

## MBR and Alternate Cycles Processes: Advanced Technologies for Liquid Wastes Treatment

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The paper deals with the application of an alternate cycles process with a membrane ultrafiltration unit to treat liquid wastes. The choice of these best available technologies permits to obtain an elevated ammonia removal higher than 93% and a net decrement of the main heavy metals. The effect of the chemical physical pre-treatment determines some hydrolysis phenomena augmenting the COD availability for the denitrification phase. The denitrification performances, supported by the real nitrates uptake rates measured, change in the range from 45% to 87% without any strict correlation with the COD/TN ratio.

### 1. Introduction

The necessity to produce treated liquid wastes with high quality in terms of macro and micro pollutants, implies the adoption of very effective processes in terms of performances and effluent concentrations. Among the best available technologies (BAT), the membrane bioreactor (MBR) is supposed to be the best choice (Fatone et al. 2005). This technology represents a new available approach to treat by biological way the liquid wastes coupled with a preliminary physical – chemical treatment phase (screening, grit removal, coagulation and flocculation). A remarkable number of studies showed that the MBRs have the capacity to perfectly remove suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD) as well as heavy metals and organic micropollutants (Liu et al., 2005). Biological removal of carbon and nutrients in MBRs can be accomplished by a number of options. Among the schemes, dynamic systems can be more flexible when automatic controls are introduced to easily manage the process. The process design can be implemented in sequencing batch reactors or in continuously fed reactors intermittently aerated (Wang et al., 2005). In this way, when the matrix treated is liquid wastes, could be suitable the choice to couple the MBR technology with an alternate cycles (AC) process (anoxic/oxic) automatically controlled with a continuous feeding in a stirred reactor. This approach, based on dissolved oxygen and oxidation reduction potential device, permits the optimization of the biological performances despite the complex and variable characteristics of the liquid wastes treated. Moreover, the flexibility of the alternate cycles to the influent loads, the application of submerged mixers to maintain in suspension the biomass during the anoxic phase and the absence of the internal recycle is a proper solution to minimize the operational and maintaining costs for an integrate process AC and MBR. In the light of this scenario, the paper deals with the treatment of liquid wastes in a platform characterized by an MBR combined with an alternate oxic and anoxic cycles process.

## 2. Materials and Methods

### 2.1 Analytical methods and chemical-physical characterization

The chemical and physical determination of the single liquid wastes discharged to the platform was made by a grab sample in terms of macropollutants. The mixed wastewater influent and effluent to the plant was characterized, according to the Standard Methods (APHA, 2005), with daily averaged samples once a week for the period from April to November 2010. Moreover from October 2010, the average macropollutants were measured in the influent to the biological reactor after the chemical physical pretreatments. The heavy metals concentrations in the main influent and in the effluent 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 and nitrates of the biological process was measured.

## 3. Results and Discussion

### 3.1 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, 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 physically pre-treated (screening step). Later, the two flows were submitted to a chemical coagulation and flocculation (acid-base treatment) 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 total nitrogen (TN) load and to assure the denitrification process, despite the low COD/TN value. The biological AC unit (1000 m<sup>3</sup>) was designed with an elevated hydraulic retention time (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) (85,000 PE). The liquid wastes of line 3, characterized by a high organic content, are mainly fed to mesophilic digester of the municipal WWTP or used as internal organic source.

### 3.2 Influent matrix: amount and macropollutants characteristics

The evaluation of the amount of liquid wastes discharged during 2009 and 2010 shows an average value of 120 td<sup>-1</sup> (Table 1) and a variation from 82 td<sup>-1</sup> to 168 td<sup>-1</sup> in the same period. This fluctuation is related to the main contribution to the influent flow by the landfill leachate (European Waste Catalogue 19.07.03), that could greatly improve during the wet periods, with a percentage from 70% to 85% of the total wastes (Table

1). The leachate brings mainly slowly or not degradable organic load (1300 mgCODl<sup>-1</sup>) and nitrogen compounds formed by ammonia (550 mgNH<sub>4</sub>-Nl<sup>-1</sup>) (Table 1). The other liquid wastes, came from urban origin (EWC 200304, 160799), represent from 15% to 30% of the global amount discharged, mainly contributing in terms of COD (29000 mgCODl<sup>-1</sup>) in the average matrix treated (Table 1).

