Over a Decade of Experience with the ANAMMOX® Reactor Start-up and Long-Term Performance

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ABSTRACT

There is an increasing interest in anaerobic digestion of sewage sludge, organic wastes and industrial effluents for a sustainable way of purification combined with production and utilization of biogas. Reject waters from sludge dewatering and effluents derived from anaerobic treatment of industrial processes contain significant amounts of ammonium. Dedicated separate treatment of these waters via the anammox route, which stands for "anaerobic ammonium oxidation" reduces energy consumption and allows for a more compact reactor. Paques has built experience applying this process for more than a decade, through designing and building ANAMMOX® reactors for a wide range of wastewaters. This article presents the results from start-up and operation of recent and long running full-scale ANAMMOX® reactors.

HISTORY OF THE ANAMMOX TECHNOLOGY

Already in 1941 an assumption was made by a research group in Washington (Hamm and Thompson, 1941), that anaerobic ammonium oxidation (anammox) could be a possible nitrogen-sink in the oceans. More than 20 years later, observations by Richards (1965) showed a water column with disappearing ammonium under anoxic conditions. This was then explained by the oxidation of ammonium with nitrate. The anammox pathway was first presented in theory as being a possible way to perform denitrification, using ammonium as an electron donor by Broda (1977), a German physicist, based on the substantial release of Gibbs free energy by the reaction (-358kJ/mol). Ten years later, in 1989, at Gist Brocades, a pharmaceutical company (now part of DSM) in Delft, the Netherlands, a gap was witnessed in the N cycle, that could only be explained by the anammox process (Mulder, 1989; Mulder *et al.*, 1995).

The group of bacteria able to perform the anammox reaction was then identified at Delft University (van der Graaf *et al.*, 1996), and also found back in other treatment plants showing that it was more commonly present than previously thought. Anammox bacteria are slow growers and they have a doubling time of 11-20 days (Strous *et al.*, 1999). Their doubling time was however recently found to be feasibly shortened to 3 days under optimal conditions, in a membrane bioreactor (Lotti *et al.*, 2015). Other bacteria commonly found in the same environments are much faster growing, with a doubling time generally below one day (Metcalf & Eddy, 2003), the fraction of the anammox reaction in the nitrogen cycle was therefore generally negligible in high rate wastewater treatment plants.

In 1998, TU Delft and Paques came to a license agreement aiming at making the ANAMMOX® technology viable as a treatment process. This was done by means of granulation of the anammox bacteria to optimize their selective retention in the bioreactor. The first full-scale

ANAMMOX® reactor was built and started in Rotterdam, NL, in 2002, in the frame of a European subsidy in cooperation with Paques, TU Delft and the Dutch Waterboard association (STOWA). It was then a 2-steps process, with partial nitritation (½ of $NH_4^+ \rightarrow NO_2^-$) taking place in a SHARON reactor before entering the ANAMMOX® reactor (Abma *et al.*, 2006).

Since 2006, both partial nitritation and anammox processes take place in a single ANAMMOX® reactor. This was successfully tested and first implemented in Olburgen, (Abma *et al.*, 2010). It is since then the way all new ANAMMOX® reactors are designed. As of January 2016, there are 32 full-scale ANAMMOX® reactors worldwide, of which 28 are based on the 1-step principle, with both the nitritation and anammox reactions taking place in a single reactor (Table 1).

PRINCIPLE OF THE ANAMMOX® REACTOR

The reaction in the ANAMMOX® reactor of Paques consists of two processes conducted by 2 groups of bacteria. The first group of bacteria are the ammonium oxidizing bacteria (AOBs) which convert about half of the ammonium (NH_4^+) into nitrite (NO_2^-) using oxygen as an electron acceptor. This first part of the reaction is called (partial) nitritation (equation 1). The second group of bacteria are the anammox bacteria per se which convert the rest of the ammonium into dinitrogen gas (N_2) using nitrite as an electron acceptor (equation 2) while 10 to 15% of nitrate (NO_3^-) is produced due to growth of the anammox bacteria (van der Star, 2008). The overall reaction taking place in the ANAMMOX® reactor is shown in equation 3.

$$1\ NH_4^+ + 1.5\ O_2 \rightarrow 1\ NO_2^- + 1\ H_2O + 2\ H^+ \qquad (1)$$

$$1\ NH_4^+ + 1.32\ NO_2^- + 0.13\ H^+ \rightarrow 1.02\ N_2 + 0.26\ NO_3^- + 2.03\ H_2O \qquad (2)$$

$$1\ NH_4^+ + 0.85\ O_2 \rightarrow 0.11\ NO_3^- + 0.44\ N_2 + 1.14\ H^+ + 1.43\ H_2O \qquad (3)$$

The biomass is present in the reactor in a granular form. The granules are red clusters of bacteria, with a diameter ranging from 1 to 5 mm. The centre of the granule is populated by the anammox bacteria and the granule is covered with a biofilm of AOBs which perform the partial nitritation. ANAMMOX® granules from a full-scale reactor are shown in Figure 1.

