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Removal and fate of total and free cyanide treating real low loaded petrochemical wastewater in a pilot membrane bioreactor (MBR)

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This paper deals with about one year experimentation of a pilot MBR operated in parallel with the world's largest industrial MBR and treating continuously real industrial wastewater coming from a petrochemical area. The removal of free and total cyanide was investigated to find an operating solution to face the problems linked to the low organic inloadings, which influenced the composition of the activated sludge and its biosorption and/or biodegradation potentials. In order to gain a deeper understanding on the mechanisms of cyanide removal, several laboratory batch tests were carried out in a range of conditions, using the activated sludge drawn from the pilot and full scale MBR. Results showed good (almost complete) biodegradation of free cyanides, influenced by the F:M ratios, and high stability of iron-complexes. Also, comparing the bench scale, pilot and full scale results, minimal specific removal rate for free cyanides were found to be in the range 0.2÷0.4 μg/gVSS*h, where the limiting substrate concentration was lower than 10 μgCN/L and the biodegradation was the major removal mechanism.

1. Introduction

Cyanide is a toxic pollutant contained in a number of industrial wastewater (i.e.: mining, coke or steel industries) at concentration up to hundreds of mg/L. Dealing with cyanide-related environmental hazard, an important distinction must be made between free cyanide, strong and weak metal-cyanide, which may have very different behaviour and toxicity. In fact the mechanisms of removal and their toxicity are likely related to their physical-chemical proprieties and particularly to their tendency to dissociate releasing free cyanides.

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Several reviews summarized the treatment feasibility of cyanides by biological and physical-chemical methods (Akcil, 2003). However, the consolidated treatments are often not able to reach the stringent standards for discharge in very sensitive water bodies, such as the Lagoon of Venice, where few µg/L are allowed to be discharged. Therefore, there is a lack of information concerning the best available techniques (BATs), behaviour and final destiny of cyanides treating wastewater with around (or less than) one hundred µg/L of cyanides. This may just be the case of wastewater collected from a large petrochemical industrial area, where a first source treatment is performed by consolidated techniques and a further advanced treatment is necessary to reach a final cyanide content of few µg/L.
This paper deals with removal and final fate of free and complex cyanide treating real low-loaded industrial wastewater, coming from a large petrochemical area, in a pilot membrane bioreactor (MBR). In the area the ongoing reduction of the industrial productions is causing a strong decrease of macro-pollutants (i.e.: COD,BOD,TKN) concentrations in the wastewater. Therefore, major experimental focus has been put on the effect of low loadings (i.e.: F:M ratio) to the bioreactor behaviour. Finally, the removal performances and mechanisms are quantitatively discussed, so to outline the treatment potentials and actual limits of the MBR technology.

2. Material and methods

The pilot MBR was operating in parallel with the world's largest industrial MBR (Cattaneo *et al.*, 2008) for the treatment of petrochemical wastewater. The pilot plant had reaction volume of 4,2 m^3, divided in multizone predenitrification-nitrification scheme with a separate filtration chamber, and was equipped with hollow fibre submerged UF membrane module (ZeeWeed 500c - filtration area of 21,7 m^2). The ultrafiltration system was operated continuously and automatically by cyclic aeration, for membrane scouring, and mixed filtration cycles (combination of permeation, relaxation and backwashing) analogous to the full scale parallel MBR. A number of parameters (ORP, MLSS, DO, T, turbidity, TMP, flowrates) were on-line monitored and logged, then periodically downloaded for further data processing.
Over nine months of experimentation, the sludge age was in the range 60÷100 days and three experimental runs were carried out treating influent wastewater of some 6÷7 m^3/d according to the main process conditions of Table 1.

