denitrification with different C-sources

C/N requirement	**Definition of C, N**	**Sort of carbon source**	**Author**	**How determined?**
$COD/N=4.5\pm0.6$	biodegradable COD	VFA from biologically hydrolysed sludge	Æsøy and Ødegaard (1994)	denitrification study with lab-scale biofilm contactor
$BOD_7/N>3$		wastewater	Andersson and Rosén (1990)	full-scale pre-denitrification system
$BOD_7/N=6\text{-}8$ $BOD_7/N=5\text{-}6$		raw wastewater methanol	Andersson et al (1994)	pre-denitrification system post-denitrification
BOD/N= 4.0	BOD of wastewater exclusively used for denitrification;	wastewater	Barth et al. (1968)	estimation
C/N=1.38 C/N=1.46	C:N, mol/mol	ethanol acetate	Constantin and Fick, (1997)	practice
COD/N > 12.5-14.3	C: total COD influent N: N_{Kj} influent	wastewater	Ekama et al., (1984)	practice for Phoredox process
COD/N= 8.6	COD totally biodegradable	municipal wastewater	Ekama and Marais (1984)	
COD/N=3-4	COD filtered	methanol	after EPA (1975)	
COD/N=11-13		wastewater	after EPA (1975)	full-scale experience at Oswego, N.Y.
COD/N>15		wastewater	after EPA (1975)	bench-scale pre-denitrification-nitrification systems
COD/N=4.5		methanol	Henze and Bundgaard (1982)	
COD/N= 4.2 COD/N=5-10		glucose wastewater	Henze (1991) Henze and Harremoës (1992)	theoretically estimated practice, COD/N depends on process configuration
COD/N= 3.5-4	minimum ratio, the rest not defined	wastewater	Henze and Harremoës, (1990)	
COD/N= 3.5-4.5	when no part of COD is lost through oxidation with oxygen	wastewater	Henze et al. (1994)	
COD/N=4-5.5	separate process			
COD/N=6-11	recirculation process			
COD/N=6-11	alternation process			
COD/N= 6-15	simultaneous process			
COD/N= 4.5		hydrolysate from primary sludge	Isaacs and Henze. (1995)	pilot-plant experiments (Biodenipho)
COD/N= 3.71		methanol	McCarty et al. (1969)	estimation based on biochemical formulation
COD/N=7.35 COD/N=4.4 COD/N=3.9		methanol ethanol methanol	Nyberg et al. (1992) Nyberg et al. (1996)	full-scale post denitrification reactor (WWTP Klagsham in Malmö, Sweden)
$BOD_5/N= 2\text{-}2.5$ $BOD_5/N= 4\text{-}5$	for 'far reaching' denitrification (total effluent $N<10\ mg.\ell^{-1}$)	settled wastewater acetate	STOWA (1992a,b)	pilot plant studies with pre-denitrification at low organic sludge loading rate
FOC/N=0.71-3.7	C: filtered C N: nitrate N	industrial wastes	after WPCF (1983)	

LIST OF SYMBOLS AND ABBREVIATIONS

ASM	Activated Sludge Model
DC	denitrification capacity (mgN.ℓ^{-1})
DO	dissolved oxygen (mgO_2.ℓ^{-1})
DP	denitrification potential (mgN.ℓ^{-1})
k_D	specific denitrification rate (mgN.gVSS^{-1}.h^{-1})
N	nitrogen (mgN.ℓ^{-1})
NUR	nitrate utilisation rate
N_{Kj}	Kjeldahl nitrogen (mgN.ℓ^{-1})
N_{org}	organic nitrogen (mgN.ℓ^{-1})
OUR	oxygen utilisation rate
Q_i	wastewater influent flow (ℓ.h^{-1} or m^3.h^{-1})
Q_{ic}	internal, nitrate-rich recycle flow (ℓ.h^{-1} or m^3.h^{-1})
Q_{ir}	return sludge flow (ℓ.h^{-1} or m^3.h^{-1})
r_D	volumetric denitrification rate; subscripts 1: in presence of S_S from influent, 2: in presence of S_S from X_S hydrolysis; 3: endogenous (mgN.ℓ^{-1}.h^{-1})
SRT	sludge retention time (d)
S_I	soluble, inert COD (mgCOD.ℓ^{-1})
S_{ND}	soluble, readily biodegradable organic N (mgN.ℓ^{-1})
S_{NH}	ammonia (mgN.ℓ^{-1})
S_{NI}	soluble inert N_{org} (mgN.ℓ^{-1})
S_{NO3}	nitrate (mgN.ℓ^{-1})
S_{NO2}	nitrite (mgN.ℓ^{-1})
S_{O2}	oxygen (mgO_2.ℓ^{-1})
S_S	soluble, readily biodegradable COD (mgCOD.ℓ^{-1})
t	time (h)
V_D	denitrification volume (ℓ or m^3)
X_a	active biomass (g.ℓ^{-1})
X_I	particulate, inert COD (mgCOD.ℓ^{-1})
X_{ND}	particulate, slowly biodegradable organic N (mgN.ℓ^{-1})
X_{NI}	particulate inert organic N (mgN.ℓ^{-1})
X_S	particulate, slowly biodegradable COD (mgCOD.ℓ^{-1})
X_V	volatile concentration of activated sludge (g.ℓ^{-1})
Y_{HD}	heterotrophic anoxic growth yield (mg $COD_{biomass}$.mgCOD$_{utilised}^{-1}$)

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2

A method to estimate denitrification potential for pre-denitrification system using batch NUR-test

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ABSTRACT

Nitrate utilisation rate (NUR) batch tests with wastewater or acetate as carbon source were carried out for systems with pre-denitrification. A pulse dosage of wastewater to activated sludge in anoxic conditions enabled to estimate the denitrification potential of the considered wastewater and the endogenous denitrification potential of the considered activated sludge. From the same NUR-test the concentration of readily and slowly biodegradable COD-fractions (S_S and X_S respectively) and the resulting denitrification rates on wastewater fractions and endogenous material could be determined. Based on the denitrification rates the anoxic utilisation rates of S_S and X_S could be estimated. The denitrification potential of the wastewater, defined as the amount of nitrate that can be reduced with both biodegradable COD-fractions, and the endogenous denitrification allow to calculate the overall denitrification potential of a given treatment plant. In combination with system characteristics it is possible to predict the denitrification capacity and the theoretical nitrate effluent quality. With the estimated denitrification kinetics, the overall denitrification rate could be modelled as a function of the anoxic sludge loading in the pre-denitrification volume by using a simple model.

If the denitrification potential of a plant is not sufficient to satisfy required effluent quality standards, the addition of an external carbon source may be considered to enhance denitrification. The denitrification kinetics from a NUR-test with acetate was used to model the relation between the obtainable denitrification rate and the acetate sludge loading rate. Such a relational model can be implemented to design the rate of an external carbon dosage or it can be used for the design of the volume of a post-anoxic reactor where the external carbon source has to be utilised. The relational model can also be used for the development of a control strategy.

The possible transfer of the presented methodology to practical conditions is considered and bottlenecks in the performance of a NUR-test are mentioned. For a correct interpretation of results from a batch NUR-test, attention should be paid on an accumulation of nitrite. When nitrite is formed, it should be included in any calculations. The feasibility of the NUR-test for wastewater characterisation is limited for activated sludge with an enhanced biological phosphorus removal activity. Further, the estimation of the wastewater characteristics is sensitive for the value of the yield factor Y_{HD}.

2.1 INTRODUCTION

When it was observed that, in terms of respiration activity, the activated sludge behaviour in aerobic and anoxic conditions is not the same for different wastewater biodegradable organic fractions, the need for a detailed wastewater characterisation appeared. In activated sludge models (e.g. DOLD ET AL., 1980, HENZE ET AL., 1987, 1996) the assumption was made that a large number of specific organic wastewater compounds can be grouped into soluble readily biodegradable (S_S), particulate slowly biodegradable (X_S) and inert soluble and particulate (S_I, X_I respectively) COD-fractions. For respiration processes, like aerobic respiration and denitrification, S_S- and X_S-fractions are of significant importance, while to predict the sludge production the knowledge about X_I is necessary. Compared with the general lump parameters like COD or BOD_5, the introduction of S_S and X_S can be considered as an important step towards a more adequate estimation of the denitrification potential of an activated sludge system and it may allow for a more precise design and optimisation of the overall denitrification process and an optimal usage of carbon sources in the wastewater.

Existing methods for wastewater characterisation can be divided into physical-chemical and biological methods. For activated sludge processes the biological methods deserve more attention since they allow to gain characteristic results about the activity of the heterotrophic biomass, due to a stoichiometric relation between biomass growth and electron acceptor utilisation (SOLLFRANK AND GUJER, 1991). The biological methods are generally based on the measurement of the respiration rate under aerobic or anoxic conditions, respectively the oxygen utilisation rate (OUR) or the nitrate utilisation rate (NUR). OUR-tests have been often used for the characterisation of biomass kinetics (e.g. EKAMA ET AL., 1986, SPANJERS AND VANROLLEGHEM, 1995, VANROLLEGHEM ET AL., 1999), wastewater characterisation (e.g. EKAMA ET AL., 1986, SOLLFRANK AND GUJER, 1991, SPANJERS AND VANROLLEGHEM, 1995, BROUWER ET AL., 1998) and estimation of the heterotrophic yield coefficient (e.g. CECH ET AL., 1984, SOLLFRANK AND GUJER, 1991). The NUR-tests were used to characterise denitrification kinetics (CLAYTON ET AL., 1991, NAIDOO ET AL., 1998), the fraction of denitrifiers (HENZE, 1986, 1992, KRISTENSEN ET AL., 1992) and biodegradable COD-fractions of the wastewater (SCHEER AND SEYFRIED, 1994, SCHEER, 1995, ÇOKGÖR UBAY ET AL., 1998, NAIDOO ET AL., 1998). NUR-tests in combination with OUR-tests allow for an estimation of the reduction factors for the biomass respiration activities under anoxic conditions in comparison with aerobic conditions, like growth, X_S-hydrolysis and endogenous respiration (HENZE, 1986, KRISTENSEN ET AL., 1992, ORHON ET AL., 1996). These reduction factors are used in several model approaches. Besides, NUR-tests can be used for the estimation of the required COD/N-ratio to attain a complete nitrate reduction for a specific wastewater and activated sludge.

The heterotrophic yield (Y_H), defined as mass of biomass COD produced per mass of consumed COD, is of great importance in model and design approaches for the estimation of the amount of produced biological sludge and for the estimation of the electron acceptor consumption during the utilisation of a given amount of substrate (SPERANDIO ET AL., 1999). In activated sludge models (DOLD ET AL., 1980, HENZE ET AL., 1987) and in respirometric procedures for wastewater characterisation (e.g. EKAMA ET AL., 1986) it is assumed that Y_H has the same numerical value under aerobic and anoxic conditions ($Y_H=Y_{HD}$). However, it is known that the use of nitrate as electron acceptor will affect the energy released by the oxidation reaction and consequently anoxic yield factors are lower than aerobic yield factors (e.g. ORHON ET AL., 1996, NAIDOO ET AL., 1998, SPERANDIO ET AL., 1999). To obtain a reliable wastewater characterisation using respirometric techniques a proper choice of Y_H or Y_{HD} is of significant importance (SCHEER AND SEYFRIED, 1994).

Some denitrification design approaches use the denitrification rate for the calculation of the anoxic volumes (EKAMA ET AL., 1984, SDA, 1989, RANDAL ET AL., 1992). Denitrification rates are often related to the implemented anoxic sludge loading rate (STENSEL, 1981, BURDICK ET AL., 1982, HOFMANN, 1985, PÖPEL, 1986, METCALF&EDDY, 1991) based on BOD_5 or COD, while subsequent wastewater fractions are usually not taken into account. Design procedures employing empirical parameters may under- or overestimate the required denitrification volume because of the unique characteristics of each wastewater and activated sludge.

This chapter describes an experimental procedure to determine the denitrification potential for systems with pre-denitrification. Batch NUR-tests with pulse addition of wastewater enables to make a distinction between denitrification rates on S_S, X_S and endogenous material and in addition, the concentrations of S_S and X_S can be estimated. Via the estimated denitrification potential the effluent nitrate concentration can be predicted and this information and can be used for an optimisation of the overall denitrification efficiency of an existing WWTP. A simplified denitrification model, based on estimated parameters and wastewater characteristics, enables to predict the denitrification rate as a function of the sludge loading. This approach was tested in a set-up for NUR-tests with a continuous dosage of substrate. The same type of relational model can be formulated for systems using external carbon sources not requiring biomass adaptation. A relation between the external carbon addition rate and attainable denitrification rate can be employed, for instance for calculating the required dose of carbon, volume of the post-denitrification reactor and in control strategies for a temporary enhancement of denitrification in stress conditions (ISAACS AND HENZE, 1995). Implementation of the presented methodology is further discussed and obstacles regarding interpretation are named.

2.2 MATERIAL AND METHODS

2.2.1 ACTIVATED SLUDGE AND WASTEWATER

The activated sludge for the experiments originated from a compartmentalised plug-flow N-removal pilot-plant with pre-denitrification, characterised by an organic sludge loading rate (B_{XCOD}) of approximately 0.1 $gCOD.gMLSS^{-1}.d^{-1}$. The activated sludge samples were taken from the last compartment of the pilot plant.

During the experimental period, the plant operated in a temperature range of 15 to 20°C. The wastewater, provided to the plant and used in the tests, was of municipal origin with an average influent COD/N-ratio of 7 and total N (=N_{Kj}) of 60 mgN.ℓ^{-1}. To evaluate the proposed method for systems with pre-denitrification and biological phosphorus removal, tests were carried out with an activated sludge sample originating from a plug-flow pilot-plant (B_{XCOD} = 0.08 gCOD.gMLSS^{-1}.d^{-1}) with biological nitrogen- and phosphorus removal.

2.2.2 EXPERIMENTAL SET-UP

For the NUR-tests a batch set-up consisting of 10 lab-scale vessels with a volume of 2.5 ℓ (Figure 2.1) was used. A big number of reactors enabled to perform several tests at the same time with increasing substrate dose. To estimate the relation between the obtainable denitrification rate and sludge loading a batch reactor with an active volume of 80 ℓ (Figure 2.2) was used. To the small vessels organic substrate (wastewater or acetate) was added in a pulse mode while to the batch reactor substrate was added in a continuous mode.

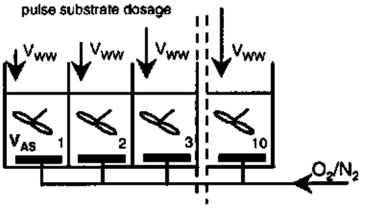

Figure 2.1 Batch set-up for a NUR-test with pulse dosage of substrate (wastewater, acetate)

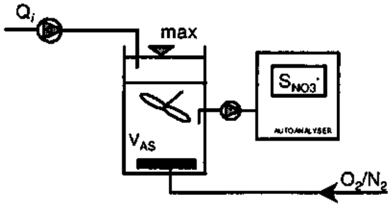

Figure 2.2 Batch set-up for a NUR-test with continuous dosage of substrate (wastewater, acetate)

In the beginning of each NUR- or continuous test, endogenous conditions were ensured by aerating the activated sludge for approximately 30 minutes and controlling its aerobic respiration rate. After the endogenous respiration was reached the aeration was switched off. When the dissolved oxygen (DO) concentration in the bulk dropped below 0.1 mg $O_2.\ell^{-1}$, nitrogen gas was purged through to maintain an oxygen-free environment throughout the duration of the experiment. The nitrate concentration of the sludge mixture was adjusted to 15-30 mg N.ℓ^{-1} using a 1M KNO_3 solution.

NUR-test in pulse mode

The tests with pulse dosage were performed at substrate/biomass ratio's (S/X_V) varying from 0.02 to 0.07 gCOD.gVSS^{-1}. The S/X_V-ratio's resulted from the applied volumetric wastewater fraction (f_{ww}) in relation to the total mixture of wastewater (V_{ww}) and sludge (V_{AS}), the total COD of the wastewater and the volatile activated sludge concentration (X_V). The value of f_{ww} varied between 0.15 and 0.5. The average applied S/X_V-ratio's were in general comparable with the values at the inlet of the pilot-plant from which an activated sludge sample was taken.

By taking grab samples at set time intervals the denitrification course was followed. The samples were immediately filtered through a paper filter (4.4 µm Schleicher&Schuell) and the concentration of nitrate (S_{NO3}), nitrite (S_{NO2}) and soluble ortho-phosphates (S_{PO4}) were determined on a Segment Flow Analyser (Skaiar, the Netherlands).

With an operation in pulse mode denitrification rates on different COD-fractions can be measured and wastewater characteristics can be estimated. A successful distinction between denitrification rates on different COD-fractions (Figure 1.1), will depend on:

- ensuring endogenous conditions of activated sludge in the beginning of the test;
- providing anoxic conditions to initialise the synthesis or activate N-oxides reductases before the addition of substrate;
- avoidance of oxygen input, especially with the addition of substrate;
- appropriate choice of initial S/X_V ratio and nitrate concentration.

Batch test in continuous mode

In reactors with a constant influent flow (Q_i) the overall denitrification rate is expected to be constant under conditions that the wastewater composition (qualitative and quantitative) is constant. When for such a reactor the rate of dosage is increased, experiments can be performed on the denitrification rate in relation to the sludge loading. With the batch test in continuous mode the effect of an increasing sludge loading rate was simulated by increasing the wastewater flow and by not withdrawing effluent and sludge from the batch vessel. To assess the relation between denitrification rate and sludge loading rate it was necessary to use the same time intervals for estimation after an increase of the wastewater flow. The course of nitrate was followed by an on-line auto-analyser (Skalar SA-9000).

2.3 RESULTS AND DISCUSSION

2.3.1 SIMPLIFIED DENITRIFICATION KINETICS

In Figure 2.3 a nitrate and nitrite course is presented after a pulse dose of settled municipal wastewater to activated sludge in endogenous, anoxic conditions. In this representative NUR-curve three slopes can be observed. The highest volumetric nitrate utilisation rate (r_{D1}) in the first 30 minutes reflects the simultaneous denitrification on S_S, hydrolysed X_S and endogenous substrate. This is followed by a lower volumetric denitrification rate (r_{D2}) resulting from the anoxic utilisation of hydrolysed X_S and endogenous activity. The endogenous volumetric denitrification rate ($r_{Dend} = r_{D3}$) is reached in this test after circa 175 minutes. These results show that the contribution of X_S in the overall denitrification potential is prevailing for the studied system.

During NUR-tests an accumulation of nitrite is not always negligible and it is proposed that for any parameter estimation the NUR-curve should be built of the sum of the nitrate and so-called nitrite-nitrate equivalent ($S_{NO} = S_{NO3}+0.6\cdot S_{NO2}$). Implementation of the nitrite-nitrate equivalent results from the fact that the reduction of 1 g S_{NO2} to 1 g N_2-gas needs the same amount of electrons as the reduction of 0.6 g S_{NO3} to 0.6 g N_2 (e.g. HENZE, 1986, ÇOGHOR ET AL., 1998). In this way both, the amount of biodegradable COD utilised for the partial process of nitrate reduction to nitrite ($S_{NO3} \rightarrow S_{NO2}$) and the COD amount for the entire denitrification process ($S_{NO3} \rightarrow S_{N2}$) are taken into account.

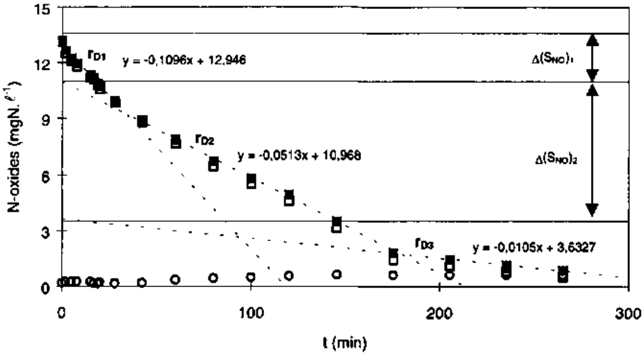

Figure 2.3 Course of nitrite (S_{NO2}) - o, nitrate (S_{NO3}) -□ and the sum of nitrate and nitrite-nitrate equivalent (S_{NO}) - ■ after a pulse dose of settled municipal wastewater (f_{ww}=0.29, COD = 430 mg.ℓ^{-1}, S/X_V=0.045 mgCOD.mgVSS^{-1}, T=18°C)

The denitrification kinetics from the experimental results can be calculated using below listed formulas. The volumetric denitrification rates ($r_{D1..D3}$) in Figure 2.3 are given by:

$$r_D = \frac{\Delta(S_{NO_3} + 0.6 \cdot S_{NO_2})}{t};\ \text{mgN}.\ell^{-1}.h^{-1} \tag{2.1}$$

$$r_{D1} = r_{DSS} + r_{DXS} + r_{Dend} \tag{2.2}$$

$$r_{D2} = r_{DXS} + r_{Dend} \tag{2.3}$$

$$r_{D3} = r_{Dend} \tag{2.4}$$

so:

$$r_{DSS} = r_{D1} - r_{D2} \tag{2.5}$$

$$r_{DXS} = r_{D2} - r_{D3} \tag{2.6}$$

Instead of the volumetric rate the specific denitrification rate can be used:

$$k_D = \frac{r_D}{X_V};\ \text{mgN.gVSS}^{-1}.h^{-1} \tag{2.7}$$

In series of NUR-tests with a pulse dose of settled municipal wastewater to activated sludge a variation was found in the maximum specific denitrification rate from 2 to 4 mgN.gVSS^{-1}.h^{-1} (k_{D1}). The specific denitrification rate on S_S (k_{DSS}) varied from 1 to 3 mgN.gVSS^{-1}.h^{-1} with an average of 2 mg N.gVSS^{-1}.h^{-1} and for X_S (k_{DXS}) from 0.6 to 1 mgN.gVSS^{-1}.h^{-1} with an average of 0.85 mgN.gVSS^{-1}.h^{-1}. For the specific endogenous denitrification rate (k_{Dend}) values were found in a range from 0.2 to 0.6 mgN.gVSS^{-1}.h^{-1}.

In Table 2.1 the ranges of specific denitrification rates for different carbon sources are given, and compared with literature values extracted from Table 1.2 from chapter 1. From the comparison the conclusion can be drawn that the measured values of the specific denitrification rates were rather low in this study but within reported ranges. It is especially of interest that the denitrification rate at presence of S_S as carbon source attained in this study a low value. This can be explained by a low activity of the biomass, what is characteristic for low-loaded systems and by a low actual concentration of S_S in the bulk. Concerning the values of the two subsequent specific denitrification rates (k_{DXS} and k_{Dend}) the difference was less remarkable and characteristic for sludge from low-loaded systems.

Table 2.1 Ranges and average values of specific denitrification rates (mgN.gVSS^{-1}.h^{-1}) on different carbon-sources, found in literature (chapter 1, Table 1.2) and in this study

	S_S, acetate or other VFA's (k_{DSS})	**X_S from wastewater (k_{DXS})**	**Endogenous metabolism (k_{Dend})**
Literature	2-25[1)]	0.5-4.6[1)]	0.1-2.2
This study	1-3	0.6-1	0.2-0.6

[1)] some values from this range can include endogenous denitrification

The volumetric anoxic utilisation rate of S_S and X_S can be calculated based on results from Figure 2.3 using equation 2.8 and 2.9:

$$r_{SS} = \frac{2.86(r_{D1} - r_{D2})}{1 - Y_{HD}} \text{ ; mg COD.g. } \ell^{-1}.h^{-1} \tag{2.8}$$

$$r_{XS} = \frac{2.86(r_{D2} - r_{D3})}{1 - Y_{HD}} \text{ ; mg COD.g. } \ell^{-1}.h^{-1} \tag{2.9}$$

The anoxic heterotrophic yield (Y_{HD}) was for this study determined with a NUR-test with a pulse dosage of acetate. Hereby, it was assumed that the biodegradability of influent S_S and products of X_S-hydrolysis (also S_S) can be compared with the biodegradability of acetate. Pulse dosage of acetate to sludge in anoxic conditions results in a S_{NO}-curve course as presented in Figure 2.4.

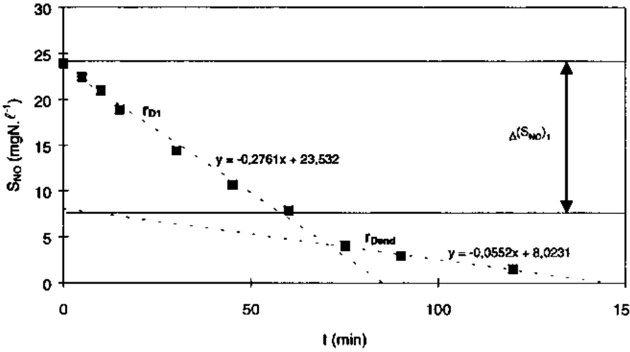

Figure 2.4 Course of S_{NO} in a batch NUR-test with pulse dosage of acetate (5 ml 1M NaAc· $3H_2O$ + 2.2 ℓ of activated sludge)

Acetate is a substrate of a uniform character and the NUR-curve will be built of two lines, a fast declining line due to denitrification on this readily biodegradable substrate and a slowly declining line representing the endogenous denitrification rate. Because the amount of added acetate (S_{Ac}) is known, Y_{HD} can be calculated from experimental results with equation 2.10:

$$Y_{HD} = 1 - \frac{2.86 \cdot \Delta(S_{NO_3} + 0.6 \cdot S_{NO_2})_1}{S_{Ac}} = 1 - \frac{2.86 \cdot \Delta(S_{NO})_1}{S_{Ac}} \qquad (2.10)$$

In Table 2.2 the average kinetic parameters from the tests with acetate are presented. In comparison with the majority of literature values (Table 1.1), the obtained specific maximum denitrification rate was rather low with $k_{DI} = 3.6 \pm 0.37$ mgN.gVSS^{-1}.h^{-1}.

Table 2.2 Kinetic parameters from batch experiments with acetate as carbon source

Kinetic parameter	Unit	Average Value
k_{DI}	mgN.gVSS^{-1}.h^{-1}	3.60 ± 0.37
k_{DSS}	mgN.gVSS^{-1}.h^{-1}	3.00 ± 0.45
k_{Dend}	mgN.gVSS^{-1}.h^{-1}	0.60 ± 0.32
Y_{HD}	mgCOD.mg COD^{-1}	0.66 ± 0.053
k_{SS}	mgCOD.gVSS^{-1}.h^{-1}	26.0 ± 3.82

This low value can again be explained by a high SRT and a low biomass activity of the examined system. With a longer exposure of activated sludge to acetate (repetition of the NUR-test with the same amount of added acetate and the same sludge population), probably a higher rate could be attained (HALLIN ET AL., 1996). On the other hand, the average specific denitrification rate on acetate (k_{DSS}) was 1.5 times higher than on the S_S-fraction from the wastewater. This can be explained by a higher actual concentration of acetate than of S_S in the bulk at the start of the experiment.

In the NUR-tests with acetate an average anoxic yield factor (Y_{HD}) of approximately 0.66 was found, under assumption that no internal storage of soluble COD occurred. SCHEER (1995) found Y_{HD} varying from 0.52 to 0.74 in anoxic batch tests with wastewater of 4 treatment plants and NAIDOO ET AL. (1998) examined 7 European WWTP's and found a range of Y_{HD}-values from 0.57 to 0.71. SPERANDIO ET AL. (1999), using the Carbon Dioxide Evolution Rate technique, found Y_{HD} in a range from 0.44 to 0.57. These variations indicate that Y_{HD} is specific to each type of activated sludge and should be estimated for each situation.

From the NUR-test with a pulse dose of settled municipal wastewater and with the estimated Y_{HD} of 0.66, average anoxic specific utilisation rates of S_S and X_S were found of respectively k_{SS}=16.4 and k_{XS}=7.1 mg COD.gVSS^{-1}.h^{-1}.

The obtained denitrification kinetics are valid for the examined sludge and for the temperature in which the appropriate NUR-tests were performed. Most kinetic parameters of the activated sludge process are influenced by temperature and depending on their further implementation, care should be taken and a temperature correction should be introduced (e.g. VAN HAANDEL ET AL., 1981, HENZE ET AL., 1987).

2.3.2 DENITRIFICATION POTENTIAL AND CAPACITY

The denitrification potential (DP) of a pre-denitrification system primarily depends on wastewater characteristics and can be calculated using the results of a NUR-test as presented in Figure 2.3. In the following equations the DP is expressed as the amount of nitrate (mg N) that can be denitrified with the S_S- and X_S-fractions in one litre (ℓ) of wastewater.

$$DP_{SS} = \frac{\Delta(S_{NO_3} + 0.6 \cdot S_{NO_2})_1}{f_{ww}} \text{ ; mgN.}\ell^{-1} \qquad (2.11)$$

$$DP_{XS} = \frac{\Delta(S_{NO_3} + 0.6 \cdot S_{NO_2})_2}{f_{ww}} \text{ ; mgN.}\ell^{-1} \qquad (2.12)$$

The denitrification potential of the wastewater fractions does not depend on the biomass concentration (MLSS or VSS) in the mixed liquor. In case of a varying MLSS level the amount of nitrate that can be denitrified on different wastewater fractions remains the same, only the reduction rate is changing. When the sum of S_S and X_S in the wastewater is not sufficient to denitrify completely the required amount of nitrate formed from the nitrification of ammonia-N, the effluent standards for total nitrogen may be fulfilled with the endogenous denitrification potential (DP_{end}). When this is still not sufficient an external carbon source has to be supplied. The DP_{end} (basic DP of activated sludge) depends on the volumetric endogenous denitrification rate (r_{Dend}), the total denitrification volume (V_D, including pre- and post-denitrification if any) and the wastewater flow (Q_i):

$$DP_{end} = \frac{r_{Dend} \cdot V_D}{Q_i} \text{ ; mgN.}\ell^{-1} \qquad (2.13)$$

In case of systems operating with varying biomass concentrations, the specific endogenous denitrification potential ($DP_{end(X_V)}$) should be used:

$$DP_{end(X_V)} = \frac{r_{Dend} \cdot V_D}{X_V \cdot Q_i} = \frac{k_{Dend} \cdot V_D}{Q_i} \text{ ; mgN.gVSS}^{-1} \qquad (2.14)$$

The total denitrification potential (ΣDP) of the system depends on the characteristics of the wastewater and the basic denitrifying activity of the sludge.

$$\sum DP = DP_{SS} + DP_{XS} + DP_{end(X_V)} \cdot X_V \text{ ; mgN.}\ell^{-1} \qquad (2.15)$$

Using ΣDP, the theoretical concentration of nitrate and nitrite ($S_{NO,e(theor)}$) in the effluent from a N-removal activated sludge system, where biodegradable COD is exclusively used for denitrification (optimised pre-denitrification and alternating systems), can be predicted by:

$$S_{NO,e(theor)} = N_{Kj,i} - S_{NH,e} - N_{org,e} - \frac{i_N \cdot P_X}{Q_i *} - \Sigma DP \text{ , mgN.}\ell^{-1} \qquad (2.16)$$

* Q_i in $\ell.d^{-1}$

where:

$S_{NO,e(theor)}$	theoretical concentration of nitrate and nitrite in the effluent ($mgN.\ell^{-1}$);
$N_{Kj,i}$	N_{Kj} in influent ($mgN.\ell^{-1}$);
$S_{NH,e}$	ammonia-N in effluent ($mgN.\ell^{-1}$);
$N_{org,e}$	organic N in effluent ($mgN.\ell^{-1}$);
i_N	N fraction in sludge (-);
P_X	amount of daily removed excess sludge (= sludge growth) ($mg.d^{-1}$).

To use equation 2.16 for predicting the nitrate effluent quality, one has to make sure that S_S and X_S are exclusively utilised in the pre-denitrification volume and are not transported into the aeration volume (thus lost for denitrification). When the organic biodegradable wastewater fractions, their anoxic utilisation rates and endogenous denitrification rate are known it can be estimated which part of wastewater denitrification potential is indeed utilised in the system. From the S_S- and X_S-load entering the pre-denitrification volume and their anoxic substrate utilisation rates, the required denitrification volume can be calculated for a complete utilisation of S_S ($V^*_{D,SS}$):

$$V^*_{D,SS} = \frac{S_S \cdot Q_i}{k_{SS} \cdot X_V} \text{ ; } \ell \tag{2.17}$$

and X_S ($V^*_{D,XS}$):

$$V^*_{D,XS} = \frac{X_S \cdot Q_i}{k_{XS} \cdot X_V} \text{ ;} \ell \tag{2.18}$$

When $V^*_{D,SS}$ and $V^*_{D,XS}$ are smaller than the available pre-denitrification volume (V_{PD}) equation 2.16 is valid to estimate the nitrate effluent quality. In the opposite situation the calculated wastewater denitrification potentials have to be reduced with a factor V_{PD}/V^*_D. To obtain a more realistic nitrate effluent quality, equation 2.16 should be modified to:

$$S_{NO,e} = N_{Kj,i} - S_{NH,e} - N_{org,e} - \frac{i_N \cdot P_X}{Q_i^*} - \left(\frac{V_{PD}}{V^*_{D,SS}} DP_{SS} + \frac{V_{PD}}{V^*_{D,XS}} DP_{XS} + DP_{end}\right) \text{ ; } mgN.\ell^{-1} \tag{2.19}$$

* Q_i in $\ell.d^{-1}$

The denitrification capacity (DC), the amount of nitrate that can be removed from a system with given wastewater characteristics, process configuration and activated sludge characteristics can be estimated using equation 2.20, which constitutes part of eq. 2.19:

$$DC = \frac{V_{PD}}{V^*_{D,SS}} DP_{SS} + \frac{V_{PD}}{V^*_{D,XS}} DP_{XS} + DP_{end} \text{ ; } mgN.\ell^{-1} \tag{2.20}$$

From a series of NUR-tests with settled wastewater and activated sludge from a N-removal pilot-plant, a number of wastewater denitrification potentials was obtained with average values of $DP_{SS} = 8.7$ and $DP_{XS} = 16$ $mgN.\ell^{-1}$. With the total denitrification potential of the wastewater, approximately 41% of the influent N_{Kj} could be denitrified. These values characterised wastewater of an average total COD of 430 $mg.\ell^{-1}$ and N_{Kj} of 60 $mgN.\ell^{-1}$.

Equation 2.19 was implemented to predict the nitrate effluent quality of the pilot plant, fed with the same wastewater as examined in the NUR-tests. Taking into consideration the amount of N removed via biomass assimilation (7.6 $\text{mgN.}\ell^{-1}$, 13% of total N load), the basic potential of the biomass (DP_{end}=13.7 $\text{mgN.}\ell^{-1}$, 23% of total N load), S_{NHe} = 0.5 and $N_{org,e}$= 0.7 $\text{mgN.}\ell^{-1}$, the predicted effluent nitrate quality was 12.8 $\text{mg N.}\ell^{-1}$. This was in close accordance with the average results from the pilot plant measured at this time.

2.3.3 WASTEWATER CHARACTERISATION FOR BIOLOGICAL N-REMOVAL SYSTEM

NUR-tests with a pulse dose of wastewater enable to characterise the wastewater for S_S and X_S. The biodegradable fractions be estimated from a NUR-test (Figure 2.3) with the following equations:

$$S_s = \frac{2.86 \cdot \Delta(S_{NO_3} + 0.6 \cdot S_{NO_2})_1}{1 - Y_{HD}} \cdot \frac{1}{f_{ww}} = \frac{2.86 \cdot \Delta(S_{NO})_1}{1 - Y_{HD}} \cdot \frac{1}{f_{ww}} \text{; mgCOD.}\ell^{-1} \qquad (2.21)$$

$$X_s = \frac{2.86 \cdot \Delta(S_{NO_3} + 0.6 \cdot S_{NO_2})_2}{1 - Y_{HD}} \cdot \frac{1}{f_{ww}} = \frac{2.86 \cdot \Delta(S_{NO})_2}{1 - Y_{HD}} \cdot \frac{1}{f_{ww}} \text{; mgCOD.}\ell^{-1} \qquad (2.22)$$

With the characterisation of wastewater, by following the denitrification rate in a NUR-test, problems can appear when a possible nitrite accumulation is not taken into account. When the accumulation of nitrite is negligible, the nitrite gradient in equation 2.21 and 2.22 can be neglected. When accumulation of nitrite attains a certain level but it was neglected, the wastewater characterisation will be less accurate regarding S_S and X_S. For instance, a presence of 10% S_{NO2} on every mg of S_{NO3} (e.g. S_{NO2}=2 $\text{mg.}\ell^{-1}$, S_{NO3}=20 $\text{mg.}\ell^{-1}$), when not included in calculations, causes approximately 6% underestimation for both S_S and X_S.

For the estimation of wastewater characteristics an improper choice of Y_{HD} has even more significant consequences for the accuracy of the method. For example, a change of Y_{HD} from 0.6 (measured value) to 0.67 (default value, e.g. HENZE ET AL., 1996) causes an overestimation of S_S with 21%. This shows that the measurement or a proper choice of Y_{HD} is advisable.

2.3.4 WASTEWATER CHARACTERISATION FOR BIOLOGICAL N&P-REMOVAL SYSTEMS

For activated sludge systems with biological P-removal the presented method to estimate the denitrification potential and capacity can be used but precaution is recommended, especially for the interpretation of the wastewater characterisation. Due to co-existing processes of denitrification and release and uptake of phosphates at anoxic conditions the clear difference between denitrification rates on S_S, X_S and endogenous substrate can be deteriorated.

In Figure 2.5 a NUR-test result is presented with a pulse dose of acetate to activated sludge from a plant with biological N&P-removal. Two substrate denitrification rates are observed. In phase 1, according to recent reports (BARKER AND DOLD, 1996), three processes occur simultaneously:

(1) utilisation of external COD for anoxic respiration by denitrifiers (S_{NO}-utilisation);
(2) utilisation of external COD by P-accumulating organisms (PAO's) (P- release);
(3) utilisation of S_{NO} by denitrifying PAO's using stored COD (P-uptake) (IWEMA AND MAUNIER, 1985, GERBER ET AL., 1986, 1987).

Assuming that all external COD was utilised (uptaken) in phase 1, the third process will be the dominant process in phase 2. The endogenous volumetric denitrification rate (r_{D3}) is not shown in Figure 2.5.

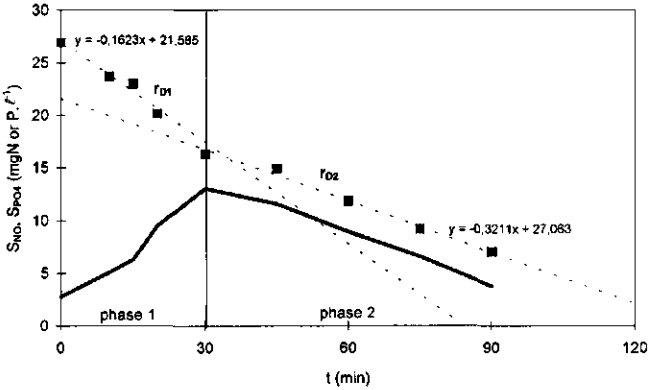

Figure 2.5 Reduction rate of S_{NO} (■) measured in NUR-test after addition of acetate to a suspended mixture originating from a system with biological N&P removal. Additionally phosphate course plotted (solid line). The second denitrification rate (r_{D2}) cannot be identified as endogenous rate since it still exposes a significant value.

When a NUR-test is conducted with wastewater instead of acetate and active PAO's are present in the activated sludge, four denitrification rates could be theoretically observed. Beside the denitrification rates on S_S, X_S and endogenous substrate, a denitrification rate on internally stored COD could be measured. The distinction between all four rates (on S_S, X_S, internally stored COD and endogenous) in such a NUR-test may become unclear and in this way the wastewater characterisation becomes unreliable, probably leading to an underestimation of S_S and an overestimation of X_S. Also the Y_{HD} of activated sludge with PAO's will be overestimated because of an internal storage of COD.

Regardless the problems with the interpretation of the results for wastewater characterisation with sludge from N&P-removing systems, NUR-tests can be implemented for an estimation of the denitrification kinetics and denitrification potential. However, the experimental procedure may become more complex, depending on the implemented process configuration.

2.3.5 DENITRIFICATION POTENTIAL IN RELATION TO SLUDGE LOADING

In literature (e.g. STENSEL, 1981, BURDICK ET AL., 1982, HOFFMAN, 1985, SCHLEGEL, 1987) relations are given between the specific denitrification rate (k_D) and the organic sludge loading rate in the pre-denitrification volume or the total activated sludge volume (Figure 2.6), expressed as $gBOD_5.g\ MLSS^{-1}.d^{-1}$ or $gBOD_5.gVSS^{-1}.d^{-1}$ (B_{XBOD5}). These relations result from a number of examined full-scale pre-denitrification systems working under non-saturated COD conditions, so a maximum denitrification rate cannot be given.

When wastewater characteristics in terms of S_S and X_S, their maximum anoxic utilisation rates (k_{SS}, k_{XS}), the endogenous denitrification rate (k_{Dend}) and the anoxic yield factor (Y_{HD}) are known the dependency of the overall denitrification rate (k_D) on the sludge loading rate (B_X) can be modelled using the following combination of simplified Monod-type and zero-order kinetics:

$$k_D = \frac{1-Y_{HD}}{2.86}(k_{SS} \cdot \frac{S_S^{'}}{K_S + S_S} + k_{XS} \cdot \frac{X_S^{'}}{K_S + X_S}) + k_{Dend} \text{ ; mgN.gVSS}^{-1}.h^{-1} \tag{2.23}$$

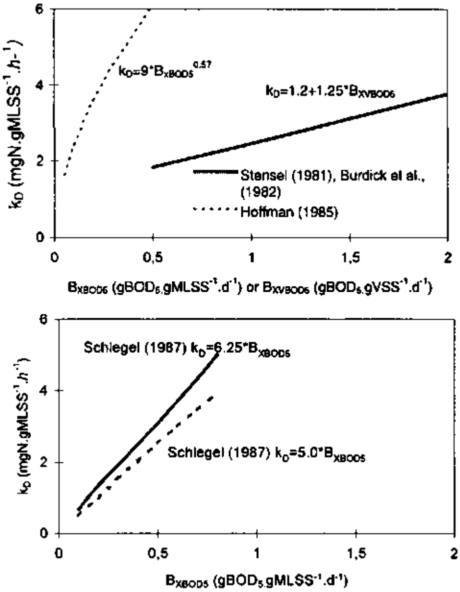

Figure 2.6 Specific, overall denitrification rate (k_D) as a function of anoxic sludge loading rate in systems fed with wastewater - literature values.

The denitrification process is modelled under assumption of a zero-order reaction with regards to nitrate. In the Monod-type relation for expressing the S_S- and X_S-utilisation rate, the same half-saturation coefficient is used for both compounds. For implementation of equation 2.23, an assumption is made that the denitrification volume represents a completely mixed reactor. The actual concentrations of biodegradable wastewater fractions in the bulk (S_S' and X_S') result from mass balances for the pre-denitrification reactor (Figure 2.7).

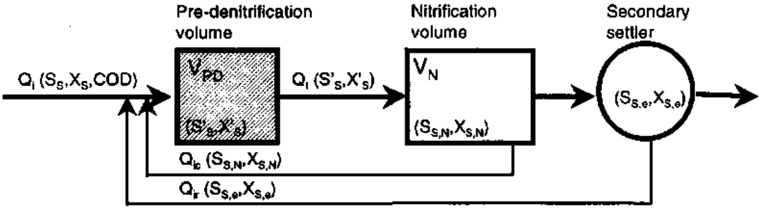

Figure 2.7 Biodegradable substrate mass balance for the pre-denitrification reactor

The anoxic sludge loading is calculated based on the total COD of the wastewater as:

$$B_{XCOD} = \frac{Q_i \cdot COD \cdot 24}{X \cdot V_{PD}} \text{ gCOD.gMLSS}^{-1}\text{.d}^{-1} \qquad (2.24)$$

Using the experimental set-up with continuous feeding, experiments were carried out to test the accuracy of the simple model expressed by equation 2.23. With a continuous feeding of wastewater to denitrifying sludge, and without the withdrawal of effluent and sludge, S_S and X_S will accumulate when the substrate loading exceeds the substrate utilisation rate.

In such a situation the denitrification rate will depend not only on the sludge loading but also on a consequent choice of the time interval where the denitrification rate is calculated. The overall denitrification rate, resulting from the actual S_S- and X_S-concentrations in the mixed liquor, was calculated from the nitrate utilisation rate after 60 minutes of the start of dosing. In Figure 2.8 the measured overall specific denitrification rates at different sludge loading rates are shown. Some variations in the measured values result from the fact that the experiments were carried out on different days, so some variation in the wastewater characteristics could appear.

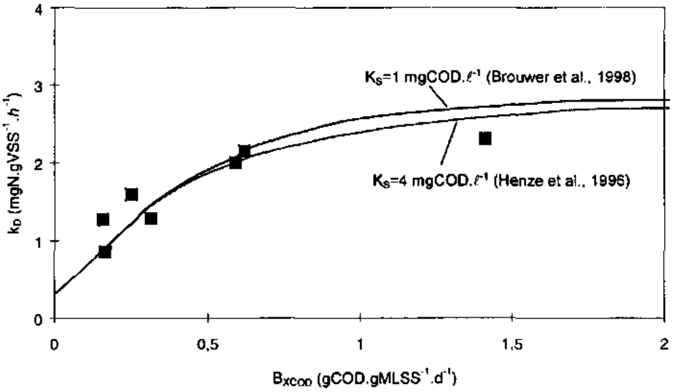

Figure 2.8 Overall specific denitrification rate (k_D) in relation to the anoxic sludge loading rate (B_{XCOD}) of the pre-denitrification reactor obtained after the first hour of the continuous test with different dosing rates of settled wastewater (■) and simulated (solid line); (T=20°C).

Based on equation 2.23 and the mass balances for S_S, X_S and nitrate over the batch system the overall denitrification rate (k_D) was simulated as a function of the sludge loading (B_{XCOD}). With the measured average values for k_{SS}, k_{XS}, and k_{Dend} and with default values for K_S of 1 and 4 mgCOD.ℓ$^{-1}$ (HENZE ET AL., 1996, BROUWER ET AL., 1998) the modelled relations are given in Figure 2.8. The S_S- and X_S-fractions were separately estimated using batch NUR-test and attained the average values of 73.3 and 134.6 mgCOD.ℓ$^{-1}$, while B_{XCOD} was calculated using equation 2.24. From Figure 2.8 it can be concluded that the modelled relation is in a reasonable accordance with the measured values.

Implementing this simplified relational model for existing systems together with mass balances over the pre-denitrification volume, the obtainable overall denitrification rate can be predicted as a function of the applied anoxic sludge loading. With this approach optimisation strategies can be evaluated for increasing the overall denitrification rate by increasing B_{XCOD} or the COD/N-ratio. Possible measures are for instance an increase of X_S by bypassing a primary clarifier or increasing S_S by adding an external carbon source. However, for implementation of 'drastic' optimisation steps like a significant change of anoxic sludge loading rate or addition of external carbon source, requiring an adaptation period from biomass, a precaution should be taken against a change in biomass activity, thus also kinetic parameters. A possible way to overcome this problem is carrying regular NUR-tests during the optimisation period in order to update denitrification process kinetics.

When an external carbon source has to be considered to enhance the denitrification potential and capacity, the similar approach can be implemented to determine the relation between the denitrification rate and the dosage rate of a chosen carbon source. The modelled relation uses again the combination of Monod-type kinetics and zero order kinetics:

$$k_D = \frac{1-Y_{HD}}{2.86} \cdot \left(k_{Ac} \cdot \frac{S_{Ac}}{K_S + S_{Ac}} \right) + k_{Dend} \text{ ; mgN.gVSS}^{-1}.h^{-1} \qquad (2.25)$$

Several continuous experiments with different dosage of acetate were performed from which the measured and simulated overall denitrification rates are plotted together with values found in literature in Figure 2.9.

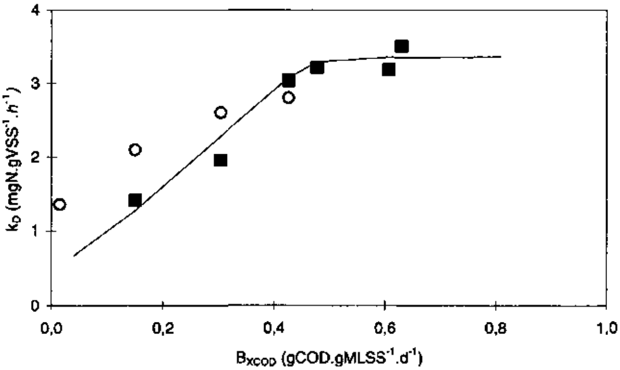

Figure 2.9 Overall specific denitrification rate as a function of anoxic sludge loading rate measured (■), simulated (solid line) after the first hour of continuous acetate dosing (T=20°C) and reported in literature (○) (ISAACS AND HENZE, 1995)

The half-saturation coefficient for acetates from the Monod-type equation is assumed to be $K_S = 1$ mg COD.ℓ^{-1} and the kinetic parameters are taken from Table 2.2. The modelled relation is again in reasonable accordance with the measured data. Comparison of Figure 2.8 and 2.9 clearly indicates the importance of substrate composition to attain a maximum process performance. The maximum k_D for wastewater was approached at B_{XCOD} of approximately 1.5 gCOD.gMLSS^{-1}.d^{-1} while for acetate at 0.5 gCOD.gMLSS^{-1}.d^{-1}.

The information about the relation between the sludge loading rate and the obtainable denitrification rate for the external carbon source is of interest in processes where denitrification has to be enhanced. Possible implementations are the design or optimisation of the anoxic reactor volume, calculation of the dosage rate of the carbon source and for the development of control strategies where the rate of external carbon dosage constitutes a control variable.

2.4 CONCLUSIONS

Anoxic NUR-tests, with a pulse dosage of wastewater to activated sludge from pre-denitrification systems, can provide with a detailed description of the denitrification kinetics. Denitrification rates associated with the influent S_S- and X_S-fractions, endogenous denitrification rate and anoxic utilisation rate of S_S and X_S can be estimated. With the same anoxic batch experiment the wastewater characterisation regarding biodegradable COD fractions (S_S and X_S) can be determined. The estimation of the anoxic yield factor (Y_{HD}) for the examined activated sludge and for the given wastewater is hereby essential.

For a successful and comprehensive interpretation of the NUR-test results, the endogenous denitrification rate must be reached and this depends on the initial nitrate concentration of the experiment and the applied S/X_V-ratio. For estimating the kinetic parameters or the wastewater characterisation precaution should be taken against the accumulation of nitrite and biological phosphorus removal activity. Beside nitrate, it is advised to follow nitrite and phosphate throughout the duration of a NUR-test.

A NUR-test allows to determine the denitrification potential of the wastewater and to estimate the overall denitrification potential of the plant. In that way the minimal obtainable nitrate effluent quality can be predicted and decisions can be made about improving the process when necessary. Determining the denitrification potential based on the wastewater and activated sludge characteristics in combination with a good description of the existing system give more precise information about the denitrification capacity than the COD/N-ratio, which is often used for design and optimisation decisions.

When kinetic parameters are known the relation between the overall denitrification rate and the applied anoxic sludge loading of the pre-denitrification volume can be modelled. This relation provides information for optimising the denitrification by, for instance, increasing the organic load or COD/N-ratio with respect to S_S and/or X_S and this can be useful for decision making about enhancing the process with e.g. an external carbon source.

