Influence of Fluctuation in Nitrate Loads on the Biological Denitrification of Industrial Wastewater Containing RO Brine, Using MBDEN Technology

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ABSTRACT

A field study was conducted at a fertilizer production plant to examine the biological nitrate removal from a combined wastewater stream, consisting of Reverse Osmosis (RO) brine and processed wastewater, using Moving Bed Denitrification (MBDEN). The Aqwise treatment system received WW effluent from an existing WWTP on-site and RO brine, with nitrate that needs to be removed before discharge. The system had to cope with nitrate concentrations that vary from ~10-150 mg/l NO_3 as N depending on the WWTP. The RO brine stream was continuous and had a stable nitrate concentration of 10-20 mg/l NO_3 as N. Throughout the course of the study, nitrate concentrations were effectively reduced and were below discharge regulations. This paper presents results from the Aqwise treatment system demonstrating that nitrate can be efficiently biologically removed even with significant variation in nitrate loads over short time periods of a few hours and/or days.

KEYWORDS: MBDEN, Denitrification, Reverse Osmosis, Brine, Nitrate, Wastewater

INTRODUCTION

The discharge of non-organic nitrogen components to the environment result in several different negative effects including changing water bodies biological balance and possible hazardous for both human and animal health. Specifically, nitrate pollution and remediation is a worldwide problem and a challenge (Arbel *et al*. 2013 and Beliavsky *et al*. 2010). The most common technologies for nitrate removal from water are based on physico-chemical processes, namely ion exchange (IX), RO and electro-dialysis. The main disadvantage, of those physico-chemical methods, is the production of concentrated brine that needs to be removed and/or treated further. Therefore, the biological treatment of WW operated by denitrifying bacteria is found to be the best solution for nitrate removal due to the conversion of nitrate to nitrogen gas (N_2) – a harmless and environmentally friendly product, without the setback of brine residue production (Briones and Raskin 2003, Curtis *et al.* 2003). In the absence of dissolved oxygen (DO) or under limited DO concentration, the nitrate reductase enzyme in the electron transport respiratory chain is induced, and helps to transfer hydrogen and electrons to nitrate as the terminal electron acceptor. The nitrate reduction reactions involve the following reduction steps presented in equation 1.

$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ **(Eq.1)**

Several environmental factors control the denitrification process such as DO, carbon source, temperature, pH, alkalinity, salinity and stable conditions. The presence of DO will suppress the enzyme system required for denitrification. Denitrification will be inhibited at DO concentrations above 0.2 mg/l though inhibition might occur in concentration above 0.13 mg/l (Santos *et al.* EPA, 2009). In case of treated water carbon source shortage it is essential to provide an external carbon sources in order to allow biological denitrification. Methanol, Ethanol or Acetic acid are usually used as an external carbon source and each one influence the kinetics differently. Specific denitrification rate using Ethanol is higher than Methanol by 1.6 to 2.3 times (Fillos *et al*. 2007). Temperature and pH are among the most important environmental conditions for bacterial growth. At temperatures above 40°C, the denitrification rate reduces. The reaction is best accomplished at temperature above 25°C and the rate decreases as the temperature decrease. When the temperature decreases from 25°C to 15°C denitrification rates are expected to be reduced by 70% (EPA, 1974, 2009). Concerning the influence of pH, it has been established that there is a maximum denitrification rate at pH range of 7 to 8.5, whereas out of that range, there is a sharp decrease in the denitrification activity (Haandel *et al*. 2012). Denitrification takes up hydrogen ions, which is equivalent to generating alkalinity. By considering nitrate as electron acceptor, it can be shown that for every mg nitrate denitrified, 3.57 mg alkalinity as $CaCO_3$ is produced (Henze *et al*.2008). Water salinity can also affect the growth rate of the denitrifying bacteria. Previous research showed significant reduction in denitrification performance at salt concentrations above 2% (Steichen *et al.* 2011). For biological WW treatment, including denitrification, variable influent concentrations and peaks are less favored for biological treatment. Stable operational conditions will contribute to the process efficiency.

