CHEMICAL ENGINEERING TRANSACTIONS Volume 17, 2009
Editor Sauro Pierucci
 ISBN 978-88-95608-01-3 ISSN 1974-9791
DOI: 10.3303/CET0917041

Biological nitrogen removal at high performances in platform for the treatment of industrial liquid wastes

Anna Laura Eusebi[1*], Cecilia Troiani[1], Francesco Fatone[2], Paolo Battistoni[1]

[1]Department of Hydraulic, Roads, Environment and Chemistry, Marche Polytechnic University. Via Brecce Bianche, 60100 Ancona, Italy. E-mail: a.l.eusebi@univpm.it
[2]Department of Science and Technology - University of Verona, Strada Le Grazie 15, Cà Vignal 37134 Verona, Italy.

The paper deals with the results obtained as nitrogen removal in a platform for the treatment of industrial liquid wastes. The reaching of the optimal reduction percentages was related, at first, with the choice of a flexible treatment flow scheme characterized by the application of best available technologies. The advanced alternate cycles process in the biological reactor determined, after three months of experimental work, removal performances on average equal to 97% for the ammonia and 77% for TN. Moreover, the best nitrification results were achieved despite the complex mixtures of different chemical species in the main influent that can inhibit the NH_4-N reduction. The ammonia uptake rate measured was 0.112 $kgNO_x$-$NkgVSS^{-1}d^{-1}$ at 20 °C. The denitrification process was assured also at COD/TN condition lower than 5.

1. Introduction

In the past ten years the water quality regulations (Directive 91/271/EEC) changed focusing on nutrients removal to avoid the eutrophication of surface water. In this direction the nitrogen reduction cannot interest only the civil discharges but also all the flows characterized by the high nitrogen loads, for example the anaerobic supernatants and the industrial liquid wastes. The specific treatment of high nitrogen load streams is developed in literature evaluating different biological process applications on the supernatant from the anaerobic digestion. In fact, the supernatant containing as much as 2 $kgTNm^{-3}$ (Strous *et al.*, 1997) is typically recirculated to the headworks of the wastewater treatment plant (WWTP) and it accounts for 15-20% of the influent nitrogen load (Jonsson *et al.*, 2000). Separate collection and treatment of the supernatant is now a promising alternative. This flow, characterized by an elevated ammonia concentration, a low COD/NH_4-N ratio, on average equal to 1, and by an high percentage of NBCOD, hardly can be treated by a conventional biological activated sludge process of nitrification and denitrification requiring an high addition of external carbon source. A number of biological methods alternative to the conventional ones has been developing to reduce the carbon addition. The SHARON process (Hellinga *et al.,* 1998), operating with aerobic phases longer than the anoxic, and the ANAMMOX process (Fux *et al.*,

Please cite this article as: Eusebi A.L., Troiani C., Fatone F. and Battistoni P., (2009), Biological nitrogen removal at high performances in platform for the treatment of industrial liquid wastes, Chemical Engineering Transactions, 17, 239-244 DOI: 10.3303/CET0917041

2003) are mainly applied for nitrogen removal and they both determine an average ammonia removal of 85%. On the other hand the treatment of the industrial liquid wastes meets a lot of troubles related with their physicochemical characteristics and with the choice of the optimal flow scheme and biological process. In fact, the influent to the platform is defined by a complex mixtures of different substances, including potentially toxic compounds, recalcitrant organic matter, heavy metals (Oygard *et al.*, 2007) and high salinity. The nitrogen concentration in this wastewater ranges from 230 $mgTNL^{-1}$ (Battistoni *et al.*, 2001) to 2000 $mgTNL^{-1}$ (Chen, 1996). Also when the TN load isn't elevated, the presence of the mentioned chemical species determines the difficult to apply directly the common biological nitrogen removal method (nitrification and denitrification). In fact, the specific ammonia uptake rate decreased at high salinity, about 30000 $mgNaClL^{-1}$, up to 0,005 $KgN\text{-}NH_4KgMLSS^{-1}d^{-1}$ (Panswad et al., 1999). Furthermore, the industrial liquid wastes require the external addition of easy biodegradable organic carbon to sustain the denitrification process. The introduction of suitable chemical and physical pretreatments, as Fenton process, represents the main solution to reduce inhibitory effects on the biological process. For partially removing the influent nitrogen load, coagulation-flocculation and ammonia stripping or evaporation are normally used. Really they need of a consistent amount of chemicals determining a net increment of the salinity. To minimize this negative impact on the biological kinetic rates, the chemical precipitation of struvite (Battistoni *et al.*, 2002) or its crystallization represent an alternative solution. The paper deals of a platform for the treatment of municipal solid waste landfill leachate, liquid wastes from urban origin and olive oil mill and dairy wastewaters. The mixture of these liquid wastes couples an high nitrogen influent load and a low COD/TN ratio with the presence of heavy metals and toxic compounds. The study demonstrates as an appropriate flow scheme and a suitable and flexible biological process (Alternate Cycles) can avoid the inhibitory and toxic effect and determine an optimal nitrogen removal.

