Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.708558

50 (2012) 132–139
December

Taylor & Francis
Taylor & Francis Group

Processes comparison for nickel and chrome removal from urban landfill leachate

Martina Santinelli[a,*], Anna Laura Eusebi[a], Francesco Fatone[b], Enrico Carniani[a], Paolo Battistoni[a]

[a]*Department SIMAU, Polytechnic University of Marche, Via Brecce Bianche 12, 60100 Ancona, Italy*
Tel. +39 071 220 4911; Fax: +39 071 220 4729; email: m.santinelli@univpm.it
[b]*Department of Biotechnology, University of Verona, st. le Grazie 15, 37134 Verona, Italy*

Received 2 March 2012; Accepted 5 June 2012

ABSTRACT

This study aims to examine the feasibility of chemical, physical and biological processes on municipal landfills leachates, to mainly evaluate Nickel (Ni) and Chrome (Cr) removal. Flocculation/coagulation methods were investigated on laboratory scale, by dosing ferric chloride ($FeCl_3$) and aluminium polychloride to three leachates, at a natural pH of 8. The oxidation treatment with sodium permanganate ($NaMnO_4$), applied on the leachate with higher metals content, defined an increment of Ni (from 9 to 50%) and Cr (from 31 to 80%) removals, compared with the previous chemical treatments. Further, the metals biosorption capacity on the biomass flocs was investigated in a pilot scale membrane bioreactor, previously tested on laboratory scale. The different percentages of added leachate showed efficiencies up to 93% for Cr and 58% for Ni, defining the different removal roles of the adsorption and of the membrane layer effect.

Keywords: Landfill leachate; Nickel; Chrome; Coagulation–flocculation; Adsorption; MBR

1. Introduction

Recent scientific and legislative guidelines force the adoption of active strategies to control and reduce the pollution of surface and ground waters caused by anthropogenic emission of organic and inorganic micropollutants, representing a significant risk for the entire environment. The 2000/60/EC Directive [1], a framework in the field of water policy, aims the prevention, protection and improvement of the water quality through specific actions for the progressive reduction and interruption of discharge of non-hazardous and hazardous priority substances, respectively. The Italian Decree 367/2003 [2], established in Annex A quality standards for water environment, chronologically more restrictive to be obtained within 2008 and 2015. Further in Annex B, it is required that non-hazardous liquid wastes (municipal solid waste landfill leachate, septic tank wastes, industrial wastewaters of various origin) cannot be co-disposed at municipal waste water treatment plant (WWTP) but need to be pre-treated, before the inlet to WWTP.

Municipal solid wastes landfill leachate represents high-strength wastewater that plays an important role in liquid waste management, as sanitary landfill is currently the primary method used for municipal solid wastes disposal in many countries. Landfill leachate is a complex mixture of different chemical species, including potentially toxic substances, and its composition exhibits noticeably temporal and site variations. Leachates from young landfills (<5 years) are usually characterized by pH <6.5, high chemical oxygen

---

*Corresponding author.

demand (COD) values (>10 g L^{-1}) and high five day biochemical oxygen demand (BOD_5)/COD ratios (>0.5). In contrast, stabilized leachate from old landfills (>10 years) show a pH > 7.5, moderate COD amounts (<5 g L^{-1}) and low BOD_5/COD ratios due to the presence of high concentrations of recalcitrant organic matters [3]. The principal classes of hazardous contaminants contained in the landfill leachate are represented by toxic recalcitrant organic components and heavy metals. Recalcitrant organic matter comprises natural high molecular weight humic and fulvic-like materials and synthetic components [4]. The concentrations of metals in the leachate widely vary from microgram to milligram per litre. Heavy metals may be present in landfill leachate in different chemical/physical forms: hydrated free ions, colloidal precipitates, labile and non-labile complexes, crystalline precipitates or associated with colloidal or particulate matter. Size charge fractionation (SCF) studies performed by different authors [5,6] have demonstrated that the main part of heavy metals in landfill leachate is strongly associated with organic matter, to form organic complexes and bounded to small-size colloids. Only a small fraction of the metals (<10%) is present as free ions. The complex capacity of the organic substances depends on the presence of functional groups (carboxylic, phenolics, etc.) and is influenced by the pH of the system, as the metal binding is in competition with H^+ ions. Christensen et al. [7] stated that the formation of Cd, Ni and Zn complexes increases with increasing pH. Redox potential is another important factor that influences the oxidation state and the binding mechanism of the metal ions. It should be pointed out that the treatment of landfill leachate can be troublesome due to a high concentration of organic matter, ammonia and the presence of numerous toxic compounds that are difficult to remove.