The main goal of the study was to evaluate the influence of fluctuation in nitrate loads on biological nitrate removal, using the Moving Bed Denitrification (MBDEN) technology. The MBDEN uses biomass carriers with a large effective surface area of 650 m^2/m^3, to increase biomass concentration within the biological reactor. The biomass carriers are typically shaped as small open cylinders for biomass growth and mass transfer (EPA, 2009). Aqwise Biomass Carriers (ABC) used in this field study are presented in Figure 1.

Figure 1. Aqwise Biomass Carriers (ABC)

METHODOLOGY

The field study was conducted at a fertilizer production facility, manufacturing fertilizers containing potash, phosphorus and nitrogen for agriculture and chemical use. The fertilizer production facility has an existing WWTP on-site that includes treatment of ammonium, phosphorus and solids removal. However, high nitrate concentrations are not being treated and are above the discharge limits of 8 mg/l as N. The overall industrial WW stream is divided to two main streams, WW and RO brine, to be treated:

- WW: This stream consists of water from production runoff, rain, WW from cleaning and drainage tanks, or any WW from spills and accidents on-site – with a flow rate of 200 to 700 m^3/day. The WW flow rate from the treatment plant depends on the WW volume and varies throughout the year due to seasonal changes. During summer (May to Oct.), the WWTP operates for 10 days/month and during winter (Nov. to Apr.), flow is continuous, although the volume varies depending on rain and runoff.
- RO brine: Six RO purification units for desalination are used to treat 5000 m^3 water/day. The RO brine is constantly produced and the flow rate depends on the number of working units (usually 4-5) at an average flow of 1200 m^3/day. The brine concentration is 5 to 10 times higher than the source water. Nitrate reduction is required in RO brine for disposal to sea or other water bodies.

When both streams (WW + RO brine) are combined, the nitrate concentration can reach concentrations as high as 150 mg/l NO_3-N.

Aqwise Treatment System

The feed to the treatment system includes RO brine and effluent from the industrial WWTP. The RO brine stream contributes nitrate at a level of 10-20 mg/l NO_3-N. The nitrate level in the combined stream, including RO with WWTP effluent, was typically in the range of 40-80 mg/l NO_3-N. Since the WWTP effluent flow is not constant, fluctuations in nitrate concentrations to the pilot occurred on an hourly, daily, and weekly basis. During the study, different flow rates (1.5 to 2.5 m^3/hour) were evaluated in order to estimate the system's performance at different loads as well as shorter hydraulic retention times (HRT) (1.1 to 1.8 hour). The flow rates and the average influent nitrate concentrations are presented in Table 1.

Table 1. Nitrate concentrations in different flow rate and time periods

Date (D.M.Y)	Influent source	Flow rate m^3/hour	Nitrate mg/l as N (influent)
10.09-24.09.13	RO	1.5	9.9
25.09-06.10.13	RO+WW	1.5	46.4
07.10-14.10.13	RO+WW	2.0	56
15.10-30.10.13	RO	2.0	19.6
31.10-06.11.13	RO+WW	2.0	73.6
07.11-11.11.13	RO+WW	2.2	56.9
12.11-19.11.13	RO+WW	2.5	49.7
20.11-02.12.13	RO	2.0	13.7
03.12-10.12.13	RO+WW	2.0	90
11.12.13-01.01.14	RO+WW	1.5	31.3

As previously mentioned, the MBDEN technology was used for this study as it is known to be based on biomass growth in the form of biofilm and able to manage fluctuations in loads better than the suspended biological based technologies.

System Configuration

WW with various concentrations of nitrate was pumped to an equalization tank in-which pH was adjusted. Downstream to the equalization tank, the WW flows (at rates of 1.5 to 2.5 m^3/hour) to two consecutive Deoxidizing (DeOX) stages for DO uptake, and then followed by an anoxic reactor. Carbon and phosphorous sources were dosed to the first DeOX reactor. A schematic diagram of the pilot's configuration is presented in Figure 2. Reactors were filled with floating Aqwise Biomass Carriers on which biomass, in the form of biofilm, is present for the biological treatment. The carriers fill ratio, in the reactors, was between 20 to 50%.

