Nitrogen and Carbon Removal from Organic Loaded Effluens

Chemical Engineering Methods and Technology

Marlene Roeckel • Estrella Aspé
Karin Walter

Novinka

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MARLENE ROECKEL
ESTRELLA ASPÉ
AND
KARIN WALTER

NOVINKA

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PREFACE

This book searches to clarify and to compare the process of denitrification/anaerobic digestion/ nitrification for the simultaneous removal of nitrogen and carbon from organic loaded effluents for: (a) only one reactor, and (b) within a series of reactors. In the first type of process, nitrification and denitrification simultaneously take place in the same reactor (SND). In the second type of process, there is a hybrid reactor with an internal recycle, where denitrification and anaerobic digestion take place; then followed by an aerobic reactor where nitrification occurs recycling in the anoxic/anaerobic stage. We attempt to analyze the different factors that affect both processes, such as: (1) dissolved oxygen (DO), (2) carbon and nitrogen ratio in the influent (C/N), (3) hydraulic residence time (HRT), (4) effect of the recycle ratio, and (5) the presence of salt (NaCl) in the influent. Additionally, the variety of SND reactors and integrated processes that have been reported (short-cut nitrification denitrification) are presented, identifying the engineering principles on which they are based and explaining the effects produced by reactor stratification and the formation of microenvironments in the reactor's biofilm. Finally, nitrogen and organic matter removal efficiencies are compared for both treatment processes. The actual tendency is towards more compact reactors with fewer stages because they combine savings in biological treatment supplies, control systems, and the installation costs with a robust and flexible system.

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Chapter 1

INTRODUCTION

Most countries are now environmentally conscious, and therefore, government authorities control industrial and urban effluents discharged in water systems and on the ground. At present, there are several wastewater treatment alternatives, in which it is not only important to obtain high organic matter and nitrogen removal efficiencies but also to extensively evaluate the costs involved in the treatment process.

Developed countries use effluent treatments that consider nitrification, denitrification and anaerobic digestion; but developing countries have yet to achieve complete removal of carbon and nitrogen when using biological treatment for effluents. Effluent treatment is incomplete in developing countries principally because the laws are less strict and the high cost of implementation for a complete process would increase the cost of the final product. Since industries in developing countries base their decisions more on economic reasons than environmental ones, economic and effective treatments for effluents need to be developed and introduced.

When selecting a treatment process for a wastewater treatment plant or modifying an existing one, the decision should be based on complete information: the characteristics, advantages and disadvantages of different alternatives offered must be known in order to choose between simultaneous or separate steps.

Several industries give rise to large amounts of saline liquid residues with high organic load, such as the salmon-processing and fish industries that use seawater in some of their processes and their effluents have high concentrations of salt and protein (Mariángel *et al.*, 2008).

The simultaneous nitrification and denitrification seems to be a process that will replace the traditional effluent treatment because it offers similar organic load and nitrogen efficiencies in a smaller reactor, involves lower installation and operation costs; can handle variations in the influent's organic load providing greater operational stability. This chapter compares both treatment systems and the factors that affect their performance.

Chapter 2

SIMULTANEOUS NITRIFICATION AND DENITRIFICATION PROCESS (SND)

To understand the chemical oxygen demand (COD) and total nitrogen (TN) removal processes, the processes of nitrification and denitrification must be understood. Nitrification corresponds to the oxidation of ammonia to nitrite by chemolithoautotrophic bacteria, where the most important genera is *Nitrosomonas* and the oxidation of nitrite into nitrate is produced by *Nitrobacter*. Denitrification is the catabolic use of nitrate to produce N_2. Denitrification by chemolithoautotrophic bacteria has been used successfully to treat drinking water. Nearly all denitrifiers are able to use NO_2^- instead of NO_3^- as an electron acceptor and a large number of different organics for as electron donator or energy source (Wiesmann, 1994). The following equations describe the process indicated (Wiesmann *et al.*, 2007).