Biological treatments, both aerobic and anaerobic, are extensively applied with satisfactory results for the reduction of BOD, COD, ammonia and biodegradable organic matter, but these treatments are less effective for the removal of organic recalcitrant compounds and heavy metals. As far as metals removal in activated sludge system, the importance of biosorption and bioprecipitation phenomena and the significant role of extracellular polymeric substances (EPS) have been widely stated [8]. Recent experiences have demonstrated the potential of membrane bioreactors (MBRs) for enhancing the removal of metals and organic xenobiotics from wastewaters with respect to the conventional activated sludge system [9,10].

Nevertheless, due to the complexity of the leachate composition, it appears difficult for a single process to meet the stringent limits set by the recent legislation, thus suggesting the utilization of a selective multistage process. Among the best available techniques (BAT), physico-chemical processes such as chemical oxidation or coagulation/flocculation are recommended for the pre-treatment of landfill leachates, particularly with the scope of reducing the inorganic residue and toxic substances mainly related to the particulate phase. Moreover, the treatment of this matrix using the membrane process was demonstrated to be an efficient technology for the main macropollutants removal (COD and total suspended solids [TSS]) and for the decrement of the heavy metals concentrations linked with the solid phase [11]. More complex is to evaluate the role of these technologies in the removal and the transformation of the recalcitrant heavy metal complexes and free metals ions. The main scope of our study is to evaluate the Nickel and Chrome removal performances, in terms of soluble and complex metals ions, by MBR, oxidation or coagulation and flocculation technologies applied to the landfill leachate. The specific phenomena of advanced oxidation, optimization of coagulation and flocculation and adsorption of activated sludge in the MBR process were studied to remove Nickel and Chrome. The results of laboratory oxidation and flocculation/coagulation tests, as well as laboratory and pilot plant biosorption and bioprecipitation tests using a submerged module of hollow fibre membrane, will be examined and discussed. Moreover, technical applicability and reliability of the process will be evaluated.

2. Materials and methods

2.1. Landfill leachates

The tested leachate samples (called A, B, C, D) were taken from four different municipal solid waste old landfills located in the province of Ancona (Italy). The samples were stored in polyethylene bottles refrigerated at 4°C and the characterization of macropollutants was performed according to Standard Methods [12]. The non-biodegradable soluble COD ($NBCOD_S$) values were determined by submitting the leachate samples to biological degradation for 72 h in a reactor of 1 L capacity, filled with the WWTP activated sludge. Heavy metal concentrations, of nickel and total chrome, were determined by using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyzer (mod. Agilent Technologies 700 ICP/OES). The analytical data were confirmed by using a Varian mod. AA 240-FS spectrometer equipped with a vapour generating accessory for the analysis of Hg and As by cold vapour atomic adsorption.

2.2. Laboratory coagulation/flocculation and oxidation tests procedures

Several laboratory batch tests were performed to evaluate the best conditions for coagulation/flocculation of the leachate samples (A, B and C) using different dosages of ferric chloride and aluminium polychloride (PAC). The dose of coagulant was added to 200 mL of leachate introduced into a glass container and, after an initial rapid mixing for chemicals dispersion, the sample was subjected to slow agitation for 10 min to favour flocs formation and growing. After a sedimentation time of 30 min, a fraction of the supernatant was siphoned off and filtered for relevant analyses. Experiments were performed using a vertical variable mixer IKA-WERK model RW 20 DZM and a stainless steel blade stirrer. Further coagulation/flocculation tests were performed by using polyorganosulphide (POS) as the trapping agent, sodium sulphide as the coagulant and ferric chloride as the flocculant. A solution of sodium permanganate was used for the oxidation of the leachate with the scope of removing and transforming recalcitrant heavy metal complexes in short-chained compounds that are easily treatable. An anionic polyelectrolyte has been added to the sample as a coagulant that aids to increase the flocs settling rate. The samples were left to react with $NaMnO_4$ for 1 h under slow stirring. With the strategy of reducing environmental impact and chemicals consumption, all the physico-chemical tests were performed at pH 8, that is appropriate to the subsequent biological treatment without any pH adjustment.