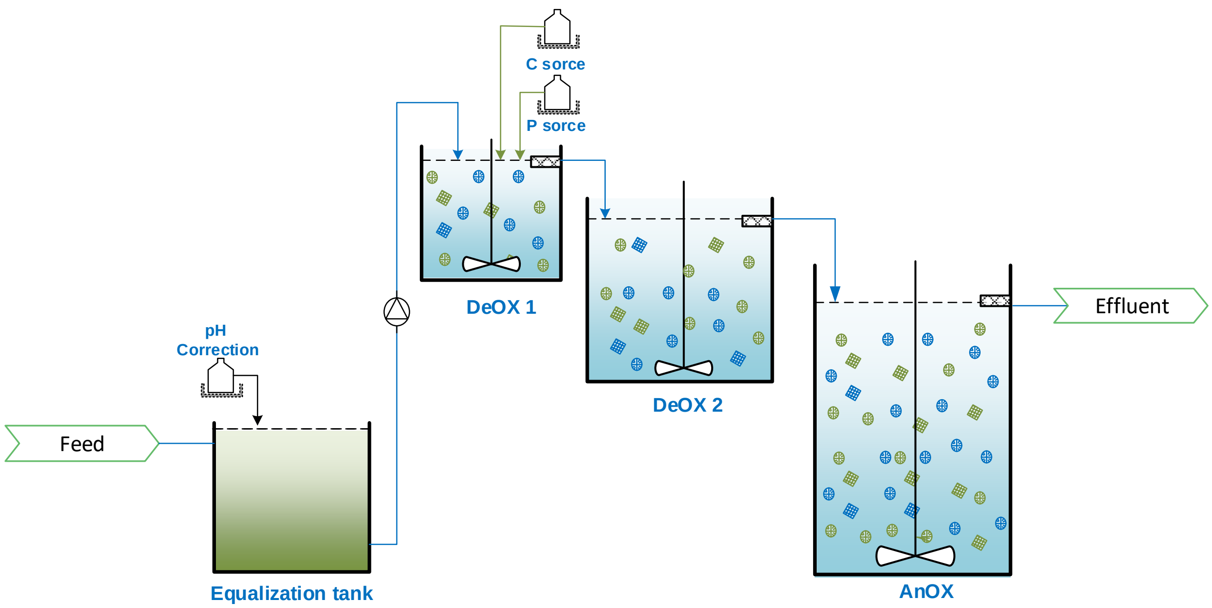

Figure 2. Schematic view of the pilot

During the field study, parameters such as pH, DO, temperature, conductivity, alkalinity, nitrite and nitrate were measured. The required effluent values for total nitrogen and nitrate are less than 10 mg/l and 8 mg/l as N, respectively.

RESULTS AND DISCUSSIONS

The main goal of the study was to demonstrate efficient biological denitrification, treating effluent form industrial WWTP and RO brine at unsteady nitrate loads. Figure 3 presents the influent and effluent nitrate loads (gr/hr) measured during the study period.