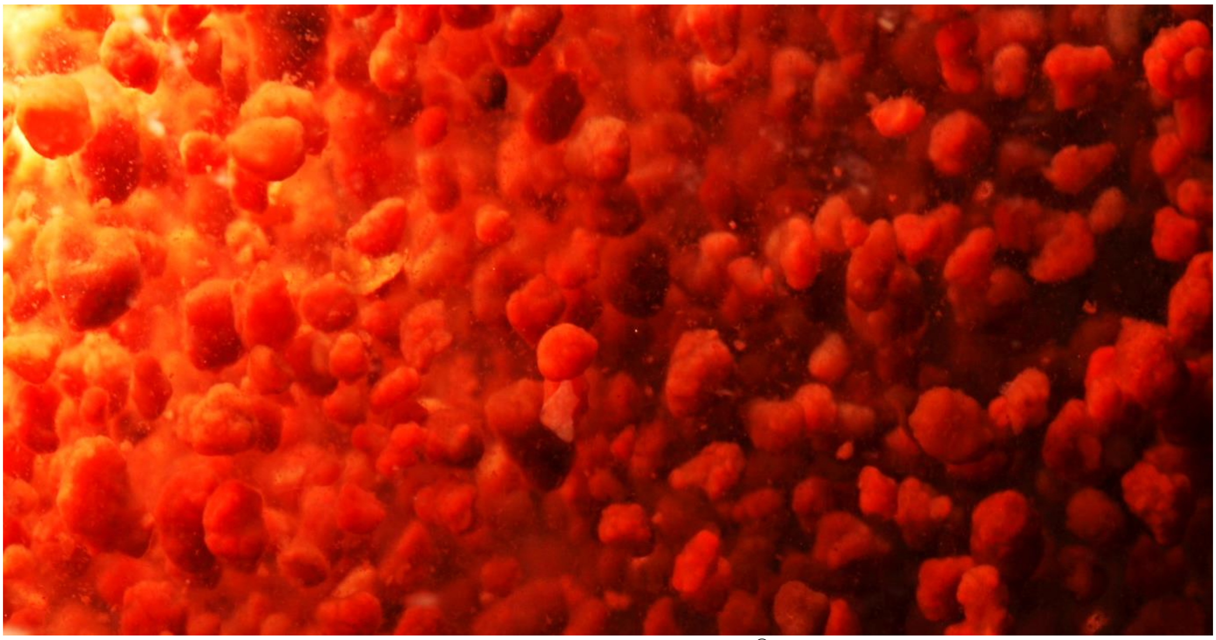

Figure 1: Picture of ANAMMOX® granules

The ANAMMOX® reactor of Paques is a completely mixed system with granular biomass. It is continuously fed with ammonium rich wastewater and continuously aerated. The granular form of the biomass allows for its easy selective retention in the reactor. While the anammox/AOB granules remain in the reactor, other undesired micro-organisms (such as heterotrophs and nitrite oxidizing bacteria (NOB)) and miscellaneous suspended solids are not retained by the internal biomass retention device and are washed out of the reactor with the effluent. The granular biomass also contributes to the high robustness of the system when disturbances happen as the slow growing anammox bacteria are protected by the layer of rapidly regenerating AOBs. In practice, shocks, such as pH disturbance, high nitrite concentrations in the reactor or peak solid loads entering with the influent are well handled by the reactors and do not result in irreversible damages to the biomass.

APPLICABILITY OF THE ANAMMOX® REACTOR

The ANAMMOX® reactor is particularly suited to treat effluents from an anaerobic treatment step, where biogas is produced. Those effluents are traditionally rich in ammonium (NH_4^+) which is formed in the anaerobic step during the degradation of nitrogen containing organics. Those effluents are also relatively poor in BOD (Biological oxygen demand) as it was used to produce the biogas. High ammonium and low BOD concentrations do not allow performing the conventional N-cycle (Figure 2) where nitrification and denitrification are involved without high requirements in aeration and external BOD source (e.g. methanol).