2.3. Laboratory adsorption batch tests

The potential of the activated sludge as a biosorbent at low metal concentrations was evaluated by bench scale equilibrium tests, with the purpose to calibrate the pilot plant experiments. A stock solution of 3,000 $mg\,L^{-1}$ of Ni^{2+} was prepared by dissolving in deionised water $NiSO_4{\cdot}6H_2O$ (assay 100% w/v) of analytical grade. Tests were performed by mixing in a reactor 10 L of activated sludge, supplied by a WWTP at three different MLSS concentrations (in the range 500–8,000 $mg\,L^{-1}$), with 10 mL of the metal stock solution, so as to have an initial ion concentration of 3.0 $mg\,L^{-1}$ for Ni. The test continued until equilibrium conditions were reached. The activated sludge has a ratio MLVSS/MLSS = 0.53 and a pH of about 8.0. Aeration and sufficient mixing were provided by a diaphragm pump, in order to avoid sludge sedimentation in the reactor. The temperature was maintained at about 20°C. Samples of 100 mL were taken at different time intervals. A portion of each sample was analyzed for pH, MLSS and MLVSS concentrations according to Standard Methods [12]; the remaining amount was pre-filtered at 20 μm, then filtered at 0.45 μm and analyzed for the metal content in the filtrate. All tests were performed at natural pH without any chemical addition. The amount of metal up-taken by the sludge was calculated by the mass balance equation and the Freundlich adsorption isotherm, in view of the high statistical approximation, was used to quantify the affinity between the biomass and the different metals.

2.4. MBR pilot plant facilities

The pilot membrane system was a stainless-steel tank with a working volume of 1,400 L, equipped with an industrial module of submerged hollow fibre membrane (manufactured by GE-Zenon-nominal pore-size of 0.04 μm and membrane area of 21.6 m^2) and with a number of on-line sensors/analysers. An air diffuser located beneath the membrane module provided aeration, mixing and membrane scouring to prevent fouling. The system could automatically operate, according to constant permeate fluxes and different filtration cycles (permeation/backwashing/relaxation), with time set points adjustable by a Programmable Logic Controller (PLC). The pilot plant was installed in proximity of a full scale Italian municipal wastewater treatment plant (60,000 PE). Two experimental campaigns were carried out using two different plant configurations.

2.5. MBR assisted biosorption of metal ions

In the first campaign the benefit of membrane biosorption of a synthetic solution of metal ions was tested in a continuous operating MBR. The pilot plant was fed with a mixture of sludge (MLSS content of 9 $g\,L^{-1}$) and effluent coming from the secondary sedimentation tank of a full scale WWTP and was charged with a synthetic solution of $Ni(NO_3)_2$ (assay 100% w/v) diluted with tap water, so as to have in the reactor a constant concentration of 5 $g\,L^{-1}$ of MLSS and a constant concentration of 2 $mg\,L^{-1}$ of the metal (Fig. 1). The membrane-filtered effluent was extracted by a centrifugal pump at a rate of 9 $L\,m^{-2}\,h^{-1}$, equivalent to about 200 $L\,h^{-1}$, in constant flux mode. To reduce membrane fouling, the pilot plant operated automatically for 300 s in the filtration mode and for 30 s in the backflushing mode. The experiment was run for 5 hours at a natural pH of about 8 and continuously aerated. The first permeate sample was collected after

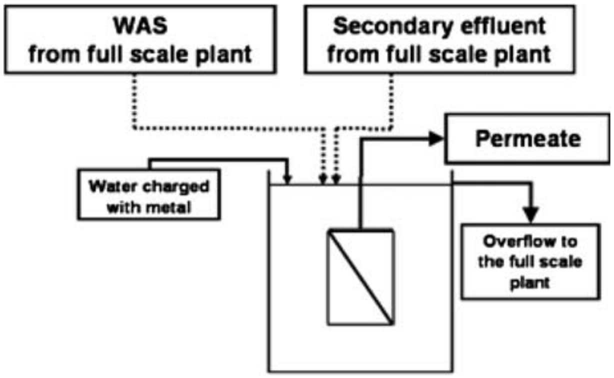

Fig. 1. Configuration of the membrane pilot plant charged with metal ions.

