# AMMONIUM RICH WASTEWATER TREATMENT VIA NITRITE: A CASE STUDY

Viorel Patroescu, Costel Bumbac, Mihaela Moise

National Research and Development Institute for Industrial Ecology ECOIND, 90-92 Panduri Av., sector 5, Bucharest, Romania, tehnologi@incdecoind.ro

#### Abstract

Several kinds of wastewater are characterized by low carbon to nitrogen ratios and very high ammonia concentrations. Some examples are wastewater coming from sludge dewatering, fertilizer industry, explosive industry or some pharmaceutical processes. A feasible treatment of this kind of effluents is the combination of a partial nitritation, where 50% of ammonia is oxidized into nitrite in an aerobic reactor, and a subsequent anaerobic ammonium oxidation (Anammox), where ammonia is oxidized by nitrite in a second tank. This paper presents the results obtained in a nitritation reactor treating a wastewater from sludge dewatering with different ammonium concentrations in order to obtain a proper ammonium: nitrite ratio of 1:1 suitable for the anammox process and the results obtained during the start-up of an anammox reactor.

**Keywords:** ammonium, nitrite, wastewater treatment, nitritation, anammox

#### Introduction

Intensifying the sludge anaerobic digestion process in WWTPs leads to the increase of ammonium concentration and quantity in the centrate or filtrate from sludge dewatering which is recirculated into the main wastewater treatment flow. It is estimated that aprox 10 to 20% of the nitrogen load of the biological step influent is the contribution of this wastestream recirculated from sludge dewatering. This has a negative impact on the COD/N ratio and affects the conventional biological nitrogen removal processes.

Therefore, in the last 10 years, worldwide WWTPs revamping projects are considering the pre-treatment of the wastestream from sludge dewatering prior to recirculating it into the main treatment flow of municipal wastewater.

#### INCD ECOIND – INTERNATIONAL SYMPOSIUM – SIMI 2011 "THE ENVIRONMENT AND THE INDUSTRY"

Considering the specific characteristics of these wastestream (pH, high NH<sub>4</sub><sup>+</sup> concentration, alcalinitate, low COD/N ratio), the most promising nitrogen removal processes are the ones via nitrite:

(a) nitritification + denitritification (SHARON process), which allows a theoretical aeration energy saving up to 25% and organic carbon savings up to 40% compared to conventional nitrification denitrification process.

Nitritification:  $NH_4^+ + 1.5 O_2 \rightarrow NO_2^- + 2H^+ + H_2O$ 

Denitritification:  $2NO_2^- + 6H^+ + 6e^- \rightarrow N_2 + 2OH^- + 2H_2O$ 

Organic carbon source/ electron donor can be represented either by (1) methanol, (2) WWTP denitrification step influent or (3) primary sludge. The process can be performed in a single tank or two tanks bioreactor system.

(b) nitritification + anammox, which allows a theoretical aeration energy saving up to 60% and a carbon source saving up to 100% (since it is an autotrophic process) compared to conventional nitrification denitrification process:

Nitritification:  $NH_4^+ + 1,5 O_2 \rightarrow NO_2^- + 2H^+ + H_2O$ 

Anammox:  $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$ 

Nitritification+Annamox can be performed in two steps (SHARON + Anammox process) or in a single tank bioreactor (CANON/ OLAND process).

#### Material and method

## Sharon experimental setup

<u>Nitiritification experiment with automatic pH control</u> was performed in a 3.9L (useful volume) bioreactor with continuous stirring (200 rpm) automatic temperature and pH control (fig.1., photo 1.). The control of hydraulic retention time and dissolved oxygen concentration was performed manually. The bioreactor was fed continuously with effluents from the industrial sludge dewatering installation of the municipal WWTPs Pitesti.

Experiment duration was 35 days.