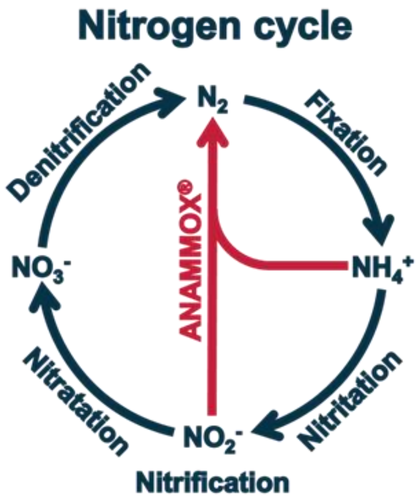

Figure 2: Schematic representation of the place of ANAMMOX® in the Nitrogen cycle

The streams treated by ANAMMOX® reactors can be of municipal or industrial origin. For applications in the municipal market, the ANAMMOX® reactors are placed on the side stream, from the sludge digestion after dewatering and before getting back to the head of works to reduce the N load on the STW (sewage treatment works). In the industrial market, ANAMMOX® reactors are found after an anaerobic treatment step (e.g. UASB) and have been successfully applied for a wide range of industries, from food-industry to semiconductors.

The superiority of the ANAMMOX® reactor is based on the advantages it brings when compared to going through the conventional nitrification-denitrification cycle (Ludzack and Ettinger, 1962):

- Aeration requirement decreased by 60%
- Sludge production decreased by 90%
- Compact system with achievable loads > 2 $kgN/m^3.d$
- No need for an external carbon source
    - The organics can be converted to valuable biogas in a pre-treatment
    - No dosing of methanol required

There are currently, as of January 2016, 32 full-scale ANAMMOX® reactors running or under construction, treating a combined load of over 85 tons of ammonium per day. A list of those references can be found in Table 1. The cumulative amount of installations and ammonium load over time are represented in Figure 3. The references in bold-italic in the table are presented in this article.

Table 1: List of the full-scale ANAMMOX® installations worldwide from Paques

Country	Application	Design load (kg_N/d)	Year
The Netherlands	Sludge liquor	500 (2 steps)	2002
The Netherlands	Tannery	325 (2 steps)	2004
Switzerland	Sludge liquor	60 (2 steps)	2006
Japan	Semiconductor	220 (2 steps)	2006
The Netherlands	***Potato/Sludge Liquor***	***1,200***	***2006***
China	Glutamate	11,000	2009
China	Yeast	1,000	2009
China	Glutamate	9,000	2010
China	Amino acids	10,000	2011
China	Sweetener	2,000	2011
China	Starch	7,000	2011
Poland	Destillery	900	2011
United Kingdom	Sludge liquor	4,000	2012
China	Winery	500	2012
The Netherlands	Sludge liquor	600	2012
The Netherlands	***Rendering***	***6,000***	***2012***
China	Winery	1,100	2012
China	Amino acids	11,500	2012
China	Winery	500	2013
The Netherlands	Sludge liquor (THP)	2,000	2013
United Kingdom	Sludge liquor	3,000	2013
Brazil	Animal waste	720	2013
Denmark	***Co-digestion***	***800***	***2014***
China	Kitchen waste	850	2014
China	Animal manure	1,100	2014
China	Animal manure	2,000	2014
China	Animal manure	1,100	2014
China	Animal manure	2,100	2015
China	Animal manure	1,100	2015
China	Chemicals	5,000	2015
China	Distillery	320	2015
China	Food Industry	600	2015

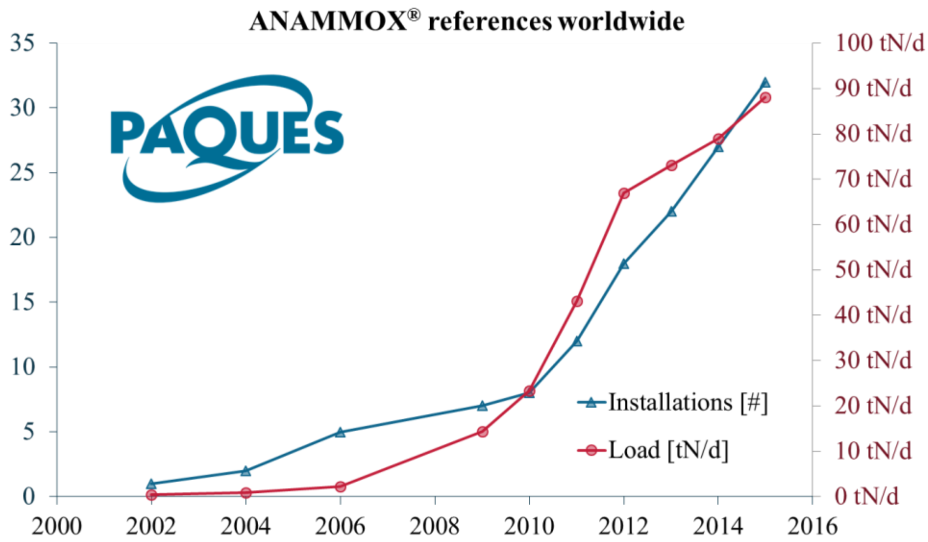

Figure 3: Cumulative amount of ANAMMOX® installations worldwide and the combined ammonium load over time