Table 1. Amount and average chemical physical characterization of each liquid waste

		2009											
		J	F	M	A	M	J	J	A	S	O	N	D
Liquid wastes	td <sup>-1</sup>	146	135	114	132	106	109	82	82	74	105	102	127
		2010											
Liquid wastes	td <sup>-1</sup>	118	113	134	149	161	168						
AVERAGE CHARACTERIZATION													
		leachate		liquid wastes from urban origin									
Min percentage on total amount		%		70									
Max percentage on total amount		%		85									
COD		mg l <sup>-1</sup>		1318									
BOD <sub>5</sub>		mg l <sup>-1</sup>		288									
NH <sub>4</sub> -N		mg l <sup>-1</sup>		556									
NO <sub>2</sub> -N		mg l <sup>-1</sup>		1									
NO <sub>3</sub> -N		mg l <sup>-1</sup>		32									
TP		mg l <sup>-1</sup>		9									

In this scenario, the matrix entered to the pretreatment unit is mainly characterized as reported in Table 2. During the period from April to October 2010 the influent flow changed in the range from 119 m<sup>3</sup>d<sup>-1</sup> to 168 m<sup>3</sup>d<sup>-1</sup>, with a variability of the COD concentrations from 3900 mgCODl<sup>-1</sup> to 5600 mgCODl<sup>-1</sup> and from 1100 mgTSSl<sup>-1</sup> to 3000 mgTSSl<sup>-1</sup> (Table 2). The nitrogen contents vary from 940 mg l<sup>-1</sup> to 1660 mg l<sup>-1</sup>, composed largely by ammonia and organic nitrogen with an average NH<sub>4</sub>-N/TKN value of 0.7. The TP concentrations were evaluated from 21 mg l<sup>-1</sup> to 53 mg l<sup>-1</sup>. The high salinity, always higher than 1400 mgCl l<sup>-1</sup> up to 2500 mgCl l<sup>-1</sup>, could, theoretically, determine a reduction of the specific ammonia uptake rate (Table 2).

Table 2. Main influent parameters

		Influent									
2010	Q in	COD	TSS	NH <sub>4</sub> -N	NO <sub>2</sub> -N	NO <sub>3</sub> -N	TKN	TN	TP	Cl	
	m <sup>3</sup> d <sup>-1</sup>	mg l <sup>-1</sup>	mg l <sup>-1</sup>	mg l <sup>-1</sup>	mg l <sup>-1</sup>	mg l <sup>-1</sup>	mg l <sup>-1</sup>	mg l <sup>-1</sup>	mg l <sup>-1</sup>	mg l <sup>-1</sup>	
A	149	3933	1631	673	1.0	0.4	946	947	21	1411	
M	161	4640	3054	753	0.7	0.7	1310	1311	36	1709	
J	168	5555	2714	910	0.0	0.4	1304	1305	53	1943	
J	157	4628	1107	1024	0.1	0.4	1304	1305	29	2504	
A	146	4534	1428	1118	0.2	0.7	1644	1645	31	2549	
S	119	4798	1168	1026	0.4	1.5	1406	1408	31	2256	
O	120	5676	2225	1024	1.0	3.7	1398	1402	46	2223	

### 3.3 Biological reactor: influent characterization and operative parameters

The average effect of the pretreatments on the influent flow is reported for the October and November 2010 in Table 3. Obviously, a decrement of phosphorous compounds and of TSS is registered after the chemical and physical units. In fact, values of  $1400 \text{ mgTSSl}^{-1}$  and  $20 \text{ mgPO}_4\text{-Pl}^{-1}$  are remarkable in the biological influent. Moreover, the high hydraulic retention time of the liquid wastes discharged in the pretreatment phase determines a fermentation effect on the COD influent. The management condition is related to the choice that any external carbon source hasn't to be used in the biological reactor. The COD concentration increased and was measured equal to  $5600 \text{ mgl}^{-1}$  during the period evaluated (Table 3). This phenomenon is coupled with a reduction of the ammonia nitrogen before the biological reactor ( $648 \text{ mgl}^{-1}$ ) (Table 3) linked with the acid – base treatment in the chemical coagulation and flocculation unit and with a partial stripping process in the equalization basin where submerged mixers are installed.