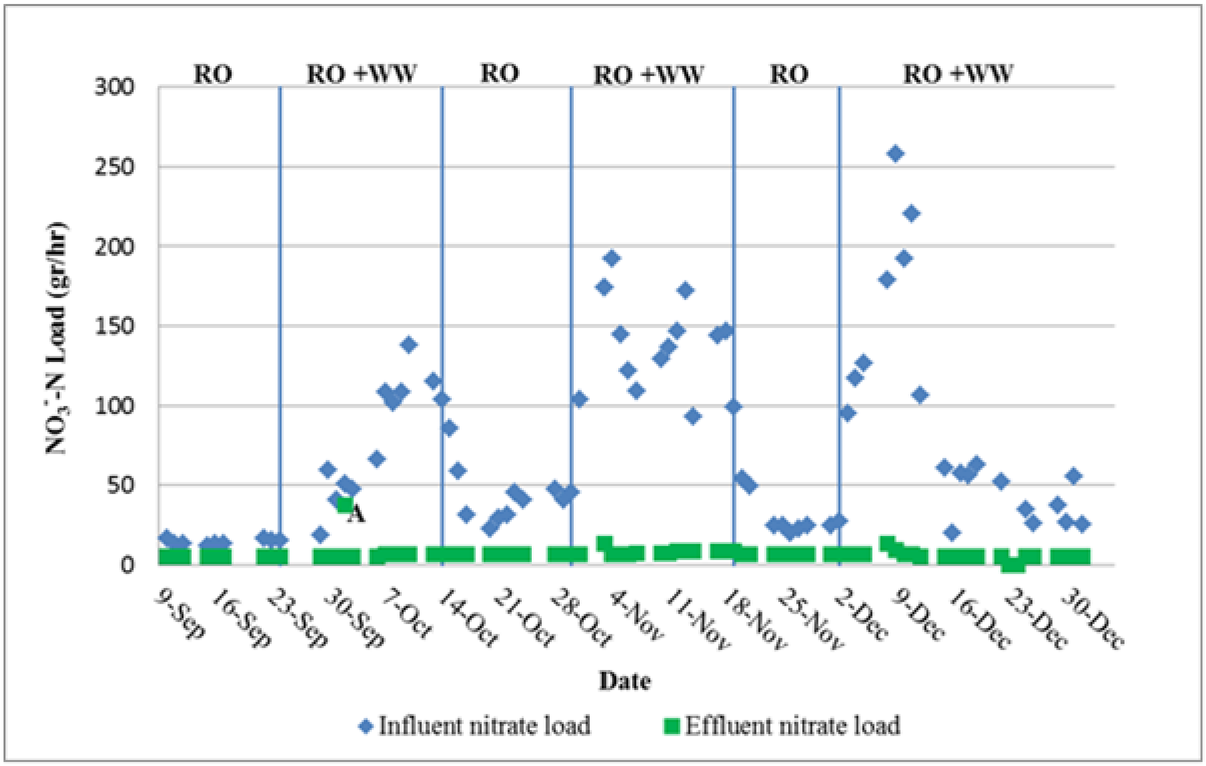

Figure 3. Influent and effluent nitrate (NO_3^--N) loads

Results indicate that the fluctuation in the influent nitrate loads did not inhibit the biological treatment and effluent nitrate concentrations were successfully reduced. In one occasion (Displayed as A, in the figure), nitrate levels exceeded the desired effluent values (8 mg/l NO_3-N). This was due to technical problem with the dosing pump which caused insufficient dosing of carbon source.

Figure 4 presents the effluent nitrate and nitrite concentrations measured during the study. The measured nitrate concentrations in the effluent, during most of the analysis performed, were lower than 3.4 mg NO_3-N/l (below the kit's detection limit). Once a week, samples were tested using a more sensitive test kit to obtain more accurate results and to confirm the data. Results obtained presented nitrate values lower than 1 mg/l as N.

Nitrite, which is a toxic element to the environment and to the denitrifying biomass, is usually formed as a by-product when the denitrification process is incomplete. The results demonstrate that the nitrite levels were below the detection limit (<0.076 mg/l as N) and deviate only in rare occasions, when the carbon source added was insufficient (Figure 4).

The discharge limits of total nitrogen (TN) concentration (10 mg/l TN) are represented by the red horizontal line in Figure 4. The TN is a value calculated by summarizing the nitrate, nitrite and Total Kjeldahl Nitrogen (TKN) concentrations.