LIST OF SYMBOLS

B_{XCOD}	COD sludge loading rate (g COD.g MLSS^{-1}.d^{-1})
B_{XBOD5}	BOD_5 sludge loading rate (g BOD_5.g MLSS^{-1}.d^{-1})
COD	total COD concentration of wastewater (mg.ℓ^{-1})
DO	dissolved oxygen (mgO_2.ℓ^{-1})
DP	denitrification potential, subscripts: S_S-on S_S, X_S-on X_S and end- endogenous (mg N.ℓ^{-1})
ΣDP	total denitrification potential of a system (mg N.ℓ^{-1})
f_{ww}	volumetric wastewater fraction in the total volume of mixed liquor (-)
i_N	fraction of N in activated sludge (mgN.mgMLSS^{-1})
k	anoxic maximum specific substrate utilisation rate; subscripts: Ac - of acetate-COD, S_S - of S_S, X_S - of X_S (mgCOD.g VSS^{-1}.h^{-1})
k_D	specific denitrification rate; subscripts: Ac - on acetate, end - endogenous, tot – total, S_S, X_S on the S_S-, X_S-fraction (mgN.gVSS^{-1}.h^{-1})
K_S	half-saturation coefficient from Monod-type equation for S_S or X_S utilisation (mg COD.ℓ^{-1})
ML(V)SS	mixed liquor (volatile) suspended solids (g.ℓ^{-1})
N_{Kj}	Kjeldahl-N; subscript: *i* – influent; in COD/N ratio N=N_{Kj} (mg N.ℓ^{-1})
N_{org}	Organic nitrogen (mg N.ℓ^{-1})
NUR	nitrate utilisation rate
OUR	oxygen utilisation rate
P_X	removal rate of surplus sludge (mg MLSS.d^{-1})
Q	flow; subscr. *i,e* – influent, effluent, t – total, *ic* – internal recycle, *ir* – return sludge (ℓ.h^{-1})
r	volumetric substrate utilisation rate, subscr. S_S- of S_S, X_S- of X_S (mg COD.ℓ^{-1}.h^{-1})
r_D	volumetric actual denitrification rate: subscripts: S_S-on S_S, X_S-on X_S, end-endogenous, 1,2,3 - subsequent as measured in the NUR-test (mg N.ℓ^{-1}.h^{-1})
S/X_V	initial substrate to microorganisms ratio (g COD.g VSS^{-1})
S_{AC}	concentration of acetate in the bulk, subscript: i - initial (mgCOD.ℓ^{-1})
S_I	soluble inert COD (mgCOD.ℓ^{-1})
S_{NH}	soluble ammonia-N (mg N.ℓ^{-1})
S_{NO}	sum of nitrate and nitrite-nitrate equivalent (mgN.ℓ^{-1})
S_{NO2}	nitrite-N (mgN.ℓ^{-1})
S_{NO3}	nitrate-N (mgN.ℓ^{-1})
S_{PO4}	ortho-phosphate (mgP.ℓ^{-1})
S_S	soluble, readily biodegradable COD; superscript: ‘ - actual in the bulk, N – in nitrification zone, e - effluent (mg COD.ℓ^{-1})
t	time interval (*h*)
V_{AS}	activated sludge volume (ℓ)
V	volume; subscripts : PD - pre-anoxic, SD – secondary anoxic, N - nitrification (ℓ)
V_D	total anoxic volume (including pre- and post-anoxic zone) volume (ℓ)
V^*_D	required denitrification volume; subscripts: S_S, X_S - required to utilise all S_S, X_S respectively (ℓ)
V_{WW}	wastewater volume (ℓ)
X_I	particulate inert COD (mgCOD.ℓ^{-1})
X_s	particulate, slowly biodegradable COD; superscript: ‘ - actual in the bulk, N – in nitrification zone, e - effluent (mg COD.ℓ^{-1})
X_V	volatile activated sludge (gVSS.ℓ^{-1})
Y_H	heterotrophic aerobic yield (mg $COD_{biomass}$.mg$COD_{utilised}^{-1}$)
Y_{HD}	heterotrophic anoxic yield (mg $COD_{biomass}$.mg$COD_{utilised}^{-1}$)
2.86	oxygen equivalent of nitrate-N in oxidation-reduction reaction (mgCOD.mgN^{-1})

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3

Methodology to estimate reduction factors for denitrification with respiration based techniques

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ABSTRACT

Activated sludge, exposed under anoxic and aerobic conditions to organic substrate, shows a similar respirometric behaviour pattern. Depending on the type of organic substrate different respiration rates are observed. The subsequent respiration rates are usually observed to be smaller under anoxic conditions. To describe mathematically the denitrification process, the aerobic activated sludge model can be used if appropriate reduction factors (η) are included in the equations describing the subsequent respiration rates.

In this chapter a methodology is presented to estimate three reduction factors for anoxic respiration rates: S_S-utilisation (η_1), X_S-hydrolysis (η_2) and endogenous respiration (η_3), under assumption that the same distribution of organic wastewater fractions was recognised under aerobic and anoxic conditions. The methodology consists of two integrated parts: an experimental part and an estimation procedure. The experimental part implemented two respiration tests: oxygen utilisation rate (OUR) and nitrate utilisation rate (NUR) performed under well-defined and analogous experimental conditions. For the estimation procedure two simplified models were used: an aerobic COD-oxidation model and a denitrification model. The type of substrate determined the range of information that could be attained from the series of respiration tests. Except of conversion kinetics (S_S-oxidation, X_S-hydrolysis and endogenous respiration) some attention was paid on the magnitude of difference for the heterotrophic yield coefficient and biodegradable organic wastewater fractions as found under aerobic and anoxic conditions. A differentiation between the anoxic and aerobic heterotrophic yield coefficient may contribute in a more precise description of the denitrification process.

Some respiration tests were performed with settled domestic wastewater and different activated sludge samples. Inherent estimation procedures were implemented. It revealed that the values of reduction factors vary strongly in function of activated sludge characteristics and process configuration.

3.1 INTRODUCTION

3.1.1 GENERAL

Pulse addition of a wastewater sample to activated sludge, under aerobic and anoxic conditions, shows usually a similar three-phase behaviour of respectively the oxygen and nitrate consumption. In the first phase a high respiration rate results from utilisation of soluble readily biodegradable COD (S_S). It is followed by a slower respiration on hydrolysis products of particulate slowly biodegradable COD (X_S). Finally the slowest, endogenous respiration is reached when all extracellular substrate is terminated (STERN AND MARAIS, 1974, WILSON AND MARAIS, 1976, MARSDEN AND MARAIS, 1976). The first attempts to model denitrification with the same equations as for aerobic substrate oxidation, resulted in a higher simulated anoxic respiration than measured (VAN HAANDEL ET AL., 1981a,b). This suggested the introduction of reduction factors, which enabled to model the aerobic and anoxic kinetics with the same relations. Several approaches appeared, some suggesting that all respiration rates are retarded under anoxic conditions and others that only anoxic respiration on S_S is slower. No consensus has been reached till now. The following literature review describes some approaches.

3.1.2 REDUCTION FACTORS FOR MODELLING THE DENITRIFICATION

VAN HAANDEL ET AL. (1981a,b) undertook an attempt to incorporate denitrification kinetics into the aerobic kinetic model of DOLD ET AL. (1980), by assuming a bi-substrate character of the wastewater, regarding the biodegradable organic fractions S_S and X_S. For an experimental plug-flow reactor the oxygen profile was simulated and compared with the measured nitrate profile expressed in nitrate-oxygen equivalents (1 mg S_{NO3} = 2.86 mg O_2). A three-phase behaviour appeared in both profiles with comparable slopes in the primary phase (S_S-oxidation) and less steep slopes in the second and third phase of the denitrification profile (Figure 3.1). Furthermore, the removed amount of nitrate-oxygen equivalents in the primary phase was equal to the removed amount of oxygen in the primary phase. This allowed them to conclude that under anoxic conditions the same amount of S_S is utilised as under aerobic conditions, at approximately the same rate. This was confirmed by STILL ET AL. (1986) with aerobic and anoxic tests using sludge from systems with an anoxic-aerobic sequence.

The similarity of the nitrate and oxygen profiles was sufficiently evident to accept in general the aerobic kinetic model of DOLD ET AL. (1980) as a basis for the modelling of denitrification behaviour. However, to allow a quantitative description, a modification had to be made. Because the removal rate of nitrate-oxygen equivalents in the second and third phase was lower than the corresponding simulated removal of oxygen, the utilisation rate of X_S and/or the endogeneous respiration in an anoxic environment must have been lower. With a reduction factor η_H= 0.38 expressing the decreased anoxic hydrolysis rate of X_S, it was possible to simulate the experimental nitrate profile in the second and third respiration phase with close correspondence. The authors hypothesised that the reduced anoxic activity concerning the last two respiration phases, can be a result of reduced enzymatic activity.

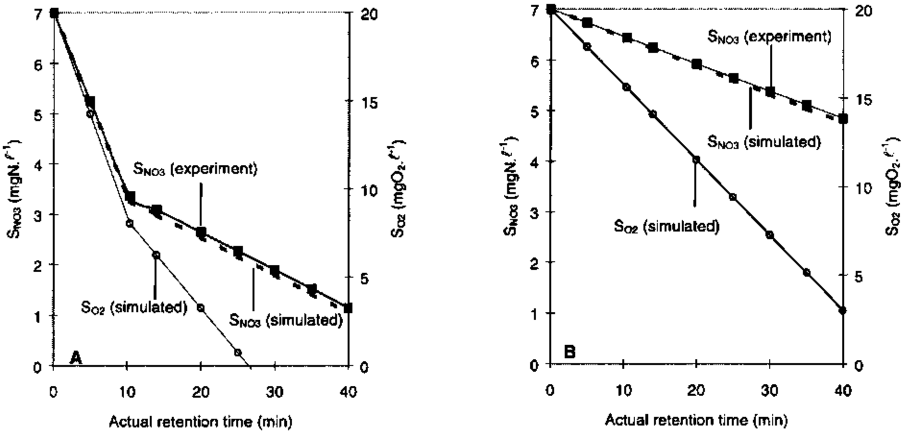

Figure 3.1 Experimental and simulated S_{NO3}-profiles in a pre- (A) and post-anoxic (B) plug-flow reactor and the simulated S_{O2}-profile in the same volumes (redrawn after v. Haandel et al., 1981a).

To incorporate biological P-removal, the model for N-removal of v. Haandel et al. (1981) was extended and further modified (Wentzel et al., 1991, 1992). For poly-P organism enhanced culture kinetics nearly all model constants could be retained except of the reduction factor η_H. This factor was examined over a wide range of configurations and conditions and resulted in a mean value of $\eta_H = 0.6$.

In Activated Sludge Model No. 1 (ASM1) (Henze et al., 1987) the growth rate of heterotrophs (μ_H) and consequently utilisation rate of S_S are reduced under anoxic conditions by the factor η_g. This is a result of the assumption that not all heterotrophs can denitrify and/or that the anoxic growth rate (μ_{HD}) is smaller than the aerobic growth rate (μ_H). The anoxic hydrolysis of X_S proceeds with a lower rate than under aerobic conditions, and is expressed with the factor η_H. The biomass decay rate in ASM1 is independent on the level and sort of electron acceptor but the conversion of its resultant product X_S is reduced by the factor η_H.

The correction factors η_g and η_H in ASM1 have different values, with commonly $\eta_H < \eta_g$. From a limited number of measurements it appeared that values for η_g ranged from 0.6 to 1 and for η_H a value of 0.4 (Dold and Marais, 1986) was common. These values confirm closely the observations of van Haandel et al. (1981a,b). The authors of ASM1 presume to simplify the approach that, when the correction factors are once measured, these values are fixed and constant for a given wastewater. It was not examined to which extent η-values can be influenced by different process configurations.

In ASM2 (Henze et al., 1996) the statements about lower anoxic heterotrophic growth- and hydrolysis rates are sustained. However, the typical values of the reduction factors are changed with regards to ASM1. The growth rate is reduced with a factor $\eta_g = 0.80$ while the hydrolysis rate is reduced with $\eta_H = 0.60$. Decay and lysis of heterotrophs remain independent of electron acceptor conditions.

In ASM2d (HENZE ET AL., 1999) the overall process description becomes more complicated because bio-P organisms (phosphate accumulating organisms, X_{PAO}) are divided into organisms that can and cannot denitrify. This fact induced the necessity to introduce additional reduction factors, for the anoxic storage rate of polyphosphate (0.60) and for the growth rate of X_{PAO} (0.60).

In ASM3 (GUJER ET AL., 1999) the decay approach is replaced by an endogenous respiration, which describes all forms of biomass loss and energy requirement for its maintenance. The endogenous respiration rates under anoxic conditions are in ASM3 50% of these under aerobic conditions. Hydrolysis of X_S is active with the same rate, independent of electron acceptor conditions.

In design approaches that use the general parameter BOD_5 instead of detailed wastewater characteristics, one overall reduction factor (η) is used. KAYSER (1983) assumes that the degradation of BOD_5 under anoxic condition is 25% slower than under aerobic conditions. The same reduction factor (η=0.75) is introduced in the steady state HSA-model (BÖHNKE ET AL., 1989, ATV, (1991)). ARGAMAN (1995 a,b) implements a reduction coefficient η=0.85 for modelling the removal rate of 'effective' BOD under anoxic conditions. In recent design approaches of KAYSER (1997) a bi-substrate character of wastewater is introduced by a division of BOD into soluble and particulate BOD. For the growth, hydrolysis and endogenous respiration rates under denitrifying conditions he introduced three different reduction factors, respectively $\eta_g = 0.9$, $\eta_H = 0.7$ and $\eta_E = 0.6$, based on experimental evidences of ERMEL (1983), TEICHGRÄBER (1988), HARTWIG (1993) and KRAUTH AND SCHWENTER (1994).

In the following paragraphs, justifications are given for the necessity to apply reduction factors in activated sludge models as proposed by different authors for different respiration phases. Further, more examples of proposed numerical values are listed.

3.1.3 ANOXIC HETEROTROPHIC GROWTH OR DENITRIFIERS' FRACTION

A general agreement to introduce a reduction factor for the anoxic growth rate of heterotrophs or the amount of denitrifiers in a heterotrophic population was supported by many investigations and associated hypothesis on the nature of this phenomena. KLAPWIJK (1978) found a fraction of denitrifiers of 20-40% in activated sludge populations from aerobic systems. He concluded that conditions where organic substrate becomes oxidised, determines the denitrifying capacity of heterotrophs or the fraction of denitrifiers. A high fraction will be found in systems where the organic substrate is oxidised mainly under anoxic conditions. PÖPEL (1986) postulated that the lower anoxic substrate oxidation rate (circa 20 to 30%) is a consequence of the fact that not all heterotrophs are able to use nitrate as a terminal electron acceptor. HENZE (1986), basing on respiration experiments, concluded that the denitrifying respiration activity may range from 0 to 80% of the aerobic activity, depending on wastewater and activated sludge. A fully aerated system will expose a lower ratio (average η_g=0.2) than an adapted denitrifying plant (average η_g= 0.6). In his further attempt to estimate the fraction of denitrifiers (HENZE, 1987), η_g was estimated in a range from 0.4 to 0.9 for different plant configurations, wastewater composition and process parameters. The fraction of denitrifiers was also supposed to be influenced by factors as inlet fraction of denitrifiers and sludge retention time (SRT). By performing OUR- and NUR-tests, KRISTENSEN ET AL. (1992) found a fraction of denitrifiers of 41-73% in denitrifying plants while in nitrifying plants this fraction was only 15-20%. BERNARDES (1996) calibrated the fraction of denitrifiers in a model study at 45%. He represents the opinion that variations in denitrifying fraction are a result of a change in wastewater characteristics, biomass composition and activity.

ARGAMAN (1985) found by using a bacterial count that in the most cases the denitrifiers count was equal to the total count, what indicated that practically all heterotrophs (X_H) in the activated sludge are denitrifiers (X_{HD}). Based on this, he hypothesised that a reduced oxidation activity under anoxic conditions should be a result of a lower μ_H under anoxic conditions ($\mu_{HD}/\mu_H<1$).

In the respirometric study of SÖZEN ET AL. (1998), the correction factor for the reduced growth of denitrifiers (η_g) varied from 0.32 to 0.98 with a mean value of 0.58 for domestic wastewater. In the estimation procedure the same heterotrophic yield for aerobic and anoxic conditions ($Y_H=Y_{HD}$) was used. SPERANDIO ET AL. (1999), using a carbon dioxide evolution rate technique for two different activated sludge samples and substrate, obtained a value for η_g in the range of 0.37 to 0.72. In the last study Y_{HD} was separately assessed and not taken as default value.

3.1.4 ANOXIC HYDROLYSIS

The introduction of a reduction factor for modelling the anoxic hydrolysis (η_H) is often considered as a significant simplification, resulting from limited knowledge on the nature of the hydrolysis process (HENZE ET AL., 1987, GUJER AND HENZE, 1991, GOEL ET AL., 1999).

HENZE AND MLADENOWSKI (1991) followed the hydrolysis through the conversion of suspended organic nitrogen to soluble organic nitrogen and further to ammonia under aerobic, anoxic and anaerobic conditions. From their results the anoxic hydrolysis reduction factor appeared to be very low ($\eta_H = 0.25$) but the question arose whether the hydrolysis of particulate nitrogenous compounds can be directly compared with the hydrolysis of particulate organic compounds. GOEL ET AL. (1999) concluded from studies on enzymatic activities in SBR-reactors, that the hydrolysis rate was not affected by different electron acceptor conditions because of the low turn-over, stability and nature of extracellular hydrolytic enzymes. Although the electron acceptor might affect the synthesis of enzymes, the activity of the synthesised enzymes is not. SÖZEN ET AL., (1998) performing OUR- and NUR-tests found a mean η_H value of 0.90 for domestic wastewater.

3.1.5 ANOXIC DECAY OF HETEROTROPHS, ENDOGENOUS RESPIRATION

The same biomass decay coefficients under anoxic or aerobic conditions ($b_{HD} = b_H$) were stated by STERN AND MARAIS (1974) and HEIDE (1975). Performing aerobic and anoxic endogenous respiration tests, KRISTENSEN ET AL. (1992) indicated that the hydrolysis of sludge-COD (endogenous respiration) takes place with the same rate under aerobic and anoxic conditions. KLAPWIJK (1978) determined endogenous respiration rates and found that the anoxic rate was approximately 0.4 of the aerobic rate ($\eta_E = 0.4$). AVCIOUGLU ET AL. (1998), testing a respiration based procedure, found b_{HD} to be 0.55 of b_H under assumption that all X_H participates in the anoxic respiration. SIEGRIST ET AL. (1999) suggest that in the absence of oxygen a reduced decay rate of heterotrophs ($b_{HD} < b_H$) may explain the reduced anoxic endogenous respiration rate.

3.1.6 ANOXIC HETEROTROPHIC YIELD

Based on experimental evidence, STERN AND MARAIS (1974) and HEIDE (1975) indicated that the sludge production in an activated sludge system with an anoxic volume fraction < 40%, does not appear to be significantly different from this generated in a completely aerobic system. They concluded that the heterotrophic yield (Y_H) is not significantly affected by anoxic conditions if the anoxic volume fraction does not exceed 40%. Also PAYNE AND WIEBE (1978) assumed that the electron transfer rates and yield for denitrifying organisms are close to those for oxygen respiring organisms. All IAWQ-models (ASM1..ASM3) do not relate the electron acceptor environment to a difference in Y_H. For a multicomponent substrate (e.g. wastewater) default values of $Y_H = Y_{HD} = 0.67$ (HENZE ET AL., 1987) or 0.63 (HENZE ET AL., 1996, 1998, GUJER ET AL., 1999) are recommended.

In contrast, based on the electron transport pathway and related formation of the high energy compound ATP, it can be deduced that the yield with N-oxides (Y_{HD}) will be substantially lower than with oxygen (MCCARTY, 1972, CASEY ET AL., 1994). Literature reports experimental evidence for Y_{HD} to be approximately two-third of Y_H (HADJIPETROU AND STOUTHAMER, 1965, KOIKE AND HATTORI, 1975, JUSTIN AND KELLY, 1978, STOUTHAMER, 1988, COPP AND DOLD, 1998). SPERANDIO ET AL. (1999) estimated Y_{HD} to be 0.66 - 0.85 of Y_H.

ORHON ET AL. (1996) calculated Y_H and Y_{HD} based on energetics of the related metabolic processes. For different organic substrates (domestic sewage, protein and lactate) they obtained Y_{HD} 20% lower than Y_H. Since the reduction factor η_g from ASM's is a conjunction between X_{HD} and μ_H they propose a Y_{HD} of 0.5 $gCOD_{biomass} \cdot gCOD^{-1}$ as a default value for domestic sewage. Also ÇOKGÖR UBAY ET AL. (1998) reported a significantly lower Y_{HD}, based on an an energetic basis. MCCLINTOCK ET AL., (1988) found in experiments with synthetic wastewater a maximum microbial anoxic yield to be circa 50% of the value found under aerobic conditions (0.40 versus 0.74 g/g).

From extended series of batch experiments SCHEER AND SEYFRIED (1994) found a slightly lower anoxic than aerobic yield. This confirmed the statement of OBERMANN (1982) that the surplus energy to anoxic metabolism stages is only 5 to 10% lower than of the aerobic metabolism stage. KLAPWIJK (1978) estimated heterotrophic yields theoretically on energetic basis and experimentally using several model substrates and found also a negligible difference between Y_{HD} and Y_H.

3.1.7 SUMMARY

The reduced rate of anoxic hydrolysis (η_H) was as first incorporated in activated sludge models (V. HAANDEL ET AL., 1981a,b) but still no established fundamental explanation grounds this approach. As next, the reduction factor for anoxic S_S-oxidation (η_g) was introduced (e.g. HENZE ET AL., 1987) Contrary to η_H, more experiments and electron transport energetics considerations supported the use of η_g. A decreased rate of the anoxic endogenous respiration was later incorporated in the models (e.g. KAYSER, 1997, GUJER ET AL., 1999). The reduction factors that are reviewed in the previous sections expose a high variation (Table 3.1).

Table 3.1 Reported values of reduction factors. The factor η_g stands for reduced growth of heterotrophs under anoxic conditions or a lower fraction in the heterotrophic population. The factor η_H reflects the retarded hydrolysis of the particulate fraction X_S while η_E is the factor for a decreased anoxic decay rate or endogenous respiration. The factor η is a general reduction factor for anoxic biodegradation in approaches where no fractionation of biodegradable COD takes place.

Author(s)	η_g	η_H	η_E	η
KLAPWIJK (1978)	0.2-0.4		0.4	
V. HAANDEL ET AL., (1981a,b)		0.38		
KAYSER (1983)				0.75
HENZE (1986)	0-0.80			
HENZE (1986)	0.20-0.58			
HENZE ET AL., (1987)	0.8	0.4		
HENZE (1987)	0.4-0.9			
BÖHNKE (1989)				0.75
HENZE AND MLADENOWSKI, (1991)		0.25		
WENTZEL ET AL., (1991, 1992)		0.6		
ARGAMAN (1995 a,b)				0.85
HENZE ET AL., (1996)	0.80	0.60		
BERNARDES, (1996)	0.45			
KAYSER (1997)	0.90	0.70	0.6	
AVCIOGLU ET AL., (1998)			0.55	
GUJER ET AL., (1999)	0.60[2)]		0.50	
HENZE ET AL., (1999)	0.80 (0.60)[1)]	0.60		
SÖZEN ET AL., (1998)	0.32-0.98 (0.58)	0.67-1.48		
SPERANDIO ET AL., (1999)	0.37-0.72			

1) η_g=0.6 refers only to denitrifying X_{PAO}; [2)] anoxic storage (X_{STO}) and growth on X_{STO};

3.1.8 OBJECTIVE OF THE STUDY

In this chapter a methodology is proposed to estimate reduction factors for a simplified denitrification model (chapter 4 and 5). The denitrification in this simplified model is described via anoxic oxidation of S_S and anoxic endogenous respiration. The source for S_S is the influent and the hydrolysis of X_S. These three processes were expected to be retarded under anoxic conditions when comparing with aerobic respiration what could be described by respectively three reduction factors: η_1, η_2 and η_3. Respiration based techniques (OUR- and NUR-tests) were implemented to estimate these three reduction factors. Some considerations about the differentiation between aerobic and anoxic heterotrophic yield, as well as the comparison between estimated aerobic and anoxic wastewater characteristics were carried out. Main concern was to develop and test the methodology, rather than to generate applicable data for different activated sludge- and wastewater samples. Several tests were performed with activated sludge from pilot-plants with different process configurations but fed with the same domestic wastewater. The obtained results are briefly discussed in light of literature values.

3.2 MATERIALS AND METHODS

3.2.1 EXPERIMENTAL SET-UP FOR OUR-TEST

For the OUR-test the automated respiration unit RESCUE (BROUWER AND KLAPWIJK, 1997) was used in its simplest configuration, consisting of a completely mixed, double-wall batch reactor (V_B=40 ℓ) and a respiration vessel (V_R=1.5 ℓ) (Figure 3.2). The content of the batch reactor was aerated while the respiration vessel was thoroughly stirred (magnetic stirrer, CAT M5). A pump secured a continuous circulation of activated sludge mixture between the batch reactor and the respiration vessel with a constant flow (q_R). The alternating operation of two pairs of valves changed the flow direction through the respiration vessel each 30 seconds what enabled to measure the oxygen respiration rate related to the substrate level in the bulk, using one dissolved oxygen (DO) sensor (WTW EO 190-1,5) centrally installed in the respiration vessel (SPANJERS AND KLAPWIJK, 1990). Each minute an oxygen consumption ($S_{O1}(t)$-$S_O(t)$) was obtained and in combination with the retention time of the activated sludge sample in the vessel the respiration rate (R) could be calculated according to equation 3.1.

$$R = \frac{q_R}{V_R} \cdot \left(S_{O1}(t) - S_O(t)\right);\ \mathrm{mgO_2.\ell^{-1}.h^{-1}} \qquad (3.1)$$

The pH and temperature in the reactor were controlled on chosen set-points (pH=7.2 and T=20°C) with respectively a pH-controller (Endress&Hauser, Liquisys CPM 240) and a heat exchanger (Julabo, MH, F25). The respiration unit was connected to a personal computer (PC) via an interface, which provided the communication between the software of the PC and the instrumentation of the respiration unit. The software, which controlled the operation of the respiration unit, was written in MATLAB. The measuring frequency of R, pH and temperature was once per 1 minute.

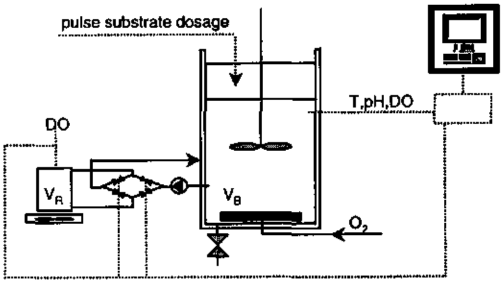

Figure 3.2 Experimental set-up for OUR-test.

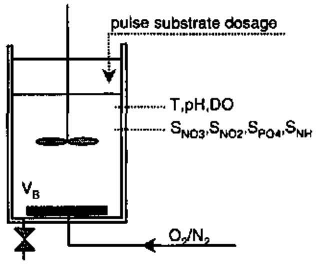

Figure 3.3 Experimental set-up for NUR-test.

3.2.2 EXPERIMENTAL SET-UP FOR NUR-TEST

The experimental set-up for a NUR-test consisted of a double-wall batch reactor (V_B=30 ℓ) equipped with a centrally installed, mechanical stirrer and a fine-bubble diffuser to provide nitrogen gas or oxygen if necessary (Figure 3.3). The pH was manually adjusted to the value of 7.2 using a solution of sodium hydroxide (2.65% NaOH) or hypochloric acid (2.58% HCl). The temperature in the batch vessel was maintained constant at a level of 20°C (Julabo, MH, F25).

3.2.3 PERFORMANCE OF OUR-TEST

To estimate wastewater characteristics (S_S and X_S) and their conversion kinetics a 16-20 ℓ sample of activated sludge was transferred to the batch reactor. A sufficient, high DO level (6-8 $mgO_2.\ell^{-1}$) was ensured with fine-bubble aeration. The course of respiration was measured directly after addition of the activated sludge sample in order to detect its endogenous stage. After a stable endogenous respiration rate was attained, a dose of allylthiourea (ATU) was added (10 $mg.\ell^{-1}$) to suppress the nitrifiers' activity. After 10 min a known volume of settled wastewater from Bennekom village was added at an average substrate/biomass ratio (S/X_V-ratio, § 2.2.2) of 0.05 $mgCOD.mgVSS^{-1}$. The respiration rate was continuously measured until a stable endogenous respiration rate (r_{end}) was attained again (Figure 3.4).

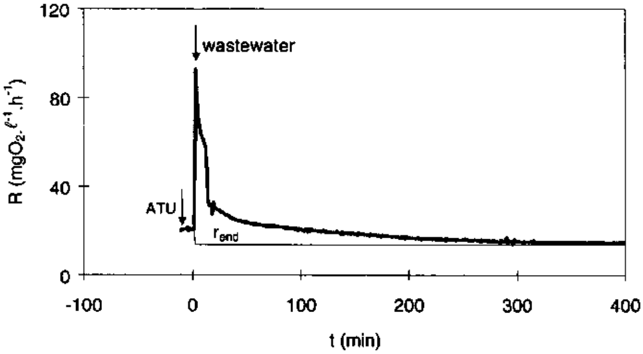

Figure 3.4 Result of OUR-test with wastewater (OUR-curve) and nitrification suppression.

To estimate the aerobic heterotrophic yield coefficient (Y_H) and oxidation kinetics, the OUR-test procedure as described above was repeated but instead of wastewater a known amount of sodium acetate solution (0.5 M $CH_3COONa{\cdot}3H_2O$) was added to a fresh sample of activated sludge in endogenous stage. The environmental conditions (pH, T, DO) were sustained as in the experiment with wastewater and there was no need to suppress the nitrification activity. The course of the respiration rate was followed (Figure 3.5).

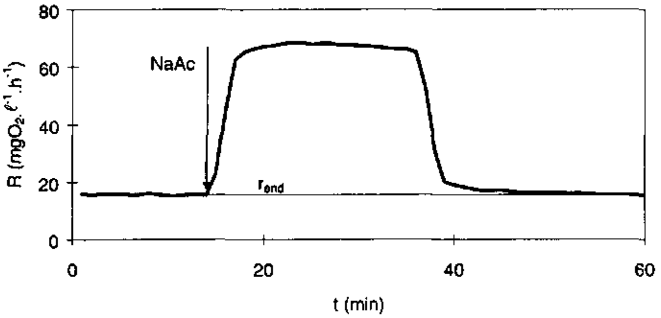

Figure 3.5 Result of OUR-test (OUR-curve) with acetate.

3.2.4 PERFORMANCE OF NUR-TEST

To estimate wastewater characteristics (S_S and X_S) and their conversion kinetics a 14-20 ℓ sample activated sludge - of same origin and sampled at the same time as for the OUR-test - was transferred to the batch reactor. It was brought to endogenous conditions by aerating it as long as in the OUR-test (at DO=6-8 mgO$_2$.ℓ$^{-1}$). After the endogenous respiration was reached, ATU was added and the sample was still aerated for approximately 10 min until the respiration rate stabilised. The aeration was stopped and nitrogen gas was purged to lower rapidly the DO-level to a negligible concentration and to sustain anoxic conditions during the experiment. After the DO concentration dropped to ~0 mgO$_2$.ℓ$^{-1}$, the concentration of nitrate in the mixture was adjusted, if necessary to a level of 10-40 mg N.ℓ$^{-1}$, by addition of a nitrate potassium solution (1 M KNO_3). The whole mixture was sustained in anoxic, endogenous conditions for a period of around 15 min before the wastewater sample was added. A sample of settled wastewater - of the same origin and composition as for the corresponding OUR-test - was added to the anoxic suspended mixture. The average S/X_V-ratio used for the NUR-tests was lower than for the OUR-test (average S/X_V =0.035 mgCOD.mgVSS^{-1}). The duration of each NUR-tests was restricted to 4 *h* on average basis. One minute after wastewater addition (assumed as sufficient for the complete equalisation of the reactor's content) the first sample was taken. Grab samples of 10 mℓ were taken in defined time intervals for nitrite (S_{NO2}), nitrate (S_{NO3}) phosphate (S_{PO4}) and ammonia (S_{NH}) determination. The samples were immediately filtered through a paper filter (Schleicher&Schuell, 595^1/$_2$, pore size 4.4 μm). The analysis was performed on the Segment Flow Analyser (SKALAR, the Netherlands).

To assess denitrification kinetics based on nitrate reduction to nitrogen gas (complete denitrification) the NUR curve was built of S_{NO3}+0.6·S_{NO2}=S_{NO} (Figure 3.6). This allowed for a direct comparison with the aerobic respiration rate because formation and optional accumulation of the intermediate product nitrite is included (see also §2.3.1).

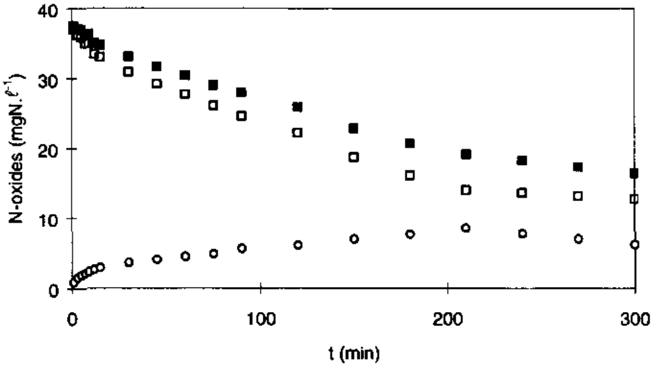

Figure 3.6 Results of NUR-test with wastewater; ○–S_{NO2}, □ -S_{NO3} and ■–S_{NO}.

To estimate the anoxic heterotrophic yield coefficient (Y_{HD}) and kinetics under anoxic conditions, the NUR-test procedure was followed but instead of wastewater a known amount of NaAc-solution (0.5 M $CH_3COONa{\cdot}3H_2O$) was added to a fresh sample of endogenous activated sludge. The typical course of S_{NO2}, S_{NO3} and S_{NO} is shown in Figure 3.7.

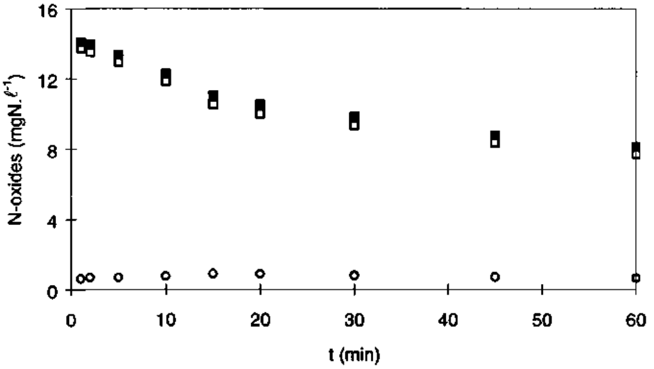

Figure 3.7 Results of NUR-test with acetate; ○–S_{NO2}, □ -S_{NO3} and ■–S_{NO}.

3.2.5 CHARACTERISTICS OF ACTIVATED SLUDGE AND WASTEWATER

A few different activated sludge samples were examined to test the methodology for estimating reduction factors, wastewater characteristics and kinetic parameters. They originated from different pilot-plants (Experimental Hall, Bennekom) operating at different configurations and operational conditions (Table 3.2).

For all experiments the settled wastewater from Bennekom village was used. Grab samples of wastewater were usually taken in the middle of the day (between 12 and 14 o'clock). Before providing it as a substrate for the considered experiment, it was stirred thoroughly and divided into three volumes: for an OUR- and a NUR-test and for standard analysis.

Table 3.2 Characteristics of activated sludge samples used for OUR- and NUR-tests.

Activated Sludge sample	Reactor type	Organic loading rate (B_{XCOD}) gCOD/gMLSS.d	Nitrification	Denitrification	Bio-P removal
AS1	SBR	0.1	YES	NO	NO
AS2	CSTR	0.2	YES	NO	NO
AS3a	CSTR, alternating system, few days after switching from aerobic only to anoxic-aerobic mode (rain weather)	0.1	YES	YES	NO
AS3b	as above but longer operating in anoxic-aerobic mode	0.2	YES	YES	NO
AS4	plug-flow reactor (A^2/O, anaerobic/ anoxic/aerobic)	0.1	YES	YES	YES
AS5	plug-flow reactor (anoxic/aerobic/ anoxic)	0.17	YES	YES	NO

To obtain identifiable results of OUR- and NUR-tests an appropriate choice of S/X_V ratio is essential (EKAMA ET AL., 1986). For the purpose of this study S/X_V is defined as:

$$\frac{S}{X_V}=\frac{COD\cdot f_{ww}}{X_V}\text{, gCOD.gVSS}^{-1} \tag{3.2}$$

where: COD total COD of wastewater ($g.\ell^{-1}$);

f_{ww} volumetric wastewater fraction in the total experimental batch volume ($\ell.\ell^{-1}$);

X_V volatile activated sludge concentration ($g.\ell^{-1}$).

If S/X_V is too low it will be especially difficult to extract precisely the S_S-concentration and its oxidation rate (e.g. Figure 3.8).

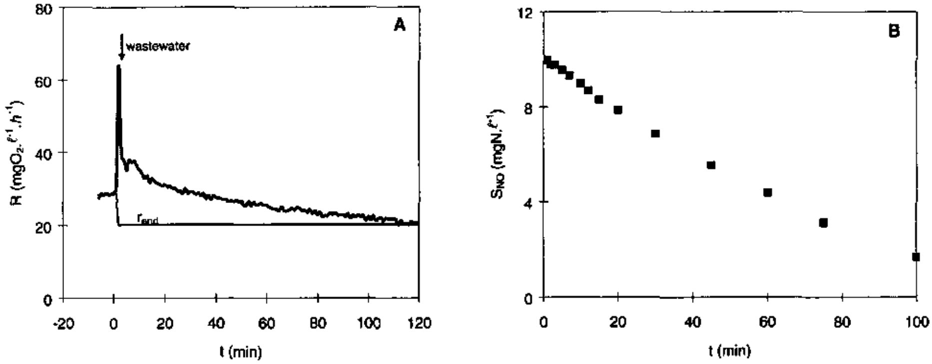

Figure 3.8 Results of OUR- and NUR-tests performed at too low S/X_V-ratios. In case of OUR curve (S/X_V= 0.014g/g) the maximum rate of S_S-utilisation was not reached. In case of NUR curve (S/X_V=0.011g/g) the distinction between denitrification rates on S_S and X_S (§ 2.3.1, Figure 2.3) was not obvious.

Also in the opposite case the differentiation between the respiration rates resulting from subsequent wastewater fractions will not be obvious. Moreover, higher loading rates contribute in an increased biomass growth, causing changes in the actual characteristics of the population (CHUDOBA ET AL., 1992).

A correctly chosen S/X_V ratio allows distinguishing different utilisation rates without a significant impact of change in population dynamics in short term experiment. Due to a slower respiration activity under anoxic conditions, S/X_V should be chosen smaller for NUR-tests. For examined wastewater and activated sludge it was experienced that the optimal S/X_V for OUR-tests was in the range 0.05-0.07 $gCOD.gVSS^{-1}$ while for NUR-tests around 0.03-0.05 $gCOD.gVSS^{-1}$.

3.2.6 ANALYSIS

The concentration of total and volatile suspended solids (MLSS, MLVSS) was measured at the end of each OUR- and NUR-test. The wastewater sample was controlled for the concentration of total COD. Analysis performed according to Standard Methods (APHA, 1992).

3.3 ESTIMATION PROCEDURE

3.3.1 WASTEWATER CHARACTERISTICS, OXIDATION KINETICS AND Y_H UNDER AEROBIC CONDITIONS

An obtained respirogram from an OUR-test with wastewater (Figure 3.4) is composed of the oxygen consumed for endogenous respiration ($r_{end}=k_{end} \cdot X_V$) and for the oxidation of readily biodegradable organic substrate (S_S). The fraction S_S originates from the influent and is generated from the hydrolysis of particulate, slowly biodegradable substrate (X_S). Because the nitrification activity is completely inhibited by ATU no oxygen for ammonia-nitrogen (S_{NH}) oxidation is consumed.

Such wastewater OUR-curve can be described with a simplified model, like presented in matrix form in Table 3.3. In this model the oxidation rate of S_S ($r_{SS}=k_{SSm} \cdot X_V$) is expressed by a Monod-type mixed-order reaction while the hydrolysis rate of X_S (r_{XS}) by a first-order reaction. The total respiration rate (R) is the sum of oxygen (S_{O2}) consumed for S_S-oxidation and endogenous respiration modelled as a zero-order process (processes 1 and 3 in Table 3.3).

Table 3.3 Simplified model to fit the OUR-curve

No	Process	S_S	X_S	S_{O2}	Rate equation
1	Aerobic S_S-oxidation	-1		$-(1-Y_H)$	$k_{SSm} \frac{S_S}{K_S+S_S} \cdot X_V$
2	Aerobic X_S-hydrolysis	1	-1		$k_H \cdot X_S$
3	Aerobic endogenous respiration			-1	$k_{end} \cdot X_V$

For the identification of the OUR-curve a parameter estimation was carried out with an optimisation method (Excel, Solver) where the model from the matrix (Table 3.3) was fitted to the measured data (Figure 3.9).

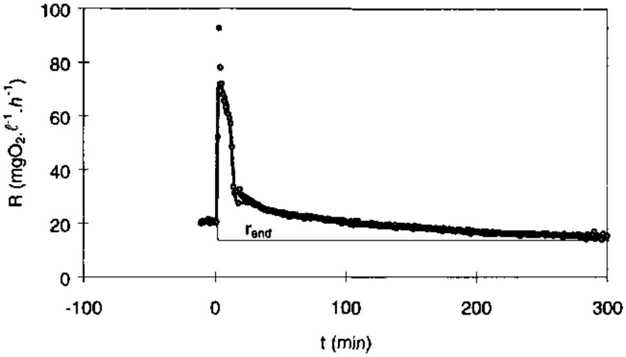

Figure 3.9 Measured (o) and simulated (solid line) OUR-curve resulting from batch experiment with wastewater. Nitrification suppressed by addition of ATU (S/X_V=0.06 gCOD.gVSS^{-1}).

A least-square method was used to minimise the deviation between the measured and simulated respiration rate. Assuming that Y_H was known (estimated from OUR-test with model substrate or taken as default value) the number of optimised parameters amounted five (S_S, X_S, k_{SSm}, k_H, K_S). Such a significant number of parameters will often lead to a quite satisfactory model fitting while parameter values can be erroneous (e.g. VANROLLEGHEM ET AL., 1995). To minimise this problem, two of the five parameters, k_{SSm} and K_S, can be estimated separately using the same activated sludge and a model substrate, e.g. acetate. K_S can also be taken as default value (e.g. HENZE ET AL., 1996, BROUWER ET AL., 1998)

The acetate OUR-curve is built of the oxygen consumed for oxidation of S_S (acetate) and the endogenous respiration (Figure 3.10). Because acetate is a substrate of uniform nature, the model for parameters identification from this respirogram is simpler than for wastewater (only process 1 and 3 from the matrix in Table 3.3). Since the initial concentration of substrate in the bulk is known the number of parameters to be optimised amounts maximally two (k_{SSm} and K_S) under assumption that Y_H is known.

The yield factor Y_H from the OUR-test with acetate may be estimated separately without the necessity of model fitting and optimisation procedure, using eq. 3.3:

$$Y_H = 1 - \int_{t_0}^{t_e} (R(t) - r_{end})dt \frac{1}{S_{Ac}}; \tag{3.3}$$

To implement equation 3.3 for estimation of Y_H one has to make sure that the storage of S_S in bacterial cells can be neglected. Poly-P accumulating bacteria (X_{PAO}) are known to store products of fermentation (acetate) in a high rate and the proposed method may lead to an erroneous value of Y_H when the activated sludge contains (active) poly-P organisms.

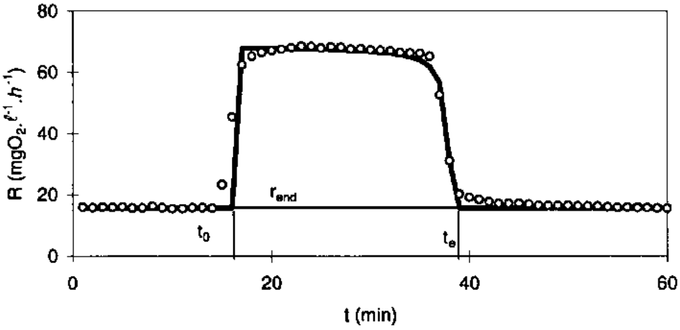

Figure 3.10 Measured (o) and simulated (solid line) oxygen respiration rate to estimate the kinetic parameters of acetate oxidation (S_{Ac} =69.3 mgCOD.ℓ$^{-1}$)

3.3.2 WASTEWATER CHARACTERISTICS, OXIDATION KINETICS AND Y_H UNDER ANOXIC CONDITIONS

Organic biodegradable wastewater fractions (S_S+X_S) can be estimated from NUR-tests (Figure 3.11) using the following equations (see also §2.3.3):

$$S_s = \frac{2.86 \cdot \Delta(S_{NO})_1}{(1-Y_{HD})} \cdot \frac{1}{f_{ww}} \text{; mgCOD.ℓ}^{-1} \qquad (3.4)$$

$$X_s = \frac{2.86 \cdot \Delta(S_{NO})_2}{(1-Y_{HD})} \cdot \frac{1}{f_{ww}} \text{; mgCOD.ℓ}^{-1} \qquad (3.5)$$

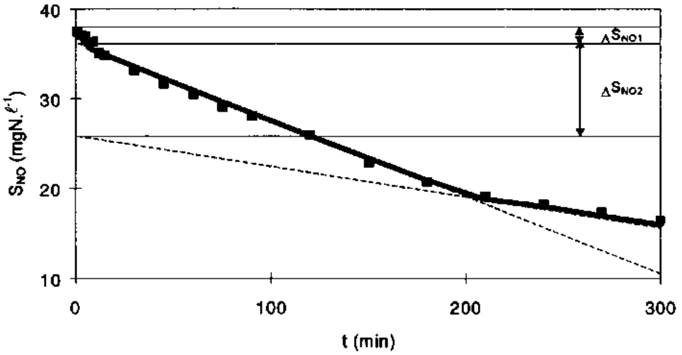

Figure 3.11 Measured (▪) and simulated (solid line) NUR-curve with the anoxic COD-oxidation/endogenous respiration model (Table 3.4); S/X_V:0.048 gCOD.gVSS^{-1}.

A complete NUR-curve can be described with a simplified model as shown in matrix form in Table 3.4. The S_{NO}-consumption in a batch NUR-test with wastewater results from anoxic oxidation of S_S (process 4) and anoxic endogenous respiration (process 6). The fraction S_S originates from influent and is generated from the anoxic hydrolysis of X_S (process 5). The anoxic S_S oxidation is modelled with an aerobic Monod-type function multiplied with the reduction factor η_1. The anoxic hydrolysis rate is expressed with a first-order, with respect to X_S, aerobic reaction multiplied with the reduction factor η_2. As last, the decreased rate of endogenous respiration under anoxic conditions is expressed by the factor η_3.

Table 3.4 Simplified anoxic COD-oxidation model used for the NUR-curve identification

No.	Process	S_S	X_S	S_{NO}	Rate equation
4	Anoxic S_S-oxidation	-1		$-\frac{1-Y_{HD}}{2.86}$	$\eta_1 \cdot k_{SSm}\frac{S_S}{K_S+S_S}\cdot X_V$
5	Anoxic X_S-hydrolysis	1	-1		$\eta_2 \cdot k_H \cdot X_S$
6	Anoxic endogenous respiration			$-\frac{1}{2.86}$	$\eta_3 \cdot k_{end} \cdot X_v$

Analogously to the OUR-test, Y_{HD} can be calculated from a NUR-test with acetate, using equation 3.6:

$$Y_{HD} = 1 - \frac{2.86 \cdot \Delta(S_{NO1})}{S_{Ac}}; \tag{3.6}$$

where the amount of consumed S_{NO} for oxidation of acetate (ΔS_{NO1}) is estimated as shown in Figure 3.12. Like in an OUR-test, possible storage of acetate during the experiment may lead to incomplete recovery of added substrate and an erroneous estimation of Y_{HD}. This refers especially to populations containing X_{PAO}'s. The acetate S_{NO}-curve can be fitted with the model presented in Table 3.4 (process 4 and 6).

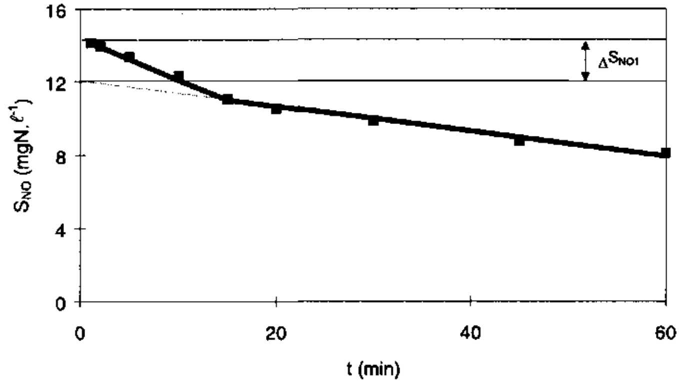

Figure 3.12 NUR-curve from a NUR-test with acetate; measured (■) and simulated (solid line) with the simplified anoxic COD-oxidation model (Table 3.4); (S_{Ac}=27.8 mgCOD.ℓ$^{-1}$).

3.3.3 ESTIMATION OF REDUCTION FACTORS FROM WASTEWATER RESPIROGRAMS

From a NUR-curve with wastewater two reduction factors (η_1 and η_2) can be estimated by fitting the S_{NO}-curve (Figure 3.11) with the model as presented in Table 3.4. The aerobic substrate conversion kinetics (parameters k_{SSm}, k_H and optionally K_S) are obtained from the identification of the corresponding OUR-curve. The heterotrophic yields (Y_H and, if distinction is made between aerobic and anoxic conditions, Y_{HD}) are estimated from the OUR- and NUR-curve with acetate, or taken as default values when simplifying the approach. The wastewater fractions (S_S and X_S) are obtained from the same NUR-curve or from a corresponding OUR-curve, when the assumption is valid that the same fractions are recognised under aerobic and anoxic conditions.

The reduction factor η_3 can be directly calculated by comparing the measured specific endogenous respiration rates from corresponding OUR- and NUR-tests, using the following relation:

$$\eta_3 = \frac{2.86 \cdot k_{Dend}}{k_{end}} = \frac{2.86 \cdot r_{Dend} \cdot X_{V(OUR)}}{r_{end} \cdot X_{V(NUR)}} \tag{3.7}$$

The reduction factors η_1 and η_2 remain the only parameters to be numerically estimated from the wastewater S_{NO}-curve, by using an optimisation method.

3.3.4 ESTIMATION OF REDUCTION FACTORS FROM ACETATE RESPIROGRAMS

From acetate respirograms only two reduction factors can be estimated: η_1 and η_3. The acetate S_{NO}-curve is fitted with a model (Table 3.4, processes 4 and 6) in which the oxidation kinetics (k_{SSm} and optionally K_S) are obtained from a corresponding OUR-test with acetate. The parameter Y_{HD} is estimated from a considered NUR-test with acetate, using equation 3.6. Because η_3 can be directly derived using equation 3.7, η_1 is the only optimised parameter.

3.3.5 SUMMARY OF METHODOLOGY

The methodology to estimate the relation between anoxic and aerobic respiration rates, expressed by reduction factors η_1, η_2 and η_3, is comprehensively summarised with scheme in Figure 3.13.