#### Process parameters:

- temperature: 36 + 0,5 °C;
- pH = 7.3 + 0.3;
- stirring: 200 rpm;
- HRT = 1.7 days;
- Dissolved oxygen concentration varied between: 0,8 5,2 mg/l.
- NH<sub>4</sub>+infl.= 315 mg/L;
- I<sub>N-NH4</sub> = 0.145 kg N-NH<sub>4</sub>+/ day\* m<sup>3</sup> reactor;
- Alkalinity infl. =  $27.4 \text{ mval/L}(1671 \text{ mg HCO}_3\text{-/L});$
- Alkalinity efl. = 12.8 20 mval/L(781-1220 mg HCO<sub>3</sub>-/L);



Fig.1. Representation of nitritification bioreactor and operational parameters.



Foto 1. Nitritification installation

<u>Nitritification experiment without pH control</u> were performed in a 14.6 L bioreactor (useful volume) with mechanical stirring (200-300 rpm) and automated temperature control and manual control of dissolved oxygen

#### INCD ECOIND – INTERNATIONAL SYMPOSIUM – SIMI 2011 "THE ENVIRONMENT AND THE INDUSTRY"

concentration. The bioreactor was fed continuously with filtrate from the industrial sludge dewatering installation of Focsani municipal WWTP. Experiment duration was 65 days.

Process parameters for Sharon without pH control were:

```
-HRT = 1,36 days;

-NH<sub>4</sub>+infl.= 105– 347 mg/L;

-I<sub>N-NH4</sub> = 0.06 – 0.212 kg N-NH<sub>4</sub>+/ day* m³ reactor;

-Alkalinity infl. = 16.07 – 20.78 mval/L(981– 1268 mg HCO<sub>3</sub>-/L);

-Alkalinity efl. = 2.35 – 8.62 mval/L(82.5– 525.8 mg HCO<sub>3</sub>-/L);

-pH infl.= 8.14 – 8.58;

- pH effl.= 6.06 – 8.04;
```

## **Anammox experimental setup**

After obtaining and enrichment of the inoculum specific for anammox process – anaerobic bacteria capable to oxidize, autotrophicaly, ammonium with nitrite to gaseous nitrogen, a bioreactor with both suspended and fixed biomass and with continuous feeding was setup.

The experimental setup was represented by a column type bioreactor (fig.4) with 3.8 L useful volume, a vertical settler, influent feeding pump and ascendant recirculation pump, a thermostated heater and an automation panel with programmable logic controller.

The column bioreactor was filled with a plastic, cylindrical shaped, network type, support material (biofilm development surface = 0.84m<sup>2</sup>) for biofilm development while the inner hallow of the column ad suspended biomass.

Experiment duration was 230 days. The influent used to feed the installation were either filtrate from sludge dewatering installations of Focsani or Pitesti municipal WWTPs, diluted and enriched with NO<sub>2</sub>-, either effluents of the Sharon experimental bioreactor (last part of the experiment duration).

Process parameters were:

```
-HRT = 2.17– 3.80 days;

-T= 33-34°C;

-DO= 0.39– 1.08 mg/L;

-pH reactor= 7.10 – 8.67;

-N-NH<sub>4</sub>+infl.= 7.7– 90 mg/L;

-N-NO<sub>2</sub>-infl.= 4.7– 92 mg/L;

-N-NO<sub>3</sub>-infl.= 0,5 – 16 mg/L;

-N-NO<sub>2</sub>-infl./ N-NH<sub>4</sub>+infl.= 0.7– 1.4;

-N-NH<sub>4</sub>+effl.= 0.1– 55 mg/L;

-N-NO<sub>2</sub>-effl.= 0.02– 21 mg/L;

-N-NO<sub>3</sub>-effl.= 0.3– 41 mg/L;

-Alkalinity effl. = 2.25 – 5.68 mval/L(137.5– 346.8 mg HCO<sub>3</sub>-/L);

-I<sub>N</sub> = 0.004 – 0.066 kg N/ zi* m<sup>3</sup> reactor;
```