START-UP OF ANAMMOX® REACTORS

The data presented in Figure 4 show the evolution of the ammonium concentration during the first one and a half months of start-up of an ANAMMOX® reactor treating wastewater from a rendering plant in the Netherlands. The plant treats wastes originating from Dutch slaughterhouses and animal carcasses. This reactor is composed of three parallel tanks each designed to treat 2000 kg NH_4-N per day and is shown if Figure 5. The reactor is downstream of a high-rate anaerobic bioreactor (BIOPAQ® IC) and a pre-aeration tank used to decrease residual concentrations of BOD and sulphide. The influent is a digestate stream and the effluent of the combined treatment is entering a membrane bioreactor where the remaining pollutants are further degraded. The aim of the ANAMMOX® reactor is to decrease the loads towards the MBR. The compactness of the reactor was an advantage as the place was limited. The reactor was started with seed granular biomass coming from the first one-step ANAMMOX® reactor at Olburgen (NL).

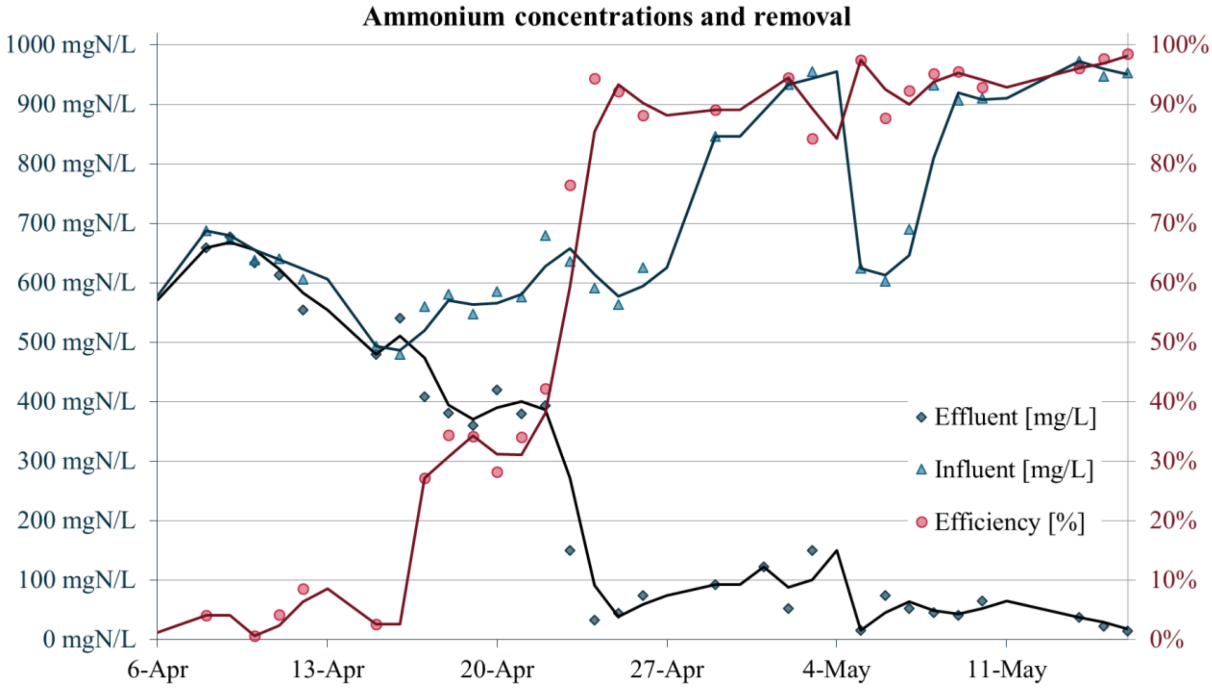

Figure 4: Ammonium concentrations in the influent and effluent during the start-up of the ANAMMOX® reactor at a rendering plant (NL)

Figure 5: Picture of the installation during start-up treating waste water from a rendering plant (NL)

After one week of adaptation of the biomass, the reactor already reached an ammonium removal efficiency of 90%. The subsequent increase of the ammonium concentration of the influent was matched by the ANAMMOX® reactor and the effluent quality was maintained. Initially, only one of the 3 reactors was started as the installation was designed to allow further increase of the loads in the future (Figure 5). The granular biomass produced in this reactor was later used to seed the remaining 2 reactors and they are currently all running in parallel, reaching an ammonium removal efficiency of up to 95%.