Table 1. Main process conditions over the three experimental runs

		Run 1	Run 2	Run 3
T	°C	22,5	27,8	32,2
MLSS	g/L	3,7	3,0	3,6
MLVSS/MLSS	%	72,0	78,0	72,4
F/M	kgCOD/kgVSS*d	0,048	0,042	0,109
$F/M_{\text{to oxic tank}}$	kgCOD/kgVSSox*d	0,036	0,064	0,127
NLR	KgN-NH4/ m^3*d	0,005	0,006	0,007
NLR'	$KgTKN_{biodegradable}$/ m^3*d	0,009	0,015	0,018

Run 1 was carried out to validate the pilot MBR as reliable scale-down of the full scale MBR. From Run 1 one may observe that the low organic content led to F:M typically not sufficient for the biomass maintenance. Then, generally, the experimental strategy

was aimed to find out the best MBR configuration to improve the characteristics/composition of the activated sludge (i.e.: fraction of active biomass) in a way to optimize macro and micro-pollutants removal. In particular, considering that the aerobic biomass decay is about five times higher than the anoxic (Siegrest et al. 1999), influent and recycle fluxes were moved and adjusted in a way to increase the F:M to the aerobic zone, always taking into account what would have been actually feasible and sustainable in the parallel full scale MBR.
Therefore, in Run 2 the influent wastewater was moved to the aerobic compartment, so to increase the F:M to the aerobic zone with the only influent, so obtaining a nitrification-postdenitrification scheme. In Run 3 a minimal, but proper, organic loading to the aerobic zone was provided by means of an additional external dosage of acetic acid, up to F/M ratio of about 0,15gBOD_5/gVSSd. Additionally, the initial predenitrification-nitrification scheme was applied again.
In each experimental run the influent and effluent wastewaters were characterized for macro-parameters according to the Standard Methods, while total cyanide were analyzed according to the APAT IRSA 29/03 4070. Also, the speciation between freecyanide and metal-cyanide were determined by ion chromatograph and UV revelation. The activated sludge was analyzed for MLSS, MLVSS and by respirometric analyses (AUR, NUR, OUR) so to evaluate the activity and possible inhibiting/toxic effect of cyanides on the biomass activity. Finally the analysis of free and total cyanides in the sludge of full scale and pilot MBR allowed us to calculate mass balances and evaluate the mechanisms of removal of free and complex cyanides and, also, to estimate the specific removal rates. The cyanide removal rates in the pilot plant in each run was also calculated using the cyanides conversions over the whole experimental runs and the kinetic equations of a CSTR reactor.
Furthermore, removal mechanisms were investigated through bench scale batch tests, by using synthetic solutions at several initial concentrations (range of 50-300 µg/L) of either free-cyanide or metal-cyanide complexes (either strong (FE^{III}) or weak (Ni^{II}) complexes). Batch tests were carried out by using the acclimated activated sludge from either the pilot or the full scale MBRs under aerobic or anaerobic conditions (the latter conditions in order to minimise the biodegradation and ascertain the role of biosorption). For the same purpose, aerobic tests with unacclimated sludge (coming from the civel wastewater treatment plant) were also performed, where the residual content of cyanides in the sludge after removal from solution was also determined.

3. Results

The preliminary study of the operational parameters of the full scale MBR showed two main characteristics: the low loadings of the influent wastewater and the poor quality of the biomass of the reactor. In fact, the influent wastewater contains concentrations of macropollutants as low as follows: COD=100÷150 mg/L; BOD = 60÷80 mg/L; Ntot = 5÷15 mg/L ; Ptot = 0,5÷1 mg/L; TSS = 5÷15 mg/L. Therefore, the full scale (and the pilot) MBR resulted oversized, up to about $500L_{reactor}$ per PE calculated on COD basis, and under loaded both for organic substances and for nutrients (FM ratio of 0,04 gBOD_5/gMLVSS, NLR of 40 g TKN/m^3_{Vox}*d) with direct impact on the fraction of active biomass, esteemed in the range 40÷50% of the MLVSS. The impact of the low