Nitrification (catabolism and anabolism):

$$55\ NH_4^+ + 76\ O_2 + 109\ HCO_3^- \rightarrow C_5H_7NO_2 + 54\ NO_2^- + 57\ H_2O + 104\ H_2CO_3 \quad (1)$$

$$400\ NO_2^- + NH_4^+ + 4\ H_2CO_3 + HCO_3^- + 195\ O_2 \rightarrow C_5H_7NO_2 + 3\ H_2O + 400\ NO_3^- \quad (2)$$

Denitrification (catabolism) using acetic acid as electron donor:

$$5\ CH_3COOH + 8\ NO_3^- \rightarrow 4\ N_2 + 10\ CO_2 + 6\ H_2O + 8\ OH^- \quad (3)$$

$$3\ CH_3COOH + 8\ NO_2^- \rightarrow 4\ N_2 + 6\ CO_2 + 2\ H_2O + 8\ OH^- \quad (4)$$

Denitrification using methanol as energy source (Wiesmann *et al.*, 2007):

$$6\ NO_3^- + 2CH_3OH \rightarrow 6NO_2^- + 2CO_2 + 4H_2O \quad (5)$$

$$6\ NO_2^- + 3CH_3OH \rightarrow 3N_2 + 3CO_2 + 3H_2O + 6OH^- \quad (6)$$

$$6\ NO_3^- + 5CH_3OH \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^- \quad (7)$$

The process of simultaneous nitrification and denitrification (SND) is based on the sequential decomposition of ammonia into nitrite by nitrification (eq.1) and further nitrite into nitrogen by denitrification (eqs. 4 and 6) in one reactor. In order to increase global process efficiency, the aerobic and anoxic steps from nitrite to nitrate (eq. 2) and nitrate to nitrite (eq. 5) should be avoided. In other words, to accomplish the previous goal, it is necessary to avoid the growth of *Nitrobacter* bacteria, which is responsible for the nitrite oxidation, by controlling adequately the reactor's aeration and pH (Gao *et al.*, 2009; Wang *et al.*, 2008; Li *et al.*, 2008; Collivignarelli and Bertanza, 1999; Nakano *et al.*, 2004).

Recent studies (Ros and Vrtovsek, 1998; Chui *et al.*, 2001; Del Pozo and Diez, 2005) have shown the feasibility of the simultaneous nitrogen and carbon removal from industrial effluents by using an anaerobic/anoxic/aerobic biofilm packed bed reactor. Martins dos Santos *et al.* (1998) provide an extensive review of nitrogen removal in compact systems by immobilized microorganisms until 1998. They show that the most effective, compact bioreactors involve immobilized cell technology and tend to be designed at height. This design contrasts with the reactors presently operating in treatment plants that are mainly based on large tanks with suspended bacteria.

2.1. Advantages of SND

One of the advantages of carrying out the SND process is the reduction of oxygen used in nitrification (up to a 40% reduction in the requirement of organic load in the denitrification step), an increase of 63% in the denitrification rate, 300% less of biomass production during anaerobic growth, and the absence of toxic effects to the reactor's microorganisms (Wang *et al.*, 2008).

According to Li *et al.* (2008) and Hu *et al.* (2008), the use of a membrane bioreactor (MBR) for the SND process offers the following advantages over a conventional process:

- It eliminates the need of two tanks operating in series or an intermittent aeration in one tank.
- It uses 22-40% less carbon source and reduces sludge production in the aerobic step in up to 30%.
- The pH is neutral and a lower alkalinity is required.
- It consumes less energy due to the reduction in aeration.

SND technologies show savings of 25% in consumed oxygen, 40% in the organic matter, 1.5-2 times higher denitrification rate and lower carbon dioxide emissions in correspondence to the conventional process (An *et al.*, 2008). According to Chu *et al.* (2006), sludge production is low because the main part of the influent organic load was anaerobically removed.

As can be observed, SND is an interesting alternative to improve water treatment plants since it can reach high removal efficiencies, involves minimum interference (low investment) in existing facilities, and uses simple technologies (low costs). For example, in a biological treatment plant with a design size of 2500 Person Equivalent (p.e.), the same efficiency of nitrogen and Chemical Organic Load (COD) removal could be achieved with 20% less reactor volume than in the conventional process and with 50% energy savings (Collivignarelli and Bertanza, 1999). Additionally, this savings comes with stable COD removal in the effluent even with COD changes in the influent (Hu *et al.*, 2008).

Chui *et al.* (2001) demonstrated that a single combined filter reactor for an integrated process is slightly more efficient than separate units; and that in such a system, the volume of various zones can be adjusted to treat wastewater with different COD and nitrogen concentrations.