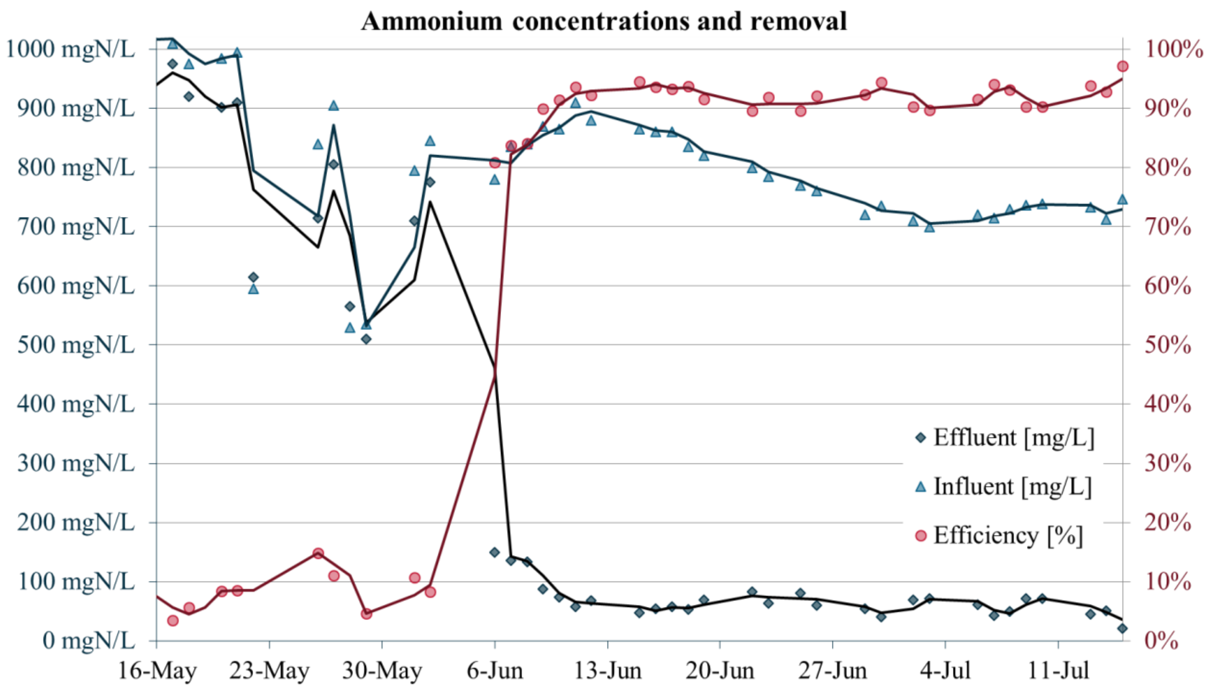

Figure 6: Ammonium concentrations in the influent and effluent during the start-up of the ANAMMOX® reactor at a Co-digestion plant (DK)

The data presented in Figure 6 show the evolution of the ammonium concentration during the first two months of start-up of an ANAMMOX® reactor treating wastewater from a co-digestion plant in Denmark. The plant treats the centrate from a digester treating a combination of municipal biomass and industrial waste. The reactor was started with seed granular biomass coming from the ANAMMOX® reactor at the rendering plant shown in figure 4. The removal efficiency of 90% was reached after two and a half weeks of operation of the plant.

The earliest start-up of ANAMMOX® reactors were taking up to 6 months. The experience gained in the last decade, combined with the larger availability of seed biomass, allowed for a remarkable shortening of start-up of as little as a couple of weeks.

LONG-TERM PERFORMANCE OF ANAMMOX® REACTORS

The Olburgen ANAMMOX® reactor has been operational since 2006 and Figure 7 shows the operational data of these ten years of operation. The Olburgen reactor treats a mixture of municipal reject water and wastewater from a potato processing factory after a pre-treatment in an UASB to remove the organic fraction. It is situated on the grounds of the local wastewater treatment plant and operated by Waterstromen. The ANAMMOX® reactor is downstream of a Phospaq™ reactor where magnesium oxide is dosed to recover phosphate as struvite ($MgNH_4PO_4 \cdot 6H_2O$). The plant is designed to treat 1200 kg NH_4-N per day and shown in Figure 8.