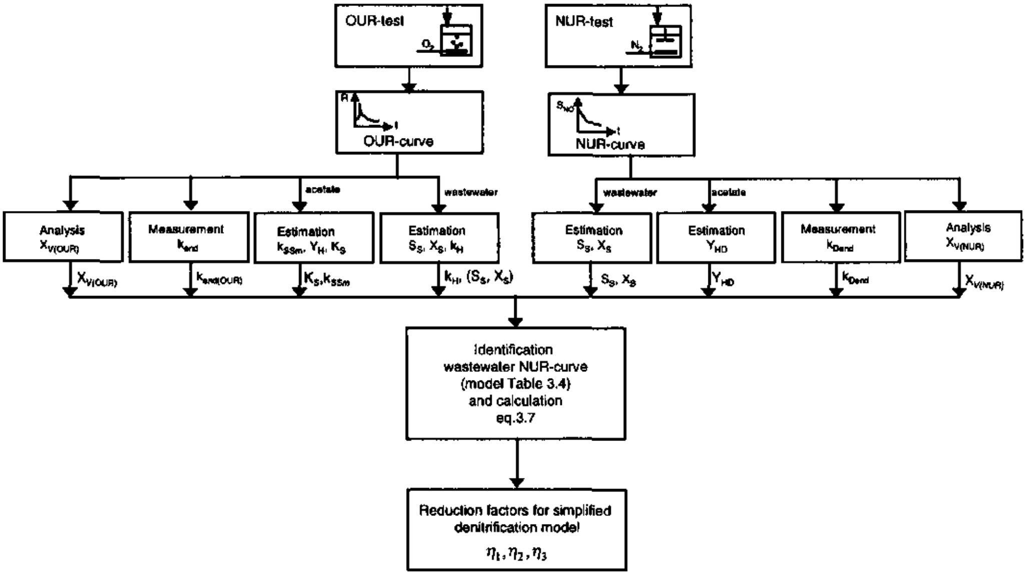

Figure 3.13 Schematic representation of the methodology to estimate reduction factors for anoxic respiration for the simplified denitrification model approach.

3.4 RESULTS AND DISCUSSION

3.4.1 OUR- AND NUR-TESTS WITH WASTEWATER

From a series of OUR- and NUR-tests a number of OUR- and NUR-curves was obtained. For visual comparison of the results, the obtained measurements are converted. The S_{O2}-respirograms are presented as cumulative oxygen consumption curves and the results of the NUR-tests are presented as cumulative S_{NO}-S_{O2} equivalent (nitrate-oxygen equivalent, $NOE=2.86 \cdot S_{NO}$) consumption curve. The obtained results are shown in Figure 3.14, plotted in pairs for the same activated sludge samples.

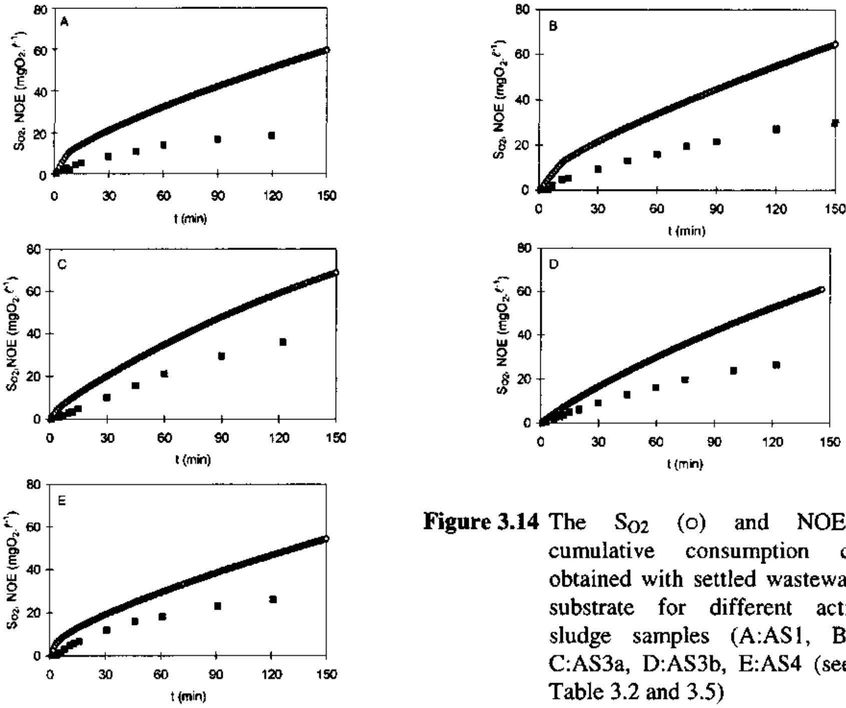

Figure 3.14 The S_{O2} (○) and NOE (■) cumulative consumption curves obtained with settled wastewater as substrate for different activated sludge samples (A:AS1, B:AS2, C:AS3a, D:AS3b, E:AS4 (see also Table 3.2 and 3.5)

Since the average initial conditions for corresponding OUR- and NUR-tests usually differed (Table 3.5), the objective of presenting Figure 3.14 was to visualise the order of difference between aerobic and anoxic respiration rates in general and in relation to the activated sludge origin.

From Figure 3.14 it is evident that the subsequent anoxic respiration rates are lower than the corresponding aerobic rates and this is relevant to each phase of respiration: direct S_S-oxidation, X_S-hydrolysis and endogenous respiration. However, the magnitude of these differences varies between different activated sludge samples and this is the reason why the values of reduction factors cannot be considered as constant for each activated sludge system.

Table 3.5 Experimental conditions of OUR- and NUR-tests performed with activated sludge samples originating from different systems (Table 3.2) (pH=7.2, T=20°C)

AS sample	Respiration test	f_{ww} $\ell.\ell^{-1}$	COD mgCOD.ℓ^{-1}	X_V gVSS.ℓ^{-1}	S/X_V gCOD.gVSS^{-1}
AS1	OUR	0.30	570	3.41	0.051
	NUR	0.20	570	3.25	0.035
AS2	OUR	0.33	652	3.41	0.063
	NUR	0.27	652	3.71	0.048
AS3a	OUR	0.33	528	2.43	0.072
	NUR	0.24	528	2.77	0.045
AS3b	OUR	0.29	200	3.98	0.015
	NUR	0.24	200	4.17	0.011
AS4	OUR	0.33	451	4.19	0.036
	NUR	0.33	451	4.08	0.037

The main goal of this study was to develop the methodology to estimate the reduction factors, to test it and to give some idea about a dependency of denitrification reduction factors on the characteristics of the activated sludge or system configuration. The attention was paid to trace some of these relations but not to assess any 'universal' default values or hypothesis supported by a significant number of experiments. The acquired values of three reduction factors using the estimation procedure for activated sludge samples AS1..AS4 are listed in Table 3.6.

Table 3.6 The reduction factors for denitrification estimated from OUR- and NUR-tests with settled domestic wastewater for several activated sludge samples originating from configurations as summarized in Table 3.2.

Activated sludge sample	η_1	η_2	η_3
AS1	0.22	0.60	0.22
AS2	0.56	0.64	0.40
AS3a	0.40	0.54	0.28
	1	0.63	0.30
AS3b	0.57	0.68	0.4
AS4	0.54	0.68	0.19

Activated sludge AS1 originated from the low-loaded SBR pilot-scale reactor, fed with settled domestic wastewater. It was a fully aerated system, able to nitrify completely the supplied nitrogen load during each cycle. Oxygen was supplied in excess and probably anoxic conditions hardly appeared, also not during the sedimentation phase.

The anoxic S_S-oxidation in the first respiration phase (Figure 3.14A) was significantly lower than the aerobic S_S-oxidation. Probably due to the fact that AS1 was not adapted to denitrifying conditions, a low reduction factor η_1 of 0.22 was estimated. Klapwijk (1978), Henze (1986) and Kristensen et al. (1992) found similar values for fully aerated systems while estimating the fraction of denitrifiers in the total heterotrophic population (η_g). The factor η_g is comparable with the factor η_1 in this study. Due to a limited duration of the first respiration phase during the NUR-test (low actual S_S-concentration) the synthesis of specific N-oxides reductases probably could not reach a high level because activated sludge was not adapted to denitrifying conditions. The X_S-hydrolysis under anoxic conditions was reduced with a factor

η_2 = 0.6. This value is similar to other findings and often used as default for modelling purposes (e.g. HENZE ET AL., 1987). The estimated reduction factor for the anoxic endogenous respiration of $\eta_3 = 0.22$ was low as compared with literature values (Table 3.1).

Activated sludge AS2 originated also from a fully aerated reactor (Table 3.2) but subjected to a two-fold higher sludge loading (B_{XCOD}) than AS1. The oxygen supply was controlled on a level just needed for a complete nitrification and probably the activated sludge was subjected to anoxic conditions in the secondary settler or due to difussion limitation of oxygen, the activated sludge floc was partly anoxic. Although AS2 was not really adapted to anoxic conditions, it exposed higher anoxic respiration rates than AS1 (Figure 3.14B). The reduction factors η_1 and η_2 amounted 0.56 and 0.64 respectively. Similar values are also proposed in new ASM versions (η_g and η_H =0.6) (HENZE ET AL., 1999, GUJER ET AL., 1999). The factor η_3 was estimated at 0.4, which is close to the values proposed in literature (e.g. KLAPWIJK 1978, AVCIOGLU ET AL., 1998, GUJER ET AL., 1999). Higher values for all reduction factors might suggest that AS2, except of partial adaptation to anoxic conditions, was characterised by higher biomass activity (higher B_{XCOD}) resulting in a higher enzymatic activity.

Activated sludge AS3a originated from the same pilot-plant as AS2 but the plant operation was switched from an aerobic- to an alternating anoxic-aerobic mode. Although the wastewater influent flow to the pilot-plant did not change, B_{XCOD} was lowered due to rain weather conditions during the experimental period. Two series of respiration tests were performed with sludge AS3a. From the first tests (Figure 3.14C) it turned out that all anoxic reduction factors decreased in relation to AS2. The reduced values of η_1 (=0.4), η_2 (=0.54) and η_3 (=0.28) could be explained by a temporary lowered activity of activated sludge because it was fed with a low-strength wastewater. Moreover, the air supply for the nitrification was not controlled and this could lead to an excessive DO-concentration in the beginning of the anoxic phase. All these facts could contribute in decreased anoxic respiration rates of AS3a.
The NUR-test was repeated with the same sludge (AS3a) after 12 *h* of endogenous anoxic conditions. The estimated anoxic S_S-oxidation rate was equal to the aerobic rate ($\eta \approx 1$) and higher values for η_2 (0.63) and η_3 (0.30) were found. The higher level of specific N-oxides reductases and enzymes for X_S-hydrolysis after a long exposure of activated sludge to anoxic conditions could explain the higher estimated values of the reduction factors.

Activated sludge AS3b originated from the same pilot-plant as mentioned above. After 2 weeks of operation in an alternating anoxic/aerobic mode, the respiration tests were performed (Figure 3.14D). The subsequent reduction factors seemed to be hardly effected with regards to the same sludge when it was only aerated (AS2).

Activated sludge AS4 (Figure 3.14E) originated from a low-loaded plug flow reactor, operating in an A^2/O configuration with an additional post-anoxic zone. In this configuration complete nitrification, a high-rate biological P-removal and a partial denitrification were performed. The ability of this sludge to oxidise S_S anoxically was reduced with a factor of

0.54 when compared with the aerobic value, while anoxic hydrolysis proceeded relatively fast (η_2=0.68) in relation to the aerobic value. The anoxic endogenous respiration rate was much lower than under aerobic conditions (η_3=0.2).

3.3.2 OUR- AND NUR-TESTS WITH ACETATE

Some of the activated sludge samples described in the previous section, were used to perform OUR- and NUR-tests with the addition of acetate as carbon source. The main objective of the respiration tests with acetate was to assess the heterotrophic yield coefficients (Table 3.7, Figure 3.15) but as mentioned earlier also k_{SSm} and optionally K_S could be estimated. The obtained S_{O2} and NOE cumulative consumption curves are presented in Figure 3.15.

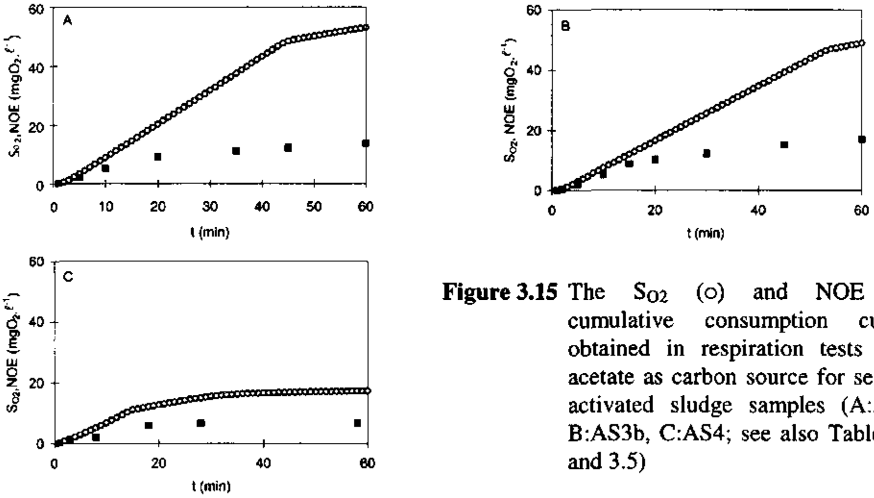

Figure 3.15 The S_{O2} (○) and NOE (■) cumulative consumption curves obtained in respiration tests with acetate as carbon source for several activated sludge samples (A:AS1, B:AS3b, C:AS4; see also Table 3.2 and 3.5)

Table 3.7 Aerobic and anoxic heterotrophic yield coefficients estimated from OUR- and NUR-tests with acetate.

Activated sludge sample	Y_H	Y_{HD}
AS1	0.73	0.65
AS3b	0.73	0.68
AS4	0.66	0.77

The estimated Y_H was identical for sludge samples AS1 and AS3b and amounted 0.73 which is much higher than the proposed value in ASM's but on the other hand found more often for a readily biodegradable, uniform model substrate. Concerning anoxic yield, both AS1 and AS3b were characterised by lower values of Y_{HD} when comparing with Y_H (0.65 and 0.68 respectively). For sludge originating from the A^2/O pilot-plant (AS4) the estimated Y_H was similar with the values used for model and design studies (e.g. HENZE ET AL., 1996, SPERANDIO ET AL., 1999). However, the obtained S_{O2}-respirogram with AS4 deviated from the 'classic' example shown in Figure 3.5 (Figure 3.16A). Such a respiration course is more often found for activated sludge containing active phosphorus accumulating organisms (X_{PAO}). Two fields of oxygen utilisation are distinguished: rapid utilisation of bulk-S_S by all heterotrophs and a slower oxidation of stored S_S by, the most probably, X_{PAO}'s. Although substrate storage appeared during the OUR-test it was only possible to calculate manually the amount of oxygen, used for utilisation of the whole amount of added substrate. The simplified aerobic COD-oxidation model in the form presented in Table 3.3 would not be able to fit the data because the storage of S_S is not included.

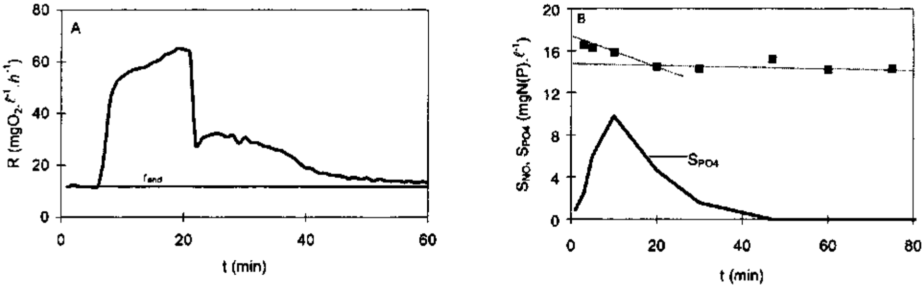

Figure 3.16 The OUR- (A) and NUR-curves (B) after addition of acetate to activated sludge containing active X_{PAO} (AS4).

A much higher Y_{HD} than Y_H was found for AS4 (0.77 vs. 0.66). This would implicate that a part of added COD could not be recovered during the NUR-test because of storage. The obtained S_{NO}-curve with two oxidation phases is very typical (Figure 3.16B). However, the second S_{NO} utilisation phase, normally considered as endogenous, could be higher because of simultaneous utilisation of an unknown fraction of stored previously acetate.

3.3.3 WASTEWATER CHARACTERISATION

From OUR- and NUR-tests the S_S and X_S concentrations could be estimated using an optimisation procedure to identify wastewater respirograms. To model the denitrification process using the same equations as for the aerobic substrate oxidation, not only the actual values of reduction factors are essential. Before a model can be used one has to make sure that the similar fractions of organic matter are recognised under aerobic and anoxic conditions. The comparison of aerobic and anoxic wastewater characterisation in terms of S_S- and X_S-fractions is given in Table 3.8.

Table 3.8 Estimated actual concentrations of S_S and X_S in settled domestic wastewater from corresponding OUR- and NUR-tests using different activated sludge samples.

Activated sludge sample	Respiration test	S_S (mgCOD.ℓ$^{-1}$)	X_S (mgCOD.ℓ$^{-1}$)
AS 1	OUR	63.3	259
	NUR	52.4	259*
AS 2	OUR	60.7	293
	NUR	50.8	293*
AS 3b	OUR	5.7	134
	NUR	4.8	148
AS 4	OUR	68.2	318
	NUR	97.3	318*
AS 5	OUR	49.1	166
	NUR	53.1	152

* X_S-values were taken as estimated from corresponding OUR-tests.

The estimation of wastewater fractions was performed using the estimated values of Y_H and Y_{HD}. For wastewater samples where yield was not estimated or where the estimated value was doubtful (e.g. AS4), the value of Y_H=0.67 was used while for Y_{HD} a 10% lower value was used (Y_{HD}=0.6)

The results listed in Table 3.8 show in general similarities in obtained S_S-fractions. The smallest deviation occurred in the tests performed with activated sludge AS3b and AS5 (Table 3.2) adapted to denitrifying conditions. The biggest deviation was noted from the tests with activated sludge from an A^2/O-system (AS4) where storage of COD disabled to obtain a reliable fractionation of biodegradable COD (see also §2.3.4).

More insight in the topic of equality of wastewater fractions recognised under aerobic and anoxic conditions can be obtained through a validation of the simplified denitrification model with wastewater characteristics obtained from an OUR-test.

3.5 CONCLUSIONS

Anoxic and aerobic respiration of activated sludge expose commonly three rates after addition of wastewater as organic carbon source: high respiration on S_S, a lower respiration on products of X_S-hydrolysis, and the lowest on endogenous substrate. The majority of observations reported in literature, as well as experimental results of this study indicate that all three respiration rates expose lower values with N-oxides than with oxygen as electron acceptor. In denitrification model approach three reductions factors: η_1, η_2 and η_3 reflect decreased rates of subsequent processes under anoxic conditions.

In this chapter a methodology is proposed to estimate reduction factors enabling to model the denitrification process using the same equation as for aerobic substrate utilisation. This methodology implements two respiration tests: the oxygen utilisation rate (OUR)- and the nitrate utilisation rate (NUR)-test.

Based on literature and results from the methodology validation it can be concluded that the values of the reduction factors are not uniform and not constant but vary as a function of characteristics of activated sludge, influenced in turn by operational conditions, wastewater characteristics and process configuration.

The most sensitive and varying is the factor η_1 for a decreased rate of the S_S-oxidation. In this study the lowest η_1= 0.22 was found for a fully aerated low loaded system, subjected 'suddenly' to denitrifying conditions in the NUR-test. For activated sludge that was exposed for some days to anoxic conditions this value was somewhat higher (η_1=0.4). For two denitrifying sludge samples, from an alternating and A^2/O systems, η_1 showed higher values (0.57 and 0.54).

The reduction factor η_2 for hydrolysis under anoxic conditions exposed less variations than η_1 and oscillated around 0.6-0.7. The configuration of the system and the operational parameters did not have an evident influence on η_2. The estimated η_2 is in the range reported in literature and advised as default value for modelling practice. The results of this study would not promote the necessity to carry extensive investigations on this parameter.
The third reduction factor, η_3, exposed values in the range of 0.2 to 0.4, and these are much lower than reported in literature. The η_3 can be calculated from a direct comparison of endogenous S_{NO}-oxygen equivalent (NOE) respiration rate with the oxygen respiration rate. The discrepancy with literature values as well as the simplicity of the estimation method promotes the necessity of the estimation of η_3 for a particular activated sludge.

From a limited number of respiration tests with acetate, the aerobic heterotrophic yield (Y_H) turned out to be approximately 10% higher than the corresponding anoxic yield (Y_{HD}) from nitrifying and nitrifying-denitrifying systems what confirms some reports from literature. The estimation of Y_H and Y_{HD} using activated sludge containing X_{PAO} with the proposed methodology is not advised because processes of substrate storage and storage product utilisation are not modelled. Default values from accepted model approaches are then an option.

The characterisation of biodegradable wastewater fractions, S_S and X_S, under aerobic and anoxic conditions result in similar values for activated sludge originating from nitrifying-denitrifying systems. Non-adapted activated sludge exposed more deviation between the estimated S_S-fractions from OUR- and NUR-tests. The most 'problematic' is wastewater characterisation with the presence of X_{PAO} in activated sludge. To prove the equality of the magnitude of S_S and X_S under aerobic and anoxic conditions, the validation of the simplified denitrification model should be carried out with wastewater characteristics from one type of respiration measurement (OUR or NUR).

LIST OF SYMBOLS AND ABBREVIATIONS

ASM	Activated Sludge Model
ATU	allylthiourea
b_H	aerobic decay coefficient of heterotrophic biomass (d^{-1})
b_{HD}	anoxic decay coefficient of heterotrophic biomass (d^{-1})
CSTR	completely stirred-tank reactor
DO	dissolved oxygen concentration ($mgO_2.\ell^{-1}$)
f_{ww}	volumetric wastewater fraction in the total experimental batch volume ($\ell.\ell^{-1}$)
k_{Dend}	specific endogenous denitrification rate ($mgN.gVSS^{-1}.h^{-1}$)
k_{end}	specific aerobic endogenous respiration rate ($mgO_2.gVSS^{-1}.h^{-1}$)
k_H	hydrolysis rate of X_S (h^{-1} or d^{-1})
k_{SS}	specific S_S oxidation rate, subscript: m - maximum ($mgCOD.gVSS^{-1}.h$)
K_S	half-saturation coefficient for S_S oxidation ($mgCOD.\ell^{-1}$)
NOE	nitrate oxygen equivalent ($mgO_2.\ell^{-1}$)
NUR	nitrate utilisation rate ($mgN.\ell^{-1}.h^{-1}$)
OUR	oxygen utilisation rate ($mgO_2.\ell^{-1}.h^{-1}$)
q_R	wastewater flow through the respiration vessel ($\ell.h^{-1}$)
R	aerobic respiration rate ($mgO_2.\ell^{-1}.h^{-1}$)
r_{Dend}	endogenous volumetric denitrification rate ($mgO_2.\ell^{-1}.h^{-1}$)
r_{end}	aerobic volumetric endogenous respiration rate ($mgO_2.\ell^{-1}.h^{-1}$)
S_{Ac}	acetate concentration in respiration test ($mgCOD.\ell^{-1}$)
SBR	sequencing batch reactor
SRT	solid retention time (d)
S/X_V	initial substrate to biomass ratio in respiration batch test ($g\ COD.gVSS^{-1}$)
S_{NH}	ammonia-nitrogen ($mgN.\ell^{-1}$)
S_{NO}	sum nitrate and nitrite-nitrate equivalent nitrogen ($mgN.\ell^{-1}$)
S_{NO2}	nitrite-nitrogen ($mgN.\ell^{-1}$)
S_{NO3}	nitrate-nitrogen ($mgN.\ell^{-1}$)
S_{O2}	oxygen concentration ($mgO_2.\ell^{-1}$)
S_S	soluble, readily biodegradable COD ($mgCOD.\ell^{-1}$)
V_B	total volume of the batch for respiration tests (ℓ)
V_R	total volume of the respiration vessel in OUR-test (ℓ)
X_H	heterotrophic biomass fraction ($mgCOD.\ell^{-1}$)
X_{HD}	heterotrophic denitrifying biomass fraction ($mgCOD.\ell^{-1}$)
X_{PAO}	phosphate accumulating organisms ($mgCOD.\ell^{-1}$)
X_S	particulate, slowly biodegradable COD ($mgCOD.\ell^{-1}$)
X_{STO}	internal cell storage products ($mgCOD.\ell^{-1}$)
X_V	concentration of volatile fraction of biomass ($g.\ell^{-1}$)
Y_H	aerobic heterotrophic yield ($mgCOD.mgCOD^{-1}$)
Y_{HD}	anoxic heterotrophic yield ($mgCOD.mgCOD^{-1}$)
η	reduction factor for anoxic substrate utilisation; often BOD_5 (literature)
η_{NO}	reduction factor(s) other than η_g, η_H and η_E (literature)
η_E	reduction factor for anoxic endogenous respiration (literature)
η_g	reduction factor for heterotrophs growth under anoxic conditions (literature)
η_H	reduction factors for anoxic hydrolysis (literature)
η_1	reduction factor for anoxic oxidation of S_S (this study)
η_2	reduction factors for anoxic hydrolysis (this study)
η_3	reduction factor for anoxic endogenous respiration (this study)
μ_H	aerobic specific growth of heterotrophs (d^{-1})
μ_{HD}	anoxic specific growth of heterotrophs (d^{-1})

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4

Respiration based simplified nitrification-denitrification model. Part I: model development

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ABSTRACT

Many models have been proposed in the last decades for the description of the activated sludge process. The most advanced allow for dynamic simulation of a single sludge process involving nitrification, denitrification and biological phosphorus removal. Calibration of advanced models requires an input of a significant number of parameters. Since the estimation of each parameter is difficult and time consuming, the choice of default values is an option but it can lead to erroneous predictions of reality. Use of complex models is inconvenient for applications like control or monitoring because it creates computational and analytical efforts. Simplified models, describing a reduced number of processes, and involving a small number of parameters, constitute an alternative. For an optimal implementation of simplified models a reliable method to obtain its actual parameters is required.

In this chapter a model is presented in which the existing simplified model for nitrification and aerobic oxidation of biodegradable COD, as described by BROUWER AND KLAPWIJK (1997) and BROUWER ET AL., (1998) was extended with a denitrification step. A characteristic feature of the resulting simplified nitrification-denitrification model was that substrate conversion was not modelled via the growth of appropriate groups of micro-organisms. Instead, experimentally estimated conversion rates were used, what contributed in a reduction of model components with regards to advanced approaches. When the conversion rates are frequently actualised, changes in biomass activity are included, despite of a variation in operational and environmental conditions. Regarding wastewater characterisation a compromise between complexity and simplicity was chosen by defining only three fractions for COD- and nitrogen conversion. These are the previously introduced fractions S_S and X_S and additionally nitrifiable nitrogen (S_{NHn}). For a frequent assessment of the majority of model parameters and wastewater characterisation, a side-stream aerobic respiration based control unit is necessary.

4.1 INTRODUCTION: DENITRIFICATION ASPECTS IN ACTIVATED SLUDGE MODELS

4.1.1 GENERAL

A lack of methods to predict the potential of treatment systems to remove required groups of wastewater components focused the attention on the development of mathematical models to identify and describe the kinetics of the systems. The development of mechanistic activated sludge models has passed through several stages by incorporating an increasing number of processes from which organic matter removal, nitrification, denitrification and phosphorus removal are the most significant. Improving fundamental knowledge about these processes and the availability of measurement techniques for the estimation of model parameters were driving forces in the improvement of models. Due to the fact that processes occur mostly in single sludge systems, models are obviously complex and characterised by a large number of reactions and a large number of components.

Several approaches are the conceptual base for the creation of a mechanistic model (e.g. ANDREWS, 1992, VAN LOOSDRECHT, 1995). For the purpose of this chapter two general model groups are of importance. Regarding the rate of complexity the models are divided into:

- complex models - attempting to include a high number of processes, and
- simplified models - restricted to a minimum number of processes.

Concerning the dynamics of the process description the models can be further grouped into:

- steady state models - restricted to constant wastewater flow and composition, and
- dynamic models - facing changes in wastewater flow and composition.

There exists no unified model to serve all model objectives as design, optimisation and control. For design purposes usually steady-state models are used and dynamic models can be used for optimisation, training and design assistance. A large number of model objectives is the main reason why a large number of model approaches exist.

In this section some representatives of the activated sludge model categories were briefly reviewed. Especially model aspects were presented that relate to biological nitrogen removal with a special attention on the denitrification process in single, suspended growth activated sludge systems. The objective was to give an impression about the variety and the rate of complexity or simplicity of the existing approaches in any way relevant to the developed simplified nitrification-denitrification model as described further in this chapter.

4.1.2 STEADY-STATE NITRIFICATION-DENITRIFICATION MODELS

The steady state denitrification model of VAN HAANDEL ET AL. (1981a,b, 1982) was one of the first denitrification approaches serving design purposes. It was developed based on the results from intensive investigations in a plug-flow Wuhrmann (post-denitrification) system and a modified Ludzack-Ettinger (pre-denitrification) system. By measuring the nitrate concentration along the length of the plug-flow anoxic reactors typical concentration profiles were observed. In a pre-denitrification reactor a two-phase linear profile was measured: (1) a fast primary phase with a short duration and (2) a slower secondary phase that persisted for the balance of time in a reactor. In a post-denitrification reactor a single linear nitrate reduction profile (3) was observed (STERN AND MARAIS, 1974, WILSON AND MARAIS, 1976, MARSDEN AND MARAIS, 1976, Figure 3.1). It was found that the amount of nitrate reduced in the first phase (ΔN_{1s}, mgN.ℓ^{-1}) was proportional to the influent biodegradable COD-concentration (S_{bi}) and independent on temperature, sludge concentration and recycle ratio (STERN AND MARAIS, 1974). The remaining amounts of nitrate reduced in the second and third phase (ΔN_{2s} and ΔN_{3s} respectively) were described by the rate constants K_2 and K_3, which were independent on sludge retention time (SRT), influent COD, sludge concentration and recycle ratios. Consequently the overall nitrate reduction in pre- and post-denitrification systems (ΔN_s), in steady-state conditions and under no limitation of organic substrate and nitrate, was expressed with equation 4.1:

$$\Delta N_S = \Delta N_{1s} + \Delta N_{2s} + \Delta N_{3s} = \alpha S_{bi} + K_2 X_a R_1 + K_3 X_a R_3\text{; mgN.}\ell^{-1} \tag{4.1}$$

where:

α	proportionality constant (mgN.mg biodegradable COD^{-1});
R_1, R_3	actual retention times in pre- and post-anoxic reactor respectively (*h* or d);
X_a	active mass concentration (g.ℓ^{-1});
K_2 and K_3	denitrification rate constants in pre- and post-denitrification reactor (mgN.gX_a^{-1}.d^{-1}).

The denitrification potential for the pre- and post-denitrification reactor enables to estimate the nitrate-effluent concentration and was formulated as follows:

$$DP = S_{bi}\left\{\alpha + \frac{Y_H SRT}{(1 + b_{HT} SRT)} \cdot (K_2 \cdot f_{x1} + K_3 \cdot f_{x3})\right\}\text{; mgN.}\ell^{-1} \tag{4.2}$$

where:

Y_H	yield coefficient (mgVSS.mgCOD^{-1})
b_{HT}	endogenous respiration rate (d^{-1})
f_{x1} , f_{x3}	fraction of sludge mass in primary and secondary anoxic reactor

Characteristic for this approach was that empirical constant values were recommended, which are related to the denitrification process (α, K_2, K_3). Regarding the nitrification process, its design was based on the minimum sludge age. For estimation, empirical kinetic parameters as maximum growth- and decay rates of nitrifiers were used, corrected by appropriate functions for pH and temperature. Also the wastewater fractionation regarding subsequent nitrogen forms in the influent and the amount of nitrogen used for biomass synthesis were calculated using empirical factors (EKAMA ET AL., 1979, VAN HAANDEL AND MARAIS, 1981).

4.1.3 ADVANCED DYNAMIC MODELS

The most often implemented advanced dynamic activated sludge models (ASM's) are developed by the IAWQ Task Group on *Mathematical Modelling for Design and Operation of Biological Wastewater Treatment Processes* and were the results of a compilation of existing approaches (e.g. DOLD ET AL., 1980, VAN HAANDEL ET AL., 1981, WENTZEL ET AL., 1988, 1992).

The first activated sludge model - **ASM1** (HENZE ET AL., 1987) describes biodegradable COD removal, nitrification and denitrification. The wastewater is characterised in detail by components grouped in organic and nitrogen fractions. The total COD is the sum of soluble readily biodegradable COD (S_S), particulate slowly biodegradable COD (X_S) and soluble and particulate inert COD (S_I and X_I respectively). Influent nitrogen is present in five forms: ammonia (S_{NH}) inert organic soluble (S_{NI}) and particulate (X_{NI}) and readily (S_{ND}) and slowly (X_{ND}) biodegradable organic nitrogen. Two general groups of microrganisms are distinguished within the activated sludge: autotrophs and heterotrophs. The conversion rates of readily degradable substrate (S_{NH} and S_S) relate to the growth rates of micro-organisms and are described using mixed order Monod kinetics. For autotrophs (X_A) S_{NH} is a supply of energy while heterotrophs (X_H) utilise directly S_S, a part for synthesis and a part for energy generation required for cell growth. The fraction X_S undergoes cell external hydrolysis to S_S, a process that is described with a surface limited reaction. No energy utilisation, thus no electron acceptor utilisation is associated with hydrolysis. The specific rate of X_S-hydrolysis is lower than the rate of S_S-utilisation. When only X_S is present, the rate of biomass growth is limited by the rate of hydrolysis. Moreover, hydrolysis is catalysed with a slower rate under anoxic than aerobic conditions, what is expressed in ASM1 by the reduction factor η_H.

Denitrification is modelled via anoxic growth (μ_H) of heterotrophs (X_H) at the precense of S_S. It is described as a one-step reaction, where nitrate (S_{NO3}) is directly transformed to dinitrogen. The maximum anoxic growth rate of heterotrophs is reduced with respect to the aerobic rate with the factor η_g. The presence of oxygen reduces the denitrification rate what is expressed by an oxygen switching function: $K_O/(S_O + K_O)$. Anoxic growth depends on the concentration of S_{NO3} and is expressed with a saturation function: $S_{NO3}/(S_{NO3} + K_{NO3})$. The matrix presented in Table 4.1 incorporates two processes of ASM1 related to denitrification.

Table 4.1 Process kinetics and stoichiometry of anoxic processes in ASM1 (the numbers of the processes j as in original model version, HENZE ET AL., 1987)

Component		S_S	X_S	X_H	S_{NO3}	**Process rate**
j	**Process**					
2	Anoxic growth of X_H	$-\frac{1}{Y_H}$		1	$-\frac{1-Y_H}{2.86 \cdot Y_H}$	$\mu_H \cdot \eta_g \frac{S_S}{K_S + S_S} \frac{K_O}{S_O + K_O} \frac{S_{NO3}}{K_{NO3} + S_{NO3}} X_H$
7	Anoxic hydrolysis	1	-1			$k_H \cdot \eta_H \frac{X_S / X_H}{K_X + X_S / X_H} \frac{K_O}{S_O + K_O} \frac{S_{NO3}}{K_{NO3} + S_{NO3}} X_H$

The nitrification process is modelled as a one-step Monod reaction of the oxidation of S_{NH} to S_{NO3} through autotrophic growth. Nitrification only takes place under aerobic conditions. Hydrolysis of entrapped X_{ND} (proportional to the rate of X_S-hydrolysis) yields S_{ND}, which is converted to S_{NH} as a result of the ammonification process (first-order reaction),. The fraction S_{NH} is required for the growth of biomass, and as energy source for X_A in the nitrification process. The nitrification model is presented in matrix notation in Table 4.2.

Table 4.2 Nitrification kinetics and stoichiometry in ASM1 (HENZE ET AL., 1987)

Component		**S_{NH}**	**X_A**	**S_O**	**S_{NO3}**	**S_{ALK}**	**Process rate**
	Process						
3	Autotrophs growth	$-i_{XB}-\frac{1}{Y_A}$	1	$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-\frac{i_{XB}}{14}-\frac{1}{7Y_A}$	$\mu_A\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_O}{K_O+S_O}X_A$

The biomass decay and lysis are ruled by several mechanisms, where X_S and X_{ND} (re-entering the cycle) and X_I (inert) are the final products (DOLD ET AL., 1980). The rate of decay in ASM1 is independent on the level and sort of electron acceptor.

ASM1 was a decade later modified to **ASM2** (HENZE ET AL., 1996) and was extended with biological phosphorus removal processes. ASM2 is more complex, not only because of the increased number of involved processes but also because the wastewater and activated sludge composition are described in more detail. The fraction S_S is subdivided in a fermentable fraction (S_F) and products of fermentation (S_A). The anoxic growth of heterotrophs takes place on both fractions and is reduced with respect to the aerobic rate by a reduction factor η_{NO} (η_g in ASM1) The modification of denitrification with regards to ASM1 is shown in Table 4.3. The growth rate of any micro-organism groups may be limited by nutrient concentration, alkalinity and temperature. The effect of temperature is modelled with an exponential expression ($a^{(T-20)}$), where the factor 'a' varies for various processes. As third group of micro-organisms, phosphorus accumulating organisms (X_{PAO}) are introduced. The hydrolysis and ammonification of N-fractions is in ASM2 simplified in comparison to ASM1 because S_{ND} and X_{ND} are assumed to be a constant fraction of S_F and X_S respectively (i_{NSF}, i_{NXS}).

Increasing experimental evidence of phosphate uptake under anoxic conditions (COMEAU ET AL., 1986, VLEKKE ET AL., 1988, KERRN-JESPERSEN AND HENZE, 1993, KUBA ET AL., 1993, BORTONE ET AL., 1994, MEINHOLD ET AL., 1999) led to the development of **ASM2d** (HENZE ET AL., 1999), being a minor extension of ASM2. Two additional processes are included describing the fact that X_{PAO}'s can utilise their storage products to convey denitrification under anoxic conditions. These are anoxic storage of polyphosphate and anoxic growth of X_{PAO}'s. The rates of both processes are reduced relative to its value under aerobic conditions by a factor η_{NO}. This accounts for the fact that not all X_{PAO}'s are capable of denitrification and additionally that these X_{PAO}'s which denitrify, perform this process with a reduced rate. With respect to ASM2, the two additional processes are presented in matrix form in Table 4.4.

ASM3 has to be seen as a modified version of ASM1 (GUJER ET AL., 1999). A new functional component is added: a cell internal storage product (X_{STO}) of heterotrophic organisms including poly-hydroxy-alkanoates (PHA), glycogen, etc. All S_S from the influent is first stored in the form of X_{STO} and later utilised by biomass. The rate of storage under denitrifying conditions is lower than under aerobic (η_{NO}). In place of the decay process as described in other ASM's, three endogenous respiration processes are introduced: endogenous respiration for X_H, respiration of X_{STO} for X_H and endogenous respiration for X_A. They describe any form of biomass loss as well as decay of storage products, both under anoxic and aerobic conditions. The endogenous rates under denitrifying conditions are lower compared with aerobic conditions. The differentiation between aerobic and anoxic heterotrophic yield coefficient is introduced. The expressions describing new process approaches under anoxic conditions are presented in Table 4.5.

For certain purposes, e.g. control strategies or 'quick' analysis of process potential, implementation of models with a large state vector (several classes of micro-organisms, detailed fractionation of wastewater, large number of kinetic and stoichiometric coefficients) may create a computational problem. Estimation of the parameter values for a particular situation is complex and a frequent update of sensitive parameters is hardly possible (analytical problem). The use of 'typical' default values may lead to an erroneous reflection of reality because of the unique, specific character of wastewater and activated sludge (depending on location, configuration, etc.). In many cases simplified models constitute an alternative.

4.1.4 SIMPLIFIED DYNAMIC MODELS

Simplified activated sludge models have been successfully used for control and monitoring purposes (e.g. VAN HAANDEL ET AL., 1981b, ISAACS ET AL., 1994, ISAACS AND HENZE, 1995, ZHAO ET AL., 1994a,b, 1995, 1999, BROUWER AND KLAPWIJK, 1997, BROUWER ET AL., 1998). One way of model simplification is to freeze the slow dynamics of the process, so microorganisms are not explicitly modelled. Simplified models are not suitable for detailed design. When applied in an adaptive fashion, by which estimated values of the parameters are periodically updated, simplified models can be applied in control schemes involving a relatively short prediction window (ISAACS AND HENZE, 1995).

One of the first simplified denitrification approaches was the model of VAN HAANDEL ET AL. (1982) and EKAMA ET AL., (1983). Accepting the presence of two biodegradable COD-fractions in municipal wastewater, the denitrification process behaviour could be expressed qualitatively in terms of the general aerobic model. A quantitative description required the change in the empirical constant that describes the slower utilisation rate of X_S under anoxic conditions ($K_{m,XS}''$). The anoxic degradation of S_S and X_S was independent on each other and described with substrate limiting Monod equations. The overall utilisation of nitrate is shown in matrix form in Table 4.6

Table 4.3 Process kinetics and stoichiometry of denitrification in **ASM2** modified with respect to ASM1 (HENZE ET AL., 1996)[1)]

Component i		S_F	S_A	X_H	S_{NO3}	Process rate
j	Process					
6	Anoxic growth of heterotrophs on S_F	$-\frac{1}{Y_H}$		1	$-\frac{1-Y_H}{2.86\cdot Y_H}$	$\mu_H\eta_g\frac{S_F}{K_F+S_F}\frac{S_F}{S_F+S_A}\frac{K_O}{S_O+K_O}\frac{S_{NO3}}{K_{NO3}+S_{NO3}}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{PO4}}{K_{PO4}+S_{PO4}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}X_H$
7	Anoxic growth of heterotrophs on S_A		$-\frac{1}{Y_H}$	1	$-\frac{1-Y_H}{2.86\cdot Y_H}$	$\mu_H\eta_g\frac{S_A}{K_A+S_A}\frac{S_A}{S_F+S_A}\frac{K_O}{S_O+K_O}\frac{S_{NO3}}{K_{NO3}+S_{NO3}}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{PO4}}{K_{PO4}+S_{PO4}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}X_H$

Table 4.4 Process kinetics and stoichiometry in **ASM2d** related to denitrification additional to these in ASM2 (the values of v_j can be computed from conservation; for details (HENZE ET AL., 1999)[1)]

Component i		S_{NO3}	S_{PO4}	X_{PP}	X_{PHA}	X_{PAO}	Process rate
j	Process						
12	Anoxic storage of X_{PP}	$v_{12,NO3}$	-1	1	$-Y_{PHA}$		$q_{PP}\eta_{NO}\frac{X_{PHA}/X_{PAO}}{K_{PHA}+X_{PHA}/X_{PAO}}\frac{K_{MAX}-X_{PP}/X_{PAO}}{K_{PP}+K_{MAX}-X_{PP}/X_{PAO}}\frac{S_O}{K_O+S_O}\frac{K_O}{S_O}\frac{S_{NO3}}{K_{NO3}+S_{NO3}}\frac{S_{PO4}}{K_{PO4}+S_{PO4}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}X_{PAO}$
14	Anoxic growth of X_{PAO}	$v_{14,NO3}$	$-i_{PBM}$		$-\frac{1}{Y_H}$	1	$\mu_{PAO}\eta_{NO}\frac{X_{PHA}/X_{PAO}}{K_{PHA}+X_{PHA}/X_{PAO}}\frac{S_O}{K_O+S_O}\frac{K_O}{S_O}\frac{S_{NO3}}{K_{NO3}+S_{NO3}}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{PO4}}{K_{PO4}+S_{PO4}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}X_{PAO}$

Table 4.5 Process kinetics and stoichiometry of denitrification in **ASM3** modified with respect to ASM1 (the values of x_j and y_j can be obtained from mass and charge conservation and compositions; for details GUJER ET AL., 1999)[1)]

Component i		S_S	S_{NH}	S_{N2}	S_{NO3}	X_{STO}	X_H	X_I	X_A	Process rate
j	Process									
3	Anoxic storage of COD	-1	y_3	$-x_3$	x_3	$Y_{STO,NO3}$				$k_{STO}\eta_{NO}\frac{K_O}{S_O+K_O}\frac{S_{NO3}}{K_{NO3}+S_{NO3}}\frac{S_S}{K_S+S_S}X_H$
5	Anoxic growth of heterotrophs		y_5	$-x_5$	x_5	$-\frac{1}{Y_{H,NO3}}$	1			$\mu_H\cdot\eta_{NO}\frac{X_{STO}/X_H}{K_{STO}+X_{STO}/X_H}\frac{K_O}{S_O+K_O}\frac{S_{NO3}}{K_{NO3}+S_{NO3}}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}X_H$
7	Anoxic endogenous respiration X_H		y_7	$-x_7$	x_7		-1	f_I		$b_{H,NO}\frac{K_O}{K_O+S_{NO}}\frac{S_{NO3}}{K_{NO3}+S_{NO3}}X_H$
9	Anoxic respiration of X_{STO}			$-x_9$	x_9	-1				$b_{STO,NO}\frac{K_O}{K_O+S_O}\frac{S_{NO3}}{K_{NO3}+S_{NO3}}X_{STO}$
12	Anoxic endogenous respiration X_A		y_{12}	$-x_{12}$	x_{12}			f_I	-1	$b_{A,NO}\frac{K_O}{K_O+S_O}\frac{S_{NO3}}{K_{NO3}+S_{NO3}}X_A$

[1)] All symbols (except of coefficients x_j, y_j, and v_j) are defined at the end of this chapter (List of symbols and abbreviations)

Table 4.6 Process kinetics and stoichiometry for denitrification process in model of VAN HAANDEL ET AL. (1981)

Component		S_S	X_S	S_{NO3}	**Process rate**
	Process				
1	Anoxic oxidation of S_S	-1		$-\frac{1-Y_H}{2.86}$	$K_{SSm}\frac{S_s}{S_S+K_S}X_a$
2	Anoxic oxidation of X_S		-1	$-\frac{1-Y_H}{2.86}$	$K^{\prime}_{XSm}\frac{P\cdot X_S}{P\cdot X_S+K_{XS}X_a}X_a$

Another example of a simplified nitrification-denitrification model where long-term changes in population dynamics are not described is the model of ISAACS ET AL. (1994). Only two bulk components are considered: ammonia- and nitrate-nitrogen (S_{NH} and S_{NO3}). The nitrification and denitrification rates are described using simple Monod-type limitation kinetics (Table 4.7) whose parameter estimates are updated periodically using on-line ammonia and nitrate measurements. Release of ammonia due to cell lysis and hydrolysis as well as its incorporation into biomass are not modelled. It is also not encountered for the transition times between aerobic and anoxic conditions where both processes may appear simultaneously at reduced rates. Since the half-saturation coefficient for nitrate is low and model predictions were not sensitive to it, a further simplification can be attained by using zero order kinetics for the denitrification rate.

Table 4.7 Nitrification and denitrification process kinetics in simplified model of ISAACS ET AL., (1994)

Component		S_{NH}	S_{NO3}	**Process rate**
	Process			
1	Nitrification	-1	1	$r_{NHm}\frac{S_{NH}}{K_{NH}+S_{NH}}$
2	Denitrification		-1	$r_{NOm}\frac{S_{NO}}{K_{NO}+S_{NO}}$

4.1.5 OBJECTIVE OF THE STUDY

The objective of this study was to develop a simplified denitrification model to predict the denitrification potential of single sludge activated sludge systems. To attain this, the existing simplified model for nitrification and aerobic oxidation of biodegradable COD (BROUWER AND KLAPWIJK, 1995, BROUWER ET AL., 1998) was extended with the denitrification process. This new simplified nitrification-denitrification approach is promoted as an alternative to existing complex approaches. The conceptual basis for the description of the processes remains similar to existing and validated complex models (such as ASM's). Regarding complexity, an attempt was undertaken to reduce the number of processes, state variables and process parameters. This can be partially attained by excluding the description of population dynamics, a method commonly used in simplified approaches. Despite of simplicity, objective was to attain a quite accurate reflection of the actual N-removal potential. That is why attention was paid on a relevant detailed wastewater characterisation, as well as the kinetics of the involved processes. To reflect the dynamic character of the process, a frequent update of model components was performed.

To minimise the analytical effort for the estimation of model components one type of measurements was employed. The applicability of respirometry was examined as a technique allowing for estimating biodegradable wastewater fractions and conversion kinetics.

4.2 DEVELOPMENT OF A NEW SIMPLIFIED NITRIFICATION-DENITRIFICATION MODEL

4.2.1 AEROBIC MODEL FOR NITRIFICATION AND BIODEGRADABLE COD-OXIDATION

Wastewater components. The influent wastewater in the simplified aerobic model was described by only three components:

- soluble readily biodegradable COD (S_S);
- particulate slowly biodegradable COD (X_S);
- nitrifiable nitrogen (S_{NHn}).

The component S_{NHn}, introduced primarily by BROUWER AND KLAPWIJK (1995), is not equivalent to S_{NH} from ASM's. The influent S_{NH}-fraction of ASM represents ammonia, which can be determined with standard chemical analysis. The S_{NHn} is defined as a fraction of influent nitrogen exclusively subjected to the nitrification process. The ammonia-N which is available for the nitrification process is the sum of influent ammonia (S_{NH} in ASM1) and ammonia produced by hydrolysis and ammonification of organic nitrogen (X_{ND} and S_{ND} in ASM1), diminished with the ammonia fraction used for biomass synthesis (both X_H and X_A). The amount of S_{NHn}, which can be measured with an aerobic respiration test, can be described using the following ASM terms:

$$S_{NHn} = S_{NH} + rX_S \cdot \frac{X_{ND}}{X_S} \cdot t_H + k_A S_{ND} X_H \cdot t_A - i_{XB} \mu_H X_H \cdot t_{gH} - (i_{XB} - \frac{1}{Y_A}) \mu_A X_A \cdot t_A \text{ ; mgN.}\ell^{-1} \qquad (4.3)$$

where:

r_{XS}	hydrolysis rate of X_S (mgCOD.ℓ^{-1}.h^{-1});
t_H	time available for X_S hydrolysis (h);
k_A	ammonification rate (ℓ.mg^{-1}.h^{-1});
t_A	time available for S_{ND} ammonification (h);
i_{XB}	N-fraction in biomass (mgN.mgCOD$_{cell}^{-1}$);
t_{gH}	time available for heterotrophic growth associated with actual S_S oxidation (h);
Y_A	yield coefficient for autotrophs (mgCOD$_{cell}$.mgN^{-1}).

Conversion processes. In the simplified model structure the microbial populations are frozen and only substrate conversions are modelled. Three of the five involved processes implicate the existence of three micro-organism groups: two types of autotrophs which are able to oxidise ammonia to nitrite (S_{NO2}) or to oxidise nitrite to nitrate (S_{NO3}), and one type of heterotrophs able to execute the oxidation of S_S. The fraction S_S originates from the influent and is produced from X_S-hydrolysis. The two-step nitrification, S_S-oxidation and endogenous respiration are related to oxygen consumption. For nitrification and aerobic oxidation of biodegradable COD the simplified model is presented in matrix form in Table 4.8 and described in more detail below.

Aerobic oxidation of S_S. The fraction S_S is directly oxidised by micro-organisms, according to the substrate limiting Monod-type relation.

Aerobic hydrolysis of X_S. Before X_S can be utilised by micro-organisms, it has to be converted into S_S via hydrolysis. Hydrolysis is modelled as a first-order reaction with respect to the X_S-concentration.