5 min, the following ones were taken every hour and analyzed for Ni concentration. In parallel, samples from the pilot reactor were filtered at 0.45 μm and analyzed for the dissolved metals in the reactor. This approach allowed to make hypothesis on the final form of the metals: (a) biosorbed on the cell wall or bioaccumulated; (b) biosorbed on the soluble EPS or bound to colloids smaller than 0.45 μm; (c) remained as dissolved cations or bound to molecules that permeate the UF membrane.

2.6. MBR assisted biosorption of landfill leachate

The second experimental campaign in the MBR pilot plant was carried out to treat the real landfill leachate coming from a municipal solid waste landfill (sample D) and showing the concentrations of Ni and Cr as reported in Table 1. The simplified flow sheet of the MBR pilot plant for the treatment of the real landfill leachate is showed in Fig. 2. To evaluate the effect of the leachate percentage on the biosorption process, the membrane reactor was filled with a mixture of waste activated sludge (WAS) and landfill leachate at three different volume ratios (volume ratios (%) leachate/(WAS + leacheate) 29, 43, 57%, respectively, for test 1, 2 and 3). Every test lasted 6 h with a pH of the mixture in the range of 7.9–8.2, as naturally established from the two mixed liquors. Every 60 min the permeation pump was switched on to take a permeate sample and at the same time a mixture sample was taken from the reactor and filtered at 0.45 μm. Both samples were analyzed for Ni and Cr concentrations.

3. Results and discussion

3.1. Characterization of the tested samples

All the samples are characterized by a pH value ≥8, typical of stabilized leachates (Table 1). The leachates A and C show higher values of alkalinity, COD and ammonia with respect to leachates B and D. Some toxic metals as Pb, As and Hg are present in concentrations lower than their detection limit, while Ni and Cr are contained in the samples at concentrations in the range of 122–317 $\mu g\,L^{-1}$ and 309–820 $\mu g\,L^{-1}$, respectively. Vacuum filtration on membrane filter at 0.45 μm was used for the distinction between dissolved and particulate fractions [13]. As a matter of fact, only the size fraction <0.001 μm must be considered as the truly dissolved fraction, whereas the size fraction between 0.001 and 0.45 μm should be regarded as small size colloidal fraction. From the

Table 1
Raw leachates macro and micro pollutants

Parameter	m.u.	A	B	C	D
pH		8.08	8.23	7.99	7.95
Specific conductivity	$mS\,cm^{-1}$	23.93	15.25	34.3	6.47
Alcalinity	$mg\,CaCO_3\,L^{-1}$	11,086	6,504	14,364	2,219
TSS	$mg\,L^{-1}$	380	360	690	174
TVS/TS	%	24.37	28.52	24.64	22.5
COD	$mg\,L^{-1}$	3,962	2,331	4,654	802
COD_S	$mg\,L^{-1}$	3,808	1,702	4,077	660
NH_4-N	$mg\,L^{-1}$	1,648	1,092	2,430	452
TKN	$mg\,L^{-1}$	1,822	1,265	2,732	511
Ni tot	$\mu g\,L^{-1}$	317	128	122	177
Cr tot	$\mu g\,L^{-1}$	748	309	820	536
Ni sol	%	91.2	99.2	98.4	96
Cr sol	%	89.0	96.4	80.6	89

Note: Detection limits defined on the basis of three times the standard deviation of the blank.

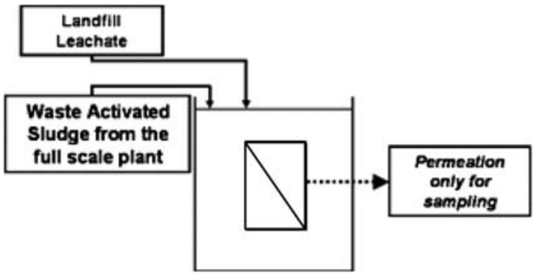

Fig. 2. Configuration of the membrane pilot plant for landfill leachate treatment.

analyses of the filtrates at 0.45 μm, it can be observed that the metals are mainly in the soluble form, on average 96.3% of Ni and 88.8% of Cr (Table 1).