2. Materials and Methods

The chemical and physical characterization of the single liquid wastes brought to the platform was made by a grab sample before the discharge. Instead, all the parameters of the influent and the effluent were determined with daily averaged samples once a week. The analytical determination of the macropollutants was made according to the Standard Methods (APHA, 1985). The heavy metals concentrations in the liquid wastes were defined with the Varian mod. AA 240-FS spectrometer equipped with a vapour generating accessory for the analysis of Hg and As by cold vapour atomic absorption. The specific uptake rate of ammonia of the biological process was measured according to Kristensen method (Kristensen *et al.*, 1992).

3. Results and discussion

3.1 The liquid wastes and the sectioning of the treatment lines

On the basis of the daily amount of the single liquid wastes brought during the years 2003-2005 it was possible to estimate the influent flows in the platform (Table 1). The average flow rate treated was 230 m^3d^{-1}. The main contribution was represented by the landfill leachate (European Waste Catalogue 19.07.03) with an average quantity of about 180 m^3d^{-1} equal to 79%. The other liquid wastes came from urban origin (EWC 200304, 160799), from the seasonal manufacturing of the olive oil (EWC 200301) and from the dairy (EWC 200599). Their amounts bore no much on the total wastes discharges (14% EWC 20304, 4% EWC 200301 and 3% EWC 200599). Moreover, the flow of municipal solid waste landfill leachate could greatly improve during the wet periods up to 280 m^3d^{-1}, in this situation the total maximum amount daily treated reached up to 330 m^3d^{-1}.

Table 1. Amount of the single liquid wastes

		Leachate	Liquid wastes from urban origin	Olive Oil wastes	Dairy wastes
EWC		190703	200304-160799	200301	200599
Q	m^3d^{-1}	180	32		
% on tot discarges	%	79	14		

The chemical and physical characterization of each liquid waste is reported in Table 2. The landfill leachate showed an elevated nitrogen concentration on average equal to about 1,100 $mgTNL^{-1}$ mainly constituted by the NH_4-N (95%). At the same time, the COD concentration was about 3,900 mgL^{-1} determining a low COD/TN ratio equal to 3. Indeed, an elevated alkalinity (7,950 mgL^{-1}) and a chlorides salinity of 720 $mgCl^{-}L^{-1}$ characterized this liquid waste. Instead, the other discharges had the highest COD from 38,270 mgL^{-1} (liquid wastes from urban origin) up to 124,650 mgL^{-1} (olive oil wastewaters) and a low ammonia concentrations. Differently from the others, the liquid wastes from urban origin highlighted an elevated TSS concentration of 31,130 mgL^{-1}. Finally, a low amount of all the heavy metals are present in the influent liquid wastes.

Table 2. Chemical and physical characterization of the liquid wastes

		leachate	liquid wastes from urban origin	dairy wastes	olive wastes
pH		8.2		5.6	5.2
NH_4-N	mgL^{-1}	1,100	230	261	172
TN	mgL^{-1}	1,160	711		
COD	mgL^{-1}	3,900	38,270	74,850	124,650
Alkalinity	mgL^{-1}	7,950	2,000		6,183
PO_4-P	mgL^{-1}	9	31	197	337
Cl	mgL^{-1}	720			1,401
TSS	mgL^{-1}	390	31,130		
COD/TN		3	54		
As	mgL^{-1}	6	2		
Cd	mgL^{-1}	0.4	0.2		
Hg	mgL^{-1}	1	26		
Cr tot	mgL^{-1}	245*	17		
Ni	mgL^{-1}	176	61		
Pb	mgL^{-1}	9	5		
Cu	mgL^{-1}	35	32		

* Cr (III) accounts for 90%

3.2 The platform flow scheme and the choice of the processes

The liquid wastes characterization determined the choice of the best available technologies and the optimal flow scheme to cope with the variability as amount and as chemical features of the influent to the platform. In fact, as reported in Figure 1, the plant was organized in three different lines: the first -line 1- for the municipal solid waste landfill leachate, the second -line 2- for the liquid wastes from urban origin and the third –line 3- for the olive oil mill and dairy wastewaters. The liquid wastes of the line 2 after the screening and grit unit, to remove the solids, were added with the stream come from the line 1 previously physical pre-treated (screening step). Later, the two flows were submitted to a chemical coagulation and flocculation to decrease the TSS and colloidal particles concentrations and to form insoluble metal salts for the heavy metals reduction. Then the supernatant was equalized and fed to the biological process. The alternate cycles (AC) process (Battistoni *et al.*, 2003) was applied in the biological reactor. By the automatic alternation of oxic and anoxic phases, the elevated control level and the best exploitation of nitrogen-bound oxygen, this technology was able to optimize the biological N reduction regardless of the intense variations of the influent TN load and to assure the denitrification process, despite the low COD/TN value.