Endogenous respiration expresses utilisation of storage compounds, decay and lysis of the biomass and is modelled as a zero-order reaction.

Nitrification. Nitrification is modelled as a two-step oxidation process where in the first step S_{NHn} is oxidised to nitrite (S_{NO2}) and in the second step nitrite to nitrate (S_{NO3}). Both conversion steps are described with a substrate limiting Monod equation (Table 4.8).

Table 4.8 Simplified model for nitrification and aerobic conversions of biodegradable COD fractions (BROUWER AND KLAPWIJK, 1995, BROUWER ET AL., 1998)

Component		1	2	3	4	5	6	Process rate
	Process	**S_S**	**X_S**	**S_{O2}**	**S_{NH}**	**S_{NO2}**	**S_{NO3}**	
1	Aerobic oxidation of S_S	-1		$-(1-Y_H)$				$r_{SSm}\frac{S_S}{K_S+S_S}$
2	Aerobic hydrolysis of X_S	1	-1					$k_H \cdot X_S$
3	Endogenous respiration			-1				r_{end}
4	S_{NHn} oxidation (1st step nitrification)			-3.43	-1	1		$r_{SNHm}\frac{S_{NH}}{K_{NH}+S_{NH}}$
5	S_{NO2} oxidation (2nd step nitrification			-1.14		-1	1	$r_{SNO2m}\frac{S_{NO2}}{K_{NO2}+S_{NO2}}$

All processes consuming oxygen are normally reduced at decreasing oxygen concentrations. To model, for instance, the transition phases between aerobic and anoxic conditions, a hyperbolic oxygen switching function, such as used in ASM's, can be added. Saturation coefficients would attain different values for each process what certainly would make the whole process description more complex. For the model testing performed in the next chapter only strict aerobic and anoxic conditions were considered the oxygen switching functions were equal to unity.

4.2.2 EXTENSION OF THE AEROBIC MODEL WITH THE DENITRIFICATION PROCESS

In contrast to nitrification, denitrification is modelled as a one-step process in which nitrate is directly reduced to dinitrogen. This approach was chosen because the reduction of any N-oxide during denitrification depends on the availability of only one substrate (S_S) while the subsequent nitrification steps are related to another substrate (S_{NH} and S_{NO2} respectively). Nitrite that was not oxidised in the aerobic zone and enters the anoxic zone of a modelled reactor is converted back to nitrate using the conversion factor 0.6 ($0.6 \cdot S_{NO2} \Rightarrow S_{NO3}$). The factor 0.6 expresses the reduced COD demand when nitrite has to be denitrified instead of nitrate to dinitrogen (see also chapter 2, §2.3.1). A consequence of this approach is that nitrite can occur in the effluent when the final compartment of the modelled reactor is aerobic. When the last compartment is anoxic the effluent nitrate reflects the sum of nitrate and nitrite-nitrate equivalent ($S_{NO}=0.6 \cdot S_{NO2}+S_{NO3}$). The overall denitrification potential depends on the availability of S_S, which is determined by the concentration of S_S in the influent, the concentration of X_S, the rate of its hydrolysis and by the endogenous activity. The denitrification capacity depends on process kinetics and reactor configuration. It is assumed that the same amount of S_S and X_S is utilised under aerobic and anoxic conditions (chapter 3). The simplified denitrification model is presented in matrix form in Table 4.9 and explained in more detail below:

Table 4.9 Simplified denitrification model

Component		**1**	**2**	**7**	**Process rate**
	Process	**S_S**	**X_S**	**S_{NO}**	
6	Anoxic oxidation of S_S	-1		$-\left(\frac{1-Y_{HD}}{2.86}\right)$	$r_{SSm} \cdot \eta_1 \cdot \left(\frac{S_S}{K_S+S_S}\right) \cdot \left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)$
7	Anoxic hydrolysis of X_S	1	-1		$\eta_2 \cdot k_H \cdot X_S$
8	Anoxic endogenous respiration			$-\left(\frac{1}{2.86}\right)$	$\eta_3 \cdot r_{end}$

Anoxic oxidation of S_S. The anoxic S_S-oxidation is described with the same process rate equation as for aerobic oxidation (Table 4.8) but extended with the reduction factor η_1. The factor η_1 expresses any effects contributing in a decreased anoxic S_S-oxidation rate with regards to aerobic conditions (chapter 3).

Since at low nitrate concentrations the denitrification rate is decreased, the nitrate inhibition function is included in the model for S_S-oxidation. Also at certain DO-concentrations, the anoxic oxidation of S_S gets inhibited (§1.3.3). To model the transition phases between anoxic and aerobic conditions, an oxygen inhibition function, such as used in ASM's, can be added. For the model testing performed in the next chapter only strict anoxic or aerobic conditions will be assumed and the oxygen inhibition function is equal to unity.

Anoxic hydrolysis. The anoxic X_S-hydrolysis is described with the same process rate equation as aerobic hydrolysis (Table 4.8) but extended with the reduction factor η_2, expressing a slower rate of this process under anoxic conditions (chapter 3).

Anoxic endogenous denitrification. Because biomass population dynamics are not modelled, the anoxic processes of biomass decay, lysis, hydrolysis of lysis products and utilisation of resulting S_S are combined in the endogenous denitrification. Experimental evidence as well as literature (e.g. KLAPWIJK, 1978, GUJER ET AL., 1999, SIEGRIST ET AL., 1999, chapter 3 of this thesis) implicate that the anoxic endogenous respiration rate is lower than the aerobic rate what is expressed by the reduction factor η_3 (chapter 3).

4.3 ESTIMATION PROCEDURE FOR MODEL PARAMETERS

4.3.1 INTRODUCTION

In order to make use of a model it must be possible to determine its parameter values. In this paragraph an adjusted procedure is presented to estimate wastewater characteristics and stoichiometric and kinetic parameters of the presented simplified nitrification-denitrification model. A majority of the model parameters and wastewater characterisation can be estimated with aerobic respiration tests (OUR-tests) and for some parameters default values from literature can be taken. NUR-tests in combination with OUR-tests aim to estimate reduction factors for denitrification (chapter 3). The estimation procedure for some parameters should be carried out relatively frequent in a side-stream of the considered activated sludge reactor. With this approach variations in biomass activity are reflected in frequently updated conversion rates. This grounds the model approach of excluding microbial population dynamics subjected to variations in wastewater characteristics, resulting process parameters and environmental conditions.

4.3.2 THE RESPIRATION BASED CONTROL UNIT RESCUE

For the model parameters estimation procedure, the respiration based control unit RESCUE (for details see BROUWER AND KLAPWIJK, 1997) was used (Figure 4.1). The essential components of the RESCUE were an aerated batch reactor ($V_6=50\ \ell$) where endogenous activated sludge was mixed with a suitable substrate and a respiration vessel ($V_R=1.5\ \ell$) where the actual respiration rate was measured.

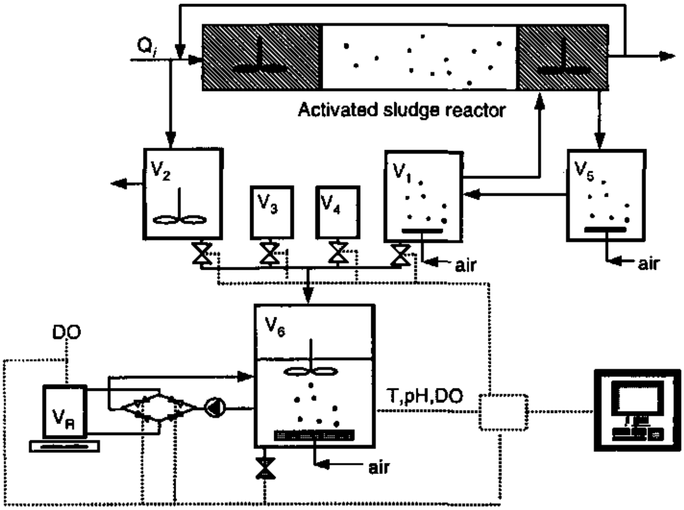

Figure 4.1 Side-stream respiration based control unit RESCUE, used for parameter estimation of the simplified nitrification-denitrification model, integrated with the activated sludge reactor.

Activated sludge was stored, equalised and aerated in an endogenous vessel (V_1=40 *ℓ*) and fed continuously with sludge from the additional vessel (V_5). Vessel V_5 was in turn continuously supplied with fresh sludge from the end of the modelled activated sludge reactor. To ensure the endogenous stage of examined sludge, the content of V_5 was aerated for approximately 2 *h*. The completely mixed influent storage vessel (V_2) was fed continuously with the same wastewater as for the modelled reactor. Nitrite and ammonium solutions ($NaNO_2$ and NH_4Cl) of a precisely known concentration were stored in bottles (V_3 and V_4 respectively). The pH and temperature in reactor V_6 were controlled on chosen set-points with respectively a pH-controller (Endress&Hauser, Liquisys CPM 240) and a heat exchanger (Julabo, MH, F25). The respiration unit was connected to a computer via an interface, which provided communication between the software of the computer and the instrumentation of RESCUE. The software that controlled the operation of the respiration unit was written in MATLAB. The measuring frequency of the respiration rate, pH and temperature was once per minute.

4.3.3 AEROBIC RESPIRATION TESTS FOR PARAMETER ESTIMATION

The estimation procedure for model parameters allowed to assess frequently wastewater components and their conversion kinetics. During one measurement cycle several respiration tests were performed with different substrates. Each cycle consisted basically of three steps in the sequence as presented in Figure 4.2 and described below.

STEP 1 **Estimation of nitrite-N (S_{NO2}) oxidation kinetics**

A known volume of endogenous activated sludge was pumped from V_1 to V_6 (Figure 4.1). When the respiration vessel (V_R) was filled with sludge, the measurement of the respiration rate started. After the endogenous respiration rate was stabilised (≈ 10 min) a known dose of $NaNO_2$-solution was added. The respiration rate was measured until the original endogenous respiration rate was detected again. The optimisation procedure started to fit the nitrite S_{O2}-respirogram with a Monod-type kinetic model of the S_{NO2}-oxidation (Table 4.8, process 5) and two parameters describing the second step of the nitrification: the maximum volumetric S_{NO2}-oxidation rate and its half-saturation coefficient from the Monod-type relation (r_{SNO2m}, K_{NO2}).

STEP 2 **Estimation of ammonia-N (S_{NH}) oxidation kinetics**

After the parameter identification procedure of the S_{O2}-respirogram with nitrite was successfully completed, a known dose of NH_4Cl-solution was spiked into reactor V_6. The same procedure as described in step 1 was repeated, with the difference that the obtained ammonia S_{O2}-respirogram was fitted with the total S_{NH}-oxidation model (Table 4.8, process 4 and 5). The kinetic parameters of the S_{NO2}-oxidation, obtained in the first estimation step, allowed to minimise a number of optimised parameters from the ammonia S_{O2}-respirogram. As a result of both experiments, the actual nitrification parameters (r_{SNO2m}, r_{NHm}, K_{NH}, K_{NO2}) were derived. Step 1 and 2 were repeated each 10-12 *h*.

STEP 3 Estimation of wastewater composition and oxidation kinetics

In the third estimation step an activated sludge from V_6 and V_R was replaced by a fresh portion from V_1 (Figure 4.1) and after the endogenous respiration rate was stabilised (10 min) a known volume of fresh wastewater was pumped from V_2. After all biodegradable wastewater components were oxidised and the endogenous respiration rate was detected again, an optimisation procedure started to fit the wastewater S_{O2}-respirogram with the model from Table 4.8. The estimated nitrification kinetics from step 1 and 2 allowed to minimise a number of parameters necessary to identify a respirogram. The parameters being optimised were the wastewater components: S_S, X_S and S_{NHn} and the oxidation/hydrolysis parameters (r_{SSm}, k_H, and optionally K_S). For a reliable identification of a wastewater S_{O2}-respirogram, a single measurement had to last for 1.5 till 2 h. Since the parameters optimisation procedure comprised a large number of parameters the initialisation was crucial for their reliable estimation. The third step was repeated 5 times, after which *the estimation procedure for nitrification kinetics started again.*

Additionally from each respirogram a volumetric endogenous respiration (r_{end}) rate of activated sludge could be measured without the necessity of model fitting.

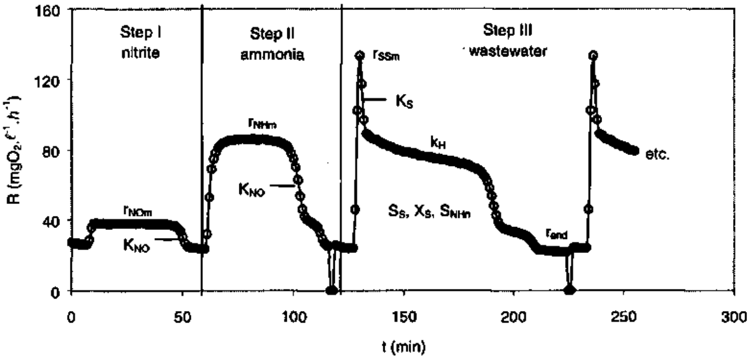

Figure 4.2 A sequence of S_{O2}-respirograms with different substrates for estimation of wastewater components and conversion kinetics of simplified nitrification-denitrification model.

An analysis of the ammonia S_{O2}-respirogram (second step of estimation procedure) explains why a two-step approach for nitrification was proposed in the simplified model instead of the commonly one-step approach. During the oxidation of S_{NH} to its final product S_{NO3}, the oxidation rate of S_{NO2} can be substantially lower than this of S_{NH}. In such a case the S_{NH}-respirogram will expose a typical so called 'nitrite tailing' (Figure 4.3). Modelling the ammonia respirogram with a one-step approach would result mostly in an unsatisfactory fit (plotted in Figure 4.3) and consequently an erroneous parameter estimation.

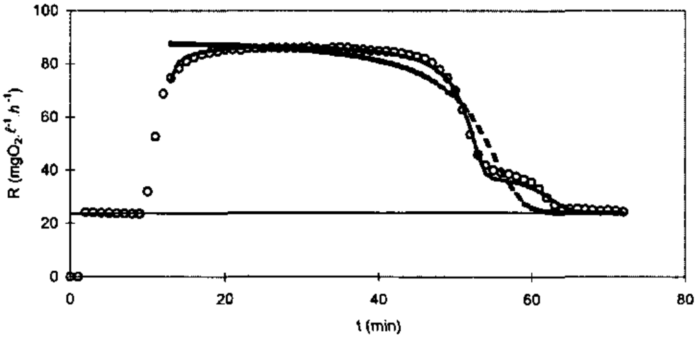

Figure 4.3 Ammonia S_{O2}-respirogram (o) with a common nitrite tailing, fitted with a one-step nitrification model such as e.g. ASM1 (dashed line) and a two-step nitrification model of BROUWER AND KLAPWIJK, 1995 (solid line).

4.3.4 ANOXIC RESPIRATION TESTS

To estimate the reduction factors for anoxic S_S-oxidation (η_1), anoxic hydrolysis (η_2) and anoxic endogenous respiration rate (η_3), the OUR- and NUR-test have to be performed in parallel with the considered activated sludge and a representative wastewater sample under well defined, adequate experimental conditions. The experimental procedure of a NUR-test, as well as the estimation procedure of anoxic reduction factors is described in detail in chapter 3. To minimise the experimental efforts, it was primarily assumed that if reduction factors were once estimated, their updating did not need to be carried out intensively. However, care should be taken for 'drastic' changes in plant operation. After a long period of rain weather and changes in the proportion between aerated and anoxic fractions, reduction factors should be updated.

Although many evidences indicate that the anoxic yield for heterotrophs (Y_{HD}) exposes a lower value than the aerobic yield (Y_H), in the presented version of the simplified nitrification-denitrification model Y_{HD} is equal to Y_H.

4.3.5 MODEL PARAMETERS

The list of all components of the simplified nitrification-denitrification model, their definitions, units and estimation methods is presented in Table 4.10.

To take into account the transition phases between an anoxic and aerobic environment in the activated sludge reactor, would probably contribute in a more precise reflection of reality. For this purpose the so-called oxygen switching functions ($S_O/(K_O+S_O)$) or oxygen inhibition functions ($K_O/(S_O+K_O)$) can be added to the appropriate processes in the simplified nitrification-denitrification model. Further improvement of the model can be achieved by differentiation of the heterotrophic yield coefficient for aerobic and anoxic conditions. These optional modifications are nevertheless not included in the testing procedures in the course of this thesis.

Table 4.10 Definition, estimation methods and occasionally default values of parameters of the simplified nitrification-denitrification model (M - measured, E - estimated, D - default).

Symbol	Parameter definition	Unit	Estimation procedure
	Wastewater characterisation (3)		
S_S	Soluble readily biodegradable COD	mgCOD.ℓ^{-1}	(E) fitting wastewater S_{O2}-respirogram with substrate oxidation/hydrolysis model (Table 4.8, processes 1-5)
X_S	Particulate slowly biodegradable COD	mgCOD.ℓ^{-1}	
S_{NHn}	Nitrifiable nitrogen	mgN.ℓ^{-1}	
	Process parameters (12) **Nitrification (4)**		
r_{NHm}	Maximum volumetric oxidation rate of S_{NH}	mgN.ℓ^{-1}.h^{-1}	(E) fitting ammonia S_{O2}-respirogram with S_{NH} conversion model (Table 4.8, processes 4-5)
K_{NH}	Half-saturation coefficient for S_{NH} oxidation	mgN.ℓ^{-1}	
r_{NO2m}	Maximum volumetric oxidation rate of S_{NO2}	mgN.ℓ^{-1}.h^{-1}	(E) fitting S_{NO2}-respirogram with S_{NO2} conversion model (Table 4.8, process 5)
K_{NO2}	Half-saturation coefficient for S_{NO2} oxidation	mgN.ℓ^{-1}	
	Aerobic oxidation of S_S (3)		
r_{SSm}	Maximum volumetric oxidation rate of S_S	mgCOD.ℓ^{-1}.h^{-1}	(E) fitting wastewater or acetate S_{O2}-respirogram with the oxidation/hydrolysis model
K_S	Half-saturation coefficient for S_S oxidation	mgCOD.ℓ^{-1}	(E) fitting wastewater or acetate S_{O2}-respirogram with the oxidation/hydrolysis model or (D) e.g. ASM2, K_S=4 (HENZE ET AL., 1996), BROUWER ET AL., (1998)
Y_H	Aerobic heterotrophic yield coefficient	(-)	(E) OUR-test with acetate as a substrate (chapter 3, § 3.3.1) or (D) Y_H=0.67 (HENZE ET AL., 1987)
	Hydrolysis of X_S (1)		
k_H	Rate constant for hydrolysis of X_S	h^{-1}	(E) fitting wastewater S_{O2}-respirogram with the oxidation/hydrolysis model (Table 4.8, process 2)
	Endogenous respiration (1)		
r_{end}	Aerobic volumetric endogenous respiration rate	mgO$_2$.ℓ^{-1}.h^{-1}	(M) OUR-test without addition of substrate
	Denitrification (4)		
η_1	Reduction factor for anoxic S_S oxidation	(-)	(E) fitting the NUR-curve with the aerobic model (Table 4.8) - η_1 and η_2 optimised parameters or (D) e.g. ASM2.
η_2	Reduction factor for anoxic hydrolysis of X_S	(-)	
η_3	Reduction factor for anoxic endogenous respiration	(-)	(M) OUR- and NUR-test without addition of substrate
K_{NO}	Inhibition coefficient for nitrate and nitrate-nitrite equivalent	mg N.ℓ^{-1}	(D) K_{NO}=0.5 (HENZE ET AL., 1996)

4.4 DISCUSSION

The simplified nitrification-denitrification model was developed conceptually based on advanced accepted approaches (e.g. ASM1 and ASM2). The simplification was attained by excluding the description of biomass population dynamics, the elimination of the influence of environmental factors (alkalinity/pH, oxygen, availability of nutrient and temperature) and by a less detailed wastewater characterisation. The comparison of complexity between the simplified model and ASM1 and ASM2 is visualised in table 4.11.

Table 4.11 Comparison of complexity for several activated sludge models in relation to COD- and nitrogen conversions.

Model	Processes	State variables	Process parameters	Wastewater components
Simplified N/D-model	8	5	13	3
ASM1	8	13	19	13
ASM2	11	13	37	13

The presented model is on the other hand characterised by a more detailed description of nitrification, denitrification and biodegradable COD-conversion processes than far simplified models (e.g. ISAACS ET AL., 1994). This brings the advantage of broader implementation possibilities. This will be validated and further discussed in chapter 5, 7 and 8. The main objectives of the development of the simplified nitrification-denitrification model were its implementations for:

- short-term analysis of a system by prediction of the N-removal potential and effluent N-quality;
- implementing control strategies to optimise directly nitrification and indirectly the denitrification processes.

To visualise the attained rate of simplicity in relation to complex advanced approaches, the comparison is given between the description of the S_S-utilisation rate (equation 4.4) in the simplified nitrification-denitrification model (second section of equation) and ASM2 (third section):

$$\frac{dS_S}{dt} = -r_{SSm} \cdot \frac{S_S}{K_S + S_S} = -\frac{\mu_H \cdot X_H}{Y_H} \cdot \frac{S_S}{K_S + S_S} \cdot \frac{S_{ALK}}{K_{ALK} + S_{ALK}} \cdot \frac{S_{NH}}{K_{NH} + S_{NH}} \cdot \frac{S_{PO4}}{K_{PO4} + S_{PO4}} \cdot \frac{S_O}{K_O + S_O} \cdot a^{T-20} \qquad (4.4)$$

The essential advantage of this model is that a majority of model parameters and wastewater components can be frequently estimated using one type of measurement - aerobic respirometry. It is remarkable for the implementation of respirometry in this approach that it allows for a qualitative and quantitative description of not only aerobic but also anoxic substrate conversion processes. It means that with one type of measurement it can possible to obtain information about the overall N-removal potential and capacity. Using a side-stream respiration unit, the actual activity of activated sludge (expressed by substrate conversion kinetics) can be frequently measured. In this way population dynamics as growth and decay, the functional groups of micro-organisms as well as effects of environmental factors do not need to be explicitly modelled (e.g. nutrients, temperature, alkalinity) and the number of default parameter values is reduced. Respirometric wastewater characterisation restricts wastewater composition to only three completely biodegradable components, which in turn allows for a further simplification of the model.

To assume that the equality given with equation 4.4 is correct, frequent independent side-stream respirometric experiments should be performed at adequate conditions with regards to the simulated reactor, with the aim to estimate the majority of model parameters. Essential environmental conditions to be met during respirometric experiments are:

- the same activated sludge concentration (ML(V)SS) which allows to use directly the estimated volumetric conversion rates instead of specific;
- the same temperature (T) as in the modelled reactor;
- the same pH as in the nitrification volume since pH influences especially nitrification kinetics already at little changes;
- similar nutrient availability.

Regarding the performance of a respirometric test the following conditions can be considered as essential:

- avoidance of a too long aeration period of an activated sludge sample without feeding (attaining endogenous stage) before each single test because it may influence the actual activity of the present biomass;
- S/X_V-ratio should be chosen carefully as a compromise between attaining the similar conditions as in the simulated reactor and duration of the experiment to obtain reliable parameter estimations (e.g. CHUDOBA ET AL., 1992, SPANJERS AND VANROLLEGHEM, 1995).

4.5 CONCLUSIONS

The simplified denitrification model was developed and combined with an existing simplified aerobic activated sludge model of BROUWER AND KLAPWIJK (1997). The overall nitrification-denitrification model is based on aerobic respirometry for wastewater and activated sludge characteristics and this implies indirectly its simplified character. The wastewater composition is restricted to only 3 components that are completely oxidisable in an activated sludge system. The substrate oxidation kinetics are modelled using conversion rates, excluding the necessity of the description of population dynamics.

In complex approaches the effect of factors as temperature, pH or nutrient availability are taken into account. In the presented simplified approach, independent estimation of substrate conversion rates at environmental conditions adequate to these in the modelled reactor, allows for a subsequent elimination of additional functions and associated parameters. Estimated actual substrate conversion rates also involve population composition and kinetics. In complex approaches these are normally expressed by concentrations of functional groups, growth and decay kinetics.

Aerobic and anoxic organic substrate conversions are modelled with the same relations while for the latter case appropriate reduction factors are added to reflect a slower activity of activated sludge under denitrifying conditions. The values of reduction factors can be estimated independently using the described methodology from chapter 3 or taken as a calibration parameter in the testing phase of the model.

To obtain maximum benefits from the presented simplified nitrification-denitrification model, the incorporation of an activated sludge system side-stream respiration based control unit for parameters estimation is necessary. To minimise maintenance and operational efforts the respiration set-up should be as far as possible automated regarding the performance of subsequent respiration tests and numerical procedures to obtain model parameters and wastewater characteristics. The validity and applicability of the simplified nitrification-denitrification model will be further tested in chapter 5.

LIST OF SYMBOLS AND ABBREVIATIONS (FOR CHAPTERS 4&5)

a	temperature factor
$b_{A,NO}$	anoxic endogenous respiration rate of X_A (d^{-1})
$b_{H,NO}$	anoxic endogenous respiration rate of X_H (d^{-1})
$b_{STO,NO}$	anoxic respiration rate for X_{STO} (d^{-1})
$i_{NSF,NXS}$	N fraction of S_F and X_S respectively
i_{PBM}	fraction P in bacterial cells,
i_{XB}	fraction N in bacterial cells,
$K_{1.2,3}$	denitrification constants associated with the utilisation of S_S, X_S and endogenous material respectively ($mgN.mgX_a^{-1}.d^{-1}$)
k_A	ammonification rate ($\ell.mg^{-1}.h^{-1}$);
K_A	half-saturation coefficient for S_A ($mgCOD.\ell^{-1}$)
K_{ALK}	half-saturation coefficient for alkalinity ($mol_{HCO3}.\ell^{-1}$)
K_F	half-saturation coefficient for S_F ($mgCOD.\ell^{-1}$)
k_H	hydrolysis constant (h^{-1} or d^{-1})
K_{MAX}	max ratio of X_{PP}/X_{PAO} ($mgX_{PP}.mgX_{PAO}^{-1}$)
K_{SSm}	max specific utilisation constant of S_S ($mgCOD.mgX_a^{-1}.d^{-1}$)
K_{XSm}	max specific utilisation constant of X_S under anoxic conditions ($mgCOD.mgX_a^{-1}.d^{-1}$)
K_{NH}	half-saturation coefficient for S_{NH} ($mgN.\ell^{-1}$)
K_{NO3}	half-saturation coefficient for S_{NO3} ($mgN.\ell^{-1}$)
K_{NO2}	half-saturation coefficient for S_{NO2} in nitrification process ($mgN.\ell^{-1}$)
K_{NO}	half-saturation coefficient for S_{NO} in denitrification process ($mgN.\ell^{-1}$)
K_O	half-saturation coefficient for S_O ($mgO_2.\ell^{-1}$)
K_{PHA}	half-saturation coefficient for X_{PHA} ($mgX_{PHA}.mgX_{PAO}^{-1}$)
K_{PO4}	half-saturation coefficient for S_{PO4} ($mgP.\ell^{-1}$)
K_{PP}	half-saturation coefficient for polyphosphate ($mgX_{PP}.mgX_{PAO}^{-1}$)
K_{PS}	half-saturation coefficient for phosphorus in storage of PP ($mgP.\ell^{-1}$)
K_S	half-saturation coefficient for S_S ($mgCOD.\ell^{-1}$)
K_{STO}	half-saturation constant for X_{STO} ($mgX_{STO}.mgX_H^{-1}$)
k_{STO}	storage rate constant ($mgS_S.mgX_H^{-1}.d^{-1}$)
K_{XS}	half-saturation coefficient for X_S ($mgCOD.\ell^{-1}$)
MLSS	mixed liquor suspended solids ($g.\ell^{-1}$)
ΔN	nitrate reduction, subscripts: 1s, 2s, 3s in the 1st, 2nd and 3rd denitrification phase ($mgN.\ell^{-1}$)
P	COD/VSS ratio ($mgCOD.mgVSS^{-1}$)
q_{PP}	rate constant for storage of X_{PP} ($mgX_{PP}.mgX_{PAO}^{-1}.d^{-1}$)
$R_{1,3}$	hydraulic retention time in respectively primary (1) and secondary (3) anoxic reactor (*h* or d)
r_{end}	aerobic, endogenous respiration rate ($mgO_2.\ell^{-1}.h^{-1}$)
r_{NOm}	denitrification rate ($mg.\ell^{-1}.min^{-1}$)
r_{SNHm}	nitrification rate, overall or 1st step ($mg.\ell^{-1}.min^{-1}$)
r_{SNO2m}	nitrite oxidation rate (2nd step nitrification) ($mg.\ell^{-1}.min^{-1}$)
r_{SSm}	max S_S oxidation rate ($mgCOD.\ell^{-1}.h^{-1}$)
S_A	fermentation products ($mgCOD.\ell^{-1}$)
S_{ALK}	alkalinity of the wastewater ($mol_{HCO3}.\ell^{-1}$)
S_{bi}	total influent biodegradable COD concentration ($mgCOD.\ell^{-1}$)
S_F	fermentable, readily biodegradable organic substrate ($mgCOD.\ell^{-1}$)
S_I	soluble inert COD ($mgCOD.\ell^{-1}$)
S_{ND}	soluble readily biodegradable N ($mgN.\ell^{-1}$)
S_{NH}	ammonium plus ammonia nitrogen, subscript: i - influent, e - effluent ($mgN.\ell^{-1}$)
S_{NHn}	nitrifiable-N ($mgN.\ell^{-1}$)

S_{NI}	soluble inert organic N (mgN.ℓ^{-1})
S_{NO}	sum nitrate and nitrite-nitrate equivalent (mgN.ℓ^{-1})
S_{NO2}	nitrite (mgN.ℓ^{-1})
S_{NO3}	nitrate; subscripts: i - influent, e-effluent (mgN.ℓ^{-1})
S_O	dissolved oxygen (mgO_2.ℓ^{-1})
S_{PO4}	inorganic soluble phosphorus, primarily ortho-phosphates (mgP.ℓ^{-1})
S_S	soluble readily biodegradable COD (mgCOD.ℓ^{-1})
T	temperature (°C)
V, V_D, V_N	respectively total, denitrification and nitrification volumes of the activated sludge tank (m^3)
X_a	concentration of active biomass (g.ℓ^{-1})
X_A	concentration of autotrophic biomass (mgCOD.ℓ^{-1})
X_H	concentration of heterotrophic biomass (mgCOD.ℓ^{-1})
X_I	particulate inert COD (mgCOD.ℓ^{-1})
X_{ND}	particulate slowly biodegradable N (mgN.ℓ^{-1})
X_{NI}	particulate inert N (mgN.ℓ^{-1})
X_{PAO}	phosphate accumulating organisms (mgCOD.ℓ^{-1})
X_{PHA}	cell internal storage products of X_{PAO}'s (mgCOD.ℓ^{-1})
X_{PP}	poly-phosphate (mgP.ℓ^{-1})
X_S	particulate slowly biodegradable COD (mgCOD.ℓ^{-1})
X_{STO}	cell internal storage product of heterotrophic organisms (mgCOD.ℓ^{-1})
Y_A	yield coefficient for autotrophic biomass
Y_H	yield coefficient for heterotrophic biomass; subscript: NO_3 - anoxic
$Y_{STO,NO3}$	anoxic yield of stored product per SS ($gX_{STO}.gS_S^{-1}$)

Greek letters

α	proportionality constant (0.028 mgN.mgS_{bi}^{-1})
η_g	reduction coefficient for heterotrophic growth under anoxic conditions,
η_h	reduction coefficient for hydrolysis under anoxic conditions,
η_{NO}	reduction coefficients for different anoxic activities in ASM2, ASM2d and ASM3
η_1	reduction factor for anoxic S_S oxidation, this study
η_2	reduction factor for anoxic hydrolysis, this study
η_3	reduction factor for anoxic endogenous respiration, this study
μ_A	max growth of X_A (d^{-1})
μ_H	max growth of X_H (d^{-1})
μ_{PAO}	max growth rate of X_{PAO} (d^{-1})

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5

Respiration based simplified nitrification-denitrification model. Part II: model testing

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ABSTRACT

The simplified nitrification-denitrification model from chapter 4 was tested using two pilot-plant configurations, named pilot-plant I and II. The majority of model parameters, like wastewater characteristics and aerobic conversion kinetics, were obtained using the side-stream automated respiration based control unit RESCUE (BROUWER AND KLAPWIJK, 1997). To describe anoxic substrate conversions, denitrification reduction factors ($\eta_1..\eta_3$) were estimated for pilot plant II using the methodology as presented in chapter 3. For pilot-plant I default values for η_1 and η_2 were taken while η_3 was estimated. For parameters having little influence on the quality of model predictions, default values were used. Steady-state and dynamic simulations were performed with satisfactory results. Potential implementations of the model for activated sludge systems are discussed, primary for an analysis of the N-removal potential and control objectives.

5.1 INTRODUCTION

Objective of this chapter was to test the simplified nitrification-denitrification model as described in chapter 4 and to indicate possible implementations. Two activated sludge systems were chosen as testing objects, characterised by a similar configuration but different wastewater characteristics and process parameters. In order to evaluate the options for model application, steady-state and dynamic simulations were carried out. Special attention was paid on the quality of model prediction regarding the denitrification process. A satisfactory quality of model predictions could also lead to the acceptance of two major model assumptions: (1) the equality of biodegradable COD-fractions (S_S and X_S) recognised and utilised under aerobic and anoxic conditions and (2) the expression of anoxic conversions using aerobic model equations modified with reduction factors. An additional aim was the validation of the applicability of aerobic respirometry to describe and reflect the denitrification process.

5.2 MATERIAL AND METHODS

The simplified nitrification-denitrification model was tested for two plug-flow pilot-plant configurations (pilot-plant I and II). The operation of both pilot-plants was controlled by adjustment of the nitrification volume to the actual load of nitrifiable nitrogen (S_{NHn}) with the side-stream automated respiration based control unit RESCUE (BROUWER ET AL., 1998). Except the operation as main control unit, the on-line operation of RESCUE enabled to assess frequently a majority of model components. The reduction factors, which are necessary for modelling the anoxic conversion kinetics, were estimated for pilot-plant I using the methodology from chapter 3 while for pilot-plant II default values were chosen.

5.2.1 PILOT PLANT I

Pilot-plant I was a 1000 ℓ plug-flow reactor with settled domestic wastewater from the Bennekom WWTP (Figure 5.1). Four functional zones (anaerobic, pre-anoxic, aerobic, post-anoxic) provided conditions for biological phosphorus and nitrogen removal (Table 5.1).

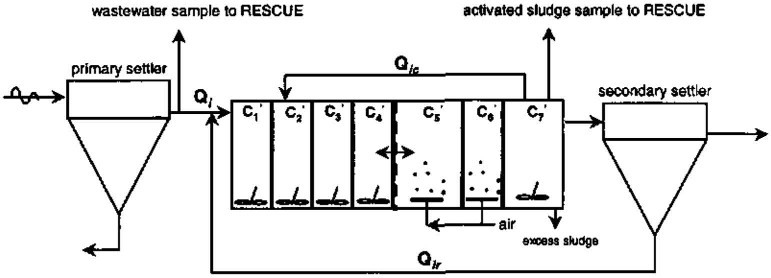

Figure 5.1 Schematic representation of pilot-plant I for simulation purposes.

The reactor was divided into ten compartments ($C_1..C_{10}$) of 100 ℓ volume each. For simulation purposes a reactor model with a smaller number of compartments was chosen to minimise computational efforts. The reactor model for simulation was divided into seven compartments ($C_1'..C_7'$) according to the scheme of Table 5.1. This division followed recommendations regarding an optimal division of a reactor for modelling purposes as proposed by e.g. MEINEMA, 1995 or HENZE ET AL., 1999.

Table 5.1 Division of compartments in pilot-plant I and the simulation model

Pilot-plant I	**Simulated reactor**	**Conditions**	**Processes**
C_1	C_1'	anaerobic	P-release
$C_2..C_4$	C_2'..C_4'	anoxic	pre-denitrification, P-uptake
$C_5..C_8$	C_5'..C_6'	aerobic	nitrification, P-uptake
$C_9..C_{10}$	C_7'	anoxic	post-denitrification

Wastewater from the primary settler, with a varying flow (Q_i), was in the simulation model mixed with return sludge (Q_{ir}/Q_i = 1.3) and then provided to the first anaerobic compartment C_1' ($V_{C1'}$=100 ℓ) for biological P-release. The nitrate-rich internal recycle stream (Q_{ic}) entered C_2' in a ratio of Q_{ic}/Q_i = 3.8. In the compartments $C_2'..C_4'$ denitrification and partial P-uptake took place. The denitrified mixture entered the aerobic compartments (C_5' and C_6') for nitrification and a further uptake of phosphate. In the last non-aerated compartment ($V_{C7'}$ = 200 ℓ), endogenous denitrification took place. This compartment also operated as deoxygenation of the mixture before entering the secondary settler. To keep the solid retention time (SRT) in the reactor at a constant level, the excess sludge was continuously removed directly from the last compartment.

The volumes of C_1' and C_7' were fixed while the proportion between the pre-denitrification and nitrification volume varied depending on the control decision. This had influence on the actual number of pre-anoxic and aerobic compartments in reality and consequently on the volume of the compartments in the simulated case. As a result of the control unit RESCUE, the average volume of $V_{C2'..C4'}$ was 400 ℓ and the average total volume of $V_{C5'+C6'}$ was 300 ℓ.

The operation of the influent pump was coupled to the operation of the influent pumps at the full-scale WWTP of Bennekom and in that way a realistic dynamic flow pattern was attained. However, the presence of a primary settler with a relatively long retention time (HRT ≅ 3.5 *h*) smoothed to some extent the influent dynamics. The side-stream respiration based control unit RESCUE ensured a flexible operation of the nitrification volume of the plant and provided a dynamic description of process kinetics and wastewater characteristics for a period of approximately two weeks (31/3/97 to 14/4/97). The activated sludge sample for respirometric tests was provided from the last compartment and the wastewater from the effluent of the primary settler.

In the operation of pilot-plant I biological phosphorus removal was incorporated. Because the simplified nitrification-denitrification model did not involve the mathematical description of bio-P removal, a significant simplification was made for simulation purposes by neglecting the role of the first anaerobic compartment of pilot-plant I in the conversion processes. In other words: compartment C_1' had only a hydraulic function.

5.2.2 PILOT PLANT II

Pilot-plant II concerned the same reactor as described in § 5.2.1 but in a technological modified configuration (Figure 5.2) and fed with pre-precipitated wastewater. Within the plug-flow reactor three functional zones were distinguished (pre-anoxic, aerobic and post-anoxic). The reactor model for simulation was divided into seven compartments (Table 5.2).

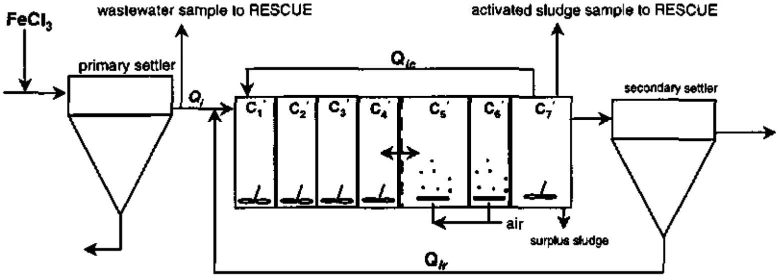

Figure 5.2 Schematic representation of pilot-plant II for simulation purposes

Table 5.2 Division of compartments in pilot-plant II and the simulation model

Pilot-plant I	**Simulated reactor**	**Conditions**	**Processes**
$C_1..C_4$	$C_1'..C_4'$	anoxic	pre-denitrification
$C_5..C_8$	$C_5'..C_6'$	aerobic	nitrification
$C_9..C_{10}$	C_7'	anoxic	post-denitrification

The volume of C_7' was fixed ($V_{C7'}$=200 ℓ), both in reality as for simulation purposes, while the proportion between the pre-denitrification and nitrification volumes varied according to the control strategy. The pre-anoxic volume comprised four simulation compartments ($C_1'..C_4'$) with an average total volume of 400 ℓ. The total nitrification volume ($C_5'..C_6'$) was increased from an average of 300 ℓ to 400 ℓ with respect to pilot-plant I.

In contrast to pilot-plant I the influent was to pilot-plant II provided with a constant flow. Both recycle streams, Q_{ir} and Q_{ic} entered compartment C_1' in average ratio's of respectively 0.8 and 2.3 in relation to Q_i. Implementation of pre-precipitation ahead of the activated sludge reactor eliminated the necessity of biological P-removal but changed wastewater characteristics with regards to the situation with pilot-plant I. Three weeks of operation with RESCUE (15/5/97 to 6/6/97) contributed in a high efficient nitrification and provided information about wastewater characteristics and aerobic conversion kinetics.

5.2.3 OPERATIONAL PARAMETERS

The average operational parameters describing each pilot-plant and used for steady-state simulations are listed in Table 5.3. The operationals parameters for pilot-plant I and II were different, mainly due to the fact that the use of pre-precipitation for pilot-plant II had a strong influence on the wastewater composition. However, for model testing it was not necessary that the operational parameters of pilot-plant I and II were comparable.

Table 5.3 Average operational parameters of pilot plants as used for the steady state simulations

Parameter	**Symbol**	**Unit**	**Pilot-plant I**	**Pilot-plant II**
Influent flow	Q_i	$\ell.h^{-1}$	55	92
Return sludge flow	Q_{ir}	$\ell.h^{-1}$	69.6	69.6
Internal recycle flow	Q_{ic}	$\ell.h^{-1}$	210	208
Anaerobic volume	V_{AN}	ℓ	100	0
Pre-denitrification volume	V_{PD}	ℓ	400	400
Nitrification volume	V_N	ℓ	300	400
Post-denitrification volume	V_{SD}	ℓ	200	200
Organic loading rate	B_{XCOD}	$gCOD.gMLSS^{-1}.d^{-1}$	0.2	0.15
Nitrogen loading rate	B_N	$gN.MLSS^{-1}.d^{-1}$	0.028	0.033
Total concentration of activated sludge	X	$gMLSS.\ell^{-1}$	2.9	4.0
Volatile fraction of biomass	X_V	%	0.75	0.68
pH in V_N	pH	-	~7.2	~7.2
Temperature	T	°C	16-17	18

1) anaerobic compartment C_1 was 'neglected' as having no influence on conversion processes of pilot-plant I

The average environmental conditions (pH and temperature) were similar for both plants with a slightly lower temperatur for pilot-plant I. The pH was measured temporary in the middle aerated compartment. In case of pilot-plant II a slight pH-adjustment was required to attain a pH-value of approximately 7.2.

5.2.4 RESULTS OF PILOT-PLANTS' OPERATION

The effluent N-quality in terms of the sum of nitrate and nitrite, and ammonia-N ($S_{NO3}+S_{NO2}$ and S_{NH} respectively) for pilot-plant I was periodically followed by an on-line analyser (Skalar SA-9000). The effluent N-quality for pilot-plant II was measured regularly in 24*h* composite samples for S_{NO3}, S_{NO2} and S_{NH}. The phosphorus concentration in the effluent was followed in 24*h* composite samples for both pilot plants.

In the period considered as steady-state (31/3/97 to 14/4/97), pilot-plant I was characterised by a high efficient biological P-removal, nitrification and denitrification. Pilot-plant II also attained a high efficient nitrification and a satisfactory P-elimination via pre-precipitation. The denitrification efficiency was low and as average not stable in the period from 15/5/97 to 6/6/97 (Table 5.4).

Table 5.4 Effluent quality of pilot-plant I and II

Parameter	Symbol	Unit	Pilot- plant I	Pilot-plant II
Ammonia-N	S_{NH}	mgN.ℓ^{-1}	2.9 ± 0.8	1.3 ± 1.5
Nitrite-N	S_{NO2}	mgN.ℓ^{-1}	not analysed	3.3 ± 1.5
Sum of nitrite-N and nitrate-N	S_{NO2+3}	mgN.ℓ^{-1}	7.1 ± 3.2	16.8 ± 5.7
Phosphate	S_{PO4}	mgP.ℓ^{-1}	< 1	0.3 ± 0.6
Total phosphorus	P_{tot}	mgP.ℓ^{-1}	< 1	0.5 ± 0.1

5.3 PARAMETERS FOR THE SIMPLIFIED NITRIFICATION-DENITRIFICATION MODEL

In order to validate the simplified nitrification-denitrification model, two types of simulations were carried out for each plant: steady-state and dynamic. For steady-state simulations the average numerical parameter values were taken. For dynamic simulations a number of model components and parameters varied in function of time. The average values are given in Table 5.5 and the courses of the model parameters are presented in Figures 5.3 to 5.5. To visualise the differences in activated sludge and wastewater characteristics the same model components and parameters of both pilot-plants are presented next to each other. The link between the performance of the system and activated sludge kinetics and wastewater composition is discussed in more detail by BROUWER AND KLAPWIJK (1997), BROUWER ET AL., (1998) for pilot-plant I and in chapter 7 of this thesis for pilot-plant II.

Table 5.5 Average values of the majority of estimated kinetic parameters and wastewater composition of the simplified nitrification-denitrification model, measured or assumed during **the entire period** of controlled operation of pilot-plant I (31/3-14/4/97) and II (15/5-6/6/97). Additionally some operational parameters are given.

Parameter	Unit	Pilot-plant I	Pilot-plant II
S_S	mgCOD.ℓ^{-1}	70 ± 13	52 ± 14
X_S	mgCOD.ℓ^{-1}	202 ± 47	149 ± 53
S_{NHn}	mgN.ℓ^{-1}	44.6 ± 8.1	39.5 ± 16.3
r_{NHm}	mgN.ℓ^{-1}.h^{-1}	9.6 ± 1.4	9.9 ± 2.3
K_{NH}	mgN.ℓ^{-1}	0.3 ± 0.04	0.5 ± 0.2
$r_{NO2m.}$	mgN.ℓ^{-1}.h^{-1}	4.7 ± 0.4	8.4 ± 1.8
K_{NO2}	mgN.ℓ^{-1}	0.28 ± 0.04	0.55 ± 0.18
r_{end}	mgO_2.ℓ^{-1}.h^{-1}	11.1 ± 1.6	13.1 ± 3.0
r_{SSm}	mgCOD.ℓ^{-1}.h^{-1}	100 – 150	100 – 150
K_S	mgCOD.ℓ^{-1}	4	4
k_H	h^{-1}	3.8 ± 0.78	2.7 ± 0.4
η_1	-	0.6	0.8
η_2	-	0.5	0.8
η_3	-	0.3	0.3
X	g MLSS.ℓ^{-1}	2.9 ± 0.2	4.0 ± 0.2
X_V	g VSS.ℓ^{-1}	2.2	2.7 ± 0.15
Q_i	ℓ.h^{-1}	55 ± 22	92 ± 6
V_N	ℓ	307 ± 91	377 ± 97

Nitrification. The estimated values of the nitrification kinetic parameters varied in a higher rate for pilot plant II throughout the controlled operation periods (Figure 5.3). Comparable maximum volumetric S_{NH}-oxidation rates (r_{NHm} = 9.6 and 9.9 mgN.ℓ^{-1}.h^{-1} respectively) were obtained regarding the first nitrification step for both pilot-plants but the specific rate was lower for pilot plant II (4.4 vs. 3.6 mgN.gVSS^{-1}.h^{-1}). The maximum volumetric S_{NO2}-oxidation rate for pilot-plant I was half of this for pilot-plant II (r_{NO2m} = 4.7 versus 8.4 mgN.ℓ^{-1}.h^{-1}). When comparing specific rates this difference was smaller (2.2 and 3.1 mgN.gVSS^{-1}.h^{-1}).

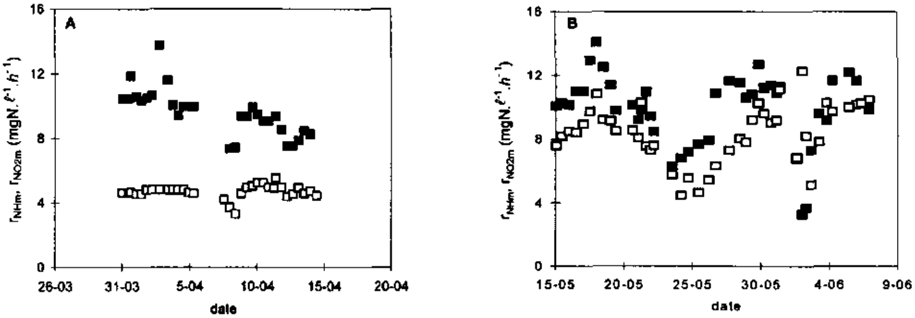

Figure 5.3 Estimated first- and second nitrification rates for pilot-plant I (A) and II (B) (■ - r_{NHm} and □ – r_{NO2m})

Wastewater characterisation. Pilot-plant I was fed with settled wastewater and pilot-plant II with pre-precipitated wastewater. The pre-precipitation influenced the distribution between wastewater fractions. The readily biodegradable soluble COD (S_S) was reduced from 70 to 52 mg.ℓ^{-1} (-25%) and the particulate slowly biodegradable COD (X_S) from an average of 202 to 149 mg.ℓ^{-1} (-26%). The distribution of the remaining COD-fractions and the effect of pre-treatment onto the total COD-removal is further given in chapter 7. The removal of nitrifiable nitrogen (S_{NHn}) attained a low common value of 11% (Figure 5.4, Table 5.5) due to pre-precipitation.

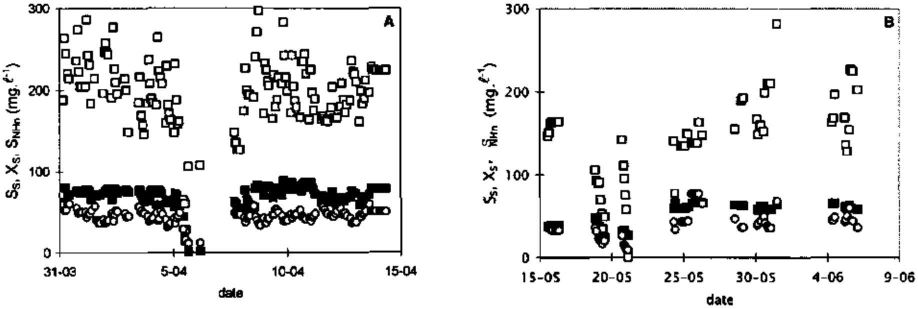

Figure 5.4 Wastewater characterisation for pilot-plant I (A) and II (B) (■ -S_S, □ -X_S and o - S_{NHn})

Oxidation and hydrolysis kinetics. The volumetric oxidation rate of S_S was for both plants estimated to be in a range of 100 to 150 mg $COD.\ell^{-1}.h^{-1}$ (Table 5.5). For simulation of both systems a constant value of 4 mg $COD.\ell^{-1}$ was taken for the half-saturation coefficient for S_S-oxidation. The average value of the hydrolysis rate was for pilot-plant I estimated on 3.8 (h^{-1}) while for pilot-plant II it attained a lower average level of 2.7 (h^{-1}). The activated sludge from pilot-plant II was characterised by a higher endogenous volumetric respiration rate of r_{end} = 13.1 $mgO_2.\ell^{-1}.h^{-1}$ while for pilot-plant I the basic sludge activity was r_{end} = 11.1 $mgO_2.\ell^{-1}.h^{-1}$. The recalculation of r_{end} into specific rates (k_{end}) resulted in an opposite order although the difference was not significant (5.1 versus 4.9 $mgO_2.gVSS^{-1}.h^{-1}$).