2.2. Why and When is SND Possible?

SND can be explained by three phenomena (Wang *et al.*, 2008; Li *et al.*, 2008; Collivignarelli and Bertanza, 1999; Guo *et al.*, 2005):

- Development of microenvironments within the aerated bioreactor as a result of the mix pattern or aeration style. This is also known as bioreactor stratification.
- Development of microenvironments within the individual floc of activated sludge or within the biofilm.
- Presence of novel microorganisms that can remove nitrogen by unknown mechanisms.

In the first case, nitrifying and denitrifying bacteria grow at different zones in the reactor. In the second case, aerobic and anoxic bacteria coexist in a microscopic scale, and SND effectiveness depends on the floc size and distribution along the biofilm.

The third case relates the SND with a microbiological phenomenon and is based on two alternate explanations. First, it occurs because the denitrifying microorganisms that metabolize during the anoxic phase, still can reduce nitrogen for a specific time period while the oxygen concentration increases. Secondly, it occurs because the denitrifying bacteria are from a higher physiological variety than previously assumed. It has been suggested that some microorganisms responsible for SND are autotrophic, which means that the need of an organic carbon source can be reduced during denitrification (Holman and Wareham, 2005).

Our research group is currently studying the first case. The study proved the feasibility of the biological treatment of high organic proteinic saline effluents in a combination of anoxic/anaerobic/aerobic steps in an one-filter reactor with different recycle ratios (0, 2 and 10), achieving values of organic matter removal efficiency higher than 98% for all reactors and values of total nitrogen removal efficiency of 46.6% and 94.3%% for recycle ratios of 2 and 10. For the reactor without recycle, 98.3% of the inlet ammonia was converted; nevertheless nitrogen is eliminated as nitrites and nitrates (Giustinianovich , 2009, not published data).

The first and second cases described earlier in this section are proved by Guo *et al.* (2005). They identify, in an airlift bioreactor with two baffles, different characteristics (width, settlement, and color) in each reactor's zone depending on if it is the anoxic, buffering, or oxic. These different characteristics lead to the presence of different types of microorganisms in each zone, proving the horizontal stratification of the media and biofilm. Batch assays also have corroborated the presence of nitrifying and denitrifying bacteria in different reactor zones, which leads to conclude that SND occurs throughout the reactor.

An example of the second case is presented by Satoh *et al.* (2003) focusing in the development of microenvironments in the flocs. Here the microenvironments within the immobilized flocs are produced due to a high density of microorganisms. Microelectrode techniques applied inside the aerated activated sludge have shown that anoxic zones exist, where denitrification has occurred, due to gradients in the oxygen concentration. The metabolic activities within the floc depend on their size and vary among samples taken in different reactors. In addition, the flow regime is an important parameter when determining what is happening in the floc, since this dynamic influences the floc diameter, resistance to mass transfer, microenvironments, and local activity.

Li *et al.* (2008) demonstrated that microenvironments develop within the biofilm in a membrane bioreactor (MBR). By introducing fibrous carriers in the reactor's down-comer for attached growth of microorganisms, considerable amount of biomass is immobilized in the bubble free anoxic compartments. Due to the absence of shear stress, a thick and rough biofilm layer develops gradually, leading to the resistance to the oxygen transfer in the layer. The resulting stable anoxic zone that develops allows growth and enrichment of denitrifiers. In this case, the development of microenvironments within the flocs can be rejected since the sizes are smaller than 50 μm and the formation of microenvironments within the same floc is not significant in suspended biomass systems.

The occurrence of SND in a biofilm has been frequently demonstrated due to the coexistence of nitrifying and denitrifying bacteria (Hu *et al.*, 2009; Xia *et al.*, 2008). In a pilot-scale submerged membrane bioreactor (SMBRs), Chen *et al.* (2008) accomplished simultaneous nitrification and denitrification, speculating that an anoxic micro-zone was formed inside the flocs where denitrification occurred due to the oxygen diffusion limitation.

Other studies indicate that the physical argument for SND is not valid alone. It has been demonstrated that in a floc of 7.754 μm size, despite the small size, SND occurs because more nitrogen species than assimilated by the microorganisms and a low consumption rate of alkalinity are observed (Zhu *et al.*, 2007).

2.3. Oxygen Effect

As indicated earlier in this review, many reports established the dissolved oxygen concentration (DO) as being responsible for SND feasibility (Gao *et al.*, 2009; Wang *et al.*, 2008; Li *et al.*, 2008; Nakano *et* *al.*, 2004; Hu *et al.*, 2008; An *et al.*, 2008). Table 1 shows the DO concentrations used for different studies.