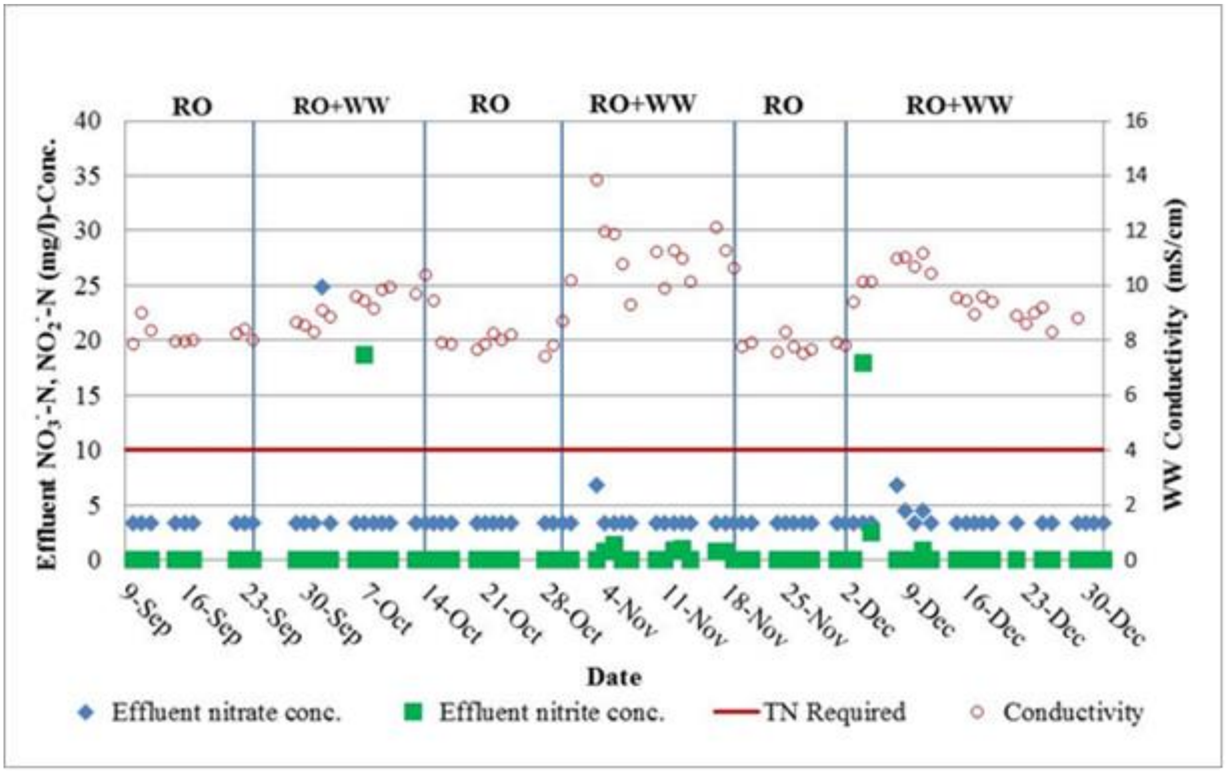

Figure 4. Effluent nitrate (NO_3^--N) and nitrite (NO_2^--N) concentrations and WW conductivity

As can be seen from the figure, the effluent concentrations of nitrate and nitrite summation is below the required TN level of 10 mg/l and can be calculated at levels less than 4 mg/l as N. Since the TKN values (data not shown) are not exceeding 1 mg/l as N, it can be concluded that the effluent TN concentrations stand within the standard requirements.

During the study, conductivity was measured to estimate the salinity. According to the results, WW conductivity ranges between 8 to 14 mS/cm, which is above drinking water values (0.05-0.5 mS/cm) and below sea water values (~50 mS/cm). Study results indicate that the WW's conductivity (i.e. water salinity), did not affect the denitrification process.

Since it is crucial to keep very low DO levels for the anoxic process, it was very important to define the DO reduction efficiency in the DeOX stages. As demonstrated in Figure 5, the DO reduction in the DeOX stages was very efficient and resulted in extremely low DO levels in the anoxic stage, in which the denitrification process is performed.