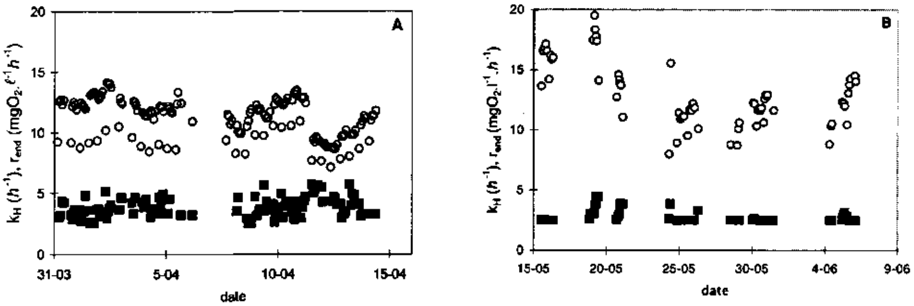

Figure 5.5 First order hydrolysis rates (estimated) and volumetric endogenous respiration rates (measured) for pilot-plant I (A) and II (B) respectively (■ - k_H and ○ - r_{end})

Reduction factors for denitrification. Since for pilot-plant I the reduction factors for denitrification were not estimated, they were assumed based on preliminary results from a system with similar operation conditions (chapter 3). The reduction factors for the anoxic S_S-oxidation and hydrolysis rates were assumed at $\eta_1 = 0.6$ and $\eta_2 = 0.5$ respectively. The anoxic endogenous respiration rate was occasionally compared with the aerobic rate and η_3 was estimated at 0.3. For pilot-plant II the methodology to assess reduction factors (chapter 3) was once implemented. The estimated reduction factors attained high values for S_S-oxidation and hydrolysis, respectively $\eta_1 = 0.8$ and $\eta_2 = 0.8$ while for η_3 a common value of 0.3 was measured.

Pilot-plant dynamics. The wastewater flow to pilot-plant I varied proportionally to the influent dynamics of the WWTP Bennekom. This explains a strong dynamic flow pattern including rain weather conditions (at 5/4/97). As a result of the dynamics in influent flow and wastewater composition, the nitrification volume was changing frequently (Figure 5.6). Pilot-plant II was fed with a constant flow so the nitrification volume was primarily dependent on wastewater composition.

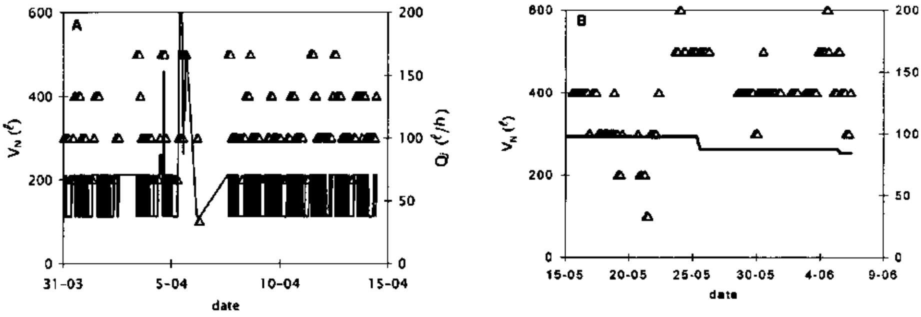

Figure 5.6 Wastewater flow and total nitrification volume dynamics characterising pilot-plant I (A) and II (B) (solid line Q_i and Δ V_N)

5.4 SIMULATIONS

For steady-state simulations average values of the estimated parameters from the considered period were used and compared with the average effluent quality (24h samples) for the measured concentrations of S_{NO} (S_{NO3}+0.6· S_{NO2}) and S_{NH} in the same time interval. For dynamic simulations, values of the most dynamic model parameters and actual functional volumes and flows of the reactor varied in function of time. The simulated dynamic S_{NO}-effluent for pilot-plant I was compared with the on-line measured sum of S_{NO3} and S_{NO2}. Model simulations were mainly focussed to predict the denitrification performance of the considered system.

5.4.1 SIMULATIONS FOR PILOT-PLANT I

The model components and operational parameters for all performed simulations of pilot-plant I, both steady-state and dynamic, are presented in Table 5.7.

Steady-state simulations

Steady-state simulations for pilot-plant I were performed for the period from 31/3/97 to 7/4/97 because only then on-line effluent N-concentrations were available. The continuity of effluent monitoring was interrupted for approximately two days (2/4/97 to 4/4/97). For S_{NH} and S_{NO} the simulated values were lower than the measured values (Table 5.6). The parameters, coefficients and plants characteristics from the first week of controlled plant operation differed to some extent from the average values from the entire period (Table 5.5 and 5.7). Regarding the default values no further calibration was carried out.

Table 5.6 Measured and simulated average effluent N-quality in the period from 31/3/97 to 7/4/97 for pilot-plant I (steady-state simulation)

Effluent quality	Unit	Measured	Simulated
S_{NH}	mgN.ℓ$^{-1}$	2.9	0.5
S_{NO}	mgN.ℓ$^{-1}$	7.1$^{1)}$	5.5

1) S_{NO} as S_{NO2} + S_{NO3}

Table 5.7 List of simplified model components values and operational parameters for all performed simulations of pilot-plant I (C-calibrated parameter, D-default, E-estimated, M-measured)

Model component	Unit	Approach	Steady state simulation	Dynamic simulations		
Wastewater characterisation			31/3/97 to 7/4/97	31/3/97	1/4/97	4/4/97
S_S	mgCOD.ℓ^{-1}	E	60.3	74.0±4.9	72.9±3.1	67.9±7.3
X_S	mgCOD.ℓ^{-1}	E	199.3	226.1±24.1	253.5±55.1	195.4±30.7
S_{NHn}	mgN.ℓ^{-1}	E	43.3	54.2±4.2	45.2±7.2	40.6±5.5
Process conversion rates						
r_{NHm}	mgN.ℓ^{-1}.h^{-1}	E	10.4	10.5	10.5	10.5
r_{NOm}	mgN.ℓ^{-1}.h^{-1}	E	4.6	4.6	4.6	4.6
r_{SSm}	mgCOD.ℓ^{-1}.h^{-1}	E	120	120	150	100
k_H	h^{-1}	E	4	3	3	3
r_{end}	mgO_2.ℓ^{-1}.h^{-1}	M	11.7	11.7	10.6	10.6
Coefficients/factors						
K_{NH}	mgN.ℓ^{-1}	E	0.30	0.30	0.29	0.29
K_{NO2}	mgN.ℓ^{-1}	E	0.27	0.27	0.25	0.25
η_1	-	E/C	0.6	0.47±0.09	0.48±0.05	0.47±0.07
η_2	-	E	0.5	0.5	0.5	0.5
η_3	-	M/C	0.3	0.3	0.2	0.2
K_{NO}	mgN.ℓ^{-1}	D	0.5	0.5	0.5	0.5
K_S	mgCOD.ℓ^{-1}	E	4	4	4	4
Y_H	-	D	0.67	0.67	0.67	0.67
Reactor volumes/flows						
V_{PD}	ℓ	M	400	406±70.4	448±93.5	451.6±73.6
V_{SC}	ℓ	M	200	200	200	200
V_N	ℓ	M	300	300±75.6	251±84.9	262.1±104.9
Q_i	ℓ.h^{-1}	M	60.3	60.3±34.2	50.9±12.9	52.8±13.6

Intermezzo:

The simplified model structure does not distinguish between nitrate and nitrite in the denitrification process and they are combined in one parameter S_{NO}. In practice, the parameter S_{NO} is always smaller than the sum of S_{NO2} and S_{NO3}, except of a situation that S_{NO2}=0 mg.ℓ^{-1}. In some simulations the predicted value for S_{NO} is somewhat lower than the measured sum of N-oxides what is in principle correct regarding the proposed approach. Unfortunately, nitrite was not separately measured so S_{NO} 'simulated' and 'measured' cannot be compared. A significantly lower oxidation rate of S_{NO2} than S_{NH} may suggest that some nitrite could be present in the effluent. On the other hand, a rather efficient denitrification process in pilot-plant I could take care of partial reduction of S_{NO2}.

Dynamic simulations

Three dynamic simulations of the S_{NO}-course in the effluent were performed for the days where a continuous nitrate/nitrite measurement was available. To obtain an acceptable fit (Figure 5.7) seven model parameters were used in function of time. These were the estimated wastewater characteristics (S_S, X_S and S_{NHn}), operational parameters (Q_i, V_{PD}, V_N) and the reduction factor for anoxic S_S-oxidation (η_1). Regarding the last parameter its primary assumed value of 0.6 (Table 5.5) varied as a result of calibration between 0.4 and 0.6. The lowest value of η_1 was always associated with the minimum available pre-denitrification volume. The small pre-denitrification volume resulted from the control decision to aerate the maximum available nitrification volume. Due to this fact more oxygen than normally could enter the anoxic volume, retarding the enzymatic activity of denitrifiers.The reduction factor for anoxic endogenous respiration was for day 1/4/97 and 4/4/97 calibrated at a value of η_3 = 0.2 instead of the once measured value of 0.3. The obtained simulation results can be considered as satisfactory regarding the reflections of tendency in the course of the nitrate-effluent (Figure 5.7) as well as the average values for the regarded period (Table 5.8).

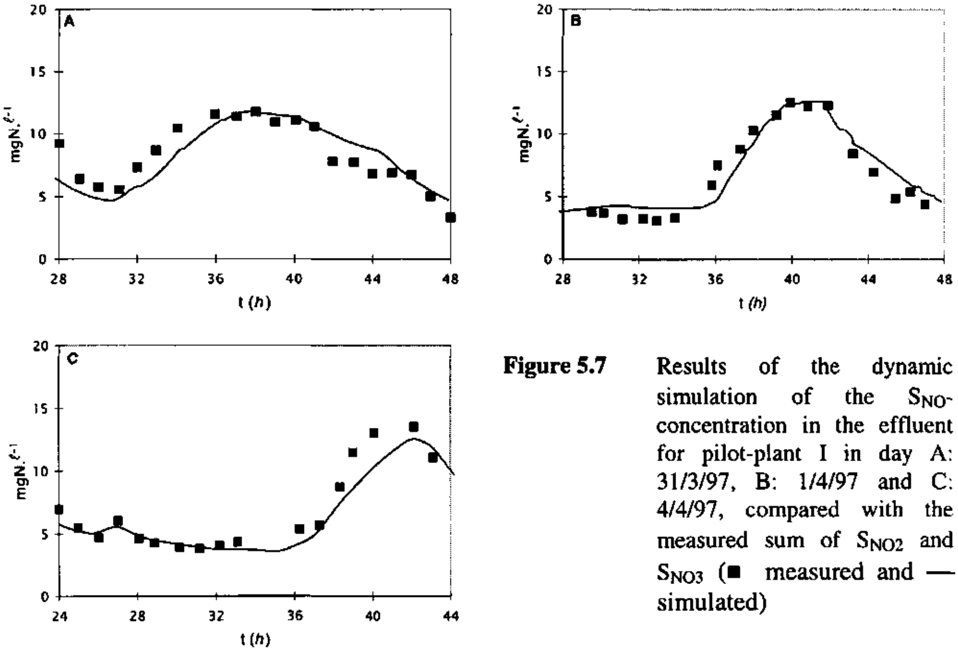

Figure 5.7 Results of the dynamic simulation of the S_{NO}-concentration in the effluent for pilot-plant I in day A: 31/3/97, B: 1/4/97 and C: 4/4/97, compared with the measured sum of S_{NO2} and S_{NO3} (■ measured and — simulated)

Table 5.8 The average measured and simulated effluent-N of dynamic simulations for pilot-plant I

Date	Unit	Measured S_{NO2}+S_{NO3}	Simulated S_{NO}
31-03-97	mgN.ℓ$^{-1}$	8.26±2.19	9.21±1.78
01-04-97	mgN.ℓ$^{-1}$	6.92±3.21	6.73±3.12
04-04-97	mgN.ℓ$^{-1}$	6.85±3.25	6.36±3.06

5.4.2 SIMULATIONS FOR PILOT-PLANT II

During the operation of pilot-plant II no on-line effluent N-quality measurement was performed, and the simplified nitrification-denitrification model was tested mainly on steady state simulations. The effluent quality was controlled for S_{NH}, S_{NO2} and S_{NO3} in 24*h* composite samples. In contrast to the situation of pilot-plant I, the simulated and measured S_{NO}-concentrations in the effluent could be directly compared. The model components and operational parameters for all performed simulations of pilot-plant II are given in Table 5.9.

Table 5.9 List of model components and parameter values for simulations of pilot-plant II with the simplified nitrification-denitrification model

Model parameter	**Unit**	**Approach**	**Steady state simulation**			**Dynamic simulation**
			Profile 29/5/97	Profile 4/6/97	Effluent 29/5/97 - 6/6/97	25/5/97 - 6/6/97
Wastewater characterisation						
S_S	$mgCOD.\ell^{-1}$	E	62.9	65.5	60.8	52.2±13.7
X_S	$mgCOD.\ell^{-1}$	E	191.5	176.2	188.7	149.2±53.0
S_{NHn}	$mgN.\ell^{-1}$	E	52.0	46.1	43.0	39.5±16.3
Process conversion rates						
r_{NHm}	$mgN.\ell^{-1}.h^{-1}$	E	11.7	9.2	9.6	10.6
r_{NOm}	$mgN.\ell^{-1}.h^{-1}$	E	9.7	9.7	9.4	10.4
r_{SSm}	$mgCOD.\ell^{-1}.h^{-1}$	E	140	120	100	100
k_H	h^{-1}	E	2.5	2.5	2.0	2.5
r_{end}	$mgO_2.\ell^{-1}.h^{-1}$	M	9.8	10.7	11.8	11.8
Coefficients						
K_{NH}	$mgN.\ell^{-1}$	E	0.31	0.31	0.35	0.35
K_{NO2}	$mgN.\ell^{-1}$	E	0.49	0.68	0.56	0.56
η_1	-	E	0.8	0.8	0.7	0.75
η_2	-	E	0.8	0.8	0.7	0.75
η_3	-	M	0.3	0.25	0.2	0.25
K_{NO}	$mgN.\ell^{-1}$	D	0.5	0.5	0.5	0.5
K_S	$mgCOD.\ell^{-1}$	E	4	4	4	4
Y_H	-	D	0.67	0.67	0.67	0.67
Reactor volumes/flows						
V_{PD}	ℓ	M	400	275	370	371±126
V_N	ℓ	M	400	525	430	428±126
V_{SD}	ℓ	M	200	200	200	200
Q_i	$\ell.h^{-1}$	M	87.1	87.1	87.1	87.1

Steady-state simulations

Two steady-state simulations of S_{NH}- and S_{NO}-profiles throughout the compartments were performed and compared with available measurements. The implemented parameter values (Table 5.9) were estimated at approximately the same time when the given profile measurement was carried out. The simulation results in Figure 5.8 were obtained without adjustment of model parameters. In both cases the predicted S_{NO}-concentrations were slightly lower in the post-anoxic compartment and the predicted S_{NH}-concentraions were slightly lower in the pre-denitrification compartments.

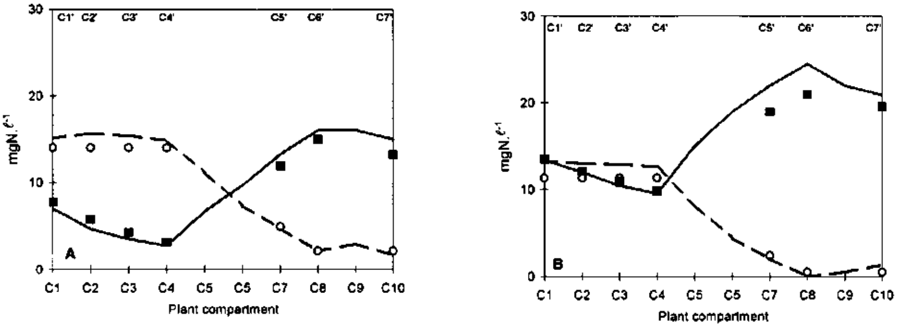

Figure 5.8 Steady-state simulation of two sets of S_{NH}- and S_{NO}-profiles throughout the compartments of pilot-plant II. Model parameters as presented in Table 5.9 for day A: 29/5/97 and B: 4/4/97 (- - - S_{NH} simulated, o S_{NH} measured — S_{NO} simulated, ■ S_{NO} measured)

For a longer period (29/5/97 to 6/6/97), steady-state simulations of S_{NO} and S_{NH} in the effluent were using average values of the estimated model parameters in this period (Table 5.9). Taking into account that S_{NO}- and S_{NH}-concentrations in the effluent were measured in 24*h* composite samples and model parameters and wastewater characteristics were less regularly supplied (from day 1/6/97 to 3/6/97 the parameters were not estimated), the prediction can be considered as satisfactory (Table 5.10).

Table 5.10 Average effluent N-quality of pilot-plant II, measured and simulated in the period from 29/5/97 to 6/6/97

Effluent quality	Unit	Measured	Simulated
S_{NH}	$mgN.\ell^{-1}$	1.7±1.6	1.3
S_{NO2}	$mgN.\ell^{-1}$	3.9±1.8	-
S_{NO3}	$mgN.\ell^{-1}$	11.4±4.2	-
S_{NO}	$mgN.\ell^{-1}$	13.7±4.4	13.1

Dynamic simulations

A dynamic simulation was performed for pilot-plant II for a period of approximately 7 days (25/5/97-31/5/97) using parameters as listed in the last column of Table 5.7. The dynamic pattern of the simulated S_{NH} and S_{NO} was compared with the effluent N-quality as measured in 24*h* composite samples. For the fitting five model parameters varied in function of time: wastewater composition (S_S, X_S and S_{NHn}) and functional volumes (V_N and V_{PD}). The dynamic simulation was performed to check the rough correlation between model prediction and measurements. As expected, some discrepancy was obtained, especially between the simulated and measured S_{NO}- concentrations in the effluent (Figure 5.8). Regarding the tendencies of S_{NH} and S_{NO} the courses were in fair agreement and the average values attained similar values (Table 5.11).

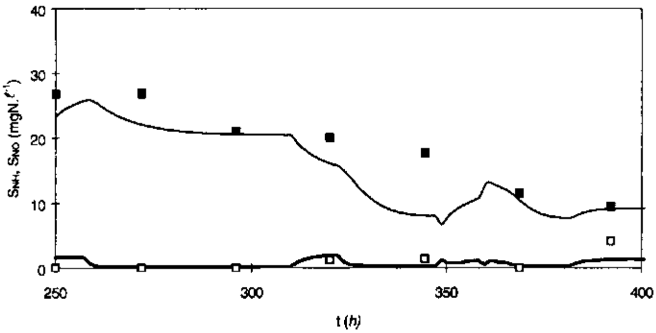

Figure 5.9 Dynamic simulation of pilot-plant II compared with 24*h* composite effluent samples in the period from 26/5/97 to 6/6/97. (□ S_{NH} measured, ▬ S_{NH} simulated, ■ S_{NO} measured, — S_{NO} simulated)

Table 5.11 Average effluent N-concentrations as obtained from dynamic simulation and measured in the period from 25/5/97 till 31/6/97 for pilot-plant II.

Effluent quality	Unit	Measured	Simulated
S_{NH}	mgN.ℓ$^{-1}$	1.3±1.5	0.7±0.5
S_{NO}	mgN.ℓ$^{-1}$	16.8±5.7	15.5±6.4

5.5 DISCUSSION

5.5.1 MODEL PARAMETERS

The test results of the simplified nitrification-denitrification model, both in static and dynamic conditions, showed that the model reflects closely the operation of the considered N-removing activated sludge system. For a general analysis of system operation with steady state simulations the model parameters and wastewater characteristics do not need to be frequently updated but the accuracy of model prediction is consequently lower. For on-line monitoring of the efficiency of the nitrification and denitrification and for control/optimisation purposes (dynamic simulation) the number of model components has to be frequently updated for satisfactory model predictions. Regarding the required frequency of estimating or updating parameters, four groups of model components can be distinguished:

(1) **Sensitive parameters**, describing influent and system dynamics that are subjected to significant changes in a time scale of hours. To this group belong: qualitative and quantitative wastewater characteristics (S_S, X_S, S_{NHn} and Q_i). If the modelled system operates with controlled, thus varying nitrification and denitrification volumes (V_N, V_{PD}), they will also belong to the group of sensitive parameters. From the first tests with the simplified model it seems that η_1 can be also classified to this group.

(2) **Less sensitive parameters**, describing mainly process conversion rates. They include effects as changes in biomass activity (growth and decay) and environmental factors (temperature, pH, inhibiting factors) which are significantly visible in a scale of days rather than hours (e.g. ISAACS ET AL., 1994). Process conversion rates belong to this group (r_{NHm}, r_{NOm}, r_{end}, r_{SSm} and k_H).

(3) **Factors and coefficients when once determined are assumed to remain constant for a period of steady-state operation.** Their update or verification should be carried out periodically, especially when the operational conditions change significantly. Two reduction factors for anoxic respiration (η_2 and η_3) and half-saturation coefficients K_S, K_{NH} and K_{NO2} belong to this group.

(4) **Default parameters**, such as e.g. K_{NO} or Y_H.

5.5.2 ACCURACY OF MODEL PREDICTION

A discrepancy between model predictions and measurements was noted, especially for some steady state-simulations (Table 5.6 and 5.10). Possible reasons for a higher measured concentration of S_{NH} in the effluent than simulated could be:

- smaller actual volume V_N due to the existence of dead zones in the aerobic compartments;
- concentration of estimated S_{NHn} was lower as a result of a different assimilation rate and/or hydrolysis and ammonification of organic-N in a batch test and in the reactor;
- slight difference in pH between respiration vessel and pilot-plant;
- higher actual wastewater flow due to a spontaneous change of influent pump capacity.

The introduction of the fraction S_{NHn} allows to model precisely the net nitrification process and to predict the S_{NH}-effluent quality. A lower simulated S_{NH} in the pre-anoxic zones (Figure 5.8) seems to be relatively simple to explain using the definition of nitrifiable-N (chapter 4, equation 4.3). Processes such as S_{NH}-assimilation under different electron acceptor conditions, as well as hydrolysis and ammonification of particulate organic nitrogen, are not included in the simplified model.

A lower simulated S_{NO}-concentration in the effluent of pilot-plant I (Table 5.6) might be a result of the negligence of biological P-removal in the model structure. Another reason of some discrepancy between simulated and measured values can be some difference between estimated S_{NHn} under batch conditions and in the modelled reactor.

5.5.3 NITRIFIABLE NITROGEN

The concentration of S_{NHn}, which is recognised during an aerobic respiration test, may differ to some extent from S_{NHn} in the reactor because of:

- different actual growth rate of biomass affecting the rate of S_{NH}-assimilation (of S_{NHn}). This is caused by different organic loading rates and electron acceptor conditions during a respiration batch test compared with the activated sludge reactor. This effect can be minimised by the choice of a similar S/X_V-ratio as in the simulated reactor;
- different electron acceptor conditions may influence N-hydrolysis and ammonification rates (HENZE AND MLADENOWSKI, 1991, GOEL ET AL., 1999). The wastewater and sludge in the simulated reactor are subjected to alternating conditions (anaerobic, anoxic, aerobic) while in the respiration test only aerobic conditions are provided.

5.5.4 CALIBRATION

Since the majority of parameters and wastewater characterisation of the simplified model can be measured frequently, an extended calibration of the model is not necessary. The first attempts of model testing proved that estimated parameters could be directly used in a function of time. The model predictions reflected closely the reality. In the initial phase of model testing only the denitrification reduction factor η_1 was calibrated.

5.5.5 DURATION OF WASTEWATER CHARACTERISATION PROCEDURE

The required time of approximately 1.5-2 *h* to estimate the actual wastewater characterisation can be considered as a limitation of the presented method to estimate parameters of the simplified model. However, the results of dynamic simulations (§ 5.4.2) reveal that this frequency did not effect negatively the quality of the model predictions.

For control applications of the simplified model, especially in the system like examined in this chapter (plug-flow and pre-denitrification), the duration of the test for the wastewater characterisation was not a bottleneck for control of the nitrification process. The information about the actual concentration of S_{NHn} in the wastewater volume, directly required for applied control strategy, was obtained before this wastewater reached the nitrification volume. In such a case respiration based control strategy of nitrification had a feed-forward character. Regarding a control strategy for denitrification, which is usually placed as first process in wastewater treatment schemes, it would have a feed-back character.

5.6 OPTIONS FOR MODEL IMPLEMENTATIONS

Development of a 'new' mathematical description of the activated sludge process requires always a justification in its possible implementation. The simplified nitrification-denitrification activated sludge model presented in chapter 4 and tested in this chapter can be used for optimisation of the nitrification and denitrification process. For nitrification one possible control strategy was validated for a plug-flow system and is described elsewhere (BROUWER ET AL., 1997, 1998). Optimisation of the denitrification process with a control strategy will depend on the process configuration. For a plug-flow pre-denitrification system the following state variables can be manipulated to improve the denitrification performance:

- internal nitrate-rich recycle stream, and
- addition of external C-source.

Choice of an optimal internal (nitrate-rich) recycle flow. An optimal recycle flow (Q_{ic}) provides a nitrate load on demand to the pre-denitrification volume (V_{PD}, Figure 5.10), and is therefore preventing nitrate limitation in any point of its volume and its very low concentration in the outflow zone. An optimal recycle ratio allows for the optimal use of denitrification potential in the considered pre-anoxic zone and minimises the oxygen input from the nitrification volume (V_N).

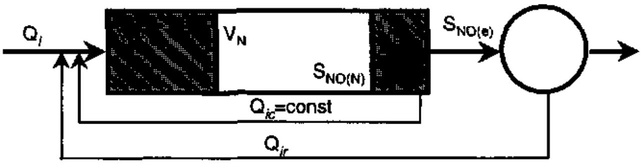

Figure 5.10 Scheme of a plug-flow pre-denitrification activated sludge system

Using the simplified nitrification model, a hydraulic model of the simulated reactor and the actual values of model and process parameters, the following can be predicted:

- nitrification efficiency in a fixed aeration volume;
- adjusted aeration volume for a complete ammonia removal (BROUWER ET AL., 1997, 1998).

In both cases the amount of produced nitrate and nitrite can be predicted and consequently the amount of S_{NO} that has to be denitrified can be calculated.
On the other hand, the estimated organic biodegradable fractions of wastewater (S_S+X_S), anoxic organic substrate conversion kinetics and anoxic endogenous activated sludge activity (denitrification model) in combination with reactor parameters allow to estimate the denitrification potential of a pre-anoxic zone (DP_{PD}). In combination with predicted S_{NO}-concentrations in the recycle streams (Q_{ir} and Q_{ic}), an optimal actual flow (Q_{ic}) to obtain the highest nitrate removal in a pre-denitrification zone can be estimated:

$$Q_{ic} = \frac{DP_{PD} \cdot Q_i - S_{NO(ir)} \cdot Q_{ir}}{S_{NO(ic)}} ;\ \ell.h^{-1} \tag{5.1}$$

Equation 5.1 is to predict the optimal nitrate-rich recycle flow and was implemented for both tested pilot-plants. The DP_{PD} and nitrate concentrations in the end-point of the nitrification zone where acquired from model simulations. It turned out that the DP_{PD} of pilot-plant I was not fully utilised due to nitrate limitation in the denitrification volume. An increase of a recycle stream from Q_{ir} = 210 to 359 $\ell.h^{-1}$ would theoretically contribute in a further nitrate reduction to approximately 3.0 mgN.ℓ^{-1} (instead of 7.1 mgN.ℓ^{-1}). In contrast, pilot-plant II was characterised by a low wastewater denitrification potential due to pre-precipitation. A too high recycle ratio was implemented and significant nitrate concentrations were still measured in the end of the denitrification zone (Figure 5.8).

Addition of external-C on demand. The unsatisfactory wastewater composition in terms of a low biodegradable organics content results in a low denitrification potential of the system and will contribute in a high effluent nitrate concentration. To fulfil the effluent N-quality, an action has to be undertaken. The most common option is the dosage of an external carbon source. In practice an excessive dosage often occurs since not many control strategies have been established till now to provide a controlled dosage on-demand (e.g. ISAACS ET AL., 1995).

The simplified, respiration based model as presented in this chapter allowed to predict the nitrate-effluent quality each 1.5-2 *h*. Taking into account the hydraulics of the plug-flow reactor, the wastewater composition and conversion kinetics were estimated in the wastewater sample that was almost entering the nitrification volume. In that case, the action to enhance denitrification efficiency should be undertaken in a post-denitrification volume.

The simplified model allows to predict the nitrate production and consequently the amount of nitrate that has to be denitrified can be calculated. Using a relational model for an external carbon source (e.g. § 2.3.5), its dose can be predicted and added to the post-denitrification volume. A possible procedure leading to the decision of a magnitude of dosage could remind the following:

(1) estimation of the denitrification potential (ΣDP, mgN.ℓ^{-1}) and denitrification capacity (DC, mgN.ℓ^{-1}) for the total system (pre- and post-anoxic zone) based on actual wastewater composition, activated sludge kinetics and reactor characteristics;

(2) estimation of the nitrate concentration to be denitrified (S_{NOd}) using the simplified nitrification model and the required effluent quality:

$$S_{NOd} = (S_{NHn} - S_{NHe} - S_{NOe});\ \text{mgN.}\ell^{-1} \tag{5.2}$$

(3) estimation of the S_{NO}-concentration to be denitrified with an external carbon source ($S_{NO}{}^{C}$):

$$S_{NO}{}^{C} = S_{NOd} - DC;\ \text{mgN.}\ell^{-1} \tag{5.3}$$

(4) estimation of the required denitrification rate in the post-anoxic zone to obtain a satisfactory S_{NO}-effluent quality ($k_D{}^{req}$):

$$k_D{}^{req} = \frac{S_{NO}{}^{C} \cdot Q_i}{V_{SD} \cdot X_V};\ \text{mgN.gVSS}^{-1}.h^{-1} \tag{5.4}$$

(5) estimation of the required flow of the external carbon source (q_C, $\ell.h^{-1}$) from a relational model (e.g. chapter 2, Figure 2.9) for a chosen carbon source of known concentration ($COD_{solution}$). In the following equation q_C is hidden in the sludge loading rate (B_{XCOD}):

$$B_{XCOD} = \frac{q_C \cdot 24 \cdot COD_{solution}}{1000 \cdot V_{SD} \cdot X};\ \text{gCOD.gMLSS}^{-1}.h^{-1} \tag{5.5}$$

Implementation of denitrification control strategies using the simplified nitrification-denitrification model can be implemented in other configurations as well, such as completely mixed systems with simultaneous nitrification/denitrification, alternating systems, SBR's, etc. In any of the mentioned systems the transition phases from anoxic to aerobic conditions and vice-versa appear, and this will influence the actual denitrification and nitrification potential. In such case oxygen switching functions should be added to the appropriate model equations (chapter 4).

5.6 CONCLUSIONS

The simplified nitrification-denitrification model was tested for two pilot-plant configurations. In both cases the automated respiration based control unit RESCUE was integrated with the considered pilot-plant. This provided frequently information about the wastewater composition and conversion kinetics as required for the developed model approach.

Acceptable results of steady-state simulations were obtained, implicating benefits that can be attained to predict the overall N-removal potential, based on a very detailed wastewater and activated sludge characterisation. The good prediction of the dynamic behaviour of the nitrate course in the effluent implicates that the model can be implemented for control strategies, e.g. for a feed-back control of the denitrification by a nitrate-rich recycle rate and/or the addition of an external carbon source. Another advantage of the model is its implementation to control the nitrification volume (BROUWER AND KLAPWIJK, 1997, BROUWER ET AL., 1998).

In the presented approach it was proved that activated sludge oxidation kinetics and wastewater composition, which were estimated with one type of respiration measurement, enable to describe very closely the overall N-removal process. The wastewater characterisation as estimated with the aerobic respiration test proved to be adequate to model the denitrification process. The reduction factors for denitrification do not need to be frequently estimated (adjusted) if the activated sludge system operates in steady-state conditions. However, strong dynamics of the system (influent dynamics and a frequent change of the ratio between pre-anoxic and aerobic zones) affects the reduction factor for S_S-oxidation under anoxic conditions (η_1).

Possible implementations of the simplified respiration based nitrification-denitrification model for a control of the denitrification process are considered as alternatives for existing approaches (chapter 1, section 1.7).

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6

Effect of pre-precipitation on denitrification potential

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ABSTRACT

An integrated biological/chemical nutrient removal process was conducted. Pre-precipitation with ferric chloride was implemented to attain total phosphorus (P_{tot}) removal up to 1 mg $P.\ell^{-1}$. Nitrogen removal was performed in a low-loaded sequencing batch reactor (SBR) with integrated pre-denitrification and nitrification. Different doses of ferric chloride, used as precipitant, were tested to find an optimal β-ratio (Fe/P molar ratio) for the required P-removal. With a normal-rate precipitant dose of $\beta=1.2$ P_{tot} was reduced to 2.4 mg $P.\ell^{-1}$ as a result of pre-treatment while in the effluent from the SBR it reached an average concentration of 1 mg $P.\ell^{-1}$.

Nitrogen removal efficiencies in systems fed with raw and pre-precipitated wastewater were compared. Special attention was paid on the effect of a change in wastewater composition on the denitrification potential and effluent quality. With $\beta=1.2$ the total COD/N ratio was decreased from 6.5 to 3.1 and consequently the wastewater denitrification potential was reduced with 42% when compared with a reference system fed with raw wastewater. The activated sludge activity differed significantly for systems fed with raw and pre-precipitated wastewater. As a result of an elimination of the majority of organic, particulate and inert material by pre-precipitation, more viable biomass per MLSS unit was present in SBRs fed with pre-precipitated wastewater. This was confirmed by higher values of the specific nitrification and denitrification rates.

A simplified nitrification-denitrification model was employed to optimise theoretically the denitrification in the SBR system with pre-precipitated influent. The results of simulations allowed to suppose that only little improvement of denitrification efficiency is possible when the denitrification potential of the wastewater is originally low.

6.1 INTRODUCTION

6.1.1 PRE-PRECIPITATION IN WASTEWATER TREATMENT SCHEMES

Among wastewater pre-treatment technologies, pre-precipitation is a potential method. Pre-precipitation is usually implemented to reduce phosphorus from wastewater. Secondary reasons for implementation of pre-precipitation are upgrading or extending the treatment plant (HENZE, 1992, BUNDEGAARD AND PEDERSEN, 1990) when available land area is limited. For treatment plants characterised by a high content of particulate material in the influent and high variations in organic pollution load, pre-precipitation smoothes the dynamics of particulate organics, organic nitrogen (N_{org}) and phosphate. This contributes in a better performance of the activated sludge system (GALIL AND REBHUN, 1990, ANDERSSON ET AL., 1992). Generally, pre-precipitation represents a low-cost option for enhancing the performance of existing plants (FIRK, 1990).

Reduction of particulate organic matter contributes in a substantial reduction of the sludge loading of the system and prolongs the sludge retention time (SRT) (KARLSSON, 1988). This is beneficial for nitrification (ANDERSSON AND ROSÉN, 1990) and decreases the biological sludge production (HENZE AND HARREMOËS, 1990). A significant reduction of the organic load allows for smaller volumes in case of new plants or will decrease the loading for existing overloaded plants. Because pre-precipitation is associated with a higher removal of solids than during conventional settling, a large amount of energy consuming organic matter is eliminated in the primary settler, resulting in a higher primary sludge production and a higher biogas production in the digestors (BUNDEGARD, 1990).

6.1.2 PRE-PRECIPITATION - BASIC ASPECTS

Pre-precipitation applied by a municipal wastewater treatment plant can be described as a process of incorporating phosphate into a particulate form, which can be removed together with the primary sludge. Using low molecular, positively charged metal salts (mostly Fe^{+3} and Al^{+3}) (SDA, 1989) or lime (ØDEGAARD, 1992) dissolved P-containing compounds like orthophosphates are precipitated. The simultaneously occurring process is a destabilisation of suspended organic matter that cannot be removed by gravity forces in conventional settling. The smaller sized organic particles of 0.1 to 100 μm (KARLSSON, 1990) are captured by hydroxide flocs of precipitants. Large aggregates are formed with high settling properties. Expressing above in numbers, the total reduction of COD with high-rate pre-precipitation varies from 60% (HENZE AND HARREMOËS, 1990) up to 75% (KARLSSON, 1990) and for suspended solids 80 - 90% (KARLSSON, 1990). For comparison, the removal efficiencies for well operating conventional primary settlers, without addition of chemicals, are 25 to 40% for COD and 50 to 70% for suspended solids (e.g. METCALF&EDDY, 1991, HENZE AND HARREMOËS, 1992). The phosphorus removal efficiency depends on the precipitant dose and may even exceed 90%, which often means that for municipal wastewater no additional efforts are necessary to fulfil the P-effluent standards.

The magnitude of dosage will vary, depending on the influent concentration of phosphorus, the chemical additive, the dosing location, the orthophosphate to total phosphorus ratio (BLISS ET AL., 1994) and the desired reduction rate. When the objective is to remove phosphorus up to 1.0 mg P.ℓ^{-1}, a normal rate pre-precipitation with a Fe/P or Al/P molar ratio of 1 to 2 can be used. This molar ratio is also known as β-ratio (SDA, 1989). When the effluent phosphorus has to be lower than 1.0 mg P.ℓ^{-1}, a high rate pre-precipitation with a much higher β-ratio has to be used. Choosing a precipitant dose, one has to keep in mind that a limitation of phosphorus for the growth of biomass should be avoided.

The choice of a β-ratio will be never accurate, because of the variability of the P-influent concentration. In practice this is solved by overdosing the metal salt at an average P-influent concentration (causing higher sludge production than necessary) or implementing control strategies based on actual wastewater flow, conductivity, P-influent concentration or turbidity (OVERATH ET AL., 1981).

The most commonly used precipitants, such as alum or ferric salts will consume alkalinity what can depress the wastewater pH according to the simplified chemical reaction where iron salt is a precipitant:

$$Fe^{+3} + H_nPO_4^{3-n} \Leftrightarrow FePO_4 + nH^+$$

If sufficient buffer capacity is not naturally present a supplemental alkalinity has be added to meet biological treatment requirements.

6.1.3 EFFECT OF PRE-PRECIPITATION ON WASTEWATER COMPOSITION AND DENITRIFICATION POTENTIAL

The actual wastewater composition determines predominantly the denitrification potential of an activated sludge system (chapter 2). The more organic matter is removed by pre-treatment, the less wastewater denitrification potential will be left. Generally, primary precipitation will remove more COD than nitrogen, lowering the COD/N-ratio (KRISTENSEN AND JØRGENSEN, 1992) and efficiency of nitrogen removal in the down-stream biological step. Reviewing the mass balances for nitrogen from pre-precipitated wastewater it can be seen that only 18% (HENZE AND HARREMOËS, 1990) to 30% (HOFFMAN AND KLUTE, 1990) of it ends in primary sludge, while for COD this can be 60 - 75% (HENZE AND HARREMOËS, 1990, KARLSSON, 1990).

The relations between different COD-fractions are changed due to pre-precipitation. The soluble readily biodegradable and inert fractions (S_S and S_I respectively) increase while the particulate and colloidal slowly biodegradable and inert fractions (X_S and X_I respectively) significantly decrease in relation to the total amount of organic matter. The major fraction of influent nitrogen is in the soluble form of ammonia (HENZE ET AL., 1987, 1996), which passes hardly changed through the pre-precipitation process.

The suspended and colloidal nitrogen, which may constitute usually up to 20-30% of total N, will be partially eliminated in the pre-precipitation process. The overall efficiency of N-removal with pre-precipitation is thus much lower than of COD. As an example, a significantly changed wastewater composition profile is presented schematically in Figure 6.1A for COD and N as representative technological influent parameters. The total COD of this representative wastewater sample of 350 $mg.\ell^{-1}$ can be subdivided into three fractions: suspended (200 $mg.\ell^{-1}$), colloidal (65 $mg.\ell^{-1}$) and soluble (85 $mg.\ell^{-1}$). Primary settling affects the suspended COD-fraction in significant rate (70% reduction). With a normal-dose pre-precipitation the rest of the suspended COD and a part of the colloidal matter is eliminated. A high dose pre-precipitation removes also completely the colloidal matter while the soluble fraction remains theoretically unaffected. For nitrogen (Figure 6.1B) the same phenomena's play a role in changing the relations between its fractions although the final effect is different due to a different original distribution of N-fractions.

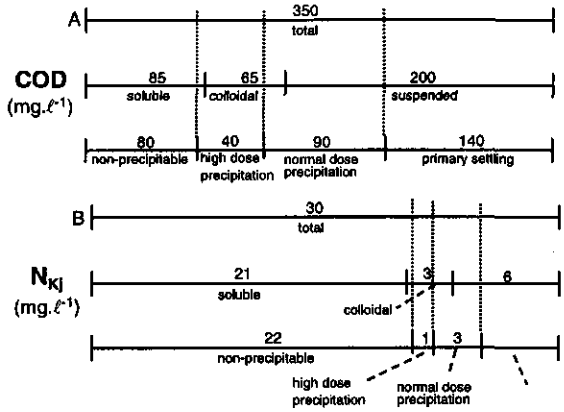

Figure 6.1 A visualisation of the effect of pre-precipitation on the wastewater composition (redrawn from HENZE AND HARREMOËS 1992, HENZE ET AL., 1994).

With pre-denitrification high nitrogen removal efficiency can be obtained when the fraction of S_S in the influent is high. However, the fraction of S_S in raw municipal wastewater accounts generally for a minor part of the total COD, 10 to 30% (e.g. SCHEER, 1995, HENZE ET AL., 1986, 1996). The fraction of X_S accounts for 30 to 60% (HENZE ET AL., 1996) of the total COD. In contrast to S_S, the X_S-fraction cannot be totally utilised in a pre-denitrification system but it plays an important role in the overall denitrification potential of the system. For the wastewater used in this study this was confirmed in chapter 2 of this thesis. Besides the actual wastewater composition, the denitrification efficiency also depends on the amount of nitrogen that has to be removed. Figure 6.2 presents the example of a change of specific denitrification rate (k_D) and denitrification potential of wastewater (DP_{ww}) as result of pre-treatment (HENZE AND HARREMOËS, 1992).

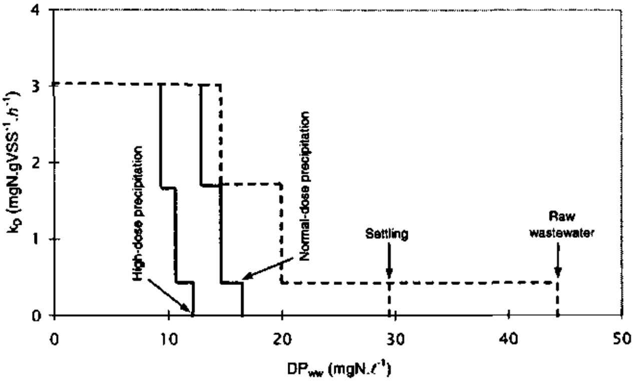

Figure 6.2 Relation between specific overall denitrification rate and denitrification potential for raw, settled and pre-precipitated municipal wastewater (redrawn after HENZE AND HARREMOËS, 1992, HENZE ET AL., 1994)

According to this figure, settling reduces the denitrification potential with approximately 33%. When the normal-dose pre-precipitation is introduced a further 30% reduction of DP can be expected while with a high-dose pre-precipitation additionally 15% of the DP will be lost. The remaining DP is mainly associated with a very high overall k_D on the soluble readily biodegradable COD. When no pre-treatment is applied, more than half of the amount of nitrate (half of wastewater denitrification potential) is reduced at a very low k_D, due to a slowly biodegradable character of a large raw wastewater COD-fraction. The nitrate removal on the colloidal COD- fraction proceeds with a higher denitrification rate of approximately 1.5 mgN.gVSS^{-1}.h^{-1} and on readily soluble biodegradable COD with the highest k_D of 3.0 mgN.gVSS^{-1}.h^{-1}.

6.1.4 OBJECTIVE OF THE STUDY

The main goal of this study was to measure the effect of pre-precipitation on wastewater composition and resulting denitrification potential, capacity and efficiency in a sequencing batch reactor (SBR) system. An important tool to achieve this goal was a fractionation of organic matter, carried out for raw and pre-precipitated wastewater using physical-chemical and biological methods. For different examined doses of precipitant, the COD/N ratio was measured and referred to the obtained denitrification efficiency. From nitrate utilisation rate (NUR) tests the simplified kinetics of denitrification process and wastewater characterisation were estimated. Using several assumptions a simplified nitrification-denitrification model was implemented to optimise theoretically the SBR system with pre-precipitated wastewater to obtain the most satisfactory effluent N-quality. Based on the results, general considerations are signalised, and worked out in chapter 7, on whether a satisfactory denitrification can be obtained in systems fed with low-strength pre-precipitated wastewater

6.2 MATERIALS AND METHODS

6.2.1 EXPERIMENTAL SET-UP

The research on the effect of pre-precipitation on denitrification potential was performed in four 3 ℓ lab-scale SBRs (named $b_1..b_4$). Two SBRs (b_1 and b_2) served as reference and were fed with raw wastwater, while the other two (b_3 and b_4) were fed with pre-precipitated wastewater. A cycle of each SBR consisted of the operational phases as presented schematically in Figure 6.3. The number of operating cycles and the duration of each operational phase were identical for all SBRs. Each cycle started with a FILL-phase of 2 min, where wastewater was provided with flow Q_i. After that, the REACT-phase begun, consisting of two sub-phases. Pre-denitrification (anoxic) and nitrification (aerobic) phases lasted each two hours. After the nitrification a SETTLE-phase started with a duration of 0.5 *h*. During the DRAW-phase the effluent was discharged (2 min) with a flow Q_e and the cycle could start again. During the DRAW-phase an effluent sample (v_S) was taken for analysis.

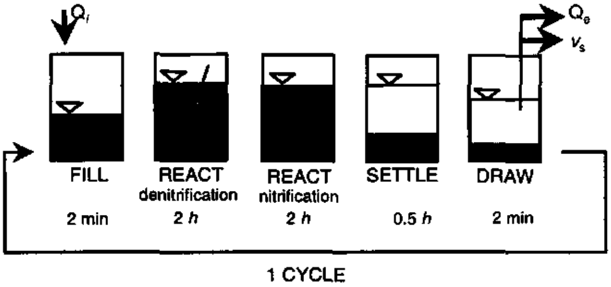

Figure 6.3 Operational phases of one SBR cycle

The raw domestic wastewater from the WWTP Bennekom was equalised in a completely mixed tank of 90 ℓ before provided to the batches b_1 and b_2 in the FILL-phase. The wastewater volume (V_{ww}) for SBR b_3 and b_4 was in the beginning of the SETTLE-phase pumped from the equalisation tank to a 3 ℓ pre-settler working in a sequencing mode (Figure 6.4). The calculated dose of precipitant (2% $FeCl_3 \cdot 3H_2O$) was added in the same time. After addition, the mixture was slowly stirred for around 15 minutes to provide conditions for flocculation. The stirrer was stopped and the flocs were separated from the wastewater for the following 15 min as a result of sedimentation. During the SBR's FILL-phase the precipitated wastewater was decanted and as influent provided to SBR b_3 and b_4 with the flow (Q_i) for the entire duration of this phase (2 min). In the same time an additional volume of pre-precipitated wastewater (v_S) was collected and stored in the refrigerator for analytical determinations.

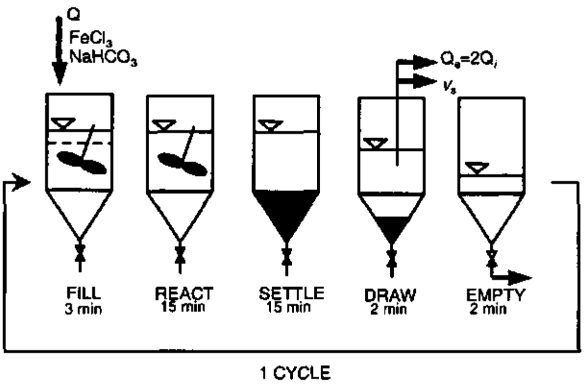

Figure 6.4 Schematic representation of pre-settler operation to produce precipitated influent to SBR b_3 and b_4.

The $FeCl_3$ dose is further expressed as β-ratio, which is a molar ratio of salt metal (Fe) to influent total phosphorus (P_{tot}). Three doses: β=1.0, 1.2 and 1.4 were tested. Each β-ratio was calculated based on an average influent P_{tot} in the period preceding the introduction of a new precipitant dose. Because of a variation in the actual influent P_{tot}-concentration also the resultant β-ratio's could slightly differ from the assumed values. The assumed and actual β-ratio's are presented in Table 6.1. A $NaHCO_3$-solution was added to maintain a pH in the reactor of circa 7.0-7.2. The whole research period was divided into four sub-periods related to the implemented β-ratio's to SBR b_3 and b_4 (Table 6.1). During all these periods the reference SBRs b_1 and b_2 remained operating in the same mode.

Table 6.1 Division of the research into experimental periods relevant to the applied different β-ratio's to SBR b_3 and b_4. SBR b_1 and b_2 remained to operate in unchanged mode throughout the entire experimental period.

Experimental period	Days	Preliminary assumed β-ratio	Actual β-ratio
0 (start-up)	0-25	0	0
I	26-56	0	0
II	56-78	1.4	1.4±0.1
III	79-119	1.0	1.1±0.2
IV	119-204	1.2	1.2±0.1

6.2.2 ANALYSIS

The influent wastewater (both raw and precipitated) was analysed for COD-, N- and P-fractions. The COD was determined in three wastewater samples: untreated (COD), filtered through a 4.4 μm paper filter (Schleicher&Schuell, S&S) (COD_f) and 0.45 μm membrane (S&S) filter (COD_m). For COD-analysis a closed reflux colorimetric method, according to Standard Methods (APHA, 1985), was used. The N_{Kj} and P_{tot} were analysed according to APHA (1985). Ammonia and soluble orthophosphate (S_{NH} and S_{PO4}) were measured spectrophotometrically on a Segment Flow Analyser (SKALAR, the Netherlands) as described by NAVONE (1964).

The filtered (S&S, 4.4 µm) effluent samples were examined for S_{NH}, S_{PO4}, nitrate and nitrite (S_{NO3} and S_{NO2}) using a SKALAR analyser. The activated sludge concentration was periodically controlled by measurement of the MLSS and MLVSS-concentration (APHA, 1985). Environmental conditions in the activated sludge bulk were controlled by regular measurements of pH (WTW pH 191), temperature and DO (WTW OXI 191).

6.2.3 SPECIFIC ACTIVITY TESTS

Denitrification activity tests with raw and precipitated wastewater as carbon source were performed in-situ during the denitrification phase of a SBR cycle. NUR-tests, as described in detail in chapter 2 of this thesis, were performed. To measure the maximum denitrification rate, acetate (1 mol $CH_3COONa \cdot 3H_2O$) was added in excess. Also nitrification activity tests were performed in-situ during the nitrification phase of a SBR cycle. From the moment that aeration started, mixed liquor samples were taken in defined time intervals. They were immediately filtered through a paper filter (4.4 µm., S&S), stored in a refrigerator and analysed after termination of the nitrification phase for S_{NH}, S_{PO4}, S_{NO2} and S_{NO3} on a SKALAR autoanalyser. The maximum nitrification rates were calculated from the linear part of the S_{NH}-depletion and S_{NO} ($S_{NO} = S_{NO3} + 0.6 \cdot S_{NO2}$) production curves.