Direct control or indirect control of DO (ORP or fluorescence NADH) can be used to maintain the low DO required (Collivignarelli and Bertanza, 1999).

Zhu *et al.* (2007) found a direct relationship between DO and SND. They also reported that simultaneous nitrification and denitrification does not occur when DO = 6.05 mg/L and the formation rate of NOx-N is almost the same as the ammonia consumption rate.

A low DO concentration limits the development and enrichment of nitrifying bacteria (Fu *et al.*, 2009). The Chemical Oxygen Demand to Total Nitrogen ratio (COD/TN) indirectly control the DO by heterotroph competition. If the COD/TN ratio decreases, increasing the percentage of nitrifiers, nitrites would be the only nitrogen species that would have to be reduced to nitrogen gas; therefore the reactor needs less aeration than a complete nitrification unit and the subsequent denitrification will consume less COD (Chu *et al.*, 2006).

Great biofilm depth produces an increment in the substrate's diffusion mass transfer resistance that leads to an increase in the demand for oxygen. Therefore, the heterotrophic communities outcompete nitrifying bacteria, and consequently nitrifying bacteria cannot efficiently remove NH_4^+-N (Hu *et al.*, 2008).

A membrane bioreactor can be classified into two zones according to DO: (1) microaerofilic, within the granular bed of the sludge, (2) aerobic, over the granular bed. The organic substances are oxidized in the microaerofilic and aerobic zones, but the nitrogen is mainly removed in the granular bed zone with limited oxygen conditions (Chu *et al.*, 2005).

Chen *et al.* (2008) studied the influence of DO concentration on organic substances and nitrogen removal in pilot-scale submerged membrane bioreactors (SMBR). The DO concentration was maintained at 0.6, 1.2, 3.0 and 5.0 mg/l. The COD removal efficiency was more than 96% for DO concentrations between 1.2 and 5.0 mg/l, but a significant decrease (from 98% to 89%) in COD removal efficiency was observed for 0.6 mg/l in the first 30 days of operation under these conditions; afterwards, it returned to its original level. The total nitrogen removal efficiency increased from 60% to 90% as the DO concentration was reduced from 5 to 1.2 mg/l, but it decreased when the DO concentration was 0.6 mg/l. Thus, the optimum DO concentration for this study is about1.2 mg/l.

Table 1. Process parameter data in compact or integrated reactors for simultaneous removal of carbon and nitrogen in high and low load effluents

Study	Reactor	Substrate	Inlet Nitrogen or Protein concentration or organic matter concentration	Nitrogen loading rate	Organic loading rate	C/N	Recycle rate	HRT or reaction time (t)	DO concentration	Efficiency and removal rate
Nitrogen removal by simultaneous nitrification and denitrification via nitrite in a sequence hybrid biological reactor (Wang *et al.*, 2008)	Sequencing batch hybrid reactor with sludge from a full-scale plant	Synthetic wastewater	71 mg TN/L 350 mgCOD/L	-------	0.5 - 4 kgCOD/ m3d	4.93 mg COD/ mgTN	-----	12 h	0.3-0.5 (mg/L)	92% COD 85% to 96% TN
Effect of oxygen concentration on nitrification and denitrification in single activated sludge flocs (Satoh *et al.*, 2003)	Single aeration batch tank	Municipal wastewater treatment plant	2280μM NH4 10μM NO2- 10μM NO3- (81.24 mg TN/L)	-----	Not informed	---	-----	10 h	10-35 (μ mol/L) (0.32-1.12 mg/L)	40% IN Nitrification Rate: 24 μmol N/MLSS/h Denitrification rate:6 μmol N/MLSS/h

Table 1. (Continued).

Study	Reactor	Substrate	Inlet Nitrogen or Protein concentration or organic matter concentration	Nitrogen loading rate	Organic loading rate	C/N	Recycle rate	HRT or reaction time (t)	DO concentration	Efficiency and removal rate
Nitrogen removal performance and microbial community structure dynamics response to carbon nitrogen ratio in a compact suspended carrier biofilm reactor (Xia *et al.*, 2008)	Compact suspended carrier biofilm reactor 35%v/v cumulated carriers	Synthetic wastewater	40 mgNH4Cl/L 120-200 mgCOD/L	10 mgNH4Cl /L/h	30-50 mgCOD/L/h	3:1 5:1 10:1	----	4 h	1.2-2.5 (mg/L)	Over 90%COD 83.3% SND TOC