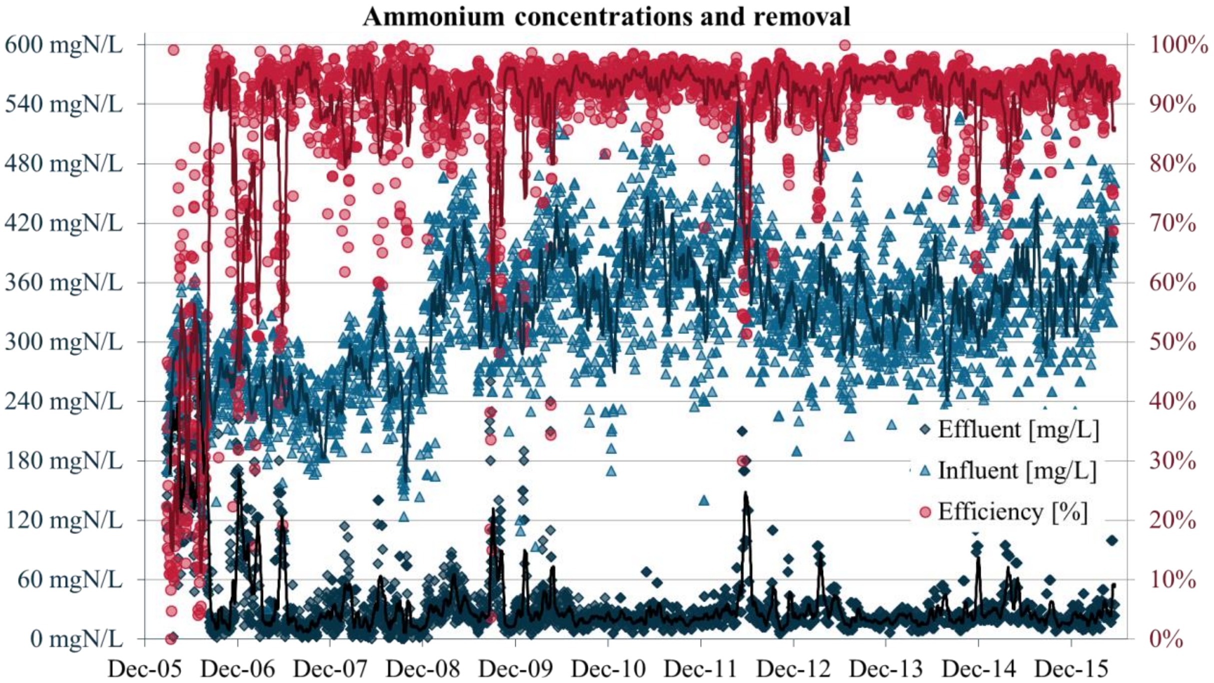

Figure 7: Ammonium concentrations in the influent and effluent of the ANAMMOX® reactor at Olburgen (NL)

Figure 8: Picture of the installation comprising the Phospaq™ and ANAMMOX® reactors at Olburgen (NL)

Despite the daily and seasonal variations in the ammonium load, a stable removal above 90% is achieved. Over the last five years, an average ammonium removal efficiency of 92% was achieved with an average effluent ammonium concentration of 28 mg/L. 8% of the removed ammonium is found back in the effluent as nitrate, which is significantly lower than the theoretical 11%. This results in an average total nitrogen removal efficiency of 85%. The latest peak in the effluent ammonium, in June 2012, was due to a temporary malfunction in the reactor that led to the wash-out of 80% of the biomass. The reactor recovered promptly without requiring addition of any external biomass. The modified design and operation of the reactor has now become a standard for Paques ANAMMOX® reactors. This installation, in Olburgen, was the first ANAMMOX® reactor based on the principle of the one-step process with the nitritation and anammox reactions occurring simultaneously in a single reactor. This was a step forward from the 2-step design (nitritation – anammox) that was applied to the first full scale ANAMMOX® reactor in the world, located in Rotterdam (NL). Due to the need for the adaptation of the ANAMMOX® biomass to the conditions in a one-step reactor, the start-up of Olburgen took six months. Since the start-up of Olburgen in 2006, all the following reactors have been based on the one-step ANAMMOX® process. Since then, due to the wider availability of one-step ANAMMOX® biomass, the start-up has been significantly reduced (see previous paragraph).