6.2.4 OPERATIONAL PARAMETERS OF SBRs

After start-up of the SBR systems, all four batches operated in the same mode and were all fed with raw domestic wastewater. In this period the operational parameters to attain effluent N-concentrations of less than 10 mg N.ℓ^{-1} were found. A stable required effluent quality was attained with the operation parameters listed in Table 6.2 for all four batches. In experimental period I the influent to b_3 and b_4 was switched to precipitated wastewater while the operation of reference b_1 and b_2 remained the same for the rest of the research (Table 6.2).

Table 6.2 Operational parameters of the SBRs fed with raw (whole experimental period) and pre-precipitated wastewater (for experimental period IV when optimal β of 1.2 was used)

Parameter	Symbol	Unit	b_1,b_2 (whole period)	b_3,b_4 (period IV, β=1.2)
Organic sludge loading rate	B_{XCOD}	g COD.g MLSS^{-1}.d^{-1}	0.07	0.04
Nitrogen loading rate	B_{XN}	g N.g MLSS^{-1}.d^{-1}	0.0095	0.012
Sludge retention time	SRT*	d	26	47
Activated sludge concentration	X	g MLSS.ℓ^{-1}	4.1	4.0
Active volume of SBR	V_{SBR}	ℓ	3	3
Wastewater volume/cycle	V_{ww}	ℓ	0.4	0.6
Nº of SBR cycles	-	d^{-1}	5.3	5.3

* SRT estimated from amount of surplus sludge removed while the suspended solids in the effluent were not controlled

Regarding the operation of b_3 and b_4 the volume of wastewater provided per cycle was increased from 0.4 to 0.6 ℓ with respect to the experimental period 0 and SBR b_1 and b_2. Besides a change in the wastewater composition, this influenced a majority of the operational parameters. The mode of SBR operation (number of cycles and length of phases) remained identical for both systems. Both SBR systems can be described as ultra-low loaded systems.

6.3 RESULTS AND DISCUSSION

6.3.1 PHOSPHORUS REMOVAL

The reference SBRs b_1 and b_2 were only designed for COD- and N-removal. Comparing the average influent and effluent concentrations for P_{tot} (Figure 6.5, Table 6.3), it was observed that approximately 2.5 mg $P.\ell^{-1}$ was removed from the system due to biomass assimilation. The P_{tot} -content measured in the sludge was 2.0%, which is common for systems without enhanced biological phosphorus removal.

After pre-precipitation was incorporated ahead of b_3 and b_4 (experimental periods I-IV), the overall reduction of phosphorus was dependent on the dose of precipitant. The various precipitant doses that were tested, aimed to find an optimal β-ratio that allowed to attain average P_{tot} concentrations in the effluent of less than 1 mg $P.\ell^{-1}$. For the examined configuration it was found that the optimal β-ratio was 1.2. The average influent P_{tot} was reduced from 7.4 to 2.4 mg $P.\ell^{-1}$ (Figure 6.5, period IV) as a result of pre-precipitation while in the effluent from b_3 and b_4 an average P_{tot} of 0.95 mg $P.\ell^{-1}$ (Figure 6.6) was measured.

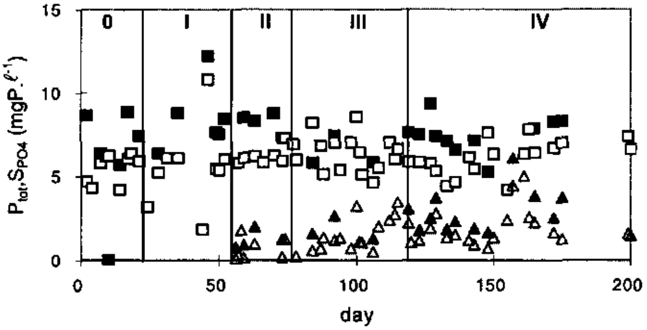

Figure 6.5 P_{tot}- and S_{PO4}-concentrations in raw and pre-precipitated influent to the SBRs in all experimental periods (■P_{tot} and □ S_{PO4} in influent to b_1 and b_2; ▲ P_{tot} and Δ S_{PO4} in influent to b_3 and b_4).

With β = 1.4, the phosphorus removal efficiency was higher than required (Table 6.3). This caused an unnecessary precipitant consumption, an excessive reduction of organic matter from the influent (COD/N-ratio dropped to 2.7) and a pH-drop in the biological step. The pH declined to 6.8 in the mixed liquor, caused a decrease in the nitrification efficiency and the necessity to use a $NaHCO_3$-solution as extra buffer capacity. The pre-precipitation efficiency with a β of 1.0 was in the examined configuration to low to fulfil the required standard. A β of 1.2 turned out to be optimal to attain a stable P-effluent quality expressed with an average P_{tot} of 1.0 mg.ℓ^{-1}.

In principle no supplemental alkalinity was needed to keep the pH above 7.0 in the biological step during all experimental periods, expect of period II. However, a preventive low-rate addition of $NaHCO_3$ in period II to IV took place.

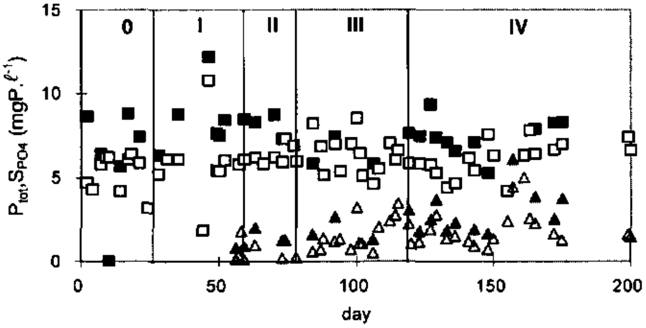

Figure 6.6 P-concentration in effluent from SBRs fed with raw and pre-precipitated wastewater throughout the entire experimental period (■P_{tot} and □ S_{PO4} in effluent from b_1, ▲ P_{tot} and Δ S_{PO4} in effluent from b_3).

Table 6.3 P-removal in function of β-ratio throughout the whole experimental period for b_3 and b_4.

β-ratio	**Influent to SBRs** (mgP.ℓ$^{-1}$)		**Effluent from SBRs** (mgP.ℓ$^{-1}$)				**Total P_{tot} removal efficiency (%)**
			b_3		**b_4**		
	P_{tot}	**S_{PO4}**	**P_{tot}**	**S_{PO4}**	**P_{tot}**	**S_{PO4}**	
0	7.4±1.9	6.1±1.3	4.9±0.3	4.3±0.7	4.7±0.6	4.2±0.6	30
1.0	2.8±0.3	1.6±1.0	**1.3±0.5**	1.1±0.4	**1.3±0.5**	1.1±0.4	82
1.2	2.4±0.7	1.4±0.6	**1.0±0.4**	0.8±0.4	**0.9±0.4**	0.6±0.5	87
1.4	1.2±0.5	0.6±0.6	**0.5±0.3**	0.3±0.2	**0.5±0.4**	0.1±0.04	93

6.3.2 COD AND NITROGEN REMOVAL BY PRE-PRECIPITATION

Wastewater characterisation. The removal of organic matter increased with increasing precipitant dose. In general, more COD than nitrogen was removed by pre-precipitation what significantly lowered the total COD/N-ratio (Table 6.4, Figure 6.7 A,C,D). The raw wastewater was characterised by a COD/N-ratio of 6.5, which as a result of pre-precipitation was reduced to 2.6 with the highest precipitant dose. The optimal precipitant dose in this study of β=1.2, contributed in the reduction of COD/N-ratio to 3.0 and with the lowest dose (β=1.0) to 3.9. The reduction of total COD varied between 49 and 66% depending on the dose (Table 6.4). This reduction is characteristic for a normal-dose pre-precipitation (e.g. HENZE AND HARREMOËS, 1990). The N_{Kj} reduction was considerably lower and amounted approximately 15%, which is also in the range reported in literature (e.g. HENZE AND HARREMOËS, 1992).

Table 6.4 Characteristics of raw and pre-precipitated wastewater

β-ratio	**COD** mg.ℓ$^{-1}$	**COD$_f$** mg.ℓ$^{-1}$	**COD Reduction (%)**	**N_{Kj}** mgN.ℓ$^{-1}$	**COD/N**	**COD$_m$** mg.ℓ$^{-1}$
0	356±88	238±62	-	55.2±8.4	6.5±1.7	32.9±7.1
1.0	179±28	141±54	49	44.3±6.4	3.9±0.5	n.m.
1.2	147±15	108±19	59	46.8±6.2	3.0±0.3	28.4±9.4
1.4	122±13	n.m.[1]	66	44.8±3.9	2.6±0.6	n.m

[1] n.m. = not measured

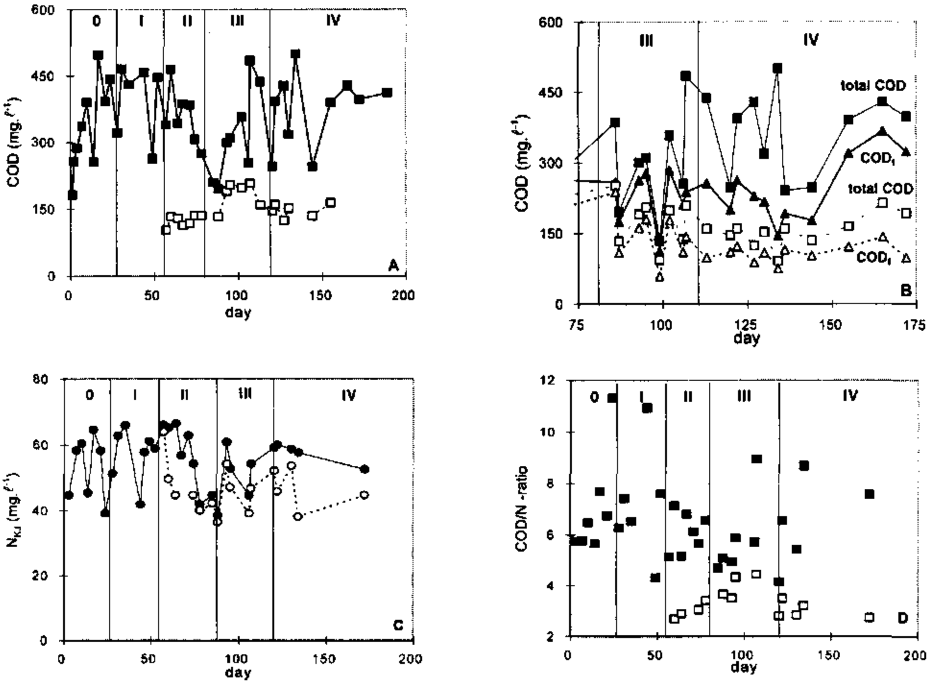

Figure 6.7 Effect of pre-precipitation on change in COD and N_{KJ} concentrations and resulting total COD/N ratio (■,▲,● - raw wastewater; □, Δ,O - pre-precipitated wastewater)

Temporary, COD was determined in wastewater samples after filtration through a filter with a pore size of 4.4 μm - COD_f (Table 6.4, Figure 6.7B). This COD represents the soluble and partially the colloidal COD fractions, since colloidal particles range in size from 0.1 to 50 μm (from 1 to 100 μm so called supra colloidal fraction, Levin et al., 1985). The COD_f was reduced significantly due to pre-precipitation. Comparison of the COD and COD_f of the pre-precipitated wastewater indicated that not all particulate and colloidal material was removed by a normal rate pre-precipitation and the COD of the pre-precipitated wastewater contained except of soluble also a fraction of small-size organic material.

According to several model approaches (e.g. Henze et al., 1987, 1996) it is assumed that total COD of wastewater consists of soluble and particulate matter which is in turn divided into biodegradable and non-biodegradable (inert) fractions. Theoretically, a bigger part of the inert particulate COD (X_I) is eliminated as a result of pre-precipitation while the inert soluble COD (S_I) should remain hardly unchanged. The COD of the effluent from b_3 and b_4, filtered through a 0.45 μm membrane filter (COD_m), amounted circa 28 $mg.\ell^{-1}$. Implementing a reduction factor of 0.9, encountering for the production of inert soluble COD during the activated sludge process (Sollfrank et al., 1992, Siegrist and Tschui, 1992), S_I in the influent would be approximately 25 $mg.\ell^{-1}$. For the system fed with raw wastewater the estimated S_I was higher and amounted circa 30 $mg.\ell^{-1}$. This difference can be explained by a partial removal by pre-precipitation of the COD-fraction with a particles size between 0.1 and 0.45 μm.

To estimate the wastewater characteristics related to the response of activated sludge and simplified denitrification kinetics, NUR-tests were performed. Some typical S_{NO}-curves for SBRs fed with raw and pre-precipitated wastewater (β=1.2) are presented in Figure 6.8.

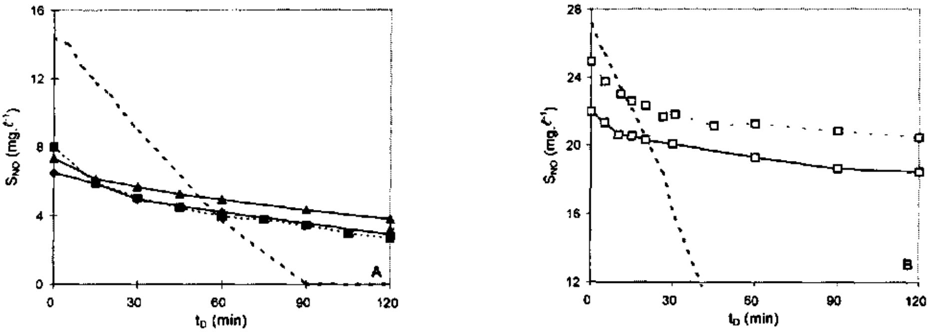

Figure 6.8 S_{NO}-curves as measured during the denitrification phase (t_D) of a SBR cycle. A: (■, ▲, ♦) SBR fed with raw wastewater; B: (□) SBR fed with pre-precipitated wastewater (dashed line: acetate for visualisation of a difference between maximum and actual denitrification rates)

Using the NUR identification procedure, as described in detail in chapter 2, the actual S_S- and X_S-fractions were estimated. For raw wastewater, the duration of the denitrification phase was limiting and consequently the S_S was accurately and X_S roughly estimated. For pre-precipitated wastewater (β=1.2) both fractions were estimated. The S_S-concentration estimated for pre-precipitated wastewater was 16% lower than for raw wastewater (Table 6.5) and amounted 50 mg.ℓ^{-1}. The average X_S-fraction was 51 mg.ℓ^{-1} for pre-precipitated wastewater and approximately 180 mg.ℓ^{-1} for raw wastewater. The sum of estimated average values of S_S, X_S and S_I in pre-precipitated wastewater was somewhat lower than the COD of the composite samples what suggests a presence of some inert particulate material (X_I) with an estimated concentration of circa 21 mg.ℓ^{-1}. For raw wastewater the value of X_I amounted circa 92 mg.ℓ^{-1}.

Regarding the accessibility of total influent nitrogen to biological conversions, not all fractions are biodegradable, analogously to COD. In a simplified approach the soluble, inert nitrogen (S_{NI}) can be determined in a filtered effluent sample from a fully nitrifying activated sludge system. The difference between N_{Kj} and S_{NH} measured in the filtered effluent sample (0.45 µm, $N_{Kj(m)}$, $S_{NH(m)}$) will constitute S_{NI}. Otherwise S_{NI} can be assumed following guidelines of ASM2 as a fraction of S_I (HENZE ET AL., 1996). Because the nitrification in all batches was complete, S_{NI} was in this study estimated using the first approach from the difference between $N_{Kj(m)}$ and $S_{NH(m)}$ and attained approximately 1.2 mg N.ℓ^{-1}. According to ASM2 guidelines for wastewater characterisation, (HENZE ET AL., 1996) the particulate inert N (X_{NI}) can be estimated as a fraction of X_I (0.5-1%) and for this study it attained values of 0.5-1 mgN.ℓ^{-1} for raw wastewater and trace concentrations of 0.1 to 0.2 mgN.ℓ^{-1} for pre-precipitated wastewater.

Table 6.5 Characterisation of raw and precipitated wastewater as obtained from physical-chemical analysis and NUR-tests.

Wastewater parameter	Method of estimation	Unit	Raw wastewater	Precipitated wastewater (β=1.2)
S_S	NUR-test	mgCOD.ℓ^{-1}	58± 11	50± 4
X_S	NUR-test	mgCOD.ℓ^{-1}	≥180±13	51±22
S_I	$COD_m \cdot 0.9$	mgCOD.ℓ^{-1}	30	25
X_I	From equation: $COD = S_S + X_S + S_I + X_I$	mgCOD.ℓ^{-1}	≤102± 37	24±17
COD	Total COD of untreated 24 *h* composite sample	mgCOD.ℓ^{-1}	373± 37	150±37
S_{NI}	Difference between N_{Kj} and S_{NH} determined in filtered effluent sample (0.45 μm)	mgN.ℓ^{-1}	1.2	1.2
X_{NI}	Fraction of X_I according to HENZE ET AL., 1996.	mgN.ℓ^{-1}	0.5-1	0.1-0.2
N	N_{Kj} of untreated 24 *h* composite wastewater sample	mgN.ℓ^{-1}	55.2±8.4	46.8±6.2
Total COD/N	COD=total COD; N=N_{Kj}		6.5	3.1
Biodegradable COD/N	COD=COD-S_I-X_I; N=N_{Kj}-S_{NI}-X_{NI}		4.4	2.1

The presence of inert COD-fractions lowers the availability of COD for denitrification and consequently also the so-called biodegradable COD/N-ratio, the presence of inert N increases it. The term biodegradable COD/N-ratio means that both components of the ratio can theoretically take part completely in the denitrification process. After analysis of the values for the biodegradable COD/N-ratio's it turned out that it was around 30% lower than the total COD/N-ratio. For raw and pre-precipitated wastewater, values were attained of 4.4 and 2.1 respectively.

6.3.3 BIOLOGICAL NITROGEN REMOVAL

Denitrification. An average total effluent N-concentration of lower than 10 mgN.ℓ^{-1} was reached after approximately 25 days of operation (end period 0) in all four SBRs fed with raw wastewater. This corresponded with an average concentration of approximately 8 mgN.ℓ^{-1} (Figure 6.9, Table 6.6) for the sum of nitrate and nitrite (S_{NO2}+S_{NO3}) in all batches (periods 0-I). This remained on the same level for batches b_1 and b_2 during the entire experimental period. After introduction of pre-precipitation ahead of b_3 and b_4 an immediate deterioration in S_{NO2}+S_{NO3}-effluent quality was noted (period II). With the optimal β-ratio of 1.2 the effluent S_{NO2}+S_{NO3} concentration achieved an average level of approximately 21.3 mg N.ℓ^{-1} (period IV) while for a β of 1.0 (period III) and 1.4 (period II) it was 19.7 and 26.3 mg N.ℓ^{-1} respectively (Table 6.6). The contribution of nitrite in the sum S_{NO2}+S_{NO3} was negligible in all batches.

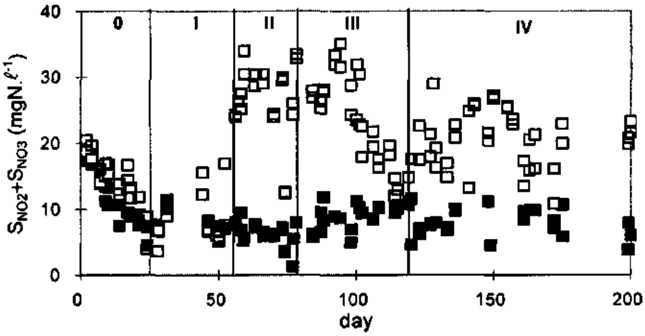

Figure 6.9 Sum of nitrite and nitrate in the effluent from SBRs fed with raw (■: b_1 and b_2) and pre-precipitated wastewater (□: b_3 and b_4).

Table 6.6 Nitrogen effluent concentrations as a function of β-ratio.

β-ratio	Batch	Experimental period	S_{NH}	S_{NO3}	S_{NO2}	N_{Kj}
			mgN.ℓ$^{-1}$			
0	b_1	I-IV	0.78±0.73	8.74±2.92	0.07±0.06	2.25±1.53
	b_2	I-IV	0.54±0.62	7.43±2.16	0.11±0.30	1.72±0.80
	b_3	I	0.32±0.30	7.86±2.36	0.12±0.16	1.71±0.38
	b_4	I	0.47±0.35	7.51±4.10	0.26±0.14	1.61±0.57
1.0	b_3	III	1.55±1.17	19.7±4.16	0.15±0.09	n.m.$^{1)}$
	b_4	III	1.67±0.97	19.63±6.44	0.13±0.12	
1.2	b_3	IV	0.37±0.73	21.9±3.33	0.16±0.33	n.m.
	b_4	IV	0.48±0.85	20.8±3.50	0.06±0.06	
1.4	b_3	II	2.26±0.85	26.12±5.31	0.24±0.16	n.m
	b_4	II	2.48±0.54	26.66±5.88	0.18±0.14	

$^{1)}$ n.m. not measured

It should be reminded that the nitrite/nitrate effluent quality for the batch systems fed with pre-precipitated wastewater was obtained after an optimised operation of SBR b_3 and b_4 by increasing the volume of added wastewater per cycle with respect to SBR b_1 and b_2 (§ 6.2.4). The denitrification potential of the SBRs fed with pre-precipitated wastewater was dependent on the precipitant dose. With a higher dose, less biodegradable COD for denitrification remained and this resulted in a lower overall process efficiency.

From NUR-tests several denitrification rates were estimated for all SBRs. The obtained denitrification rates for the experimental set-up fed with raw wastewater (b_1 or b_2) and pre-precipitated wastewater (b_3 or b_4, β=1.2) differed significantly (Table 6.7). It is remarkable that the subsequent actual specific denitrification rates on S_S, X_S and endogenous (k_{DSS}, k_{DXS}, k_{Dend}) were higher in the SBRs fed with pre-precipitated influent. Also the maximum specific denitrification rate attained with an excessive addition of acetate (k_{DAc}) turned out to be significantly higher in b_3 and b_4. Moreover, k_{DAc} was significantly higher than k_{DSS} in each case and especially for b_1 and b_2. This can be explained by a low initial concentration of S_S in the SBR's, even lower in b_1 and b_2 due to a smaller volume of wastewater provided in the FILL phase.

The much higher respective denitrification rates in the batches with pre-precipitated wastewater can result from a relatively low fraction of particulate COD (X_I and X_S) provided to such a system. The fraction X_I adsorbs on activated sludge flocs, reducing the viable biomass fraction in the MLSS. The fraction X_S adsorbs also on the sludge flocs and is slowly hydrolysed and degraded. When a little amount of X_S and X_I is provided, activated sludge can become more viable and more active than in systems subjected to wastewater with a high X_I- and X_S-content.

The specific overall denitrification rate (k_D) was determined in relation to the entire duration of the denitrification phase (t_D) in each SBR. The k_D, in contrast to respective denitrification rates, turned out to be 37% higher for batches b_1 and b_2. At first sight the difference does not seem to be significant to contribute in such a deteriorated effluent quality of b_3 and b_4. However, the effluent quality is not only dependent on the denitrification rate but also on the amount of nitrate that has to be removed. More wastewater was provided to b_3 and b_4 what resulted in a higher production of nitrate (and nitrite) in the nitrification phase. The smaller overall denitrification rate and higher initial nitrate concentration contributed in insufficient nitrate elimination in b_3 and b_4, leading finally to its high effluent concentration in steady state conditions.

The significant difference in effluent N-quality of both systems can be the best explained by a difference in wastewater denitrification potential (DP) that in this case was defined as an amount of nitrate that could be removed from 1 ℓ wastewater using the examined activated sludge (inclusive the basic endogenous denitrification potential of activated sludge). Using the DP, the difference in denitrification efficiency for SBRs fed with precipitated influent was calculated to be 42% lower than of the SBRs fed with raw wastewater.

Table 6.7 Specific denitrification rates (k_{DSS}, k_{DXS}, k_{Dend}, k_D and k_{DAc}) and wastewater denitrification potential (DP) estimated for SBR systems fed with raw (b_1, b_2) and pre-precipitated (b_3, b_4, β=1.2) wastewater

Denitrification parameter	Unit	Raw wastewater (b_1, b_2)	Precipitated wastewater (b_3, b_4, β=1.2)
k_{DSS}	$mgN.gVSS^{-1}.h^{-1}$	1.86±0.46	3.33±0.18
k_{DXS}	$mgN.gVSS^{-1}.h^{-1}$	0.69±0.20	0.82±0.13
k_{Dend}	$mgN.gVSS^{-1}.h^{-1}$	0.20	0.32±0.04
k_D	$mgN.gVSS^{-1}.h^{-1}$	0.88±0.16	0.64±0.22
k_{DAc}	$mgN.gVSS^{-1}.h^{-1}$	4.35	6.76
DP	$mgN.\ell^{-1}$	30.20±7.80	17.44±5.61

Nitrification. Complete nitrification was measured in all batches fed with raw and pre-precipitated wastewater (β=1.2). The poorer nitrification efficiency in b_3 and b_4 when wastewater was treated with a precipitant dose of β=1.4 was a result of insufficient pH correction in the SBR.

The nitrification batch tests during the nitrification phase in the SBR allowed for a simplified estimation of maximum nitrification rates. Although for both systems the final effluent quality was of the same range, the specific maximum nitrification rate (k_{NHm}) was approximately 2.2 time higher for the system fed with pre-precipitated wastewater (Table 6.8, Figure 6.10). Several reasons could contribute in this effect. The system fed with pre-precipitated wastewater was characterised by a lower organic loading, decreased sludge production and consequently a longer SRT of activated sludge. A longer SRT results in a higher fraction of nitrifiers in the whole activated sludge population. Moreover, analogously to the denitrification, the activated sludge from SBRs b_3 and b_4 could contain more viable biomass, and therefore an increased fraction of nitrifiers. Besides, SBR b_3 and b_4 were subjected to higher N-loading rates (B_{XN}), which can stimulate the nitrification rate. During the whole research period the operation temperature was 15-23 °C and was beneficial for nitrification in both systems.

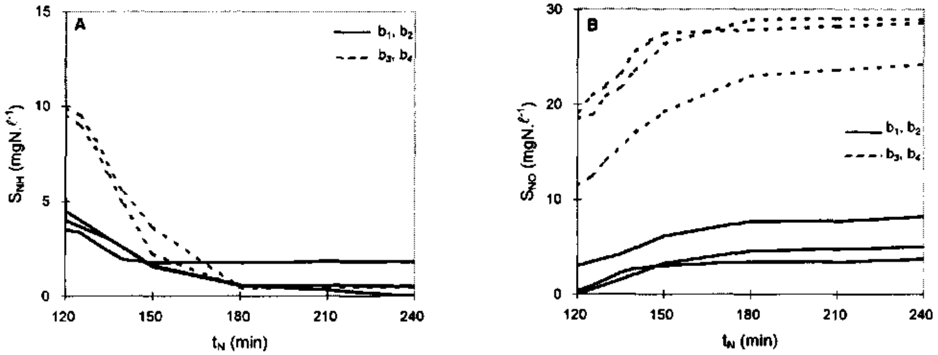

Figure 6.10 Reduction rate of S_{NH} and production rate of S_{NO} during a nitrification phase (t_N).

Table 6.8 Maximal specific nitrification rates (k_{NHm}) calculated from linear phases of S_{NH}-reduction and S_{NO}-production during the nitrification phase of a SBR cycle and nitrogen sludge loading rate for SBRs fed with raw and pre-precipitated wastewater.

SBR	k_{NHm} (mgN.gVSS^{-1}.h^{-1})		B_{XN} (mgN.gMLSS^{-1}.h^{-1})
	from S_{NH} reduction	from S_{NO} production	
b_1, b_2	2.47±0.49	2.86±0.36	0.40
b_3, b_4	5.37±0.62	6.19±0.64	0.52

6.4 THEORETICAL SYSTEM OPTIMISATION WITH A SIMPLIFIED MODEL

A simplified nitrification-denitrification model (Table 6.9) was used for a theoretical optimisation of the SBR system fed with pre-precipitated wastewater. The main question was, whether the unsatisfactory denitrification efficiency could be improved when manipulating with the duration of denitrification and nitrification phases (t_D and t_N respectively).

Table 6.9 Simplified nitrification-denitrification model used for the optimisation of the SBR system fed with pre-precipitated wastewater

Model component		S_{NH}	S_{NO}	S_S	X_S	Process rate
Process		1	2	3	4	
1	Nitrification	-1				$k_{NHm} \cdot X_V \frac{S_{NH}}{K_{NH}+S_{NH}}$
2	Anoxic S_S oxidation (denitrification)		$-(1-Y_{HD})$	-1		$k_{SSm} \cdot X_V \frac{S_S}{K_S+S_S}$
3	Anoxic X_S oxidation (denitrification)		$-(1-Y_{HD})$		-1	$k_{XSm} \cdot X_V \frac{X_S}{K_{XS}+X_S}$
4	Endogenous denitrification		-1			$k_{end} \cdot X_v$

The denitrification part of the model is described in chapter 2. A description of the nitrification process is more simplified than this of the respiration based nitrification-denitrification model in chapter 4. An introduction of a one-step nitrification where S_{NH} is directly oxidized to S_{NO3} was dictated by the lack of information about the S_{NO2}-oxidation rate. The kinetics of the nitrification process were estimated from the S_{NO} profile during the aerobic phase of the SBR system. The maximum specific nitrification rate was estimated from the linear phase of S_{NO}-production. The S_{NH} half-saturation coefficient (K_{NH}) was estimated by fitting a S_{NO} production curve with a Monod-type equation for the S_{NH}-oxidation. The concentration of nitrifiable nitrogen (S_{NHn}) was estimated from several measurements of the initial S_{NH}-concentration in the beginning of the nitrification phase (t_N=0). Organic biodegradable fractions of wastewater and denitrification kinetics were estimated from NUR-tests. The oxygen consumption, aerobic oxidation of S_S and X_S and the transition phases between denitrification and nitrification phases were not modelled. The equations describing nitrification and denitrification processes are presented in matrix form in Table 6.9 while the parameters and their values are listed in Table 6.10.

Table 6.10 Wastewater characterisation and kinetic and stoichiometric parameters used for the simulation of the SBR system fed with pre-precipitated wastewater (β=1.2).

Model component		Unit	Value
Wastewater characterisation			
Readily biodegradable COD	S_S	mgCOD.ℓ^{-1}	45
Slowly biodegradable COD	X_S	mgCOD.ℓ^{-1}	33
Nitrifiable N	S_{NHn}	mgN.ℓ^{-1}	38
Parameters			
Max specific S_S-oxidation rate	k_{SSm}	mgCOD.gVSS^{-1}.h^{-1}	22.0
Max specific X_S-utilisation rate	k_{XSm}	mgCOD.gVSS^{-1}.h^{-1}	2.5
Half-saturation coefficient for S_S	K_S	mgCOD.ℓ^{-1}	1
Half-saturation coefficient for X_S	K_{XS}	mgCOD.ℓ^{-1}	4
Max specific S_{NH}-oxidation rate	k_{SNHm}	mgN.gVSS^{-1}.h^{-1}	6.9
Half-saturation coefficient for S_{NH}	K_{NH}	mgN.ℓ^{-1}	0.6
Endogenous specific denitrification rate	k_{Dend}	mgN.gVSS^{-1}.h^{-1}	0.2 (0.25-0.4)
Anoxic heterotrophic yield	Y_{HD}	-	0.67

Simulations. The effect of prolonging the denitrification phase (t_D) within the unchanged duration of one SBR cycle was simulated. All measured S_{NH} profiles indicating that nitrification was completed half way of the aerobic phase (Figure 6.10) formed a basis for this simulation scenario. Four situations were simulated with a duration of the nitrification phase of t_N=2 (original), 1.5, 1 and 0.8 *h* respectively within an unchanged length of the total SBR cycle. The denitrification kinetic parameters were estimated from a NUR-test performed during the denitrification phase (Figure 6.11) using the estimation procedure and default values as described in chapter 2. For the performed simulations it was assumed that the shortening of a nitrification phase would not have any effect on the biomass kinetics (simplification). For the examined configuration a minimal t_N ensuring still a low effluent S_{NH}-concentration was approximately 50 minutes.

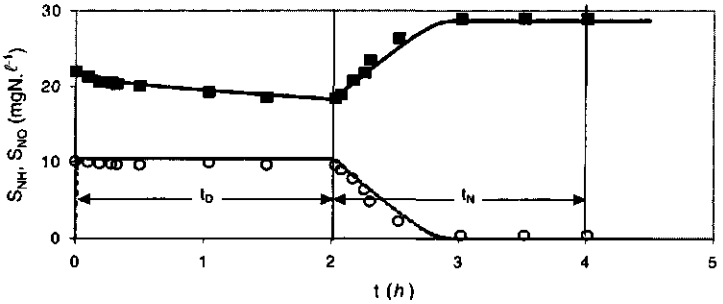

Figure 6.11 Representative course of S_{NO} and S_{NH} during one cycle of the SBR (t_D+t_N) fed with pre-precipitated wastewater (β=1.2) that served to obtain kinetic parameters of the nitrification and denitrification process. The measurements (points: ■ S_{NO}, O S_{NH}) are fitted (solid lines: S_{NO} and S_{NH}) with the simplified nitrification-denitrification model (Tables 6.9 and 6.10).

The results of simulation reveal that due to prolonging of the denitrification phase, the nitrate reduction in the additional time proceeds with the slowest endogenous rate (Figure 6.12). In case of the maximal t_D of 3.2 *h* the fraction S_{NO} would be further reduced with 0.6 mg N per litre batch mixture per cycle, with respect to the basic reduction (3.5 vs. 4.1 mgN per litre of batch mixture per cycle for t_D=2 *h* and 3.2 *h* respectively). This would in turn contribute in the improvement of the effluent quality of approximately 2.8 $mg.\ell^{-1}$ (20.1 vs. 17.3 $mgN.\ell^{-1}$ in equilibrium state of a SBR reactor).

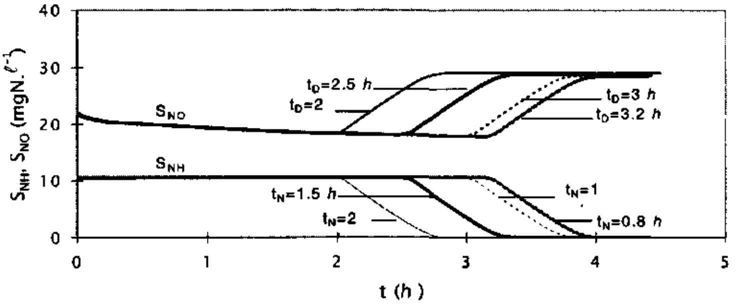

Figure 6.12 Effect of a modification of the length of the anoxic and aerobic phases (t_D, t_N) on the S_{NH} and S_{NO} courses in the SBR system fed with pre-precipitated wastewater (β=1.2).

Above results were obtained with a very low endogenous denitrification rate of k_{Dend} =0.2 mgN.gVSS^{-1}.h^{-1} as measured from the nitrate profile presented in Figure 6.11. The average k_{Dend} was however higher (Table 6.7), what suggested to perform series of further simulations with a step-wise increase of k_{Dend}-values. The resulting theoretical improvement of S_{NO}-effluent quality at k_{Dend} ranging from 0.25 to 0.40 mgN.gVSS^{-1}.h^{-1} is shown in Figure 6.13. With the highest k_{Dend} of 0.4 mgN.gVSS^{-1}.h^{-1} and t_D of 3.2 *h* the expected effluent S_{NO} could attain approximately 13.5 mgN.ℓ^{-1} what can be considered as a significant improvement of the process.

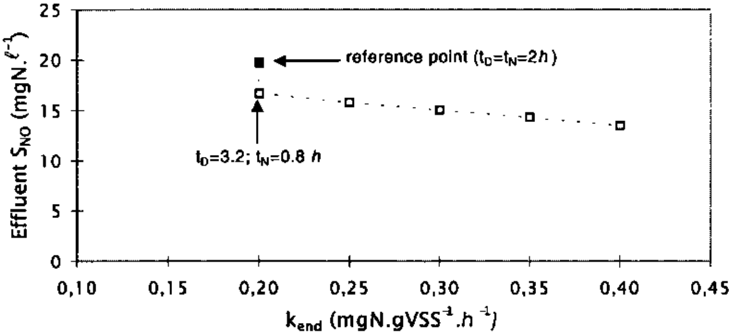

Figure 6.13 S_{NO}-effluent quality from the SBR-system fed with pre-precipitated wastewater as a function of specific, endogenous denitrification rate (k_{Dend}). Except of the reference point (basic situation t_D=t_N=2*h*) all others are characterised by t_D=3.2 *h*.

6.5 CONCLUSIONS

The effect of pre-precipitation on wastewater composition, denitrification potential and overall activated sludge process was examined in lab-scale SBR systems operating with pre-denitrification.

To remove P_{tot} up to less than 1 mg.ℓ^{-1} in the overall chemical-biological treatment, three doses of ferric chloride were tested, expressed as β-ratio: β=1.0, 1.2, 1.4. The β of 1.2 caused a reduction of total phosphorus from P_{tot} = 7.4 to 2.4 in primary treatment and around 1.5 mgP.ℓ^{-1} was removed in the down-stream activated sludge system for biomass assimilation. This β-ratio turned out to be optimal for the examined configuration, concerning P-removal.

During the whole experimental period the raw wastewater was characterised by a rather low total COD/N-ratio of 6.5. With an optimal β-ratio the total COD/N ratio was reduced to 3.1. The profile of wastewater fractions changed due to pre-precipitation. The soluble readily biodegradable and inert fractions S_S and S_I were eliminated in 14 and 17% respectively. The particulate slowly biodegradable and inert fractions, X_S and X_I, were both removed in approximately 75%.

The denitrification potential of pre-precipitated wastewater was low because its biodegradable organic content was significantly reduced. This led to high nitrate-effluent concentrations of approximately 21.3 mg.ℓ^{-1} while in the reference system fed with raw wastewater 8 mg.ℓ^{-1} was attained throughout the entire experimental period. Pre-precipitation with β=1.2 caused a 42% reduction of denitrification potential with respect to the analogous system with raw wastewater.

The activated sludge from the system fed with pre-precipitated wastewater exposed higher specific denitrification rates for different carbon sources (S_S, X_S, acetate, endogenous) than from the system subjected to raw wastewater. The higher activity of activated sludge was probably caused by the presence of a higher fraction of viable biomass due to a significant reduction of X_S and X_I from the wastewater. The overall denitrification rate measured for the whole denitrification phase was however higher for the system fed with raw wastewater.

The denitrification potential of the system depends on wastewater composition and basic respiration activity of the activated sludge. The system denitrification efficiency depends on the denitrification potential and system configuration while the nitrate-effluent quality additionally on the amount of nitrate that has to be denitrified.

The nitrification was complete in both systems, giving a high S_{NH}-effluent quality. However, the specific nitrification rates were 2.2 times higher for the system fed with pre-precipitated wastewater. The major reason contributing in this effect is an increased nitrifiers fraction in the latter case, caused by a prolonged SRT, a higher fraction of viable biomass in the total activated sludge mass and a lower COD/N-ratio.

The theoretical optimisation of the denitrification process for a system fed with low-strength pre-precipitated wastewater by using a simplified model proved that the S_{NO}-effluent quality is primarily determined by the denitrification potential of the wastewater. The optimisation of such a system is mainly restricted to take maximum advantage of the endogenous denitrification what leads to big anoxic reactors.

LIST OF SYMBOLS AND ABBREVIATIONS

$b_1..b_4$	subsequent SBR-batches used in the study described in this chapter
B_{XCOD}	organic sludge loading rate (g COD.g MLSS^{-1}.d^{-1})
B_{XN}	N sludge loading rate (g N.g MLSS^{-1}.d^{-1})
COD	total COD concentration of wastewater (mg.ℓ^{-1})
COD_f	COD measured in wastewater sample filtered through 4.4 µm filter (mg.ℓ^{-1})
COD_m	COD measured in wastewater sample filtered through 0.45 µm membrane filter (mg.ℓ^{-1})
DP	denitrification potential (mgN.ℓ^{-1})
k	specific substrate utilisation rate in the anoxic conditions, subscripts: SSm, XSm - maximum of S_S and X_S respectively (mg COD.gVSS^{-1}.h^{-1})
k_D	total specific denitrification rate; additional subscripts: Ac, S_S ,X_S - on acetate, S_S, X_S alone; o - overall (mgN.gVSS^{-1}.h^{-1})
k_{Dend}	specific endogenous denitrification rate (mgN.gVSS^{-1}.h^{-1})
k_{NHm}	specific maximum nitrification rate (mgN.gVSS^{-1}.h^{-1})
K_{NH}	half-saturation coefficient from Monod equation for S_{NH} oxidation (mgN.ℓ^{-1})
K_S	half-saturation coefficient from Monod equation for S_S oxidation (mgCOD.ℓ^{-1})
K_{XS}	half-saturation coefficient from Monod equation for X_S (mgCOD.ℓ^{-1})
ML(V)SS	mixed liquor (volatile) suspended solids (g.ℓ^{-1})
N	total nitrogen concentration; in COD/N ratio $N=N_{Kj}$ (mgN.ℓ^{-1})
N_{Kj}	total Kjeldahl nitrogen in the influent, regarding influent $N_{Kj}=N$; subscript: m - N_{KJ} measured in 0.45 µm membrane filtrate (mgN.ℓ^{-1})
NUR	nitrate utilisation rate
P_{tot}	total phosphorus (mgP.ℓ^{-1})
Q_i	wastewater flow during FILL phase of SBR cycle (ℓ.h^{-1}); $Qi \cdot t_{FILL}=V_{ww}$
Q_e	wastewater flow during DRAW phase of SBR cycle (ℓ.h^{-1})
SBR	sequencing batch reactor
S_I	soluble, inert COD (mgCOD.ℓ^{-1})
S_{NH}	soluble ammonia; subscript: (m) - S_{NH} in 0.45 µm membrane filtrate; n - nitrifiable S_{NH} (mgN.ℓ^{-1})
S_{NI}	soluble inert nitrogen (mgN.ℓ^{-1})
S_{NO}	sum of nitrate and nitrite-nitrate equivalent; $S_{NO}=S_{NO3}+0.6 \cdot S_{NO2}$ (mgN.ℓ^{-1})
S_{NO2}	nitrite (mgN.ℓ^{-1})
S_{NO3}	nitrate (mgN.ℓ^{-1})
S_{PO4}	soluble orthophosphate (mgP.ℓ^{-1})
SRT	solid retention time (d)
S_s	soluble readily biodegradable COD (mgCOD.ℓ^{-1})
t_D	duration of denitrification phase in SBR cycle (h)
t_{FILL}	length of the FILL phase of SBR cycle (h)
t_N	length of nitrification phase in SBR cycle (h)
V_{SBR}	active volume of SBR (ℓ)
v_S	volume of wastewater sample discharged in DRAW phase of SBR- and presettler cycle for analysis (mℓ)
V_{ww}	wastewater volume provided in the FILL phase of SBR or pre-settler cycle (ℓ)
X_I	particulate inert COD (mgCOD.ℓ^{-1})
X_{NI}	particulate, inert N (mgN.ℓ^{-1})
X_s	particulate, slowly biodegradable substrate (mgCOD.ℓ^{-1})
X	concentration of total biomass; subscript: V of volatile biomass (gMLSS.ℓ^{-1} or gVSS.ℓ^{-1})
Y_{HD}	heterotrophic yield coefficient (mg $COD_{biomass}$.mg$COD_{substrate}^{-1}$)
β	molar ratio of precipitant salt to phosphorus in influent wastewater

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7

Optimisation of a pre-denitrification system fed with pre-precipitated wastewater with a control strategy

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ABSTRACT

To verify the statements on the effect of pre-precipitation on the denitrification potential, as derived from the research described in chapter 6, and from contradictive evaluations appearing in literature, a supplementary research was performed. A plug-flow pre-denitrification pilot-plant with pre-precipitated wastewater was used. Its operation was optimised, by implementing a respiration based control strategy to adjust the nitrification volume to the actual nitrifiable N load. This control strategy allowed avoiding over-aeration of the system and a maximum possible denitrification fraction could be created. Further, relatively high sludge loading rates were employed, while a satisfactory nitrification efficiency could be still attained.

Pre-precipitation with ferric chloride with β-ratio of 1.0 lowered the total COD/N-ratio of the raw wastewater from 7.6 to 4.7. Despite of more beneficial wastewater characteristics comparing with the research described in chapter 6 and implementation of a well operating control strategy the denitrification efficiency was not significantly improved. Concerning the nitrate effluent quality an improvement of 5 $mgN.\ell^{-1}$ could be obtained for wastewater of the same origin in comparison with the results from chapter 6 (16.3 vs. 21.3 $mg N.\ell^{-1}$ respectively).

It was concluded that the denitrification potential of the wastewater in question determines predominantly the denitrification efficiency of a well-dimensioned activated sludge system. Any optimisation steps contribute only to a small extent in denitrification efficiency improvement.

7.1 INTRODUCTION

Before requirements for nitrogen and phosphorus (N&P) removal from wastewater became obligatory, all pre-treatment steps reducing the COD-load to the biological reactor were evaluated positively since they allowed for a reduction of the activated sludge volume and saving energy for aeration (e.g. ØDEGAARD, 1992, OOTEN ET AL., 1993). Since strict requirements for total N&P removal were introduced, the wastewater strength and composition, especially in terms of biodegradable COD-fractions, became of crucial importance and a high COD-reduction by any pre-treatment step became counteractive for N&P removal.

Pre-precipitation is an efficient pre-treatment technology for COD- and P-removal. However, it contributes often in unsatisfactory denitrification efficiency in a down stream activated sludge treatment. This implies the necessity of additional denitrification volume, addition of an external carbon source and/or implementation of advanced control strategies.

A significant reduction of organic matter from wastewater by pre-precipitation is evident. Several opinions exist concerning the influence of a changed organic profile of wastewater on the denitrification potential. According to HENZE (1994), the denitrification efficiency in systems with pre-precipitation is 30% lower compared to systems where raw wastewater is supplied. In research with an ultra-low loaded activated sludge SBR system (described in chapter 6 of this thesis) the denitrification potential was reduced with 42% after pre-precipitation was introduced in comparison with a reference system with raw domestic wastewater. Based on the results from full- and semi-full scale experiments, GIESEN and PETERS (1994) concluded that pre-precipitation in 100% of the influent stream caused a 21% reduction of the denitrification efficiency. On the other hand, denitrification was hardly effected when only a part of the wastewater flow (25%) was exposed to pre-precipitation. In both situations, the P-effluent requirements were met. KARLSSON and SMITH (1991) found by a comparison of a conventional system fed with settled wastewater and a system with pre-precipitated wastewater that in both cases approximately 9 mg $N.\ell^{-1}$ was removed as a result of denitrification. They stated that a decreased BOD/N-ratio did not have a negative effect on the denitrification in a system characterised by an anoxic retention time from 3 to 5 *h*. UIJTERLINDE and VAN DER ROEST (1994) presented the results from a system where after introduction of pre-precipitation and with an optimisation of the oxygen input a sufficiently low total nitrogen effluent quality was obtained.

The results of the research presented in chapter 6 revealed that the introduction of pre-precipitation contributed to a high concentration of nitrate in the effluent from the ultra low-loaded SBR-system with fixed nitrification and denitrification phases. The question arose, how far the denitrification efficiency can be improved when implementing any optimisation strategy. With a simplified nitrification-denitrification model the effect of the duration of anoxic and aerobic phases on the denitrification efficiency was simulated. However, the simplified character of the model did not allow to predict a change in activated sludge activity, so a real effluent quality could be only speculated. It was stated, that the denitrification potential of a wastewater is the most crucial and any optimisation attempt can improve the denitrification efficiency of a well dimensioned system only to a small extent. To draw ultimate conclusions additional research was still required.

Generally, nitrification or denitrification efficiency can be improved by using an adequate control strategy. In this part of the thesis the results are presented where aerobic respirometry was used to control the nitrification volume in a plug-flow pilot-plant with pre-precipitated wastewater. Objective was to create an optimal aerobic volume, proportional to the frequently estimated actual influent nitrifiable-N concentration. A low ammonia concentration in the effluent was a precondition. By avoiding over-aeration a maximal possible pre-denitrification volume could be created. For control of the nitrification volume the automated respiration based control unit (RESCUE, BROUWER ET AL., 1997) was used. Attention was mainly paid on how far the denitrification efficiency can be improved by manipulating the operational conditions of a system when the original wastewater denitrification potential is relatively low.

7.2 MATERIALS AND METHODS

7.2.1 PILOT-PLANT

The optimisation of the denitrification in a system fed with pre-precipitated wastewater was executed in a controlled pilot-plant (Figure 7.1). The pilot-plant consisted of a primary settler, an activated sludge plug-flow reactor and a secondary settler. Ferric chloride (4% $FeCl_3 \cdot 6H_2O$) used as precipitant was continuously dosed into the influent tube.

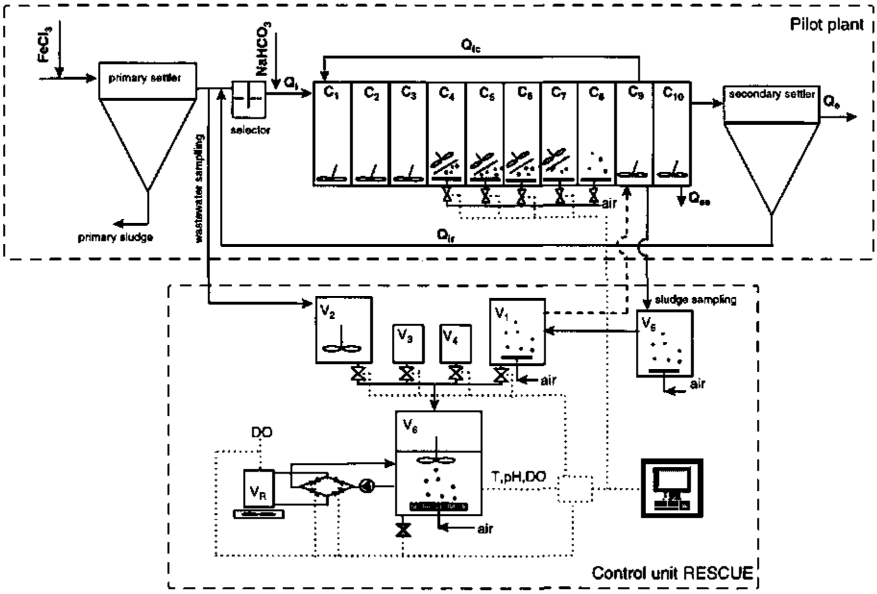

Figure 7.1 Schematic representation of the plug-flow pre-denitrification pilot-plant fed with pre-precipitated wastewater integrated with the respiration based control unit RESCUE.

The precipitant dose, defined as a molar ratio (β-ratio) of salt metal (Fe) to influent total phosphorus (P_{tot}), was set at β=1.0. The flocculation and sedimentation took place in the primary settler (volume 350 ℓ). The primary sludge was removed every hour from the conical bottom of the settler. The precipitated wastewater entered with a constant flow (Q_i) the selector (volume 28 ℓ) where it was mixed with the return sludge stream (Q_{ir}) in a Q_i/Q_{ir}-ratio of 1.25. The plug-flow activated sludge reactor with a total volume of 1000 ℓ, consisted of 10 equal compartments (named $C_1..C_{10}$) in series. The compartments C_1, C_2 and C_3 were anoxic (stirred) while C_4 to C_7 could be either anoxic or aerobic (stirred and aerated), depending on the control decision of RESCUE. Compartment C_8 was permanently aerated while C_9 and C_{10} were only stirred. From C_9 the nitrate-rich mixture (Q_{ic}) was pumped to C_1 in a ratio of 2.3 with respect to Q_i. From C_{10} the effluent (Q_e) was discharged to the secondary settler (volume 350 ℓ) from where the settled sludge was returned to the selector. The excess sludge was removed with a constant flow (Q_{es}) from C_{10}, allowing for maintenance of a constant SRT in the pilot-plant. As a result of pre-precipitation the alkalinity of wastewater was lowered. To maintain a pH in the aerobic volume at approximately pH=7.2 a sodium bicarbonate solution was dosed to the primary settler. The operational characteristics of the pilot-plant are presented in Table 7.1

Table 7.1 Average operational parameters for the pilot-plant with pre-precipitated wastewater.