3.2. Laboratory coagulation/flocculation and oxidation batch tests

The results of the analyses performed on the filtrates of A, B and C leachate samples after flocculation with ferric chloride and PAC are reported in Table 2. It can be observed that the percentages of Ni and Cr removals are quite unsatisfactory and slightly increase by increasing the coagulant dose. Cr removal is higher than Ni at all different test conditions. The best results were obtained by the addition of 200 mg/L of Al (9.4% of Ni and 31.4% of Cr reductions, respectively, for the sample B; 8.2% of Ni and 25.7% of Cr for sample A, 15.2% of Cr removal in sample C). The COD removal at the maximum dosage of flocculant ranges from 3.6 to 36.5%. Further, coagulation/flocculation tests were performed on leachate A, that contains a high concentration of heavy metals, as Cr and Ni (Table 1), using sodium sulphide (10 and 20 $mg\,S\,L^{-1}$) as the coagulant with and without the addition of ferric chloride (100 $mg\,Fe\,L^{-1}$) to improve flocs formation (Table 3). Sulfuration treatment is characterized by the low solubility of metal sulphides, lower than that of metal hydroxides. The solubility of various metal sulphide depends strongly on the pH value, (for example the minimum solubility of NiS corresponds to pH ~10) so it is difficult to obtain the combined removal of different species working at one defined pH. The results of the tests show at the dosage of 10 $mg\,S\,L^{-1}$ there is poor reduction of Ni (7.2%) and Cr (4.6%). The increasing of the Na_2S dosage and the addition of $FeCl_3$ do not change the previous results. As the insignificant changes in pH, due to the buffering capacity of bicarbonate, no pH corrections were necessary. Traditional coagulation/flocculation tests were modified by using different dosages of polyorganosulphide as the coagulant and 100 $mg\,Fe\,L^{-1}$ of $FeCl_3$ as the flocculant. According to the manufacturer specifications, the product can be applied to the removal of Cr and Ni at concentrations lower than 700 $\mu g\,L^{-1}$ in leachate landfills, in the pH range 8–9. Considering the Na_2S dosage, no difference in COD, Ni and Cr removal was noticed with or without the $FeCl_3$ dosage, with an average efficiency of about 13, 8 and 5.4%, respectively. Also referring to POS, as reported in Table 3, the results were quite unsatisfactory showing a maximum removal of about 20 and 25%, respectively, for Ni and Cr, at a polyorganosulphide dosage of 40 $mg\,L^{-1}$. By increasing the POS dosage up to 130 and 200 $mg\,L^{-1}$, the COD removal efficiency increased to about 40%, despite a net reduction in Ni and Cr removal (on the average 0 and 15% each). No significant difference was noticed for the COD removal if adding 40 $mg\,L^{-1}$ (plus 100 $mg\,L^{-1}$ of $FeCl_3$) or 194 $mg\,L^{-1}$ (without $FeCl_3$ dosage) of POS, while Ni and Cr removals reduced by more than half. Small percentage reductions obtained by the previous

Table 2
Results of $FeCl_3$ and PAC coagulation/flocculation tests at pH 8

Leachate	Coagulant dosage $mg\,L^{-1}$ as Fe/Al	Ferric chloride			Aluminium polychloride		
		COD removal (%)	Ni removal (%)	Cr removal (%)	COD removal (%)	Ni removal (%)	Cr removal (%)
A	50	22.2	4.5	8.7	0	2.8	12.3
A	100	18.7	6.0	11.7	0	5.3	14.8
A	200	17.3	4.6	20.5	6.4	8.2	25.7
B	50	19.6	0	6.8	25.4	6.3	3.6
B	100	23.7	0	11.3	34.5	8.6	14.6
B	200	31.2	0	19.7	36.5	9.4	31.4
C	50	1.1	0	0.4	0	0	0.5
C	100	8.6	0	3.5	0	0	7.3
C	200	3.6	0	14.9	8.6	0	15.2

Table 3
Coagulation/flocculation tests of leachate A at free pH

Coagulant type and dosage	$FeCl_3$ (mg Fe L^{-1})	Final pH	COD removal (%)	Ni removal (%)	Cr removal (%)
Na_2S, 10 mg S L^{-1}	0	8.31	12.0	7.2	4.6
Na_2S, 20 mg S L^{-1}	0	8.32	14.8	8.0	5.4
Na_2S, 10 mg S L^{-1}	100	8.19	12.9	8.7	5.8
POS, 28 mg L^{-1}	100	8.19	14.2	11.4	25.4
POS, 40 mg L^{-1}	100	8.13	18.2	19.6	24.4
POS, 130 mg L^{-1}	100	8.04	42.8	0	21.7
POS, 200 mg L^{-1}	100	8.04	39.5	0	11.6
POS, 194 mg L^{-1}	0	8.07	23.3	6.2	7.1