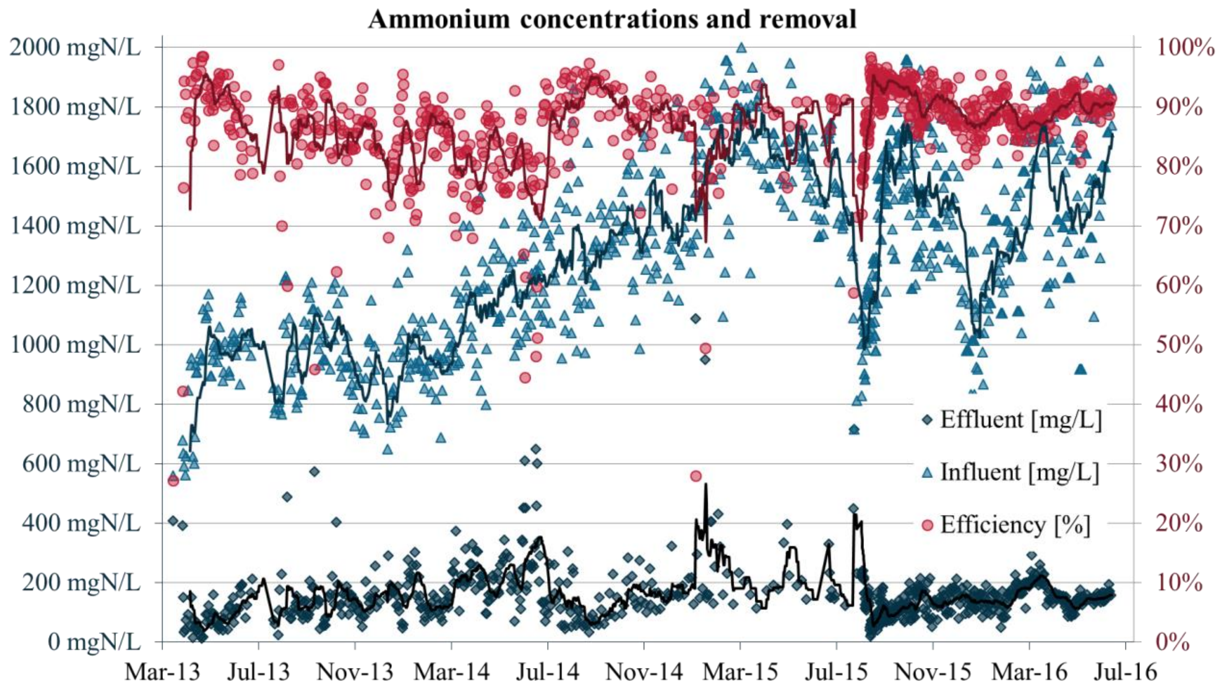

Figure 9: Ammonium concentrations in the influent and effluent of the ANAMMOX® reactor at a rendering plant (NL)

Figure 9 shows 3 years of operation of the ANAMMOX® reactor treating the wastewater at the rendering plant in the Netherlands. This ANAMMOX® reactor, composed of 3 parallel reactors of 1000 m³ each, treats a load of up to 6000 kg of nitrogen per day. Over the last year, the reactor has achieved an average ammonium removal efficiency of 90%, with an average concentration of ammonium in the effluent of 160mg/L. This effluent concentration is the set-point value sought after by the end-user. In this plant, 7% of the removed ammonium is found back in the effluent as nitrate. This results in a total nitrogen removal close to 85%. The peak in the effluent concentration that took place in August 2015 was due to a failure of the cooling system, combined with a heat wave in the Netherlands. This led to an increase of the temperature in the reactor to above 41°C (106°F). Despite temporarily loss of activity due to the too high temperature, the reactor rapidly recovered.