Table 3 Influent to the biological reactor

	Q in	COD	TSS	NH <sub>4</sub> -N	NO <sub>2</sub> -N	NO <sub>3</sub> -N	TKN	TN	PO <sub>4</sub> -P	Cl
	m <sup>3</sup> d <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>
O-N	149	5594	1407	648	2	17	757	776	20	2905

The combination between the decrement of the TN and the hydrolysis of the COD load establishes a net increment of the COD/TN ratio influent to the biological unit (Figure 1). In fact, whereas the ratio was in the range from 3 to 6.2 in the main influent discharged, it augments from 4.8 to 9.1 in the biological influent. Although the recalcitrant material and not biodegradable compounds remain in the main flow, this condition supports partially the following denitrification phase. The biological operative

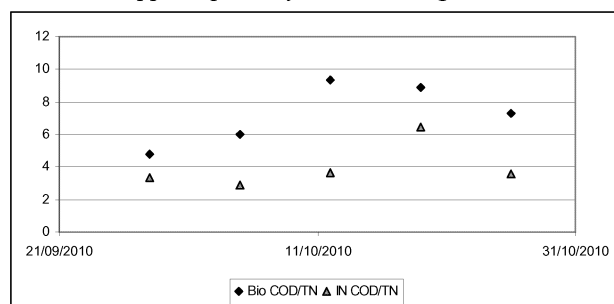


Figure 1 COD/TN of the influent to the platform and to the biological reactor

parameters are characterized by a specific nitrogen load (NLR) from  $0.10 \text{ kgTNm}^{-3}\text{d}^{-1}$  to  $0.18 \text{ kgTNm}^{-3}\text{d}^{-1}$  with a volatile biomass ratio on average equal to 42.5 % (Table 4).

Table 4. Operative biological parameters

	NLR	MLSS	VSS/SS	kn	kd with influent
	kgTNd <sup>-1</sup> m <sup>-3</sup>	mg <sup>l</sup> <sup>-1</sup>	%	kgNH <sub>4</sub> -NkgVSS <sup>-1</sup> d <sup>-1</sup>	kgNO <sub>x</sub> -NkgVSS <sup>-1</sup> d <sup>-1</sup>
05/10/2010	-	8972	42.0	0.177	0.003
12/10/2010	0.11	9002	42.5	0.197	0.045
19/10/2010	0.18	8861	42.0	0.180	-
26/10/2010	0.18	8807	42.0	0.113	0.027
04/11/2010	0.10	10700	43.0	0.132	0.013

Even though this biological situation coupled with the high salinity of the liquid wastes ( $2900 \text{ mg l}^{-1}$  Table 3), the ammonia uptake rates at  $20^\circ\text{C}$  are always higher than  $0.113 \text{ kgNH}_4\text{-NkgVSS}^{-1}\text{d}^{-1}$  (Table 4). The denitrification rates at  $20^\circ\text{C}$ , measured in batch tests using the biological influent as carbon source, highlighted variable values from  $0.003 \text{ kgNO}_x\text{-NkgVSS}^{-1}\text{d}^{-1}$  to  $0.045 \text{ kgNO}_x\text{-NkgVSS}^{-1}\text{d}^{-1}$  (Table 4) attributed to endogenous and slowly biodegradable COD presence.

### 3.4 Nitrogen performances

The final nitrogen performances obtained in the platform are showed in Figure 2. Notwithstanding the elevated NLR, the ammonia nitrification efficiency was ever higher than 93% (Figure 2). The optimal performances obtained were supported by the ammonia uptake rates measured in the biological reactor. The denitrification decrement, variable in the range from 45% to 87%, isn't strictly correlated to the COD/TN ratio, supporting the hypothesis of high concentrations of not biodegradable carbon.