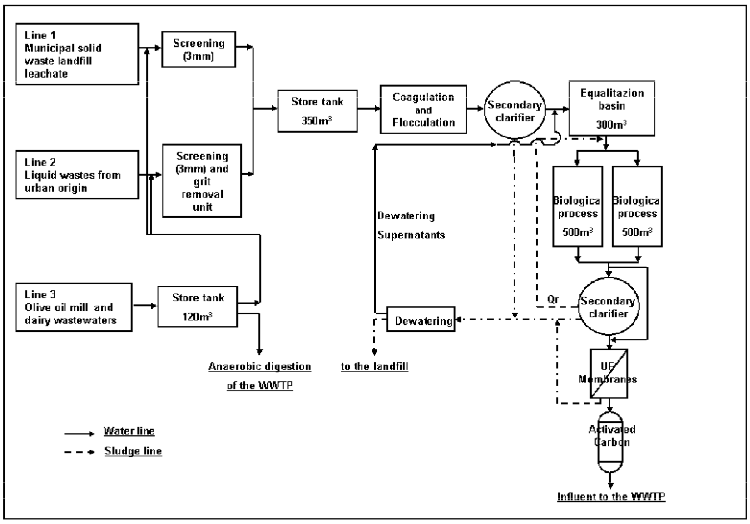

Figure 1. Block flow diagram

The biological AC unit (1000 m^3) was dimensioned with an elevated HRT (3 d) to promote the biosorption phenomena for metals removal. Moreover, the ultrafiltration membranes can be coupled with the alternate cycles as MBR section or they can be utilized as tertiary treatment (TT) after the secondary clarifier. Finally, an activated carbon adsorption unit works if the final heavy metals concentration is higher than the law limits. The effluent treated is discharged in the headworks of a municipal wastewater treatment plant (WWTP) (60,000 PE).The liquid wastes of line 3, characterized by an high organic content, are mainly fed to mesophilic digester of the municipal WWTP or sometimes used as internal organic source.

3.3 Influent/effluent characteristics and performances of the treatment

The start up was made in July 2008 and the platform was monitored for three months. The membrane unit worked in TT configuration. The main nitrogen reduction happened in the reactor managed with the AC process. During this period the average total amount treated was about of 120 m^3d^{-1} divided between 63% of leachate and 37% of the liquid wastes from urban origin. The maximum operative influent flowrate was never reached during this period. The characterization of the influent after the physical pre-treatments defined COD and TN concentrations of about 2800-6700 $mgCODL^{-1}$ and 800-1350 $mgTNL^{-1}$. After the coagulation and flocculation unit the range of the macropollutans decreased up to 1700-4000 $mgCODL^{-1}$ and 700-1000 $mgTNL^{-1}$ mainly formed by ammonia (75%). The average reduction percentages observed in the biological unit were 77% for TN, 97% for NH_4-N and 76% for COD. Specifically, the influent to the process was characterized by a nitrogen loading rate (NLR $kgTNm^{-3}d^{-1}$) from 0.095 $kgm^{-3}d^{-1}$ to 0.160 $kgm^{-3}d^{-1}$ (Figure 2). Notwithstanding the elevated NLR, the ammonia nitrification efficiency was ever higher than 92% (Figure 2). The optimal performances obtained were supported by the ammonia uptake rate measure in the biological reactor. The test showed a value of 0.112 $kgNO_x$-$NkgVSS^{-1}d^{-1}$ at 20 °C. At the same time, although the COD/TN ratio changed from 1 to 7 (average value of 3) the TN performances came from 54% to 91% (Figure 3). The successful denitrification confirms the results (Fatone *et al.*, 2005) achieved in other municipal wastewaters characterized by the alternate cycles process. In fact, previously, in a municipal full scale plant (5300 PE) and in a pilot plant (maximum influent flow 40 m^3d^{-1}) characterized by a COD/TN ratio lower than 5, the AC application determined the nitrogen removal percentages ever higher than 86%.