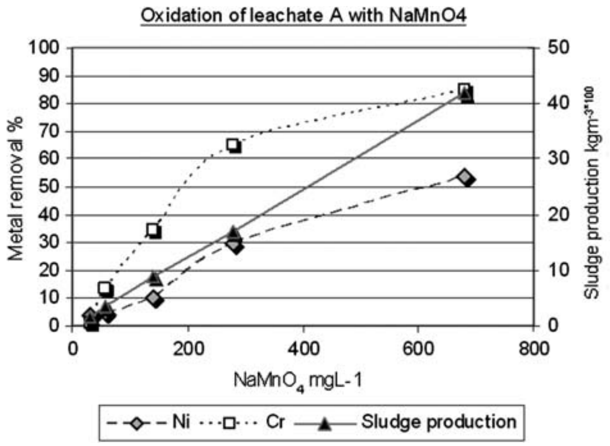

Fig. 3. Ni and Cr removals by oxidation of sample A with $NaMnO_4$.

tests were correlated to the presence of soluble non-labile Cr and Ni organic complexes, there are difficult to remove by coagulation/flocculation process. Thereby oxidation tests with $NaMnO_4$ were carried out with the scope to break up these compounds and transform them into more easily treatable components. Permanganate has been selected because it is widely used in industrial wastewater treatment system to oxidize organic and inorganic pollutants including chelated metals, As, Mn and Fe. After the dosage of $NaMnO_4$ at free pH, insoluble manganese dioxide (MnO_2) is formed as an oxidation by-product and an anionic polyelectrolite at medium anionic charge was added to the samples at the concentration of 1 mg L^{-1}, to favour MnO_2 precipitation. A little increase in pH (about 0.1–0.2 units) was observed due to the alkaline properties of permanganate. Fig. 3 shows that the removal of heavy metals increases with the dosage of the oxidant. By adding 0.68 g L^{-1} of $NaMnO_4$, reduction of about 54% of Ni and 85% of Cr was observed while the sludge production consequentially increased with the oxidant addition, from 0.02 to 0.42 kg m^{-3}. Considering the high cost of permanganate salts, it is necessary to evaluate process optimization in order to establish economical feasibility of the system.

3.3. Laboratory adsorption tests

Three adsorption tests were performed for Ni at an initial concentration of 3 mg L^{-1} and at different biomass contents. About 2 h were needed to reach the equilibrium conditions for the liquid/solid systems, but it can be observed from Table 4 that the metal ion uptake was very fast in the first 5 min, particularly at higher MLSS concentrations. The removal efficiency (E_r) for Ni increased by increasing the biomass concentration. At the highest MLSS concentrations the

Table 4
Adsorption of Ni on activated sludge at initial conc. of 3 mg L^{-1}

Parameter	m.u.	Test 1	Test 2	Test 3
MLSS	mg L^{-1}	7,579	5,822	683
C after 5 min	mg L^{-1}	0.12	0.23	1.17
C_e	mg L^{-1}	0.08	0.12	0.78
E_r after 5 min	%	96.0	92.3	61.0
E_r after 2 h	%	97.3	96.0	74.0
X/M	mg Ni g $MLSS^{-1}$	0.385	0.495	3.25

Table 5
MBR adsorption test of metal ions

Time	Ni			
	Filtrate 0.45 μm		Permeate	
	Conc. ($mg\,L^{-1}$)	Retention (%)	Conc. ($mg\,L^{-1}$)	Retention (%)
0	2			
5 min	0.18	91.0	0.03	98.5
1 h	0.17	91.5	0.10	95.0
2 h	0.17	91.5	0.13	93.5
3 h	0.18	91.0	0.14	93.0
4 h	0.18	91.0	0.16	92.0
5 h	0.18	91.0	0.17	91.5