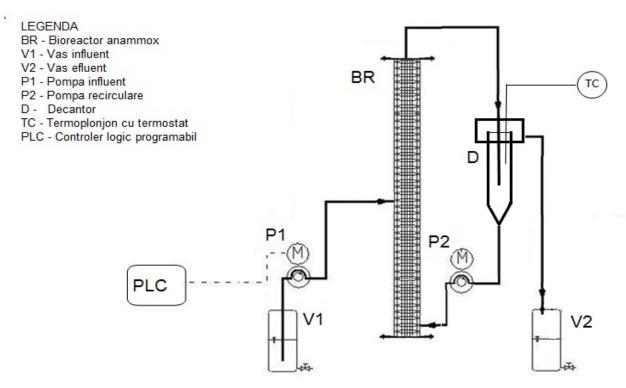


Fig.4. Anammox experimental setup

## **RESULTS AND DISCUSSION**

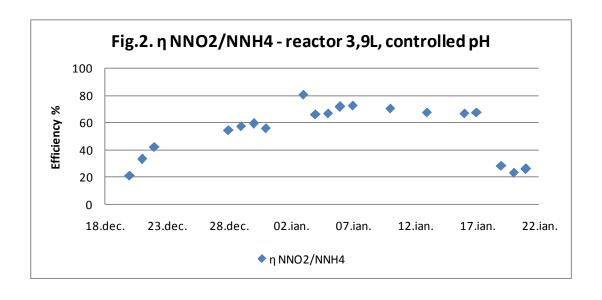
## Sharon experimental model

## Nitritification experiment with pH control

The results obtained are graphically represented in Fig. 2.

Neutralizing agent doses varied between 0.45 – 0.60 kg NaOH/ m<sup>3</sup> infl.

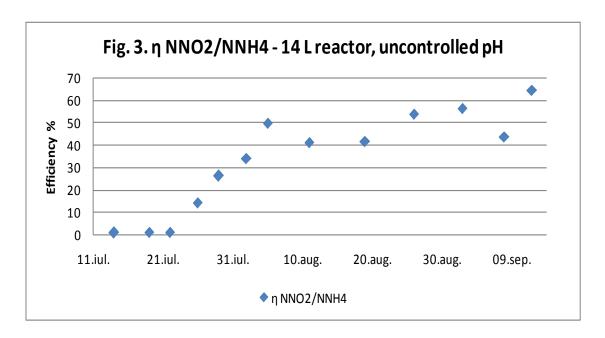
 $N-NH_4^+ \rightarrow N-NO_2^-$  transformation efficiency varied between 67 – 80%.



# Nitritification experiments without pH control

The results obtained are presented graphically in Fig.3.

 $N-NH_4^+ \rightarrow N-NO_2^-$  transformation efficiency varied between 41 – 64%.



## **Anammox experimental model**

Influets and effluents characteristics are presented Fig.5 -6. Influent nitrogen removal efficiencies varied between 30 – 89%.

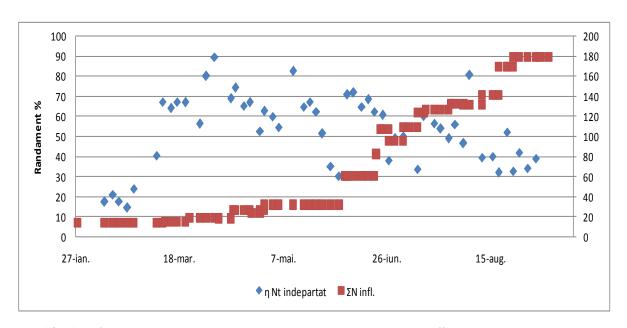


Fig.5. Influent nitrogen concentration and nitrogen removal efficiency evolution

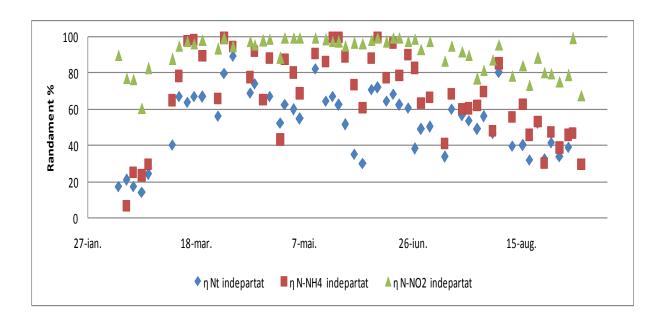


Fig.6. N-NO<sub>2</sub>-, N-NH<sub>4</sub>+ and nitrogen removal efficiencies

## **CONCLUSIONS**

## Sharon experimental model

## Sharon experiment with pH control

pH control of a Sharon process is an efficient mean to obtain a desired N-NO $_2$ -/N-NH $_4$ + ratio of 1.32 so that the Sharon effluent to be suitable for use as influent of the Anammox experimental setup. However, the neutralizing agent consumption is important.