Parameter	Symbol	Unit	Value
Influent flow	Q_i	$\ell.h^{-1}$	90.7
Return sludge flow	Q_{ir}	$\ell.h^{-1}$	69.6
Internal recycle flow,	Q_{ic}	$\ell.h^{-1}$	208.2
MLSS	X	$gMLSS.\ell^{-1}$	3.8
MLVSS	X_V	$gVSS.\ell^{-1}$	0.67*X
Organic sludge loading	B_{XCOD}	$gCOD.gMLSS^{-1}.d^{-1}$	0.15
Nitrogen sludge loading	B_{XN}	$gNgMLSS^{-1}.d^{-1}$	0.033
Precipitant dose, β		$mol_{Fe}.mol_{Pin}^{-1}$	1.0
Pre-anoxic fraction of plant	-	-	0.40
Aerobic fraction of plant	-	-	0.40
Post-anoxic fraction of plant	-	-	0.20
pH	-	-	7.2
Temperature	T	°C	18

7.2.2 CONTROL UNIT

The respiration based control unit RESCUE (Figure 7.1) was integrated with the pilot-plant. A detailed description of RESCUE's components can be found in chapter 4 (§ 4.3.2).

7.2.3 CONTROL PROCEDURE

The control approach of the nitrification volume relied on the adjustment of the nitrification volume to the actual nitrifiable-N (S_{NHn}) load and nitrification kinetics. The control procedure consisted of four steps. The control decision (step 4) was proceeded by three types of respirometric tests (step 1-3), also described in chapter 4 (§ 4.3.3):

STEP 1 Respirometric estimation of nitrite (S_{NO2}) oxidation kinetics (each 10-12 *h*).

STEP 2 Respirometric estimation of ammonia (S_{NH}) oxidation kinetics (each 10-12 *h*).

STEP 3 Respirometric estimation of wastewater composition and oxidation kinetics.

From the identification of a wastewater respirogram, using the model from chapter 4 (Table 4.8), a detailed wastewater characterisation and oxidation kinetics were obtained. For control purposes only the information about the actual concentration of S_{NHn} was of interest. The necessary duration of a single respiration test to attain reliable wastewater characteristics restricted the estimation frequency of the actual S_{NHn}-concentration to approximately each 1.5-2 *h*. Regarding the necessity to actualise the nitrification kinetics (step 1+2) every 10-12 *h*, the maximal number of S_{NHn}-values was limited to around 12 estimates per 24 *h*.

STEP 4 Control decision about the number of aerated compartments.

The actual concentration of S_{NHn} and the actual flow (Q_i) to the plant allowed to calculate the S_{NHn}-load. The aerobic volume of the pilot-plant (V_N) for a complete nitrification was calculated using equation 7.1 using the simplification of one-step zero order nitrification kinetics:

$$V_N = \frac{Q_i \cdot S_{NHn}}{r_{NHm}} \; ; \ell \qquad (7.1)$$

where: r_{NHm} – maximum volumetric ammonia oxidation rate ($mgN.\ell^{-1}.h^{-1}$)

The calculated volume was rounded up and translated into the nearest number of aerated compartments. The aerated volume was in this way always larger than calculated. Because of plant compartmentalisation the smallest change of the volume was restricted to 10%.

All respirometric tests were performed at stable pH (7.2) and temperature conditions (18°C).

7.2.4 ANALYSIS

The influent and effluent quality of the pilot-plant were measured in composite 24 *h* samples with respect to nitrogen, phosphorus and COD-fractions (§6.2.2.). Periodically, the course of ammonia, nitrite, nitrate and phosphate was controlled throughout the compartments of the entire pilot-plant by taking and analysing grab samples. The environmental conditions in the pilot-plant were monitored by regular manual measurements of temperature, dissolved oxygen (WTW OXI 191), pH (pH controller Endress&Hauser, Liquisys CPM 240) and ML(V)SS-concentration. All determinations were performed according to Standards Methods (APHA, 1992).

7.2.5 SPECIFIC ACTIVITY TESTS

To assess specific denitrification rates and denitrification potential (DP), nitrate utilisation rate (NUR) tests were performed with a pulse addition of pre-precipitated wastewater. The volumetric ratio of wastewater to the total mixture of activated sludge was similar as in the pilot-plant ($f_{ww} \equiv 0.25\text{-}0.28$). The activated sludge sample was taken from the endogenous vessel V_1 of the control unit RESCUE (Figure 7.1). Nitrification rates were obtained twice a day from aerobic respirometric tests (step 1+2 of control strategy, §7.2.3).

7.3 RESULTS

7.3.1 PHOSPHORUS REMOVAL

As a consequence of pre-precipitation with a β of 1, P_{tot} was reduced from an average of 9.2 to 3.8 mg $P.\ell^{-1}$ and S_{PO4} from 6.0 to 2.0 $mgP.\ell^{-1}$. In the effluent from the activated sludge pilot-plant, average concentrations of P_{tot} = 0.5 mg $P.\ell^{-1}$ and S_{PO4} = 0.2 $mgP.\ell^{-1}$ were measured (Table 7.2).

An optimal precipitant dose allows removing P_{tot} to such a level that it will not limit the biomass growth in the down-stream activated sludge process and that it will just reach the demanded effluent P_{tot}-concentration. In this study the P-effluent concentration was unnecessary low (P_{tot}=0.5 $mg.\ell^{-1}$ instead of the required value of 1.0 $mg.\ell^{-1}$), suggesting that further optimisation of the precipitant dose would have been possible.

Table 7.2 P_{tot}- and S_{PO4}-concentrations in raw and pre-precipitated wastewater, and in the effluent from the pilot-plant.

Parameter	Unit	Raw wastewater	Pre-precipitated wastewater (β=1)	Effluent from pilot-plant
P_{tot}	$mgP.\ell^{-1}$	9.3±0.7	3.8±0.7	0.5±0.08
S_{PO4}	$mgP.\ell^{-1}$	6.0±0.9	2.0±0.9	0.2±0.5

7.3.2 COD&N REMOVAL BY PRE-PRECIPITATION

As a result of pre-precipitation the total COD of 567 $mg.\ell^{-1}$ was reduced to 278 $mg.\ell^{-1}$ (Table 7.3). The Kjeldahl nitrogen (N_{Kj}) was reduced from 74.5 to around 60 $mgN.\ell^{-1}$ while the soluble ammonia (S_{NH}) from 49.7 to 44.6 $mgN.\ell^{-1}$.

From respiration tests performed by RESCUE the soluble readily (S_S) and particulate slowly biodegradable (X_S) COD-fractions were frequently estimated. The average concentrations of S_S and X_S amounted 52 and 149 $mg.\ell^{-1}$ respectively, estimated during 22 days of steady-state operation of the pilot-plant and the average total biodegradable COD (S_S+X_S) was 201 $mg.\ell^{-1}$.

Table 7.3 Characteristics of raw and pre-precipitated wastewater obtained with chemical-physical methods and respiration tests

Parameter	**Unit**	**Raw wastewater**	**Pre-precipitated wastewater**
COD	$mgCOD.\ell^{-1}$	567±87	281±67
S_S	$mgCOD.\ell^{-1}$	n.m.[1)]	52.0±13.7
S_I	$mgCOD.\ell^{-1}$	n.m.	27
X_S	$mgCOD.\ell^{-1}$	n.m.	149.2±52.6
X_I	$mgCOD.\ell^{-1}$	n.m.	50
N_{Kj}	$mgN.\ell^{-1}$	74.5±7.7	60.0
S_{NH}	$mgN.\ell^{-1}$	49.7±6.5	44.7±8.13
Total COD/N	-	7.6±0.9	4.7±1.1

[1)] n.m. not measured

Assuming that inert soluble COD was equal to the soluble COD (S_I) in the effluent (determined in filtrate from 0.45 μm filter), multiplied with a factor of 0.9 (S_I=30*0.9=27 mg.ℓ^{-1}) (SOLLFRANK ET AL., 1992, SIEGRIST AND TSCHUI, 1992), the particulate inert COD (X_I) from the COD balance (chapter 6, Table 6.5) would be 50 mg.ℓ^{-1}.

7.3.3 BIOLOGICAL NITROGEN REMOVAL

Nitrification. A complete nitrification with an average effluent S_{NH}-concentration of less than 1.1 mg N.ℓ^{-1} (Table 7.4) was attained with the controlled operation of the pilot-plant. This low S_{NH}-concentration was obtained with a relatively high overall nitrogen load of B_{XN} = 0.033 gN.gMLSS^{-1}.d^{-1} and beneficial operational temperature (18°C) in the nitrification zone. Moreover, the employed control strategy adjusted the aerated volume on demand. This contributed in a high-efficient oxidation of S_{NHn} and avoided its accumulation in the system. The average aerated fraction of the pilot-plant amounted 40% in the controlled period. On the other hand, high nitrite concentrations (average S_{NO2}=2.9 mgN.ℓ^{-1}) were measured during the experimental period.

Table 7.4 N-effluent quality from the pre-denitrification plug-flow pilot-plant with pre-precipitated wastewater

Parameter	**Unit**	**Value**
S_{NH}	$mgN.\ell^{-1}$	1.1±1.4
S_{NO2}	$mgN.\ell^{-1}$	2.9±1.6
S_{NO3}	$mgN.\ell^{-1}$	14.2±5.0
S_{NO2}+ S_{NO3}	$mgN.\ell^{-1}$	16.3±5.0

From the control respiration unit RESCUE the nitrification kinetics of the activated sludge could be regularly assessed. Throughout the steady-state period of plant operation, the average maximum specific ammonia oxidation rate k_{NHm} was higher than the nitrite oxidation rate k_{NO2m} (3.9 and 3.3 mgN.gVSS^{-1}.h^{-1} respectively, Figure 7.2).

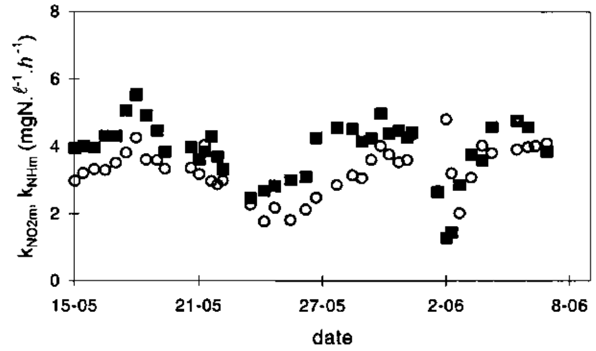

Figure 7.2 The course of specific nitrification rates (■ k_{NHm}, ○ k_{NO2m}) of activated sludge from the controlled pre-denitrification pilot-plant fed with pre-precipitated wastewater.

The average, respirometrically estimated concentration of S_{NHn} was 39.3 mgN.ℓ^{-1}. Comparison between the pre-precipitated influent concentration of N_{kj} (60 mgN.ℓ^{-1}) less the total inert N-fraction and S_{NHn}, indicates that approximately 66% of N_{Kj} was used for nitrification while for biomass assimilation around 31%.

Denitrification. The effluent quality of the pilot-plant regarding the sum of nitrite and nitrate (S_{NO2}+S_{NO3}) was unsatisfactory. The average concentration of S_{NO2}+S_{NO3} amounted 16.3 mg N.ℓ^{-1} and the average S_{NO2} was 2.9 mg N.ℓ^{-1}. This relatively high effluent S_{NO2}-level resulted from a slower S_{NO2}- than S_{NH}-oxidation (Figure 7.2) and the control of the nitrification volume was only based on the actual k_{NHm}-value (equation 7.1). Another reason for a higher S_{NO2}-level could be a limitation of biodegradable COD for complete denitrification.

Profiles of N-fractions throughout all compartments (example in Figure 7.3) depicted that an increase of the internal recirculation flow (Q_{ic}) would not be a potential factor to improve denitrification efficiency since nitrate and nitrite were still present in the last anoxic compartment. The highest nitrate reduction rate was observed in C_1 and resulted from the presence of S_S in the pre-precipitated wastewater.

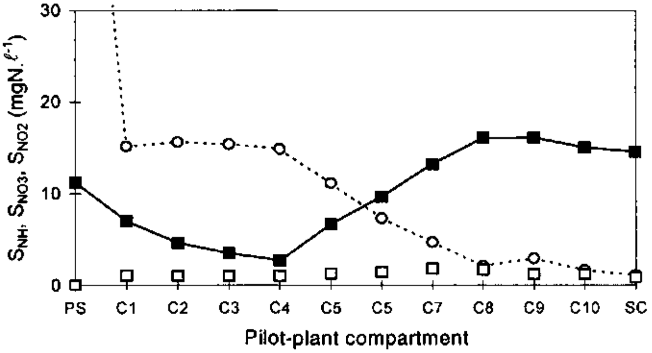

Figure 7.3 Example of S_{NH} (o), S_{NO2} ( ) and S_{NO3} (■) profiles throughout the compartments.

The slower nitrate reduction rate associated with the presence of X_S was measured in compartment C_2 and C_3. The denitrification proceeded with the slowest endogenous rate in C_4, C_9 and C_{10}. This example would suggest that in the last anoxic compartments (C_4, ultimately C_5 and C_6 depending on the control decision) the organic substrate limited the denitrification efficiency.

Occasionally batch NUR-tests were performed to estimate the denitrification potential (DP) and capacity (DC) of the examined pilot-plant (Figure 7.4). The overall DP estimated from two NUR-tests attained an average value of 23.7 $mgN.\ell^{-1}$. The average DC was calculated as a difference between S_{NHn}, effluent S_{NH} and S_{NO} and amounted 22.3 $mgN.\ell^{-1}$.

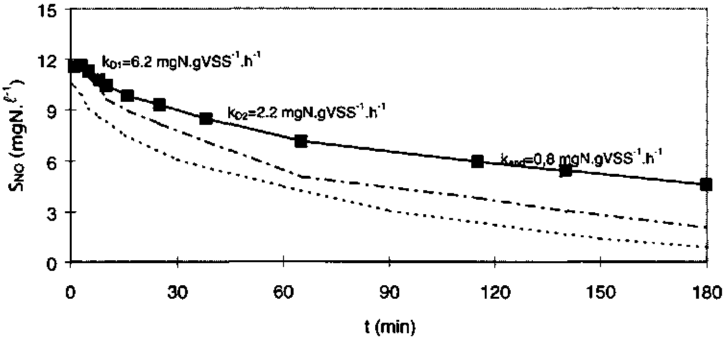

Figure 7.4 S_{NO}-curves from batch NUR-tests after pulse addition of precipitated wastewater to endogenous activated sludge from the pilot-plant (■ 24 *h* composite sample, f_{ww}=0.28, COD=349 $mg.\ell^{-1}$; the other dashed lines are for a visual comparison).

The estimated specific denitrification rates from NUR-tests associated with the anoxic oxidation of subsequent COD-fractions attained relatively high values (Table 7.5). Such high values were not measured with any other activated sludge samples like in the experiments described in previous chapters of this thesis (chapter 2, 3, 6). Implementation of a higher B_{XCOD} in this study does not explain the difference because also in the other experiments such magnitudes of organic loading were used. It seems that rather the combination of a higher B_{XCOD} and reduction of particulate COD (X_S and X_I) contributed in the formation of more viable heterotrophic biomass. This could result in higher substrate conversion rates what was also hypothesized in chapter 6 (§ 6.3.3).

7.4 DISCUSSION

A change in wastewater characteristics and sludge loading conditions affects the biomass activity. With the same quantity of wastewater but with modified characteristics (e.g. with pre-precipitation), the process efficiency and effluent quality are changed as a result of different sludge loading rate, sludge retention time (SRT) and sludge production. To reveal this, a comparison of process performance was performed between this study and the study as described in chapter 6. The data for this comparison are presented in Table 7.5.

The total COD/N-ratio for pre-precipitated wastewater was higher in this study than in the study from chapter 6 (4.7 and 3.0 respectively) as a result of a higher concentration of organics in the raw wastewater and a less efficient pre-precipitation. The nitrate effluent quality was expected to be significantly improved but the attained S_{NO2}+S_{NO3} concentration was only 5 mg.ℓ^{-1} lower (16.3 vs. 21.3 mgN.ℓ^{-1} respectively). This constitutes to some extent a proof that the value of total COD/N-ratio is certainly not universal indication of the denitrification potential for each wastewater and activated sludge system. The wastewater fractions related to the denitrification process, the activated sludge characteristics, process conditions and reactor configuration influence the value of the required COD/N-ratio for each specific situation.

Table 7.5 Effect of wastewater composition and process conditions on activated sludge process conversion rates and effluent N&P quality, based on results of the study presented in this chapter and chapter 6.

		Type reactor			
Parameter	**Unit**	**Plug-flow** (BROUWER AND KLAPWIJK, 1997)	**Plug-flow** (this chapter)	**SBR** (chapter 6)	**SBR** (chapter 6)
Wastewater characteristics and activated sludge process conditions					
Wastewater type		Settled wastewater	Precipitated wastewater	Raw wastewater	Precipitated wastewater
COD	mg.ℓ^{-1}	491	281	356	147
N_{Kj}	mgN.ℓ^{-1}	65	60	55	47
Total COD/N		7.6	4.7	6.5	3.0
Biodegradable COD/N			3.5		2.7
$S_S + X_S$	mg.ℓ^{-1}	260	201	238	101
P_{tot}	mgP.ℓ^{-1}	9.2	3.8	7.4	2.4
B_{XCOD}	gCOD.gMLSS^{-1}.d^{-1}	0.2	0.15	0.07	0.04
B_{XN}	gN.gMLSS^{-1}.d^{-1}	0.028	0.033	0.0095	0.012
β-ratio			1.0		1.2
Process conversion rates					
k_{NHm}	mgN.gVSS^{-1}.h^{-1}		3.9	2.9	6.2
k_{DSS}	mgN.gVSS^{-1}.h^{-1}		5.0	1.9	3.3
k_{DXS}	mgN.gVSS^{-1}.h^{-1}		1.4	0.69	0.82
k_{Dend}	mgN.gVSS^{-1}.h^{-1}		0.9	0.2	0.32
k_D	mgN.gVSS^{-1}.h^{-1}			0.88	0.64
N via assimilation	% N_{Kj}		31		13
N used for nitrification	% N_{Kj}		66		83
S_{NHn}	mgN.ℓ^{-1}		40		39
DP	mgN.ℓ^{-1}		23.7	30.2	17.4
DP_{ww}	mgN.ℓ^{-1}		14.9		
DC	mgN.ℓ^{-1}	34.4	22.3		
P via assimilation	mgP.ℓ^{-1}		3.3	2.4	1.4
Effluent quality					
S_{NH}	mgN.ℓ^{-1}	2.9	1.1	<1	<0.5
S_{NO2+3}	mgN.ℓ^{-1}	7.1	16.3	8	21.3
S_{NO2}	mgN.ℓ^{-1}		2.9	0.09	0.11
N_{tot}	mgN.ℓ^{-1}	11	19.5	10	23
P_{tot}	mgN.ℓ^{-1}	0.5	0.5	5.6	0.95

In the research with the same controlled pilot-plant but fed with settled wastewater (BROUWER AND KLAPWIJK, 1997), the effluent $S_{NO2+}S_{NO3}$ concentration amounted 7.1 mg N.ℓ^{-1} while a rather satisfactory nitrification was assured. It means that both raw (chapter 6) and settled domestic wastewater of the same origin was characterised by a denitrification potential allowable to attain a satisfactory effluent N-quality in an appropriate process configuration. The introduction of pre-precipitation on the plant with settled wastewater, decreased the COD-loading with 25% and increased the N-loading with 20%. This contributed in an unrecoverable deterioration of necessary conditions for a satisfactory denitrification. In other words, it deteriorated the denitrification potential of the system. A comparison of denitrification capacities (derivative of the DP) reflects this deterioration (Table 7.5).
The implemented control strategy to optimise the aerobic volume, and consequently the anoxic volume, seemed to have a negligible effect on the improvement of the denitrification performance in a system fed with low strength wastewater.

Regarding the comparison of pre-precipitated wastewater characteristics from this study and the study described in chapter 6, the following aspects can be noted:

- the concentrations of S_S and S_I were similar;
- the particulate COD-fractions (X_S and X_I) in this study were two times higher for X_S and three times for X_I. The reasons might be different initial concentrations of particulate COD-fractions in the raw wastewater and a lower rate of pre-precipitation.
- a relatively high organic sludge loading rate (B_{XCOD}=0.15 vs. 0.04 gCOD.gMLSS^{-1}.d^{-1}) caused in this study an increased biomass production, resulting in an increased demand of S_{NH} for assimilation with a factor of 2.5.
- however, the N_{Kj}-concentration in the precipitated wastewater was significantly higher in this study and the S_{NHn}-concentration was practically identical for both cases. This shows that S_{NHn} is a resultant of initial wastewater characteristics and process conditions;
- a significant difference was measured in specific S_{NH}-oxidation rates. A much lower value was obtained in this study (3.9 vs. 6.2 mgN.gVSS^{-1}.h^{-1}). A high B_{XCOD}, low SRT and lower reduction of particulate COD-fractions were the most important factors that reduced the nitrifiers fraction in the total biomass population, and therefore lowered the nitrification rate;
- on the other hand, subsequent specific denitrification rates were approximately two times higher in this study what can be explained by a higher activity of heterotrophic biomass, resulting from a higher applied B_{XCOD} and lower SRT. A lower removal efficiency of the X_S-fraction could have resulted in an increased endogenous denitrifying activity.

Pre-precipitation introduced before a biological nutrient removal system usually causes a deterioration of nitrate effluent quality. An important reason is a significant reduction of biodegradable COD, not accompanied by a proportional reduction of biodegradable N-forms. The denitrification potential on the organic wastewater fractions can be lowered significantly while the amount of nitrate that has to be denitrified will be affected in a lower rate.

In Table 7.6, wastewater characteristics, operational conditions and effluent N-quality of several activated sludge systems that used pre-precipitation are characterised. Substantial differences can be observed in influent concentrations for N_{Kj} and COD, COD/N-ratio, B_{XCOD} and B_{XN}. These factors have all a certain influence on the efficiency of the denitrification process. However, a similarity or difference in the total amount of removed nitrogen (influent N_{Kj} - effluent N_{tot}) cannot unequivocally be explained by a comparison of the different operational conditions. The measurement of the nitrifiable nitrogen fraction S_{NHn} and the estimation of the denitrification potential or capacity would provide more valuable information for an adequate comparison, and this may decide whether effluent requirements will be, or will not be reached for a certain activated sludge system.

Table 7.6 Comparison of N-removal efficiencies of the activated sludge systems fed with pre-precipitated wastewater from literature and this thesis.

Parameter	Uuterlinde and v.d. Roest (1994)	Kristensen, and Jørgensen (1994)	Kristensen, and Jørgensen (1994)	Chapter 6	This chapter
Wastewater characteristics					
N_{Kj} (mgN.ℓ^{-1})	35	37	39	47	60
COD (mg.ℓ^{-1})	240	159	155	147	281
COD/N	6.7	4.8	4.6	3.1	4.7
Process parameters					
β-ratio	1 (Fe)	0.97 (Al)	0.94 (Fe)	1.2 (Fe)	1.0 (Fe)
B_{XCOD} (gCOD.gMLSS^{-1}.d^{-1})	0.14	0.115	0.088	0.04	0.15
B_{XN} (gN.gMLSS^{-1}.d^{-1})	0.019	0.025	0.019	0.012	0.033
Aerated volume fraction (-)		0.5	0.5	0.5	0.4
Effluent quality					
N_{tot} (mgN.ℓ^{-1})	11.3	11-14.5	9-10.5	23	19.5
S_{NH} (mgN.ℓ^{-1})				< 1	<1.5
$S_{NO2} + S_{NO3}$ (mgN.ℓ^{-1})	8.2	9.5-11.5	~7.5	21.3	16.3

The S_S- and X_S-fractions that determine the denitrification potential differ in an extended range for different wastewater origin. The removal rate of X_S depends probably on the particle sizes forming this fraction, the precipitant dose and the hydraulic conditions for coagulation. The fraction S_S is removed in a low rate due to pre-precipitation. If a wastewater sample contains a high fraction of S_S and denitrification is placed as first in the treatment scheme (pre-denitrification), a low nitrate concentration can be expected in the effluent, even with pre-precipitation. When the influent is characterised by a prevailing content of X_S which potentially would determine the effluent N-quality, an unsatisfactory denitrification efficiency can be expected after pre-precipitation was introduced.

The available biodegradable COD for denitrification, the amount of N that has to be denitrified (biodegradable COD/N-ratio) and the optimal utilisation of the anoxic volume (available biodegradable COD will be oxidised only with nitrate) are some of the factors to be considered to obtain the highest possible effluent quality in nutrient removing systems fed with low-strength pre-precipitated wastewater.

7.4 CONCLUSIONS

With a precipitant dose of β=1.0, the total COD/N-ratio of pre-precipitated wastewater attained a value of 4.7 and the biodegradable COD/N-ratio a value of 5.1. Especially the last parameter was more beneficial as in the study of chapter 6 (almost two times higher). Together with an optimisation of the anoxic and aerobic activated sludge fraction this contributed only in an improvement for the S_{NO2}+S_{NO3}-effluent quality of 5 mgN.ℓ^{-1} and the standard of total N $\leq$ 10 mgN.ℓ^{-1} was still not fulfilled. This indicates that the required COD/N-ratio to attain a complete denitrification is not a universal value but is strongly dependent on wastewater activated sludge characteristics, process conditions and operational parameters.

A higher B_{XCOD} in this study contributed in higher rate of N- and P-uptake for biomass synthesis. This allowed implementing a lower precipitant dose. Besides, the fraction of nitrifiable-N (S_{NHn}) and nitrate to be denitrified in relation to the total influent N was decreased in comparison with the system examined in chapter 6.

When the denitrification potential of raw and settled wastewater in question allowed just to fulfil the required nitrate standard in the effluent from a down-stream activated sludge system, the reduction of the biodegradable COD by normal rate pre-precipitation caused a significant deterioration. Any optimisation step aiming to improve the denitrification efficiency may improve the nitrate effluent quality only to small extent and is an option in situations where the nitrate effluent level differs slightly from the demanded value.

LIST OF SYMBOLS AND ABBREVIATIONS

B_{XCOD}	organic sludge loading rate (gCOD.gMLSS^{-1}.d^{-1})
B_{XN}	N sludge loading rate (gN.gMLSS^{-1}.d^{-1})
$C_{1..10}$	subsequent compartments of the plug-flow pilot-plant
COD	total COD of wastewater (mg.ℓ^{-1})
COD_m	COD of wastewater filtrate (0.45 μm) (mg.ℓ^{-1})
COD:N	ratio of total influent COD and total influent nitrogen (=N_{Kj})
DO	dissolved oxygen concentration (mgO_2.ℓ^{-1})
DP	denitrification potential (mgN.ℓ^{-1})
f_{ww}	fraction of wastewater volume in the total volume of activated sludge mixed liquor (-)
k_D	specific denitrification rate; subscripts: 1 - associated with S_S utilisation including endogenous rate, 2 - associated with S_S utilisation from X_S hydrolysis including endogenous rate, 3 or end - endogenous, o - overall (mgN.gVSS^{-1}.h^{-1})
k_{NHm}	specific rate of ammonia oxidation (mgN.gVSS^{-1}.h^{-1})
k_{NOm}	specific rate of nitrite oxidation (mgN.gVSS^{-1}.h^{-1})
NUR	nitrate utilisation rate
P_{tot}	total phosphorus (mgP.ℓ^{-1})
Q_{es}	excess sludge flow (ℓ.h^{-1})
Q_i	influent wastewater flow to the pilot-plant (ℓ.h^{-1})
Q_{ic}	internal nitrate-rich recirculation flow (ℓ.h^{-1})
Q_{ir}	recycle sludge flow (ℓ.h^{-1})
r_{NHm}	volumetric rate of ammonia oxidation (mgN.ℓ^{-1}.h^{-1})
SBR	sequencing batch reactor
S_I	soluble inert COD (mgCOD.ℓ^{-1})
S_{NH}	concentration of ammonia (mgN.ℓ^{-1})
S_{NHn}	concentration of nitrifiable nitrogen (mgN.ℓ^{-1})
S_{NO}	concentration of sum nitrate and nitrite-nitrate equivalent (mgN.ℓ^{-1})
S_{NO2}	concentration of nitrite (mgN.ℓ^{-1})
S_{NO3}	concentration of nitrate (mgN.ℓ^{-1})
S_{PO4}	concentration of soluble orthophosphate (mgP.ℓ^{-1})
SRT	solid retention time (d)
S_S	soluble, readily biodegradable COD (mgCOD.ℓ^{-1})
T	temperature (°C)
V_N	nitrification volume (ℓ)
X	total solids concentration in activated sludge reactor (gMLSS.ℓ^{-1})
X_V	volatile suspended solids (gMLVSS.ℓ^{-1})
X_S	particulate, slowly biodegradable COD (mgCOD.ℓ^{-1})
X_I	particulate, inert COD (mgCOD.ℓ^{-1})
β	molar ratio: precipitant metal to P_{tot} in the influent wastewater (M_{Me}.M_{Ptot}^{-1})

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8

Discussion

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8.1 INTRODUCTION

Information which has been published in the last three decades on denitrification in activated sludge systems (review in chapter 1) would suggest that denitrification is a well recognised and established process and that there is no special demand for further investigations. Nevertheless, practical evidences indicate that available information is not efficiently utilised, although the need to optimise denitrification is often faced. Applied design procedures for denitrification are still based on empirical relations and general parameters (e.g. BURDICK ET AL., 1982, KAYSER, 1983, HOFFMAN, 1986, US EPA, 1987, SDA, 1988, ECKENFELDER, 1989) and the recent improvements in the design of the denitrification process are not revolutionary (e.g. KAYSER, 1999), in spite of a continuously improving theoretical understanding of the factors that influence denitrification.

The knowledge that can be gained from a detailed wastewater characterisation is an example of information that could better be utilised for studies into design and improvement of the denitrification process. In treatment plants receiving domestic wastewater, the availability of biodegradable COD is often considered as the bottleneck. Although many efforts have been done to establish relations between the type and concentration of organic carbon and the denitrification parameters, in several obliging design approaches for the denitrification a general parameter as COD/N- or BOD_5/N-ratio is used (EKAMA ET AL., 1984, KAYSER, 1999). In chapter 1 it was stated that the COD/N- or BOD_5/N-ratio's are not able to estimate the denitrification potential, capacity or efficiency and no universal default value can be given for a sufficient performance. This can be confirmed by a large number of estimated values (Table 1.1) of very extended ranges. Other conditions that determine the denitrification potential and capacity of an activated sludge system are to a big extent recognized and many of them can be secured by proper design and operation.

Implementation of empirical approaches may lead to an under- or overestimation of the denitrification volume and for economic and sustainable reasons this should be avoided. For instance inventory analysis performed for several treatment plants in the Netherlands, designed with the widely accepted HSA-method, revealed that the difference in volume between 'reality' and model prediction was as high as –25 till +35 % (STOWA, 1995). A strong need is being observed in an improved design procedure for wastewater treatment plants, based on an accurate estimation of the denitrification potential in relation to detailed wastewater and activated sludge characteristics. The denitrification potential (DP) in this thesis is defined as the maximal mass of nitrate that **can** be denitrified in the anoxic volume per unit of influent flow. The DP depends on the concentration of biodegradable COD in the influent and the sludge activity.

In this thesis a methodology is presented for the estimation of the denitrification potential in relation to wastewater and activated sludge characteristics. Two respiration techniques formed the basis for two different approaches, the anoxic nitrate utilisation rate test (NUR-test) and the aerobic oxygen utilisation rate test (OUR-test).

The approach that is based on the NUR-test is a direct method for the assessment of the denitrification potential. The approach based on the OUR-test is an indirect method because a simplified model is necessary to transform oxygen utilisation to nitrate utilisation. Both methods were validated with several case studies, characterised by different wastewater composition and activated sludge characteristics. The developed methods offer an advanced possibility for design assistance, optimisation, monitoring and control of wastewater treatment systems with nitrogen removal.

8.2 ESTIMATION OF THE DENITRIFICATION POTENTIAL

8.2.1 GENERAL

For modelling purposes it is generally accepted that biodegradable COD of domestic wastewater is divided into soluble readily biodegradable- (S_S) and particulate slowly biodegradable COD (X_S). The fraction S_S can be directly consumed by denitrifiers and results in high process rates but it forms usually a smaller fraction of the total COD in municipal wastewater. Because of its character it is essential for the process efficiency that S_S is exclusively used for denitrification and not lost by aerobic oxidation. The fraction X_S, forming usually a higher fraction of the total COD, consists of particulate material that has to be hydrolysed before it can be utilised by denitrifiers. Because of a higher concentration and a longer required time for anoxic consumption, more anoxic volume is needed to utilise X_S optimally for denitrification. The amount of nitrate that potentially can be reduced with S_S (DP_{SS}) and X_S (DP_{XS}) is called wastewater denitrification potential (DP_{ww}).

Besides the wastewater denitrification potential, each type of activated sludge is characterised by a basic or endogenous denitrification potential (DP_{end}). The endogenous denitrification in this thesis is defined as the denitrification utilising substrate from storage, adsorption and biomass decay and lysis; this substrate historically originates from the influent. The endogenous denitrification potential, in contrast to wastewater denitrification potential, is more a resultant of process configuration and parameters.

8.2.2 RESPIRATION TECHNIQUES FOR THE ESTIMATION OF THE DENITRIFICATION POTENTIAL

NUR-test, direct estimation of the denitrification potential

In a NUR-test a wastewater sample is mixed with an activated sludge sample and in an anoxic environment the utilisation rate of nitrate/nitrite is measured. The results of a NUR-test (Figure 8.1) allow for a direct estimation of the DP_{ww} and DP_{end}, and consequently the estimation of the overall denitrification potential of the examined wastewater treatment plant. Additional information that can be extracted from a NUR-test are the wastewater composition concerning organic biodegradable fractions S_S and X_S, their volumetric rates of utilisation (r_{SSm}, r_{XSm}) and the basic volumetric endogenous denitrification rate (r_{end}). In combination with reactor characteristics like influent flow, anoxic volumes and activated sludge concentration, the denitrification capacity and the effluent nitrate concentration can be assessed (Figure 8.2, chapter 2 equation 2.20). The amount of nitrate that has to be denitrified is at this stage estimated from the nitrogen mass balance taking into account the nitrogen utilised for biomass assimilation, nitrate produced from nitrification and inert N-fractions.

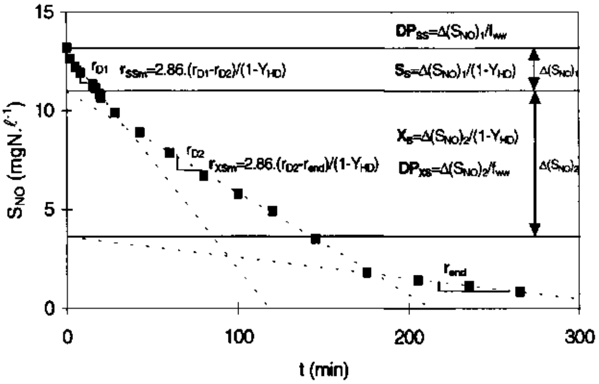

Figure 8.1 Direct estimation of wastewater denitrification potential (DP_{SS}, DP_{XS}), wastewater characteristics (S_S and X_S) and volumetric substrate conversion rates (r_{SSm}, r_{XSm} and r_{end}) from a NUR-test with wastewater (appropriate list of symbols in chapter 2). To estimate DP_{end} additional information regarding system characteristic (influent flow and anoxic volume) is needed (equations 2.13, 2.14).

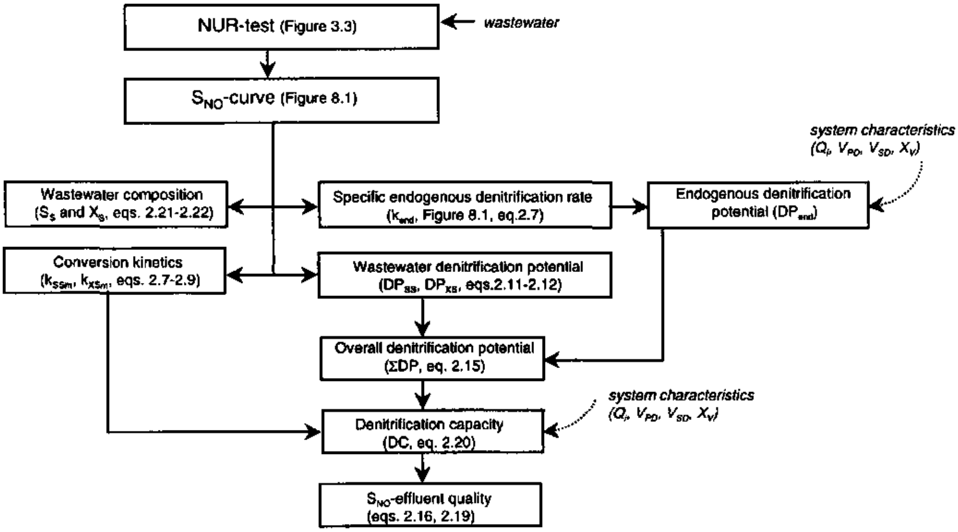

Figure 8.2 The direct methodology to estimate denitrification potential and capacity of an activated sludge system

For the identification of the NUR-curve attention has to be paid on the inclusion of nitrite, the proper choice of anoxic heterotrophic yield (Y_{HD}) and presence of poly-P organisms in the examined activated sludge mixture. The effect of nitrite production and their accumulation during the NUR-test is accounted by the introduction of a combined parameter: sum of nitrate and nitrite-nitrate equivalent (S_{NO}, § 2.3.1) forming the NUR curve (or S_{NO}-curve). In this way the distinction is made between the amount of biodegradable COD utilised for the partial process of nitrate reduction to nitrite ($S_{NO3} \rightarrow S_{NO2}$) and for the entire denitrification process ($S_{NO3} \rightarrow S_{N2}$).

The choice of Y_{HD} is essential since it affects first of all the magnitude of estimated S_S and X_S (SCHEER AND SEYFRIED, 1994). Next to the choice of the default value (HENZE ET AL., 1987, 1996), a separate NUR-test with a model substrate like acetate is an option for the estimation of Y_{HD}.

The presence of poly-P accumulating organisms deteriorates the demanded shape of the NUR curve (§ 2.3.4). In such a situation the estimation of S_S and X_S may be in most cases erroneous, while the estimated conversion rates and denitrification potentials will be relevant.

A significant number of information can be assessed from one simple NUR-test. Test performance and the numerical procedure to assess the parameters are relatively time consuming in the current form. Automation of the NUR-test and parameter identification can be similar as with the OUR-test (chapter 5, 7) and this would contribute in a more user-friendly approach. The automation of a NUR-test can be attained by implementation of a nitrate/nitrite electrode.

OUR-test, indirect estimation of the denitrification potential

In an OUR-test, aimed to estimate the denitrification potential, a wastewater sample is mixed with an activated sludge sample in aerobic conditions and the utilisation rate of oxygen is measured while the nitrification activity is suppressed. The resultant respirogram (OUR-curve or S_{O2}-curve), as presented in Figure 8.3, may provide information on the wastewater composition concerning S_S and X_S and the rates of their utilisation. To obtain the appropriate parameters a model (chapter 4, Table 4.8, processes 1-3) can be used to fit the obtained respirogram.

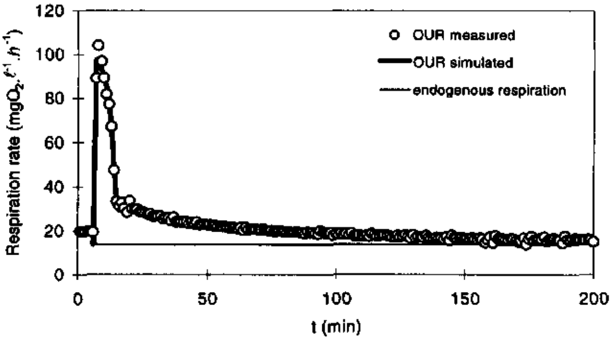

Figure 8.3 Results of an OUR-test performed with wastewater under nitrification suppression. The obtained OUR-curve can be modelled using a simplified aerobic model as presented in chapter 4 (Tabel 4.8, processes 1-3).

The indirect character of the estimation of the denitrification potential with an OUR-test is formed by the fact that the oxygen utilisation rate has to be transformed into a denitrification rate. The heterotrophic respiration with oxygen or nitrate as electron acceptor proceeds in an analogical way but the subsequent substrate conversion rates are observed to be slower under anoxic conditions (literature review chapter 3). This suggests that an aerobic substrate conversion model can be used with some modifications to describe the denitrification process. The slower process conversion rates under anoxic conditions are expressed for modelling purposes by so called reduction factors (chapter 3, 4, Table 4.9). The obtained reduction factors (estimated or defaults) can be used to model the denitrification process or a NUR-curve (Figure 8.4). For that purpose the following assumptions are made:

- amount of S_S and X_S recognised by heterotrophs under aerobic and anoxic conditions is the same;
- anoxic S_S-oxidation rate, X_S-hydrolysis rate and endogenous respiration rate are smaller than the corresponding aerobic rates which is expressed by the subsequent reduction factors η_1, η_2 and η_3;
- reduction factors are specific for each system;
- anoxic heterotrophic yield is equal to the aerobic yield (Y_{HD}=Y_H).

In chapter 3 a methodology is presented to assess reduction factors (η_1, η_2 and η_3) by a parallel performance of NUR- and OUR-tests, under well-defined analogical experimental conditions. The factor η_3 was obtained from a direct comparison of aerobic and anoxic endogenous respiration rates. The obtained S_{NO}-curve from a NUR-test was fitted with a simple denitrification model using wastewater composition and kinetic parameters as estimated from the OUR-test while the η_1 and η_2 were the only unknown parameters.

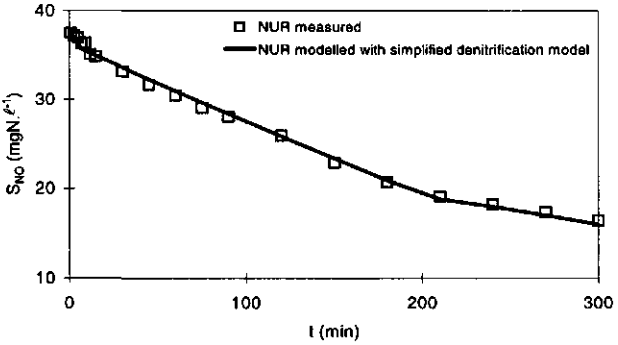

Figure 8.4 Example where NUR-curve is fitted with a simplified denitrification model. The kinetic parameters and wastewater characteristics are obtained from the identification of an OUR-curve while the reduction factors were obtained from a fitting procedure.

8.3 METHODOLOGY TO ESTIMATE THE N-REMOVAL POTENTIAL

The OUR-curve with the nitrification suppression can be modelled with the aerobic substrate (biodegradable COD) conversion model (chapter 4, Table 4.8, processes 1-3). When incorporating nitrification in the OUR-test, the obtained respirogram can be modelled using the nitrification–aerobic COD-oxidation model (chapter 4, Table 4.8, processes 1-5). To limit the amount of unknown parameters the nitrification kinetics can be acquired by performing OUR-tests with model substrates (NH_4Cl and $NaNO_2$) and identification of the attained respirograms with a nitrification model (Table 4.8, processes 4-5). Optionally the S_S-

oxidation kinetics can be estimated from an OUR-test with the model substrate acetate. Application of the aerobic COD-oxidation model to anoxic conditions by additional implementation of appropriate reduction factors in the appropriate equations results in a denitrification model (Table 4.9, processes 1-3). Integration of the simplified aerobic substrate oxidation -, nitrification- and denitrification models resulted in an overall, simplified activated sludge model for N-removal (chapter 4).

The presented model approach has a simplified character. This is because the population dynamics as well as the effect of environmental conditions are not modelled and the wastewater composition is described by only three parameters (S_S, X_S and S_{NHn}). The implementation of actual substrate conversion rates instead of biomass population dynamics allows reducing an amount of model parameters. A frequent update of the conversion rates allows for further minimisation of model parameters by excluding the effects of environmental factors.

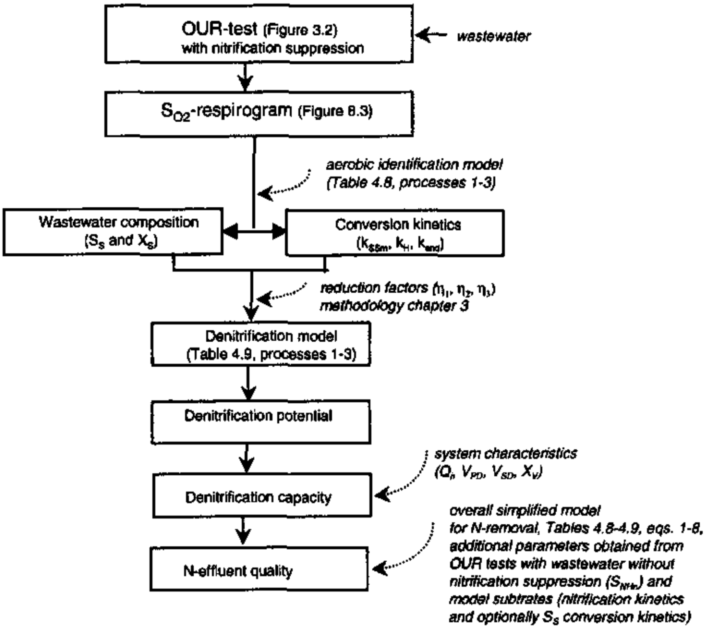

Figure 8.5 Indirect methodology to estimate denitrification potential, capacity, N-removal potential and effluent N-quality of an activated sludge system

Use of the nitrifiable N-fraction (S_{NHn}), to characterise the influent N-fraction which exclusively participates in nitrification and potentially in denitrification, allowed for a further reduction of modelled processes by excluding S_{NH}-assimilation, hydrolysis and ammonification of organic nitrogen. The simplified activated sludge model is meant to predict the overall N-removal potential of a system (Figure 8.5) and it can be employed in several monitoring and optimisation procedures.

8.4 IMPLEMENTATION AND VALIDATION OF THE DEVELOPED METHODOLOGIES

Testing and validation of the developed methodologies to estimate denitrification- and overall N-removal potential of the activated sludge system were performed using several case studies (batch tests, pilot plants) where the characteristics of activated sludge and wastewater varied. Through these studies it was proved that the methodologies were suitable:

- <u>to assess wastewater characteristics;</u>

  To model an activated sludge system a relevant wastewater characterisation is essential. Although respiration techniques have served this purpose in the last one and a half decade, it did not obtain sufficient acceptance in practice. Many examples from this thesis prove that both respiration techniques (OUR- and NUR-tests) were a source of reliable information on wastewater composition, allowing for a versatile analysis of the considered activated sludge system. Raw, settled and pre-precipitated domestic wastewater was in this way analysed (chapters 2, 3, 5, 6, 7) for biodegradable COD-fractions but also for the nitrifiable N-concentration. This allowed for example, an evaluation of the effect of pre-treatment on the distribution of the wastewater fractions (chapter 6, 7).

- <u>to estimate the denitrification potential and capacity;</u>

  Estimation of the denitrification potential allowed for a good definition of process possibilities in relation to wastewater and activated sludge characteristics. Estimation of the denitrification capacity offered an additional tool to optimise a system, both theoretically and in operation (chapter 2, 6, 7).

- <u>to predict N-removal potential of a system;</u>

  Implementation of the overall simplified activated sludge model for N-removal allowed for a precise estimation of the effluent N-quality in both static and dynamic conditions for two pilot-plants, characterised by significantly different wastewater composition (settled and pre-precipitated) and activated sludge parameters (chapter 5). Implementation of the side-stream aerobic respiration unit allowed for a frequent, reliable estimation of model parameters. Transfer of the respirometrically estimated parameters to describe both, aerobic and anoxic substrate oxidation processes gave satisfactory prediction results.

- <u>to asses reduction factors for denitrification;</u>

  Implementation of the methodology to assess denitrification reduction factors from OUR- and NUR-tests (chapter 3) allowed to obtain a number of realistic values, in relation to process configuration and parameters. It revealed that each process is characterised by a set of specific values of reduction factors and for that reason individual assessment is required. Moreover, a strongly dynamic character of an activated sludge system affects the reduction factor values. The biggest achievement of this testing was that aerobically obtained model parameters (wastewater characteristics and oxidation kinetics) can be transferred using some modification to describe the denitrification process.

- to control an activated sludge N-removal process;

  Although not extensively tested, it was signalised that with the presented methodology it is possible to control efficiently the operation of a N-removal activated sludge system. Control of nitrification by aerating the reactor volume on demand, with respect to the S_{NHn}-loading rate and nitrification kinetics, was tested in chapter 7. A stable, low S_{NH}-concentration was attained in the effluent throughout the period of controlled plant operation. Such a control strategy can partly be seen as an optimisation of the denitrification process because over-aeration of a system is avoided, the oxygen content in recycle streams is minimised and a maximal possible denitrification volume is created.

- to optimise theoretically a N-removal system.

  The presented methodologies to assess the denitrification and N-removal potentials assume the necessity to perform more or less frequently the appropriate batch tests to estimate the actual process capabilities and wastewater characteristics. They are thus especially suitable for analysis of an existing system. Since biomass population dynamics are frozen in the simplified model, the prediction of system capabilities after a significant modification is not correct without specific measurements. However, within certain limits the effect of 'little changes' on the system efficiency can be predicted using the simplified N-removal model (chapter 6).

8.5 POSSIBLE APPLICATIONS OF THE DEVELOPED METHODOLOGIES IN PRACTICE

The developed methodologies for the estimation of the denitrification potential with the NUR- and/or OUR-test suggest some possible implementations, which are discussed in the following paragraphs.

8.5.1 APPLICATION FOR EXISTING SYSTEMS

For estimation of the denitrification potential and capacity of an existing system, the method based on the NUR-test (chapter 2) is recommended. A simple NUR-test allows extracting sufficient and relevant information on the denitrification potential of an existing system without using complex approaches where biomass dynamics are used. When system characteristics as influent flow, volume and sludge concentration are available, the denitrification potential can be translated into denitrification capacity. This approach is especially useful to optimise a system by:

- increasing pre-denitrification volume to increase the magnitude of anoxic S_S- and X_S-utilisation;
- increasing post-anoxic volume in case when effluent nitrate concentration slightly differs from the required value and biodegradable COD is limiting in pre-denitrification zone;
- minimising oxygen input to the pre-denitrification volume by avoiding too high recirculation rates or minimising the oxygen content in the recycle stream;
- increasing recirculation rate to provide nitrate load on demand;

- elimination of pre-treatment step or decrease of its efficiency for the removal of biodegradable COD-fractions;
- calculating the average dose of external carbon when other measures do not help to increase the denitrification capacity, because the denitrification potential of wastewater and activated sludge is too poor.

8.5.2 ASSISTANCE IN DESIGN

For new systems to be designed, the denitrification potential can be assessed from a NUR-test when a sample of the wastewater under consideration is available. The activated sludge sample for the NUR-test can also originate from a plant characterised by similar process conditions (sludge loading rate, sludge age, configuration, etc.) and fed with a similar type of wastewater.