removal efficiency, at equilibrium conditions, was equal to 97.3%. On the other hand, the specific uptake (X/M) expressed as $mg\,Me\,g\,MLSS^{-1}$, increases for a lower value of biomass concentration. The available literature data confirmed the obtained specific uptake rate: Dias et al. [14] achieve X/M values for Ni equal to $0.4\,mg\,Ni\,g\,MLSS^{-1}$ (biomass concentration of $2\,g\,L^{-1}$) on average while a medium value of $6\,mg\ Ni\,g\,MLSS^{-1}$ was determined with a biomass concentration of $0.5\,g\,L^{-1}$ [15]. Moreover, adsorption data fit very well in the Freundlich model, with a regression coefficient $R^2 > 99\%$ and values of the constants k and $1/n$ equal to 4.0685 and 0.958, respectively.

3.4. MBR-assisted biosorption of metal ions

The MLSS concentration, monitored on line, shows an approximately constant value of $5\,g\,L^{-1}$ with a maximum variation of 5%. The transmembrane pressure was constant between −0.287 bar and −0.289 bar indicating that no appreciable fouling phenomena occurred during the test. Notwithstanding the different experimental conditions, the results of MBR treatment of synthetic solution added with $2\,mg\,L^{-1}$ of Ni, reported in Table 5, substantially confirmed the data obtained by laboratory adsorption tests as they show in the filtrate at 0.45 μm a fast metal reduction, larger than 90%, caused by sludge biosorption. At the same time higher metal removals are measured in the permeate, as the membrane, that has a nominal pore size of 0.04 μm, is capable to remove also part of colloids and macromolecules that are not retained by the membrane filter. Both the concentrations in the filtrate and in the permeate reached stable values after 2 h. It is interesting to note, that the Ni content in the permeate increases gradually with time starting from $0.03\,mg\,L^{-1}$ after 5 min to $0.17\,mg\,L^{-1}$ after 5 h of tests running, with the consequence that the additional membrane filtration effect becomes negligible. Concerning the concentration in the filtrate at 0.45 μm, the Ni amount shows a constant value of $0.17–0.18\,mg\,L^{-1}$ throughout the test. This behaviour, which is in contrast with that observed from laboratory adsorption tests, in which metal concentrations decreased with process time, is not easy to explain as the complexity of biosorption phenomenon. It can be said that Ni has significant affinity to biosorption, confirmed by the data summarized in Table 4, and that a possible layer effect of the membrane could have occurred. Hence, a progressive filling of the free membrane pores and a slow reduction of the layer effect, could have determined the slight increase in the metal concentration in the permeate.

Table 6
MBR adsorption test of landfill leachate (sample D)

	Metals	Initial conc. ($\mu g\ L^{-1}$)	Mixture filtrate at 0.45 μm		Permeate	
			Conc. ($\mu g\,L^{-1}$)	Retention (%)	Conc. ($\mu g\,L^{-1}$)	Retention (%)
Test 1	Ni	48.6	24.0	50.6	20.0	58.8
	Cr	136	17.5	87.1	9.0	93.4
Test 2	Ni	97.1	39.0	59.8	37.5	61.4
	Cr	273	16.0	94.1	11.5	95.8

3.5. MBR-assisted biosorption of landfill leachate

The results of membrane assisted-biosorption of a real landfill leachate after 2 h of tests are reported in Table 6, within the corresponding analyses performed on a mixture sample filtrate at 0.45 μm, to evaluate the metal content in the soluble fraction. For all the tests high removal of Cr was determined in the permeate, up to 95.8%, while at the same time for Ni lower removals, in the range 58.8–61.4%, were observed. The adsorption efficiencies seem to be independent of the volume ratio WAS/leachate, as better results were obtained in tests 2 with the lower WAS volume. The additional membrane filtration effect is remarkable for Cr, while lower enhancements of Ni retentions were observed in the permeate. By a comparison of the above results with those obtained from the adsorption tests of a synthetic solution of metal ions, it seems to be confirmed that the major part of the soluble Ni is present in the percolate as Ni-complexes, which, differently from metal ions, are not effectively adsorbed on the activated sludge. In a practical point of view it can be calculated from test 2 that for the biosorption process 6.75 kg MLSS m^{-3} leachate is required, corresponding to 5.4 kg of biomass per m^3 leachate, supposing a MLVSS/MLSS ratio of 0.8. Assuming an observed cell yield (Y_{obs}) = 0.35 kg MLVSS kg COD^{-1} (transformed COD considering a COD removal of 70%) and a population equivalent factor of 0.12 kg COD $P.E.^{-1}$ d^{-1}, it results that 183 P.E. are necessary to process 1 m^3 of leachate daily.