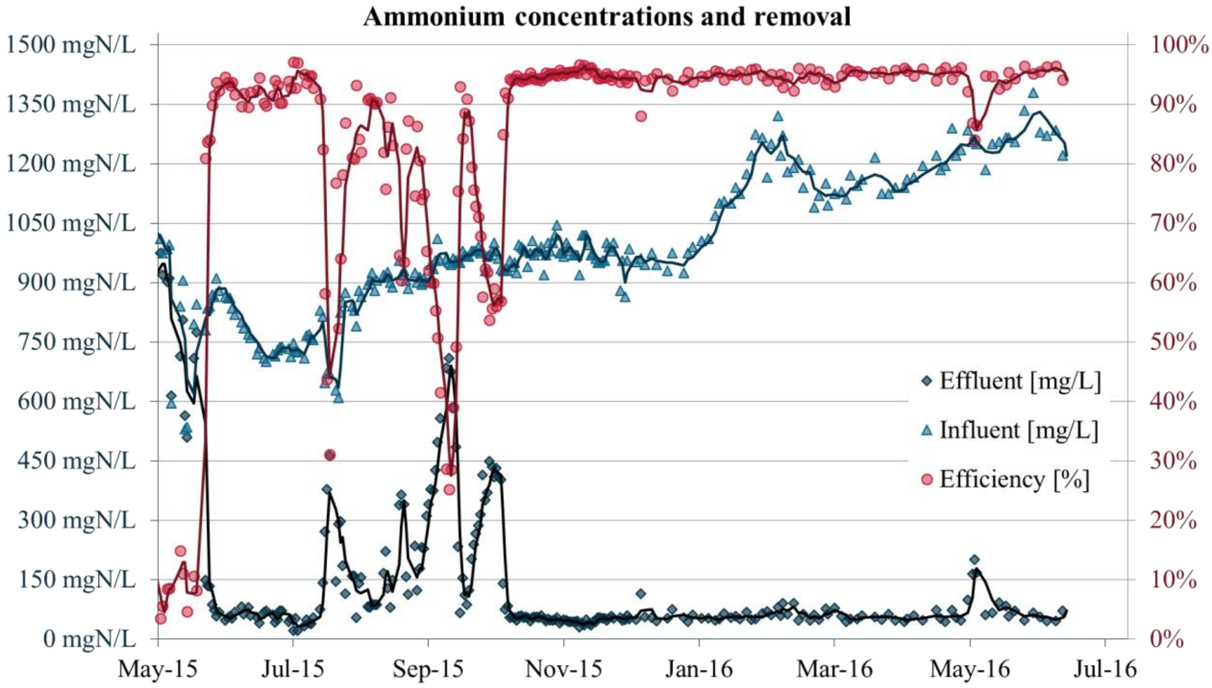

Figure 10: Ammonium concentrations in the influent and effluent of the ANAMMOX ® reactor at a Co-digestion plant (DK)

Figure 10 shows the first year of operation of the ANAMMOX® reactor treating the wastewater at a co-digestion plant in Denmark. Over the last 8 months, the reactor has achieved an average ammonium removal efficiency of 95%, with an average concentration of ammonium in the effluent of 59 mg/L. Currently, 7% of the removed ammonium is found back in the effluent as nitrate. This results in an average total nitrogen removal efficiency of 87%. After a successful and relatively fast start-up, within 3 weeks after seeding (Figure 6), a drop in the removal efficiency was witnessed after a period of one and a half month. This drop in activity was later found to be due to a lack of specific micro-nutrients that were not present in the centrate from the digester. This was solved as supplementary dosing of nutrients was installed in October 2015. The dip in the removal efficiency observed in May 2016 was due to a temporary insufficiency of the blower capacity which was promptly resolved.

ADDITIONAL REMARKS AND POTENTIAL HURDLES

The ANAMMOX® process is a proven and robust technology. Given Paques' extensive full-scale experience, potential hurdles and bottlenecks for the application of the ANAMMOX® technology have been encountered over the last decade but subsequently successfully tackled. The low growth rate of the anammox bacteria (doubling time of twelve days) initially resulted in long start-up times for the first applications, with up to six months for the first one step installations. The amount of available seeding biomass worldwide and the experience acquired in the last decade through various application on diverse wastewaters allowed for a shortening of that start-up time down to less than one month.

The granular ANAMMOX® biomass can be retained very well at high up-flow velocities with the internal retention device. This allows the process to cope with high suspended solids concentrations. Nevertheless, extremely high peak concentrations (above 10 g/L SS in the influent) result in an increased viscosity of the medium which disturbs the retention of the small granules in the reactor and, therefore, growth of biomass in the reactor. Too high phosphate concentration in the influent will result in operational problems due to uncontrolled struvite formation. For optimal operation at volumetric loading rates in excess of 2 kg N / m³.d, and therefore to allow the use of compact reactors, a minimum temperature of 30°C (86°F) is required. Operation at lower temperatures are also conceivable, but it comes at the cost of a slightly larger reactor.

When challenges are expected for the wastewater, a pretreatment step can be installed upstream of the reactor to target those problems. A Phospaq™ reactor will solve the phosphate problem while a pre-sedimentation step will address the potential troubles with high peaks of suspended solids. A pre-aeration step will address the problem of too high sulphide and/or volatile fatty acids concentrations in the influent. A careful operation of the plant upstream and of the ANAMMOX® reactor itself will prevent the toxic effect of polymers or too high nitrite concentrations in the reactor.

CONCLUSIONS

The ANAMMOX® reactor from Paques has proven to be an efficient and robust full scale technology to treat waste waters with high ammonium concentrations, such as sludge reject water from sewage plants as well as anaerobically treated industrial effluents.

The ANAMMOX® reactor is characterized by relatively low energy consumption, low sludge production, compact reactor volumes and no requirement for organic carbon.

Long term operational experience (>10 years) has proven stable performance achieving removal efficiencies on ammonium well above 90 % and on total nitrogen removal above 85%.

The current widespread availability of biomass from existing ANAMMOX® reactors allow for start-up times as short as few weeks.

Over the last decade, Paques has built up a wide experience in designing, troubleshooting and staring-up ANAMMOX® reactors worldwide, which is now used to conceive and optimize the current and future projects.

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