loadings on the activated sludge activity was well defined according to consolidated respirometry analyses that showed the following specific rates: SNR=0,2mgN-NH_4/gVSSh; SDNR=0,9mgN-NO_3/gVSSh, $SOUR_{max(acetate)}$=mgO_2/gVSSh.
As for the cyanides speciation in the influent and effluent from the full scale plant (Figure 1), the major part was composed of free cyanides and well removed in the MBR, on the other hand, metal-cyanides (probably iron-cyanide considering the following discussed results from the batch tests) were almost stable in the biological reactor. Bench scale tests showed the biodegradation to be the main contribution in the removal of free (both in aerobic and anoxic conditions) and nickel cyanides, while the iron-cyanide were not removed in aerobic tests. The free cyanides (spiked from synthetic solutions) were always biodegraded down to under the detection limit (5 µg/L). Maximum specific removal rates increased from 150 to 450 µg/gVSS d, when the initial free cyanide concentration was increased in the range 50-300 µg/L in batch tests. The aerobic and anaerobic tests showed the contribution of biosorption to be the most important in the first part of the tests while decreasing during the trials.

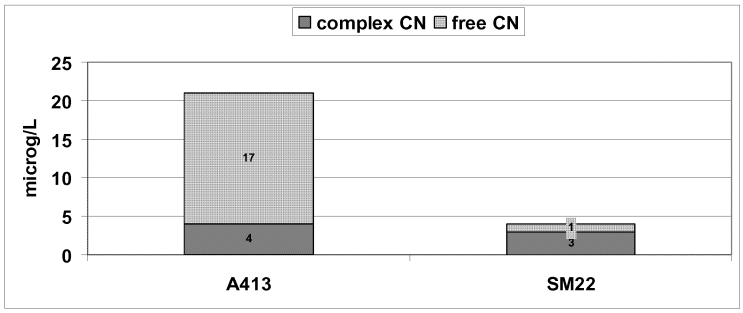

Figure 1 removal of free and complex cyanides in full MBR

Samples averaged over 24 hours were collected from the influent and effluent of the pilot MBR, and analyzed for total and free cyanides,. The results showed constant and stable total cyanide conversions over the three experimental runs, dependent on the F:M ratio. Considering the scale, the real substrate and the durations of the experimentation, these results are reliable to describe also the behaviour of the full scale MBR.
In particular, one may observe that from 0,04 to 0,1 gBOD5/gMLVSS d, the total cyanide removal rates with respect to the real influent were stable and increased from 80 to 99 %, allowing one to obtain effluent cyanide well under 10 µg/L (Figure 2)

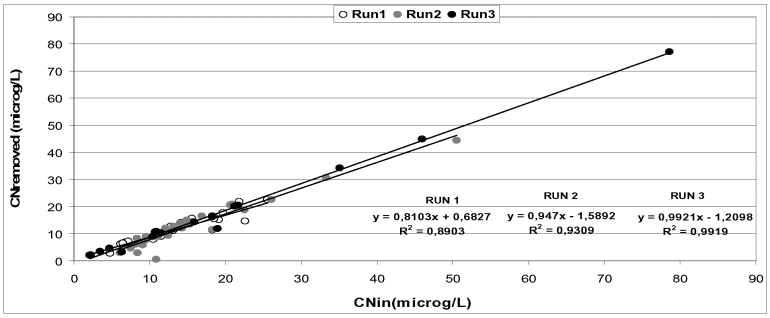

Figure 2 Removal of cyanides during the three experimental runs

Finally the cyanide removal rates calculated by mass balances and using the cyanide conversions over the whole experimental runs are shown in Table 2.

Table 2 Cyanide removal rates at the operating reactor concentration (few ppb) in pilot and full scale MBR

	FULL SCALE	**PILOT SCALE**			
Removal rate	Mass balance	Mass balance	Conversions over the whole runs		
			I run	II run	III run
µgCN/gVSS*h	0,31	0,25	0,31	0,29	0,34

Different calculation methods led to comparable removal rates of around 0,3 µgCN/gVSS*h, much slower than the values found by bench scale tests. (Figure 3a) This may demonstrate that the cyanide biodegradation reaction is substrate-limited for concentration lower than 5÷10 µg/L.