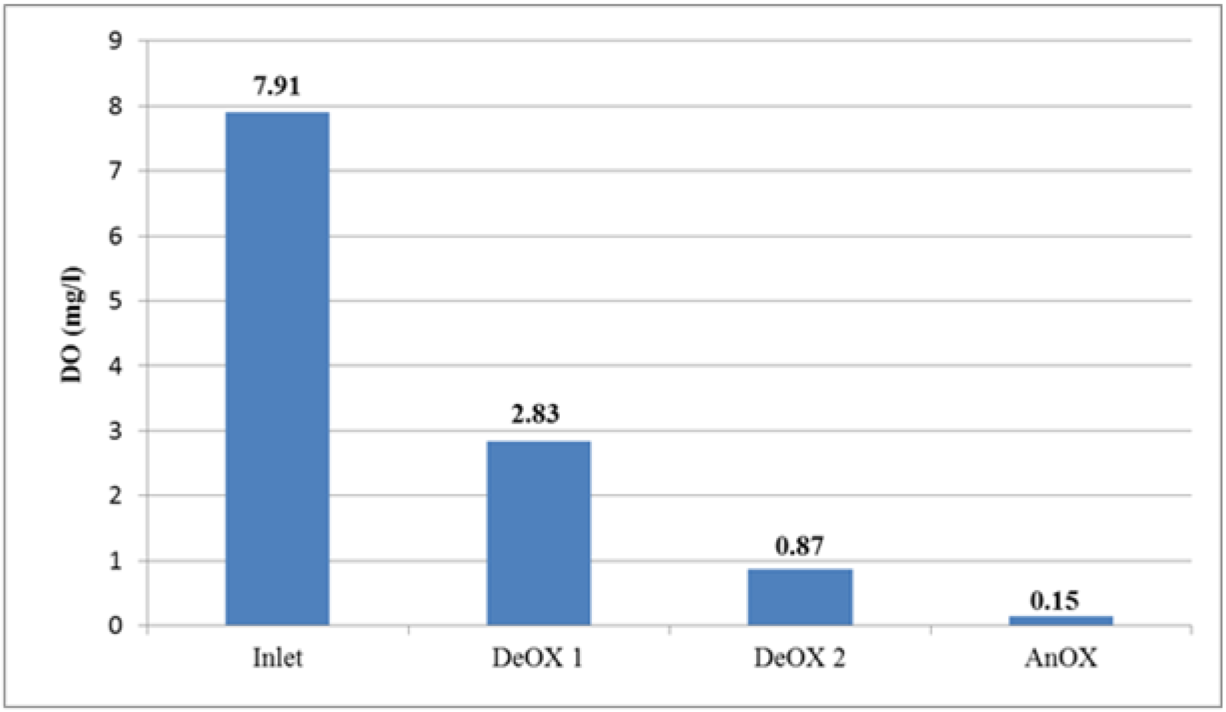

Figure 5. Average DO concentrations at different pilot's steps

To summarize, biological systems are known to perform better at stable conditions. Yet, even though the tested system had to manage with fluctuations in nitrate concentrations, it had no influence on the effluent nitrate as well as TN concentrations.

CONCLUSIONS

The Aqwise MBDEN technology adjusted for enhanced nitrate bio-removal can cope with high range influent nitrate concentrations (~10 to ~150 mg/l as N) and loads, resulting with effluent nitrate concentration below 1 mg/l as N.

Throughout the pilot, the nitrate removal efficiency was not affected by high water conductivity values ranging from 8 to14 mS/cm. Furthermore, the system was not inhibited by decreasing HRT's (1.8 to 1.1 hour).

The Aqwise MBDEN technology adjusted for enhanced nitrate bio-removal demonstrated the ability to maintain steady low TN effluent concentrations of below 10 mg/l.

In order to secure appropriate system operation and required nitrate and nitrite effluent quality, sufficient carbon source should be added.

Results from this field study prove that Aqwise MBDEN technology adjusted for enhanced nitrate bio-removal can be implemented in facilities operating at irregular nitrate loads.

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