When a wastewater sample is not available, optionally an equivalent wastewater sample from an alternative plant can be used. Similarity of the influent composition is determined by several factors, e.g. type of sewer system and industrial discharges to the sewer system. The wastewater composition plays a decisive role in the denitrification potential and therefore for economic reasons it is worth the effort to pay sufficient attention to find an equivalent wastewater sample. To minimise the experimental work in a pre-design phase of a new wastewater treatment plant, the availability of a database with information about different plant configurations and wastewater compositions could contribute in a significant progress in process design.

For a range of treatment plants, characterised by different COD- and N-loading rates (B_{XCOD} and B_{XN}) and fed by different types of wastewater (COD, N_{Kj}, S_S and X_S as % total COD), relations could be worked out in nomograms for the anoxic specific reduction rates of S_S (k_{SSm}), X_S (k_{XSm}) and the endogenous rate (k_{Dend}). With wastewater characteristics, estimated experimentally or predicted based on similar situations, the denitrification potential could be relatively precisely assessed, certainly better than based on COD/N- or BOD_5/N-ratio's.

In Figure 8.6 a scheme is presented of a procedure for the estimation of the denitrification potential for a new designed plant, leading to an assessment of the denitrification volume.

Because the development of a design procedure for the nitrification process was not the objective of this research, the calculation of the nitrification volume in Figure 8.6 is based on the commonly used HSA-model; however, there is a broader consensus on the nitrification kinetics of the HSA-model than for denitrification. For the estimation of the concentration of nitrifiable nitrogen (S_{NHn}) and the amount of nitrogen that has to be denitrified (S_{NOd}) an OUR-test without nitrification suppression can be performed or it can be assessed with the N-balance as in the HSA-model.

In the procedure for the calculation of the denitrification volume a pre-denitrification volume (V_{PD}) is taken as fraction of the total plant volume V_T. With this starting point the denitrification potential and the resulting denitrification capacity (DP, DC, mgN.ℓ^{-1})) are estimated using kinetics from available nomograms for a 'similar' situation or from a performed NUR-test (when similar wastewater and activated sludge sample are available).

The calculation of the denitrification volume is an iterative process and the V_{PD}, and if necessary the secondary anoxic volume (V_{SD}), have to be adjusted until DC becomes equal to S_{NOd}.

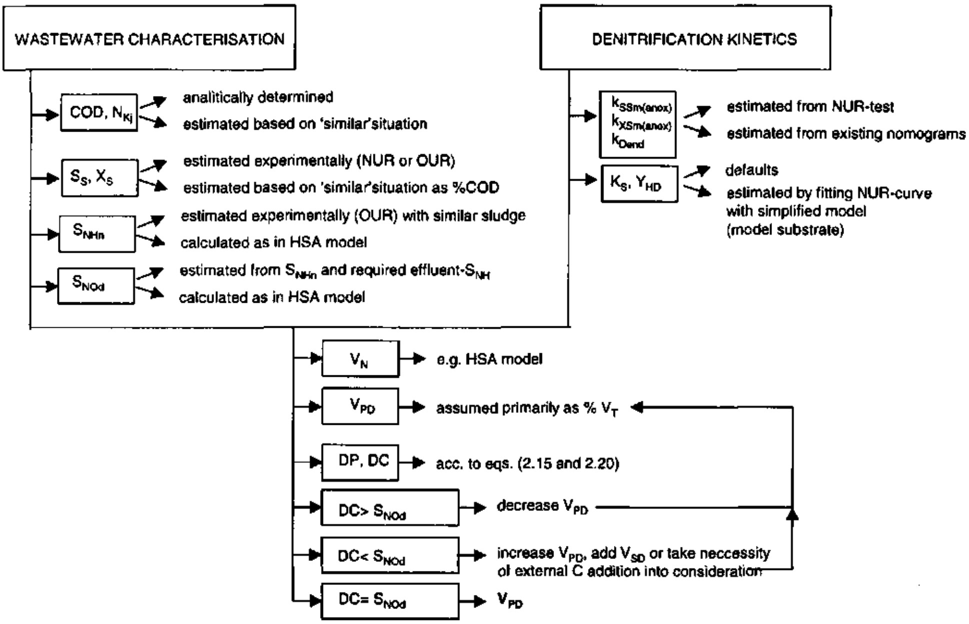

Figure 8.6 A possible procedure to estimate denitrification potential, capacity and anoxic volume for a new pre-denitrification activated sludge system using the methodology to estimate the denitrification potential with a NUR-test.

A hypothetical example of a relation between activated sludge process parameters, wastewater characteristics and denitrification kinetics is presented in Figure 8.7.

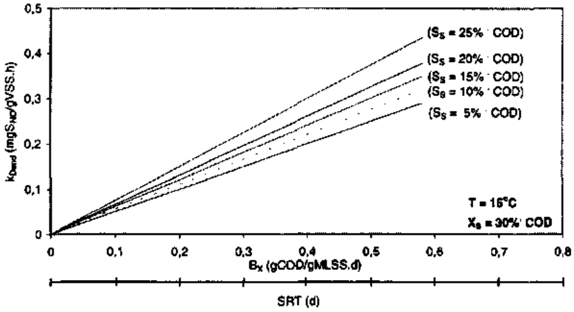

Figure 8.7 Hypothetical example of a nomogram where the relation between denitrification parameter, specific endogenous denitrification rate (k_{Dend}), process parameters and wastewater characterisation is given. The similar-type relations for different temperature, X_S and S_S-fractions and SRT should be worked out for anoxic utilisation rates of S_S and X_S ($k_{SSm(anox)}$ and $k_{XSm(anox)}$).

In this example the anoxic specific endogenous denitrification rate (k_{Dend}) is given as a function of the organic sludge loading rate (B_{XCOD}), SRT and wastewater characteristics. The wastewater in the presented example is characterised by a COD-value (hidden in B_{XCOD}), a certain X_S-fraction (as % total COD) and different S_S-fractions. The k_{Dend} should also be given for different X_S-fractions (not shown). The same relations should be available for the other denitrification parameters (k_{SSm} and k_{XSm}). The temperature influence can be predicted using exponential Arrhenius-like relationships.

One may say that attaining these relations would be time consuming and expensive. On the other hand a lot has been already done regarding a detailed wastewater characterisation for existing N-removing treatment plants (also with use of respiration techniques). An additional effort to establish denitrification kinetics in relation to different process parameters, configuration and wastewater characteristics would lead to the formulation of a more optimal design than obtained with the present empirical design approaches. It is plausible that extra costs for defining adequate starting points will be recovered on the investment costs for realisation.

8.5.3 ON-LINE SYSTEM MONITORING AND/OR CONTROL

The methodology to estimate the N-removal potential using an OUR-test is suitable to be used in an on-line monitoring and/or control strategy for nitrification and denitrification in existing systems. Because conversion kinetics and wastewater composition from OUR-tests can be transferred to predict the denitrification potential, this technique constitutes the base of an overall control strategy. Additional advantage is that nitrification kinetics can be assessed. A possible implementation of control strategies is sketched in Figure 8.8 where a pre-denitrification activated sludge reactor with an additional post-anoxic zone is given as example. The control unit implementing the aerobic respiration technique could resemble the presented in chapter 5 and 7.

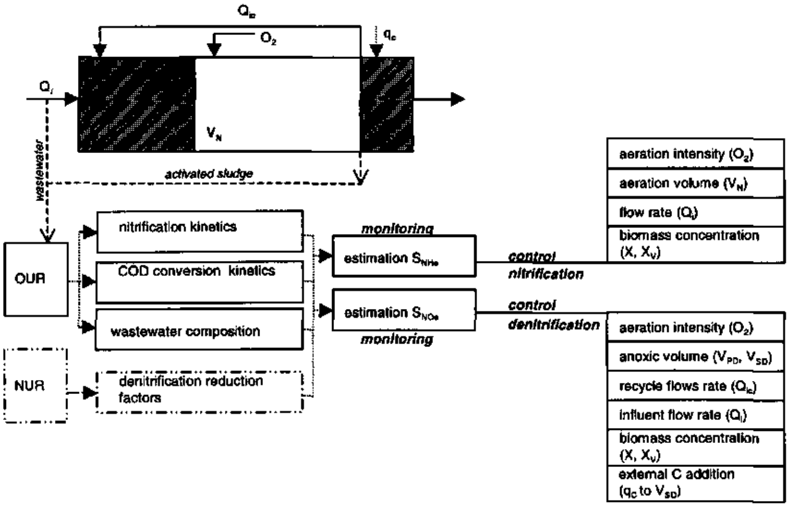

Figure 8.8 Possible control strategies using the methodology to estimate N-removal potential using respiration techniques.

The set-up for a NUR-test could be additionally implemented to assess reduction factors for anoxic respiration. However, when more would be known on the relation between reduction factors and system parameters and configuration, additional NUR-tests could be performed very occasionally or even eliminated. With the methodology that is described in chapter 3, 4 and 5, both nitrification and denitrification potential can be assessed and this in turn allows to predict the total nitrogen effluent quality.
The estimation of effluent N-quality may serve simple monitoring or control purposes. Control of the nitrification volume with the approach from Figure 8.8 (option aeration intensity or aeration volume) was successfully tested by BROUWER ET AL. (1998) and in chapter 7. Frequent estimation of actual nitrification kinetics and the S_{NHn}-concentration in the influent allows for aerating the reactor volume on demand. Depending on the technical configuration of a system (compartments, plug-flow reactor or alternating system), optimisation of the nitrification efficiency can be realised by aerating a larger or smaller reactor volume, providing more or less oxygen or prolonging or shortening the aeration phase.

Nitrification can also be affected by a modification of B_{XCOD} (or B_{XN}) and SRT by changing the influent flow (Q_i) or the activated sludge concentration (MLSS/MLVSS). Then however, effects of a control decision cannot be estimated directly.

Regarding the denitrification, estimation of its potential offers a possibility to utilise it optimally. The same control decisions as in case of the nitrification can be taken; modification of the aeration intensity or nitrification volume allows for creating more space for denitrification, and the present potential can be used more efficiently. An optimal control of the aeration intensity, except that fulfils nitrification requirements and creates optimal space to satisfy both processes, allows minimising the presence of oxygen in recycle streams.

Control of nitrate-rich recycle flow providing nitrate on-demand, especially in situations where the wastewater denitrification potential is low, allows to avoid excessive pumping costs and oxygen provision. The denitrification capacity and efficiency can be also improved by changing sludge loading conditions via a change in the influent flow or biomass concentration. When the denitrification potential of the wastewater and activated sludge do not allow to attain the required effluent N-quality (low strength wastewater as in chapter 6 and 7) it is possible with the presented methodology to predict the required amount of external denitrification potential in form of an external carbon source.

8.6 CONCLUSIONS

The achievement of this thesis can be considered as a step towards a more optimal design and optimisation of the denitrification process. This can be achieved using a relatively simple approach. The proposed approach allows for estimating the denitrification potential of an activated sludge system based on relevant wastewater and activated sludge characteristics. This information can be acquired from two types of respiration tests.

From an anoxic respiration test - nitrate utilisation rate (NUR-) test - with a wastewater sample from the concerned treatment plant, wastewater characteristics, simplified anoxic conversion kinetics and the denitrification potential of wastewater and activated sludge can be assessed directly. For more intensive implementations, an automated NUR-test could be considered as a positive development regarding the experimental and identification procedure.

The aerobic respiration test - oxygen utilisation rate (OUR-) test - with wastewater and nitrification suppression, allows obtaining indirectly the same information as from a NUR-test. To translate the results of an OUR-test to the denitrification potential of a system, a simplified denitrification model was formulated. It resembles practically the aerobic biodegradable COD oxidation model with the only difference that each equation regarding substrate conversion is multiplied with an appropriate denitrification reduction factor. The values of the reduction factors can be assumed based on other widely used approaches or estimated using parallely performed OUR- and NUR-tests.

Both approaches have a simplified character because the population dynamics and influence of any environmental factors are not explicitly modelled. All these effects are however not neglected but, if necessary, hidden in frequently actualised conversion rates.

The presented methodology to estimate the denitrification potential is further extended to the methodology to estimate the overall N-removal potential. This is assesed by extending the simplified aerobic/anoxic substrate oxidation model with a nitrification model (BROUWER AND KLAPWIJK, 1997). The nitrification kinetics is obtained from OUR-tests using a model substrate. The nitrifiable nitrogen from wastewater is obtained by fitting the obtained respirograms with appropriate models from an OUR-test with wastewater and without nitrification suppression.

The developed methodology to estimate the N-removal potential can be implemented for an advanced analysis of existing systems and an objective comparison of a number of optimisation strategies to improve the denitrification and nitrification efficiency. The developed methodology can also be beneficial in design assistance for activated sludge systems with nitrogen removal.

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Summary

Denitrification, with its prerequisite process nitrification, is a common practice to remove nitrogen from wastewater in activated sludge systems. From a large number of information published in the last three decades on denitrification it seems to be a well-recognised process. Key factors detrimental to its performance (**chapter 1**) are well known. The practical evidence indicates however that available information is not always efficiently utilised, although the need to optimise denitrification is often faced in both design and operation.

The relation between the denitrification potential and a detailed wastewater characterisation is an example of prior information that could be better utilised for design and optimisation of the denitrification process. Nowadays, in several obligatory denitrification design approaches a general parameter as COD/N- or BOD_5/N-ratio is used. With these lumped parameters it is not possible to estimate precisely the denitrification potential, capacity or efficiency. No universal default value can be given due to a unique character of each activated sludge and wastewater. This can be confirmed by a large number of estimated values (Table 1.2) of very extended ranges. Other design approaches use empirical values of the denitrification rate. The analysis of a variety of reported denitrification rate definitions and values (Table 1.1) may lead to the conclusion that this is also not the method for an optimal system design. Implementation of empirical approaches may lead to an under- or overestimation of the denitrification volume, what for economic reasons should be avoided. A strong need is observed for improved design and optimisation procedures for wastewater treatment plants, based on an accurate but relatively simple estimation of the denitrification potential in relation to detailed wastewater and activated sludge characteristics.

In this thesis a methodology is presented for the estimation of the denitrification potential in relation to wastewater and activated sludge characteristics. The denitrification potential (DP) in this thesis is defined as the amount of nitrate that **can** be reduced with biodegradable COD-fractions present in wastewater and from the endogenous respiration. The derivative of the denitrification potential, denitrification capacity, is defined as the amount of nitrate that **is** reduced in a given system. A common loss of biodegradable COD for aerobic oxidation (too small anoxic volume, oxygen recycle to anoxic volumes) or biological P-removal are examples that contribute in a lower denitrification capacity than DP.

Two respiration techniques formed the basis for two different approaches, the anoxic nitrate utilisation rate test (NUR-test) and the aerobic oxygen utilisation rate test (OUR-test). The approach that is based on the NUR-test is a direct method for the assessment of the DP. The approach based on the OUR-test is an indirect method because a simplified model is necessary to transform the oxygen utilisation rate to a nitrate utilisation rate. Both methods were validated with several case studies, characterised by different wastewater composition and activated sludge characteristics. The developed methods offer an advanced possibility for design assistance, optimisation, monitoring and control of wastewater treatment systems with nitrogen removal.

In **chapter 2** a methodology based on NUR-tests is proposed to estimate the DP of an activated sludge system. Next to the DP, attention is paid to the estimation of the denitrification capacity. Knowledge on the denitrification potential of wastewater allows to calculate the overall denitrification potential of a given treatment plant. In combination with system characteristics and simplified denitrification kinetics it is possible to predict the denitrification capacity and the nitrate effluent quality, probably more accurately than based

on COD/N-ratio or empirical denitrification rates. Using the proposed methodology, also the concentration of readily and slowly biodegradable COD-fractions (S_S and X_S respectively), denitrification rates on S_S, X_S, the endogenous denitrification rate and the anoxic utilisation rates of S_S and X_S can be estimated. With denitrification kinetics and relevant wastewater characteristics several optimisation decisions to improve the denitrification capacity of existing treatment plants can be undertaken with a simplified model.

When the internal DP of a plant is not sufficient to satisfy required effluent N-quality standards, the DP can be increased external in the form of a supplemental carbon source. Using the NUR-based approach, DP and kinetics can be acquired for any external carbon source. With denitrification kinetics from a NUR-test with e.g. acetate, the relation between the obtainable denitrification rate and the acetate sludge loading rate was modelled. Such type of relational model enables to design the rate of an external carbon dosage, the volume of the post-anoxic reactor volume and the development of a control strategy.

To obtain maximum advantage from NUR-tests, a number of experimental conditions have to be followed. For interpretation of the results special attention has to be paid on nitrite inclusion in assessment of the kinetics, presence of enhanced biological phosphorus removal and a proper choice of the anoxic heterotrophic yield factor Y_{HD}.

Chapter 3 is the prelude to a simplified activated sludge denitrification model. Activated sludge shows a similar respirometric behaviour pattern under anoxic and aerobic conditions to organic substrate. However, the subsequent respiration rates are usually smaller under anoxic conditions. In activated sludge models, where the denitrification process is mathematically described with aerobic substrate conversion equations, this fact is implemented by appropriate reduction factors (η). In chapter 3 a methodology is presented to estimate three reduction factors for three anoxic conversion rates: S_S-utilisation (η_1), X_S-hydrolysis (η_2) and endogenous respiration (η_3), since these processes are assumed to build up the denitrification in the simplified denitrification model (chapter 4 and 5). The methodology consists of two integrated parts: an experimental part and an estimation procedure. The experimental part implements the two respiration based techniques (OUR-test with nitrification suppression and NUR-test), performed under well-defined and analogous experimental conditions.
For the estimation procedure two simplified models are used: an aerobic biodegradable COD-oxidation model and a denitrification model. Wastewater characterisation and conversion kinetics can be assessed from an OUR-test by using the estimation procedure with the simplified aerobic COD-oxidation model. The NUR-curve is fitted with the denitrification model, being a modified version of the aerobic model but extended with reduction factors for each process. Since the majority of model parameters are assessed via aerobic respiration tests with wastewater or model substrates, and the factor η_3 can be determined directly, the reduction factors η_1 and η_2 are the only optimised parameters from the NUR-curve fitting. Additional attention was paid on the magnitude of difference between the aerobic and anoxic heterotrophic yield and anoxic and aerobic wastewater characterisation.

Some respiration tests were performed with settled domestic wastewater and different activated sludge samples. The results revealed that the values of reduction factors are not uniform but vary in function of activated sludge characteristics, operational conditions and process configuration. From the first validation turned out that the factor η_1 is the most sensitive. The reduction factor η_2 exposed less variation and oscillated around values commonly proposed in literature and validated model approaches (0.6-0.7). The reduction factor η_3 exposed much lower values than reported in literature.

From a limited number of respiration tests with acetate as model substrate, the aerobic heterotrophic yield (Y_H) turned out to be approximately 10% higher than the corresponding anoxic yield (Y_{HD}) from nitrifying and nitrifying-denitrifying systems. Estimation of Y_H and Y_{HD} using activated sludge with a high fraction of X_{PAO} is not advised with the proposed methodology because processes of substrate storage and storage product utilisation are not modelled. When Y_H and Y_{HD} are not assessed, the choice of default values from other validated approaches remains an option.

The characterisation of biodegradable wastewater fractions (S_S and X_S) under aerobic and anoxic conditions resulted in similar values for activated sludge originating from nitrifying-denitrifying systems. Non-adapted activated sludge exposed more deviation between the estimated S_S-fractions from OUR- and NUR-tests.

In **chapter 4** a simplified respiration based denitrification model is presented and incorporated with the existing simplified model for nitrification and aerobic COD-oxidation (BROUWER AND KLAPWIJK (1997) and BROUWER ET AL., (1998)). A characteristic feature of the resulting simplified nitrification-denitrification model is that substrate conversion is not modelled via the growth of appropriate groups of micro-organisms. Instead, experimentally estimated conversion rates are used, which fact contributes in a reduction of model components with regards to advanced approaches. When the conversion rates are frequently actualised, changes in biomass activity, by varying operational and environmental conditions (temperature, pH, nutrient availability, toxicity), are included. By defining only three biodegradable wastewater fractions, a compromise between complexity and simplicity was obtained. These fractions are the previously introduced S_S and X_S and additionally the nitrifiable nitrogen (S_{NHn}). The fraction S_{NHn} represents the nitrogen fraction participating exclusively in nitrification. This allows for a reduction of processes and associated parameters in the simplified nitrification-denitrification model. Aerobic and anoxic organic substrate conversions are modelled with the same relations but for anoxic conditions appropriate reduction factors are incorporated in conversion kinetics to reflect a slower activity of activated sludge under denitrifying conditions. The proposed model approach constitutes an alternative for both complex and far-simplified model approaches.

Calibration and implementation of advanced models requires an input of a significant number of parameters. Since the estimation of each parameter is difficult and time consuming, the choice of default values is an option but this can lead to erroneous predictions of reality. Use of complex models is inconvenient for applications like control or monitoring because it creates computational and analytical efforts. The far-simplified models, usually based on on-line measurement of process state variables (e.g. ammonia, nitrate), are applied to describe a limited number of processes with the simplest kinetics.

To obtain maximum benefits from the presented simplified model, the incorporation of a side-stream respiration based control unit for parameter estimation is necessary. To minimise maintenance and operational efforts the respiration set-up should be as far as possible automated regarding the performance of subsequent respiration tests and numerical procedures to assess model parameters and wastewater characteristics.

The validity and applicability of the simplified model was further tested in **chapter 5** with two pilot-plant configurations. The majority of model parameters, like wastewater characteristics and aerobic conversion kinetics, were obtained using the side-stream automated respiration based control unit RESCUE (BROUWER AND KLAPWIJK, 1997, BROUWER ET AL., 1998).

Denitrification reduction factors ($\eta_1..\eta_3$), necessary to describe anoxic substrate conversions, were estimated with the methodology as presented in chapter 3 or values from previous research on the examined system were taken. The same heterotrophic yield was used for both aerobic and anoxic conditions. For parameters having little influence on the quality of model predictions, default values were used. Steady-state and dynamic simulations were generally performed with satisfactory results.

Acceptable results of steady-state simulations implicate that the simplified model can be used to predict the overall N-removal potential, based on an actual detailed wastewater and activated sludge characterisation. The good prediction of the dynamic behaviour of the nitrate course in the effluent implicates that the model can be implemented for control strategies, e.g. for a feed-back control of the denitrification by a nitrate-rich recycle rate and/or the addition of an external carbon source. Another advantage of the model is its implementation to control the nitrification volume, tested already by BROUWER AND KLAPWIJK, 1997, BROUWER ET AL., 1998 and further in chapter 7 of this thesis.

The validation of the presented approach proved that activated sludge oxidation kinetics and wastewater composition, estimated with one type of respiration measurement, enable to describe very closely the overall N-removal process. In this way the scope of implementation of aerobic respirometry gets extended with the denitrification process. However, the anoxic respiration test to assess reduction factors must sometimes assist to attain better prediction results. When once assessed, the reduction factors for denitrification do not need to be frequently updated if the activated sludge system operates in 'steady-state' conditions. Strong system dynamics (influent dynamics and a frequent change of the ratio between pre-anoxic and aerobic zones) affects especially the reduction factor η_1.

In **chapter 6** the effect of pre-precipitation on wastewater composition, DP and overall activated sludge process was examined in lab-scale SBR systems. The operation of a reference system fed with raw wastewater enabled direct comparison. With a coagulant dose of β=1.2 (molar ratio metal to influent phosphorus), the total COD/N-ratio was decreased from 6.5 to 3.0. The soluble COD-fractions were eliminated in significant lower rate than the particulate COD-fractions. The significant reduction of biodegradable wastewater COD (mainly in form of X_S) led to high nitrate-effluent concentrations of approximately 21.3 mg.ℓ^{-1} while in the reference system with raw wastewater 8 mg.ℓ^{-1} was attained. The wastewater DP was reduced with 42% when compared with a reference system fed with raw wastewater.

The activated sludge from the system fed with pre-precipitated wastewater exposed higher specific denitrification rates for different carbon sources (S_S, X_S, acetate, endogenous) and higher nitrification rates than sludge from the reference system fed with raw wastewater. The higher activity of heterotrophic sludge was probably caused by the presence of a higher fraction of viable biomass due to a significant reduction of X_S and X_I from the wastewater. Longer SRT, lower COD/N-ratio and more viable activated sludge contributed in an increased activity of autotrophic biomass. The DP was however the determining factor for low denitrification efficiency in the system fed with pre-precipitated wastewater. This underlines the risk of using denitrification rates for design of activated sludge systems.

The simplified nitrification-denitrification model was employed to optimise theoretically the denitrification in the SBR system with pre-precipitated influent. The results of simulations allowed to suppose that only little improvement of the denitrification efficiency by manipulating with operational conditions is possible when the DP of the wastewater is originally low. The optimisation of such a system is mainly restricted to take maximum advantage of the endogenous denitrification what leads to big anoxic reactors.

To verify the statements on the effect of pre-precipitation on the DP, as derived from the research described in chapter 6, and because of contradictive evaluations appearing in literature, a supplementary research is described in **chapter 7**. A respiration based control strategy was implemented for optimising a pre-denitrification pilot-plant with pre-precipitated wastewater. This control strategy relies on the adjustment of the nitrification volume to an actual nitrifiable-N load, and this allowed avoiding over-aeration. In this way a maximum possible denitrification fraction could be created. Further, relatively high sludge loading rates were employed while satisfactory nitrification efficiency could still be attained.

Pre-precipitation with ferric chloride (β=1.0) lowered the total COD/N-ratio of the raw wastewater from 7.6 to 4.7. Despite of more beneficial wastewater characteristics comparing with the research described in chapter 6, and implementation of a well operating control strategy, the denitrification efficiency was not significantly improved. Concerning the nitrate effluent quality, an improvement of 5 $mgN.\ell^{-1}$ could be obtained for wastewater of the same origin (16.3 vs. 21.3 $mg\ N.\ell^{-1}$ respectively) and the standard of total $N \leq 10\ mgN.\ell^{-1}$ was still not fulfilled. The results in chapter 7 confirm that the required COD/N-ratio to attain satisfactory denitrification is not a universal value but is strongly dependent on wastewater and activated sludge characteristics, process conditions and operational parameters.

While the DP of raw and settled wastewater in question allowed to fulfil the nitrate standard in the effluent, the reduction of biodegradable COD by normal rate pre-precipitation caused a significant deterioration. Any optimisation step aiming to improve the denitrification efficiency may improve the nitrate effluent quality only to small extent; in principle it is only an option in situations where the effluent nitrate level differs slightly from the demanded value.

In **chapter 8** a comprehensive summary of the presented methodologies to estimate the DP and overall N-removal potential and the interrelation between the subsequent components of the overall methodologies is presented. Examples of validation of different methodologies are given and briefly sketched in this chapter. The discussion on possible application is divided between existing and designed activated sludge systems.

The approach based on a simple NUR-test is especially useful to optimise a system by changing functional zones, internal recycle ratio's, minimising oxygen input to the denitrification volume and evaluating the effect of pre-treatment on the process. When other measures do not help to increase the denitrification capacity, also the average dose of an external carbon source can be estimated. The implementation of a NUR-test for new systems is possible but with the precondition that a comparable wastewater sample and activated sludge sample from a plant with similar process conditions is available. To minimise the experimental effort in a pre-design phase of a new wastewater treatment plant, the availability of a database with information about different plant configurations and wastewater compositions could contribute in a significant progress in process design. For a range of treatment plants, characterised by different loading rates and fed by different types of wastewater, relations could be worked out in nomograms for the anoxic specific reduction rates of S_S, X_S and the endogenous rate. It is expected that the denitrification potential estimated in this way is much more precise than based on COD/N- or BOD_5/N-ratio's.

The methodology to estimate the N-removal potential using an OUR-test is suitable to be used in an on-line monitoring and/or control strategy for nitrification and denitrification in existing systems. Because conversion kinetics and wastewater composition from OUR-tests can be transferred to predict the denitrification potential, this technique constitutes the base of an overall control strategy. Additional advantage is that nitrification kinetics can be assessed.
The set-up for a NUR-test could be additionally implemented to assess reduction factors for anoxic respiration. However, when more would be known on the relation between reduction factors and system parameters and configuration, additional NUR-tests could be performed occasionally or even eliminated. With the methodologies described in this thesis, both nitrification and denitrification potential can be assessed and this allows for a prediction of the total nitrogen effluent quality.

Samenvatting

Voor de verwijdering van stikstof uit afvalwater is het gecombineerde actiefslibproces van nitrificatie en denitrificatie de gangbare praktijk. De hoeveelheid informatie die in de laatste drie decennia is verschenen over denitrificatie doet vermoeden dat de bepalende factoren voor de uitvoering (**hoofdstuk 1**) voldoende bekend zijn en dat het proces voldoende wordt doorgrond. De praktijk laat zien dat de beschikbare informatie echter niet altijd doelmatig wordt toegepast, terwijl de noodzaak voor een optimalisatie van het denitrificatieproces regelmatig aan de orde is bij ontwerp en bedrijfsvoering van actiefslibsystemen.

Een voorbeeld van primaire informatie die beter zou kunnen worden benut voor ontwerp en optimalisatie van het denitrificatieproces is de relatie tussen de denitrificatiepotentiaal en een gedetailleerde afvalwaterkarakterisering. In de huidige gangbare ontwerpprocedures wordt doorgaans uitgegaan van algemene parameters als CZV/N- of BZV_5/N-verhouding. Met deze somparameters is het daarentegen niet mogelijk de denitrificatiepotentiaal, -capaciteit of het rendement nauwkeurig te bepalen. Voor deze parameters bestaat geen universele waarde vanwege het unieke karakter van elk type afvalwater en actief slib. Dit kan worden bevestigd door de grote gesignaleerde variatie in benodigde CZV/N- of BZV_5/N-verhouding voor een vergaande denitrificatie (Tabel 1.2). Alternatieve ontwerpprocedures gebruiken empirische waarden voor de denitrificatiesnelheid. Een analyse van de grote variatie in gerapporteerde definities en waarden voor de denitrificatiesnelheid (Tabel 1.1), geeft aan dat ook dit niet de adequate methode is voor een optimaal ontwerp. Toepassing van bovengenoemde empirische methoden kan resulteren in een onder- of overschatting van het denitrificatievolume en uit kosten-technisch oogpunt moet dit worden vermeden. Om deze reden is er behoefte voor een verbeterde procedure voor het ontwerpen en optimaliseren van actiefslibsystemen, gebaseerd op een accurate en relatief eenvoudige bepaling van de denitrificatiepotentiaal in relatie tot een gedetailleerde karakterisering van het afvalwater en actiefslib. In dit proefschrift zijn methoden gepresenteerd voor de bepaling van de denitrificatiepotentiaal.

De denitrificatiepotentiaal (DP) van een actiefslibsysteem is gedefinieerd als de hoeveelheid nitraat die **kan** worden gereduceerd met de biodegradeerbare CZV-fracties in het afvalwater en de endogene respiratie van het actief slib. De denitrificatiecapaciteit is een afgeleide van de denitrificatiepotentiaal en is gedefinieerd als de hoeveelheid nitraat die **wordt** gereduceerd in een bepaald systeem. De aërobe oxidatie van biodegradeerbaar CZV (vanwege beperkt anoxisch volume of recirculatie van zuurstof naar de anoxische zone) en het verbruik van CZV voor de biologische P-verwijdering, zijn processen die verantwoordelijk zijn voor een lagere denitrificatiecapaciteit in vergelijking tot de DP.

Twee respiratietechieken vormen de basis voor twee benaderingen: de anoxische respiratietest voor het meten van de nitraatverbuiksnelheid (in Engels: NUR-test) en de aërobe respiratietest voor het meten van de zuurstofverbruiksnelheid (in Engels: OUR-test). De benadering gebaseerd op de NUR-test is een directe methode voor de schatting van de DP. Omdat een vereenvoudigd model moet worden gebruikt voor het omzetten van de zuurstofverbruiksnelheid naar een nitraatverbruiksnelheid, moet de benadering met de OUR-test worden opgevat als een indirecte methode. Beide methoden zijn getest voor meerdere actiefslibsystemen, met een variatie in afvalwatersamenstelling en slibkarakteristiek. De ontwikkelde procedures bieden een goede mogelijkheid voor ontwerp, optimalisatie en regeling van actiefslibsystemen met stikstofverwijdering.

Hoofdstuk 2 behandelt de procedure om de DP van een actiefslibsysteem te bepalen met een NUR-test. Naast de DP wordt aandacht besteed aan de berekening van de denitrificatie-capaciteit. Kennis over de DP van het afvalwater maakt het mogelijk om de totale DP van een actiefslibsysteem te bepalen. In combinatie met de procesparameters en een vereenvoudigde denitrificatiekinetiek is het mogelijk om de denitrificatiecapaciteit en het nitraatgehalte in het effluent nauwkeuriger te bepalen dan op basis van een CZV/N-verhouding of empirische denitrificatiesnelheden. Met de voorgestelde procedure is het tevens mogelijk om snel en langzaam biodegradeerbare CZV-fracties te bepalen (S_S en X_S) in het afvalwater, de denitrificatiesnelheden op S_S en X_S, de endogene denitrificatiesnelheid en de anoxische omzettingssnelheid van S_S en X_S. Met de denitrificatiekinetiek en relevante afvalwaterkarakterisering kunnen voor bestaande actiefslibsystemen meerdere optimalisatie-mogelijkheden worden beoordeeld met een vereenvoudigd actiefslibmodel.

Wanneer de DP van een actiefslibsysteem niet voldoende is voor het bereiken van de vereiste effluentkwaliteit, kan de DP worden verhoogd in de vorm van een externe koolstofbron. Met de voorgestelde NUR-test kunnen de DP en denitrificatiekinetiek eenvoudig worden vastgesteld van elk type koolstofbron. Voor acetaat was de relatie gemodelleerd tussen de haalbare denitrificatiesnelheid en de acetaatdosering. Met een dusdanige relatie is het mogelijk de doseerhoeveelheid van een externe koolstofbron en het extra benodigde denitrificatievolume te ontwerpen. De relatie kan ook dienen als basis voor het ontwerp van een regelstrategie voor de dosering.

Voor een juiste interpretatie van resultaten dient bij een NUR-test met een aantal experimentele condities rekening te worden gehouden. Speciale aandacht moet onder meer worden besteed aan de vorming van nitriet, de aanwezigheid van biologische P-verwijdering en een adequate keuze van de anoxische heterotrofe yield factor Y_{HD}.

Hoofdstuk 3 vormt de inleiding van het in dit proefschrift gepresenteerde vereenvoudigd denitrificatiemodel. Onder anoxische omstandigheden laat actief slib een soortgelijk respirometrisch gedrag zien als onder aërobe omstandigheden. Onder anoxische omstandigheden zijn de opeenvolgende respiratiesnelheden echter lager. In actiefslibmodellen waar het denitrificatieproces wiskundig wordt beschreven via aërobe substraatomzettings-snelheden, wordt daarom gebruik gemaakt van reductiefactoren (η). In hoofdstuk 3 is een methode gepresenteerd voor de bepaling van de reductiefactoren voor: S_S-omzetting (η_1), X_S-omzetting (η_2) en de endogene respiratie (η_3). Deze processen zijn betrokken bij de opbouw van de denitrificatie in het vereenvoudigde denitrificatiemodel (hoofdstuk 4 en 5). De methode voor de bepaling van de reductiefactoren bestaat uit een experimenteel deel en een numerieke procedure voor parameterschatting. Het experimentele deel omvat de twee respiratietechnieken (OUR-test met remming van nitrificatie en een NUR-test) onder gedefinieerde en identieke experimentele condities. Voor de numerieke procedure worden twee vereenvoudigde modellen gebruikt: een aëroob model voor de oxidatie van biodegradeerbaar CZV en een denitrificatiemodel. De afvalwaterkarakteristiek en kinetiek van de omzetting kunnen worden bepaald via een OUR-test en parameterschatting met het aërobe model. Het verloop van de NUR-test wordt 'gefit' met het denitrificatiemodel, een gemodificeerde versie van het aërobe model met reductiefactoren voor elk proces. Omdat de meerderheid van de modelparameters zijn bepaald via de OUR-test met afvalwater of een modelsubstraat en de factor η_3 direct kan worden bepaald, zijn de reductiefactoren η_1 and η_2 de enige optimalisatieparameters. Bij het uitwerken van de methode is extra aandacht besteed aan de mate van variatie tussen de aërobe en anoxische heterotrofe yieldfactor en de aërobe en anoxische afvalwaterkarakterisering.

Een aantal respiratie-experimenten is uitgevoerd met voorbezonken afvalwater en verschillende soorten actief slib. De resultaten geven aan dat de waarden van de reductiefactoren niet uniform zijn en variëren in functie van slibkarakteristiek, procesparameters en configuratie. Het bleek dat de factor η_1 de meest gevoelige factor is. De reductiefactor η_2 vertoonde minder variatie en lag rond waarden die staan vermeld in de literatuur (0,6-0,7). De bepaalde reductiefactor η_3 was lager dan gerapporteerd in de literatuur.

Van een beperkt aantal respiratie-experimenten met acetaat als modelsubstraat, bleek de aërobe heterotrofe yieldfactor (Y_H) ongeveer 10% hoger te zijn dan de corresponderende anoxische yieldfactor (Y_{HD}) voor slib van een systeem met alleen nitrificatie en van een systeem met nitrificatie en denitrificatie. Voor de bepaling van Y_H en Y_{HD} met slib met een hoge fractie aan X_{PAO}, is de gepresenteerde methode niet geschikt omdat geen rekening is gehouden met opslagproducten. Wanneer Y_H en Y_{HD} niet worden vastgesteld blijft de keuze van standaardwaarden uit de literatuur een mogelijkheid.

De karakterisering van biodegradeerbare fracties (S_S en X_S) onder aërobe en anoxische omstandigheden resulteerde in vergelijkbare waarden bij gebruik van actief slib van een nitrificerend/denitrificerend systeem. Niet-geadapteerd slib vertoonde meer variatie in de bepaalde S_S-fractie via OUR- of NUR-testen.

In **hoofdstuk 4** wordt het op respirometrie gebaseerde vereenvoudigde denitrificatiemodel gepresenteerd. Dit model wordt samengevoegd met het bestaande vereenvoudigde model voor nitrificatie en aërobe CZV-oxidatie (BROUWER AND KLAPWIJK (1997) and BROUWER ET AL., (1998)). Een karakteristieke eigenschap van het resulterende model is dat de substraatomzetting niet is gemodelleerd via de groei van de betrokken organismen. In plaats daarvan worden experimenteel bepaalde omzettingssnelheden gebruikt. Dit leidt tot een reductie van modelcomponenten in vergelijking tot geavanceerde modellen. Wanneer de omzettingssnelheid regelmatig wordt geactualiseerd, zal hierin de verandering in de activiteit van de biomassa (door variatie in temperatuur, pH of toxiciteit) worden gereflecteerd. Voor de afvalwaterkarakterisering zijn slechts drie biodegradeerbare fracties gedefinieerd; hierdoor is een compromis tussen complexiteit en eenvoud bereikt. Naast de fracties S_S en X_S wordt als extra fractie het nitrificeerbaar stikstof (S_{NHn}) geïntroduceerd. De fractie S_{NHn} representeert de stikstoffractie die exclusief deelneemt in het nitrificatieproces. Dit staat een reductie toe van bepaalde processen en betrokken parameters voor een vereenvoudiging van het model. Aërobe en anoxische substraatomzetting zijn gemodelleerd met dezelfde relatie waarbij voor anoxische condities reductiefactoren zijn gebruikt voor de beschrijving van een lagere activiteit onder denitrificerende condities. De voorgestelde modelaanpak vormt een alternatief voor zowel complexe als zeer vereenvoudigde modellen.

Calibratie en implementatie van geavanceerde modellen vereist de invoer van een significant aantal parameters. Omdat de bepaling van elke parameter moeilijk is en tijdrovend, is de keuze van standaardwaarden een optie; dit kan echter leiden tot een zeer afwijkende beschrijving van de praktijk. Het gebruik van complexe modellen voor regeldoeleinden is bovendien lastig vanwege een verhoogde kans op rekenfouten.
De zeer vereenvoudigde modellen die meestal zijn gebaseerd op on-line metingen van procesvariabelen (bijv. ammonium en nitraat), worden gebruikt voor een beperkt aantal processen met een niet-complexe kinetiek.

Om maximaal voordeel te halen van het gepresenteerde vereenvoudigde model voor nitrificatie en denitrificatie, is de combinatie met een op respiratie gebaseerde meetopstelling nodig voor parameterschatting. Om bedrijfsvoering en onderhoud te minimaliseren moet de opstelling bij voorkeur zijn geautomatiseerd voor het uitvoeren van respiratiemetingen en het bepalen van de modelparameters en afvalwaterkarakterisering via een numerieke procedure.

De geldigheid en bruikbaarheid van het vereenvoudigde model zijn verder getest in **hoofdstuk 5** met twee proefinstallaties. De meerderheid van de modelparameters zijn verkregen met een geautomatiseerde meetopstelling op basis van respirometrie (RESCUE, BROUWER AND KLAPWIJK, 1997, BROUWER ET AL., 1998). De reductiefactoren voor denitrificatie ($\eta_1..\eta_3$) zijn bepaald met de methodiek van hoofdstuk 3 of er is gebruik gemaakt van reeds eerder bepaalde factoren voor het onderzochte systeem. Dezelfde heterotrofe yieldfactor werd gebruikt voor aërobe en anoxische condities. Voor parameters met een geringe invloed op de modelresultaten werden standaardwaarden toegepast. Statische en dynamische simulaties werden doorgaans uitgevoerd met goed resultaat.

Acceptabele resultaten met statische simulaties houden in dat het vereenvoudigde model gebruikt kan worden voor een voorspelling van de totale stikstofverwijderingscapaciteit, gebaseerd op een actuele gedetailleerde afvalwater- en slibkarakterisering. De goede beschrijving van het dynamisch karakter van het nitraatverloop in het effluent geeft aan dat het model kan worden ingezet voor regelstrategieën, bijv. voor een regeling van de denitrificatie middels de recirculatie van nitraat en/of de dosering van een externe koolstofbron. Een voordeel van het model is dat het tevens geschikt is voor de regeling van het nitrificatievolume, zoals eerder getest door BROUWER AND KLAPWIJK, 1997, BROUWER ET AL., 1998 en beschreven in hoofdstuk 7 van dit proefschrift.

De validatie van de gepresenteerde aanpak geeft aan dat de oxidatiekinetiek en afvalwaterkarakterisering, bepaald met één type respiratiemeting, het mogelijk maakt om het totale proces van stikstofverwijdering goed te beschrijven. Op deze manier wordt het toepassingsgebied voor aërobe respirometrie uitgebreid met het denitrificatieproces. Anoxische respiratietests voor het bepalen van de reductiefactoren zijn desondanks nodig voor een goede beschrijving van het actiefslibsysteem. Eenmaal gemeten hoeven de reductiefactoren voor denitrificatie minder frequent te worden bepaald bij een stabiele bedrijfsvoering van het actiefslibsysteem ('steady-state'-condities). Een sterke dynamiek (influentdynamiek en een frequente verandering in de verhouding tussen het volume van de voordenitrificatie en de aërobe ruimte) heeft vooral invloed op de reductiefactor η_1.

Hoofdstuk 6 behandelt voor een SBR-systeem (Sequencing Batch Reactor) op laboratoriumschaal het effect van voorprecipitatie op de afvalwatersamenstelling, denitrificatiepotentiaal en het totale actiefslibproces. Een identiek SBR-systeem gevoed met onbehandeld afvalwater diende als referentiesysteem. Een dosering met een β van 1,2 (molaire verhouding van metaalzout tot fosfaat in het influent) resulteerde in een verlaging van de CZV/N-verhouding van 6,5 tot 3,0. De opgeloste CZV-fracties werden met een significant lagere snelheid verwijderd dan de gesuspendeerde CZV-fracties. De verwijdering van biodegradeerbaar CZV (vooral in de vorm van X_S) leidde tot nitraatconcentraties in het effluent van 21,3 $mg.\ell^{-1}$ terwijl in het referentiesysteem met ruw afvalwater een concentratie van 8 $mg.\ell^{-1}$ kon worden bereikt. De DP van het afvalwater werd door voorprecipitatie met 42% verminderd in vergelijking tot onbehandeld afvalwater.

Het actief slib van het systeem met voorprecipitatie vertoonde hogere specifieke denitrificatiesnelheden voor verschillende koolstofbronnen (S_S, X_S, acetaat en endogeen materiaal) en hogere nitrificatiesnelheden dan voor het referentiesysteem met onbehandeld afvalwater. De hogere activiteit van heterotroof slib werd waarschijnlijk veroorzaakt door de aanwezigheid van een hogere fractie aan actieve biomassa, als resultaat van een vergaande reductie van X_S en X_I uit het afvalwater. Een langere slibleeftijd, lagere CZV/N-verhouding en meer actieve biomassa droegen bij aan een grotere fractie van autotrofe biomassa in het actief slib. De verlaagde DP was echter de bepalende factor voor een verminderde denitrificatie in het systeem met voorprecipitatie. Dit deel van het onderzoek onderstreept het gevaar van het gebruik van denitrificatiesnelheden voor ontwerp.

Het vereenvoudigd nitrificatie-denitrificatiemodel was gebruikt voor een theoretische optimalisatie van het het SBR-systeem met voorprecipitatie. Simulatieresultaten geven aan dat bij onvoldoende DP in het afvalwater slechts een beperkte verbetering kan worden gerealiseerd door de procescondities aan te passen. De optimalisatie van een dusdanig systeem kan lopen via een maximale benutting van de endogene denitrificatie; dit leidt echter tot grote anoxische reactoren.

Voor een verificatie van de bevindingen over het effect van voorprecipitatie op de denitrificatiepotentiaal in hoofdstuk 6 en vanwege tegengestelde beweringen in de literatuur, is aanvullend onderzoek uitgevoerd en beschreven in **hoofdstuk 7**. Een op respirometrie gebaseerde regelstrategie was ingevoerd voor de optimalisatie van een voordenitrificatie-systeem met voorgeprecipiteerd afvalwater. De regelstrategie zorgde voor een aanpassing van het nitrificatievolume op basis van de actuele belasting met nitrificeerbare stikstof. Overmatige beluchting werd via deze regelstrategie voorkomen zodat een maximaal mogelijke anoxische volumefractie voor denitrificatie kon worden gecreëerd.

Voorprecipitatie met ijzerchloride (β=1,0) verlaagde de totale CZV/N-verhouding van het onbehandelde afvalwater van 7,6 tot 4,7. Ondanks een gunstiger afvalwaterkarateristiek dan in het onderzoek van hoofdstuk 6, en ondanks de implementatie van een adequate regelstrategie, werd het denitrificatierendement niet voldoende verbeterd. Voor afvalwater van dezelfde herkomst kon een verbetering worden gerealiseerd van 5 mgN.ℓ^{-1} in het effluent (16,3 versus 21,3 mg N.ℓ^{-1}). De effluenteis voor N-totaal $\leq$ 10 mgN.ℓ^{-1} werd dus nog niet bereikt. De resultaten in hoofdstuk 7 bevestigen dat de vereiste CZV/N-verhouding voor voldoende denitrificatie geen universele waarde is en in hoge mate afhankelijk is van afvalwater- en slibkarakteristieken, procescondities en operationele parameters.

Daar waar de DP van ruw en voorbezonken afvalwater voldoende was voor het voldoen aan de gestelde stikstofeis in het effluent, zorgde de reductie van biodegradeerbaar CZV (X_S) door voorprecipitatie voor een significante verslechtering. Elke ingevoerde optimalisatiestap voor het verbeteren van het denitrificatierendement verbeterde de effluentkwaliteit slechts in geringe mate; het is in principe alleen een optie in situaties waar de effluentkwaliteit voor stikstof de vereiste standaard reeds dicht benaderd.

In **hoofdstuk 8** is een overzicht gegeven van de gepresenteerde methoden voor het bepalen van de DP en de totale stikstofverwijderingspotentiaal. In dit hoofdstuk worden bovendien voorbeelden omschreven voor een validatie van de verschillende methoden. Voor de discussie over de toepassing is onderscheid gemaakt tussen bestaande en nieuwe actiefslibsystemen.

De methode gebaseerd op de NUR-test is vooral geschikt voor het optimaliseren van de procesconfiguratie, interne recirculatieverhouding, minimalisatie van de zuurstofinbreng in de denitrificatieruimte en de evaluatie van het te verwachten effect van een voorbehandeling van het afvalwater. Wanneer de hiervoor genoemde maatregelen niet resulteren in een verhoging van de denitrificatiecapaciteit is het via een NUR-test mogelijk de benodigde dosering van een externe koolstofbron te bepalen. De implementatie van een NUR-test voor nieuwe systemen is mogelijk; echter met de randvoorwaarde dat een vergelijkbaar monster afvalwater kan worden gebruikt en actiefslib verkrijgbaar is van een actiefslibsysteem met soortgelijke procescondities. Ter vermindering van de experimentele inbreng in een voorontwerp kan de aanwezigheid van een gegevensbestand met informatie over verschillende procesconfiguraties en afvalwatersamenstelling bijdragen aan een significante vooruitgang in procesontwerp. Voor actiefslibsystemen die worden gekarakteriseerd door een verschil in slibbelasting en afvalwaterkarakterisering kunnen relaties worden opgezet in de vorm van nomogrammen voor de denitrificatie op S_S en X_S en de endogene denitrificatie. De verwachting is dat de via deze manier bepaalde denitrificatiepotentiaal meer nauwkeurig is dan gebaseerd op CZV/N of BZV_5/N-verhouding.

De methode voor de bepaling van de N-verwijderingspotentiaal met een OUR-test is geschikt voor de monitoring en/of regeling van de nitrificatie en denitrificatie in bestaande systemen. Omdat de omzettingskinetiek en afvalwatersamenstelling van OUR-tests kunnen worden omgezet voor het voorspellen van de denitrificatiepotentiaal, omvat deze techniek de basis voor een totale regelstrategie, mede omdat de nitrificatiekinetiek kan worden vastgesteld. Door NUR-tests uit te voeren kunnen de reductiefactoren voor anoxische respiratie worden vastgesteld. Wanneer echter meer kennis beschikbaar komt over de relatie tussen reductiefactoren en procesparameters en procesconfiguratie, is een incidentele uitvoering van een NUR-test voldoende of in zijn geheel niet meer noodzakelijk. Met de beschreven methoden in dit proefschrift, kunnen zowel de nitrificatie- als denitrificatiepotentiaal worden vastgesteld en dit biedt mogelijkheden voor een voorspelling van de stikstofconcentratie in het effluent.

Curriculum vitae

Katarzyna Kujawa-Roeleveld was born the 7th of February 1968 in Żary (Poland). After graduation from the Polish secondary school (gymnasium) she started in 1986 her study at the Poznań University of Technology in Poland, faculty Sanitary Engineering at the Department of Civil Engineering. She obtained her engineer title in 1991 by defending the thesis "Optimisation of nutrient removal in small treatment plants with the UCT activated sludge model". In the beginning of 1992 she started to work as assistant at the Department of Civil Engineering, participating in educational programs for students and in some research projects. Practical experience to transform the knowledge on detailed technological and civil design of comprehensive wastewater treatment plants, she acquired when working for the engineering company AQUA as consulting engineer and for the Water Board as technologist on the Poznań WWTP (both part time). In 1995 she attained a licence of independent design engineer, necessary in Poland to authorise projects. From 1993 she visited within the EU program Tempus a few times the Department of Environmental Technology of the Wageningen University. From March 1995 to the end of 1998 she performed the experimental work as described partially in this thesis. Since July 1999 she works in the Department of Environmental Technology as researcher on the project "Decentralised Sanitation and Reuse".