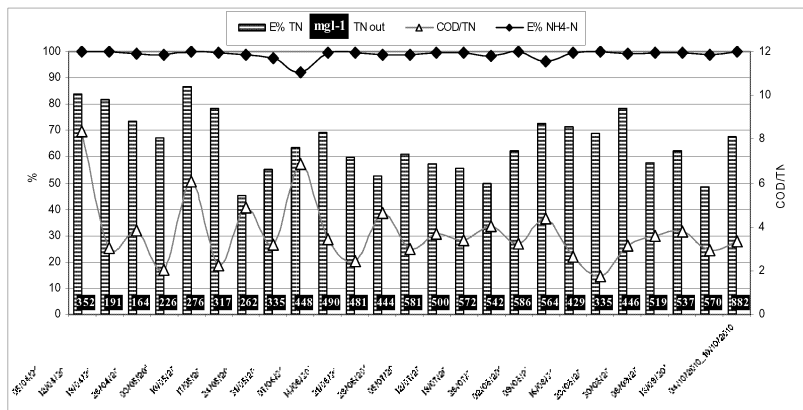


Figure 2 Nitrogen biological performances

### 3.5 Membranes operative conditions

The MBR unit, characterized by a total filtration area of  $1216 \text{ m}^2$  and coupled with the AC process, works, during the period exposed, with a filtration flow from  $3 \text{ m}^3\text{h}^{-1}$  to  $6 \text{ m}^3\text{h}^{-1}$ . The working time is 7 minutes followed by 1 minute of relaxation. Each day is applied a maintenance cleaning (MC) and when the trans membrane pressure (TMP) is lower than  $-800 \text{ mBar}$  a clean in place skid (CIP) is effectuated. Peracetic acid is utilized for the MC and the CIP. As reported in Figure 3, the working condition in over critical flux determines a reduction of the TMP under  $-700 \text{ mBar}$  and a related decrement of the specific flux  $J_s$  ( $\text{lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ ). Only after a chemical cleaning (CIP) the operative working conditions are re-established.

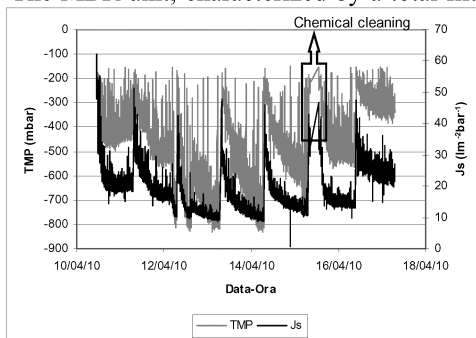


Figure 3 TMP and Js Example

### 3.6 Micropollutants performances

The metals efficiencies are related to the capability of the membrane to produce a permeate without suspended solids where pollutants are adsorbed. As showed in Table 5 all the heavy metals are characterized by an elevated variability (standard deviation) in the main influent. Good average performances are obtained as Al (91%), Pb (38%), Fe (61%), Ni (10%) and As (32%) (Table 5). The really lower influent amounts of Cd and Hg didn't permit a correct analytical evaluation of the phenomena occurred. Average increments of Zn and Cu are present in the platform probably related to the complexity of the matrix treated. About this last aspect more research activity has to be conducted.

Table 5 Micropollutants performances

		Al	Pb	Fe	Ni	Cd	Zn	As	Cu	Hg
		mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>	mg <sup>l</sup> <sup>-1</sup>
Influent	Ave.	2.58	0.021	4.61	0.41	0.0002	0.43	0.040	0.048	0.0004
	Min	0.13	0.011	2.78	0.31	0.0000	0.19	0.027	0.011	0.0000
	Max	4.39	0.030	7.55	0.46	0.0005	0.62	0.051	0.129	0.0006
	St. dev.	1.59	0.007	1.73	0.06	0.0002	0.17	0.009	0.046	0.0002
Effluent	Ave.	0.24	0.013	1.78	0.37	0.0007	0.72	0.027	0.126	0.0008
	Min	0.10	0.003	0.86	0.35	0.0003	0.42	0.009	0.064	0.0005
	Max	0.66	0.052	2.70	0.47	0.0015	1.29	0.046	0.181	0.0015
	St. dev.	0.22	0.019	0.65	0.05	0.0005	0.32	0.013	0.040	0.0004

### 4. Conclusions

The results obtained coupling the AC process with the MBR showed high performances for ammonia removal supported by an elevated  $k_n$  higher than  $0.113 \text{ kgNH}_4\text{-NkgVSSd}^{-1}$  although the influent fluctuation and the over influent nitrogen load. A denitrification performances from 45% to 87% is obtained without any external carbon source and related to the variability of recalcitrant compounds and not biodegradable carbon concentrations. The MBR effect is mainly linked with an elevated reduction of the main heavy metals present in the influent flow.

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