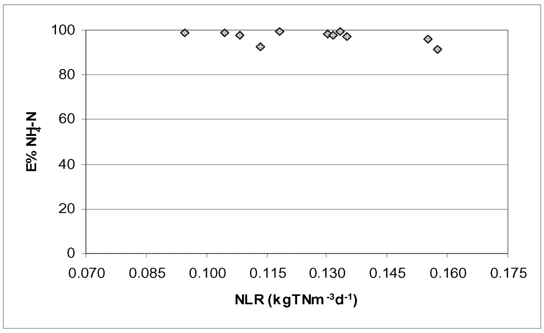

Figure 2. Ammonia performances

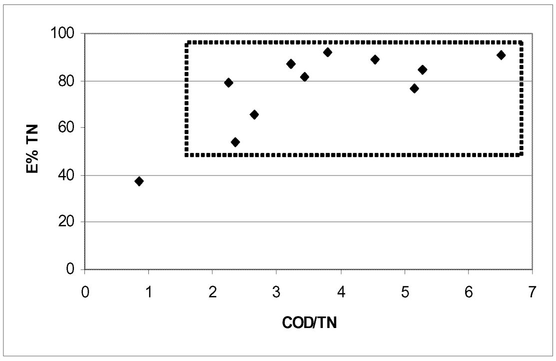

Figure 3. TN performances vs COD/TN

4. Conclusion

The paper deals of a platform for the treatment of industrial liquid wastes. The average composition of the influent couples an high nitrogen influent load and a low COD/TN ratio with the presence of heavy metals and toxic compounds. The main conclusions of the study were the following:

-the best available technologies applied and the flow scheme chosen permit to cope with the amount variability and the chemical complexity of the influent liquid wastes;

-the use of ultrafiltration membranes as MBR section, coupled with the alternate cycles, or as tertiary treatment determined an high flexibility of the process;

-the AC process in the biological reactor determined the ammonia removal performance on average equal to 97% notwithstanding the NLR changed from 0.095 $kgm^{-3}d^{-1}$ to 0.160 $kgm^{-3}d^{-1}$;

- the ammonia uptake rate of 0.112 $kgNO_x$-$NkgVSS^{-1}d^{-1}$ demonstrated an optimal activity of the nitrifying bacteria despite the complex mixtures of different chemical species in the main influent;

-the automatic alternation of oxic and anoxic phases and the best exploitation of nitrogen-bound oxygen optimized the biological TN reduction also in the COD/TN lower ratio on average equal to 3 .

References

APHA, 1985, Standards methods for the examination of water and wastewater, 16th edition, American Public Health Association, Washington D.C..

Battistoni P., Boccadoro R., Bolzonella D. and Marinelli M., 2003, An alternate oxic-anoxic process automatically controlled. Theory and practice in a real treatment plant network. Water Science and Technology, 48 (11-12), 337-34.

Battistoni P., Boccadoro R., Bolzonella D. and Pezzoli S., 2001, Optimization of chemical and physical pretreatments in a platform of treatment of liquid industrial wastes, Ind. Eng. Chem. Res. 40, 4506-4512.

Battistoni P., De Angelis A., Prisciandaro M., Boccadoro R. and Bolzonella D., 2002, P Removal from anaerobic supernatants by struvite crystallization: long term validation and process modelling. Water Res. 36 (8), 1927-1938.

Chen P.H., 1996, Assessment of leachates from sanitary landfills: impact of age, rainfall, and treatment. Environment International 22(2), 225-237.

Fatone F., Bolzonella D., Battistoni P. and Cecchi F., 2005, Removal of nutrients and micropollutants treating low loaded wastewaters in a membrane bioreactor operating the automatic alternated-cycles process, Desalination 183(1-3), 395– 405.

Fux C., Marchesi V., Brunner I. and Siegrist H., 2004, Anaerobic ammonium oxidation of am-monium-rich waste streams in fixed-bed reactors. Wat. Sci. Tech. 49(11-12), 77-82.

Hellinga C., Schellen A. A. J. C., Mulder J. W., van Loosdrecht M. C. M. and Heijnen J. J., 1998, The SHARON process: an innovative method for nitrogen removal from ammonium-rich wastewater. Wat. Sci. Tech. 37(9), 135-142.

Jönsson K., Grunditz C., Dalhammar G. and Jansen J. la C., 2000, Occurrence of nitrification inhibition in Swedish municipal wastewaters. Wat. Res. 34(9), 2455-2462.

Kristensen G.H., Jorgensen P.E. and Henze M., 1992, Characterization of functional microrganism groups and substrate in activated sludge and wastewater by AUR, NUR and OUR. Wat. Sci. Tech. 25, 43-57.

Øygard J.K., Gjengedal E. and Røyset O., 2007, Size charge fractionation of metals in municipal solid waste landfill leachate, Water Res. 41 (1), 47-54.

Panswad and Anan, 1999, Specific oxygen, ammonia, and nitrate uptake rates of a biological nutrient removal process treating elevated salinity wastewater. Bioresource Technology 70, 237-243.

Strous M., van Gerven E., Zheng P., Kuenen J. G. and Jetten M. S. M., 1997, Ammonium re-moval from concentrated waste streams with the anaerobic ammonium oxidation (Anammox) process in different reactor configuration. Wat. Res. 31(8), 1955-1962.