In fact, starting batch tests from concentration of about 80 µgCN/L, the maximum removal rate of free-cyanide was around 7÷10 µgCN/gVSS*h that demonstrate the good removal potential of the activated sludge. Moreover, the activated sludge from pilot-scale plant grown at the highest ratio showed a slightly faster removal than the one from full-scale plant, that also corresponded to a higher overall biological activity.

The latter difference was measured from parallel respirometric tests in the presence of acetate (6.19 and 4.16mgO_2/gVSS/h for pilot-scale and full-scale plant, respectively) and supports the hypothesis that the free-cyanide removal is mostly due to biodegradation. As for the removal of strong and weak metal complexes, fig. 3b shows that Fe-cyanide is not removed (at least in the time scale of the experiment) whereas Ni-cyanide complex is removed at a similar rate to the free-cyanide.

In order to better elucidate the removal mechanisms, batch tests were also performed: i) with no oxygen and the full-scale sludge, or ii) with oxygen but with an acclimated sludge. In both cases, free-cyanide removal was quite slower than in typical aerobic tests with both oxygen and acclimated sludge, so confirming that free-cyanide removal was mostly due to biodegradation..

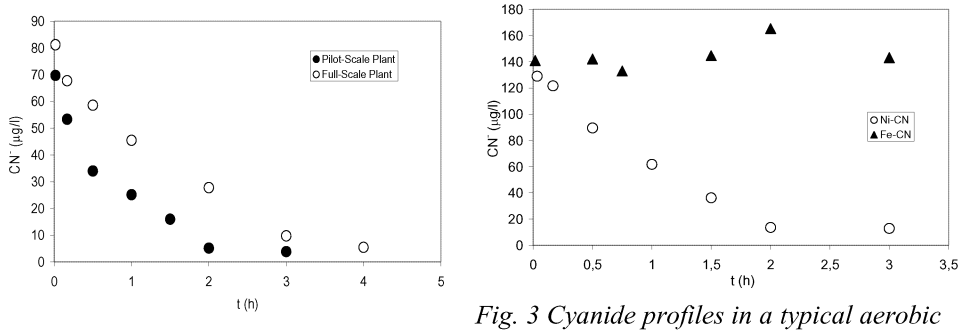

Fig. 3 Cyanide profiles in a typical aerobic batch test: A) free-cianyde with biomass from pilot-scale and full-scale plant; B) Fe-Cyanide and Ni-Cyanide with biomass from full-scale plant

Interestingly, Ni-cyanide was removed at a similar rate by acclimated and unacclimated sludge, that suggests a major contribution was due to adsorption rather than to biodegradation

As a preliminary confirmation, residual cyanides were extracted from the unacclimated sludge after a 90-95% removal of free- or Ni-cyanide had been obtained in parallel aerobic batch tests. The results (not shown) indicated that free-cyanide had been removed by 78% through biodegradation and 22% through biosorption, whereas removal of Ni-cyanide was by 49 and 51%, respectively. However, such results still require confirmation by test with acclimated sludge from pilot and full-scale plants.

4. Conclusions

Removals and final fate of free and total cyanides was investigated treating low loaded real wastewater from a petrochemical industrial area by a pilot membrane bioreactor and bench scale batch tests.

Treating influent concentration of around one hundred µgCN/L, the process was able to reach effluent concentrations lower than 5÷10 µgCN/L, which led the bioreaction to substrate-limited conditions. The major removal mechanism for free cyanides was biodegradation and removal rates passed from around 10 µgCN/gVSS*h, at about 80 µgCN/L, to around 0,3 µgCN/gVSS*h, at 5÷10 µgCN/L. On the other hand, iron-cyanide was almost inert to the biological process, whereas Ni-cyanide was removed at a similar rate to free-cyanide, even though with a different mechanism (the biosorption playing a higher role than for free-cyanide).

As for the operating parameters, stable increases of cyanides conversions (from 81 to 99%) were found increasing the F:M to the aerobic zone of the bioreactors, so to demonstrate the importance of the fraction of active biomass on the cyanide biodegradation.

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