4. Conclusions

Chemical, physical and biological processes have been investigated to evaluate Ni and Cr removal, in municipal landfill leachates. The matrixes complexity highlighted the narrow reductions (Cr 31% and Ni 9%) using high traditional chemicals dosages. The removals increment (Cr 80% and Ni 50%) was achieved with advanced oxidation ($NaMnO_4$) to the detriment of the chemical sludge production with related higher costs in a possible full scale application. The biosorpion determined on bench scale the high Nickel affinity to the biomass (3.25 mg Ni g $MLSS^{-1}$). This mechanism, tested on leachate in a MBR, defined higher efficiencies that increased to 93% (Cr) and 58% (Ni) if considering the membrane layer effect. These results define a further advantage for the full scale MBR application, added to the already ensured macropollutants removals MBR performances.

Acknowledgement

The authors acknowledge the Fondazione Cariverona for the support to the scientific activity, within the project "Biomasse di oggi e di domani: dai reflui zootecnici e dalle microalghe un contributo all'agricoltura sostenibile e all'energia rinnovabile".

References

[1] 2000/60/EC Directive. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy, 2000.

[2] Italian Decree 367/2003, Regolamento concernente la fissazione di standard di qualità nell'ambiente acquatico per le sostanze pericolose, ai sensi dell'articolo 3, comma 4, del decreto legislativo 11 maggio 1999, n. 152 (2003).

[3] A. Amokrane, C. Comel, J. Veron, Landfill leachate pretreatment by coagulation-flocculation, Water Res. 31 (1997) 2775–2782.

[4] Monje-Ramirez., M.T. Orta de Velásquez, Removal and transformation of recalcitrant organic matter from stabilized saline landfill leachates by coagulation–ozonation coupling processes, Water Res. 38 (2004) 2359–2367.

[5] J.B. Christensen, T.H. Christensen, Complexation of Cd, Ni and Zn by DOC in polluted groundwater: A comparison of approaches using resin exchange, aquifer material sorption and computer speciation models (WHAM and MINTEAQ2), Environ. Sci. Technol. 33 (1999) 3857–3863.

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

[7] J.B. Christensen, T.H. Christensen, The effect of pH on the complexation of Cd, Ni and Zn by dissolved organic carbon from leachate-polluted groundwater, Water Res. 34 (2000) 3743–3754.

[8] S. Comte, G. Guibaud, M. Baudu, Relations between extraction protocols for activated sludge extracellular polymeric substances (EPS) and EPS complexation properties Part I. Comparison of the efficiency of eight EPS extraction methods, Enzyme Microb. Technol. 38 (2006) 237–245.

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

[10] F. Cecchi, L. Innocenti, D. Bolzonella, P. Pavan, Membrane bioreactor processes: a must for the wastewater treatment plants of the lagoon of Venice, Annal. Chim. 93 (2003) 381–388.

[11] A.L. Eusebi, M. Santini, A. De Angelis, P. Battistoni, MBR and alternate cycles processes: advanced technologies for liquid wastes treatment, Chem. Eng. Trans. 24 (2011) 1057–1062.

[12] APHA, Standards Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, DC, 2010.

[13] A.J. Horowitz, K.R. Lum, J.R. Garbarino, G.E.M. Hall, C. Lemiex, C.R. Demas, Problems associated with using filtration to define dissolved trace element concentrations in natural water samples, Environ. Sci. Technol. 30 (1996) 954–963.

[14] M.A. Dias, C.A. Rosa, V.R. Linardi, R.A. Conte, H.F. De Castro, Application of factorial design to study of heavy metals biosorption by waste biomass from beverage distillery, Appl. Biochem. Biotechnol. 91–93 (2001) 413–422.

[15] M.A. Dias, H.F. Castro, P.F. Pimentel, N.C.M. Gomes, C.A. Rosa, V.R. Linardi, Removal of heavy metals from stainless steel effluents by waste biomass from Brazilian alcoholic beverage production, World J. Microbiol. Biotechnol. 16 (2000) 107–108.