#### Sharon experiment without pH control

N-NH<sub>4</sub><sup>+</sup>  $\rightarrow$  N-NO<sub>2</sub><sup>-</sup> transformation efficiency varied between 41 – 64 %. Aplication of nitritification as a first step of a two reactors deamonification process seems possible without pH control as the transformation efficiency has an acceptable value (aprox.50%) of the N-NH<sub>4</sub><sup>+</sup> / N-NO<sub>2</sub><sup>-</sup> ratio. The alkalinity of the municipal sludge dewatering effluents is high enough to maintain proper conditions.

## **ANAMMOX** experimental model

Nitrogen removal efficiencies (Ninfl.  $\rightarrow$  N<sub>2</sub>) ranged between 30-89%. Application of the Anammox process on an influent that represents the effluent of a partial nitritification process with an acceptable ratio between N-NO<sub>2</sub>-/ N-NH<sub>4</sub>+ (aprox 50%) is possible when a very good control of parameters is assured.

#### INCD ECOIND – INTERNATIONAL SYMPOSIUM – SIMI 2011 "THE ENVIRONMENT AND THE INDUSTRY"

The control of dissolved oxygen concentration in the bioreactor proved to be rather difficult during experimentation. Thus, degassing the influent or sparging a mixture of  $N_2$  and  $CO_2$ , in the column bioreactor would be necessary for both pH control and dissolved oxygen control – task which is hard to perform on the experimental model that works at very low influent flow rates.

#### References

- Hellinga, C., Schellen, A. A. J. C., Mulder, J. W., Van Loosdrecht, M., and Heijnen, J. J. (1998). "The SHARON process: an innovative method for nitrogen removal from ammonium rich wastewater." *Water Science & Technology*, 37(9), 135-142
- Mulder, J. W., Van Loosdrecht, M., Hellinga, C., and van Kempen, R. (2001). "Full scale application of the SHARON process for treatment of rejection water of digested sludge dewatering." *Water Science & Technology*, 43(11), 127-134
- Peng, Y., Zhu, G. (2006). Biological nitrogen removal with nitrification and denitrification via nitrite pathway, *Appl. Microbiol. Biotechnol.*, 73 (1), 15-26
- M.S.M. Jetten, M. Strous, K.T. van de Pas-Schoonen, J. Schalk, U.G.J.M.van Dongen, A.A. Van De Graaf, S. Logemann, G. Muyzer, M.C.M. van Loosdrecht, J.G. Kuenen. The anaerobic oxidation of ammonium. FEMSMicrobiology Reviews, 22:421–437, 1999.
- U. van Dongen, M.S.M. Jetten, M.C.M. van Loosdrecht. The SHARON-Anammox process for treatment of ammonium rich wastewater. Water Science and Technology, 44(1):153–160, 2001.
- S.W.H. Van Hulle, E.I.P. Volcke, J.L. Teruel, B. Donckels, M.C.M. van Loosdrecht, P.A. Vanrolleghem. Influence of temperature and pH on the kinetics of the SHARON nitritation process. In Proceed- ings 4th IWA World Water Congress, pages (on CD–ROM), Marrakech, Morocco, September 19-24 2004.
- R. van Kempen, J.W. Mulder, C.A. Uijterlinde, M.C.M. van Loosdrecht. Overview: full scale experience of the SHARON-process for treatment of rejection water of digested sludge dewatering. Water Science and Technology, 44(1):145–152, 2001.
- Francis CA, Beman JM, Kuypers MMM, 2007. New processes and players in the nitrogen cycle: the microbial ecology of anaerobic and archaeal ammonia oxidation. *ISME J I(2007)* 1, 19-27