Desalination and Water Treatment
www.deswater.com
9 (2009) 136–141
1944-3994/1944-3986

Treatment of landfill leachate in a bench scale MBR

J. Svojitka[a,b], T. Wintgens[a,*], T. Melin[b]

[a]School of Life Sciences, Institute for Ecopreneurship, University of Applied Sciences Northwestern Switzerland, Gründenstr. 40, CH-4132 Muttenz, Switzerland
[b]Aachener Verfahrenstechnik, Chair of Chemical Process Engineering, RWTH Aachen University, Turmstr. 46, D-52056 Aachen, Germany
email: thomas.wintgens@fhnw.ch, jan.svojitka@fhnw.ch

Received 15 September 2008; Accepted 5 November 2008

ABSTRACT

In the present work, a bench-scale MBR plant treating landfill leachate was operated for a period of 6 months. The volume of the activated sludge tank was approx. 50 L and it was coupled with a polyethersulphone (PES) tubular membrane with pore size in the ultrafiltration range. The monitoring of the pilot plant was aimed at biological parameters (removal of nitrogen, COD and BOD) and filtration properties of the membrane (permeabilities in relation to cross-flow velocity, trans-membrane pressure and sludge concentration). Because of the high content of xenoestrogenic substances in the landfill leachates, the concentration of bisphenol A (BPA) was followed in influent, mixed liquor and permeate.

Regarding the results on carbon removal, overall COD removal was less than 30% in most cases, while BOD removal was 91%. Nitrification efficiency was 90–99% (decrease of ammonia nitrogen from 1200 mg/L to 10–150 mg/L), denitrification was only possible after addition of external substrate (methanol).

Removal of BPA was highly efficient – from an initial concentration in the influent of 2100 μg/L to less than 1 μg/L in the effluent.

The membrane permeabilities varied from 3.5 to 40 L/(m²/h/bar) (LMH/bar) depending on the operational conditions (cross-flow velocity, trans-membrane pressure and biomass concentration).

Keywords: Landfill leachate; Membrane bioreactor; Bisphenol A

1. Introduction

Landfill leachate is produced in the landfill body as a result of percolation of rainwater through the waste deposited, or originating from the waste itself. It is a complex wastewater highly loaded with organic matter, nitrogen, suspended solids and heavy metals. The organic load (mainly fatty acids and humic substances) is usually between 500–20 000 mg/L COD [1, 2].

Because of the complexity of the pollutants present in landfill leachates, it is advantageous to combine more then one treatment procedure to reach the desired effluent quality. Often a concept of activated sludge process followed by one of the physical methods is used (e.g. nanofiltration, chemical oxidation, adsorption) [2].

Besides naturally occurring compounds, numerous chemicals of anthropogenic origin (xenobiotic compounds) have been detected in landfill leachates. Many of them constitute a potential risk to the environment because of their toxicity, biological activity or persistence. Xenobiotic compounds with endocrine disruptive properties (EDCs), such as bisphenol A (BPA) or nonylphenol are frequently found in landfill leachates in high concentration. (up to 17 mg/L of BPA) [4].

---

*Corresponding author.

Presented at the Conference on Membranes in Drinking and Industrial Water Production, 20–24 October 2008, Toulouse, France.

Bisphenol A is a compound widely used in the production of polymers, as development agent in a thermal paper or as anti-oxidant. Besides its estrogenic effect it is also toxic to water organisms. Contamination with BPA was found in water bodies, fish and sediments. The most important sources of this pollutant are wastewater effluents and landfill leachates. Concentrations up to 17 mg/L of BPA were found in landfill leachate [4].

It has been reported that the activated sludge process can successfully degrade EDCs including BPA. Removal efficiencies were found between 70–99.9%. The elimination is attributed to processes of adsorption and biological degradation since volatilization is negligible due to the low vapour pressure of BPA [6, 7].

The main aim of this project was to optimize the performance of a laboratory-scale MBR plant for landfill leachate treatment with respect to nitrogen and COD removal. The membrane performance was characterized by measurement of its permeability at different operational conditions. Since landfill leachates represent an important source of xenobiotic compounds, measurement of the elimination of bisphenol A was included in the project.

2. Materials and methods

2.1. Pilot plant

The scheme of the pilot plant is shown in Fig. 1 with the design parameters listed in Table 1. It consisted of an activated sludge tank (total volume 50 L) with three compartments in series (14–22 L each) which could be operated either as anoxic (denitrification) or aerated (nitrification). The biological part is followed by a membrane module, which was formed by a tubular ultrafiltration membrane made of polyethersulphone (PES). The cross-flow was induced by a screw pump with frequency regulation.

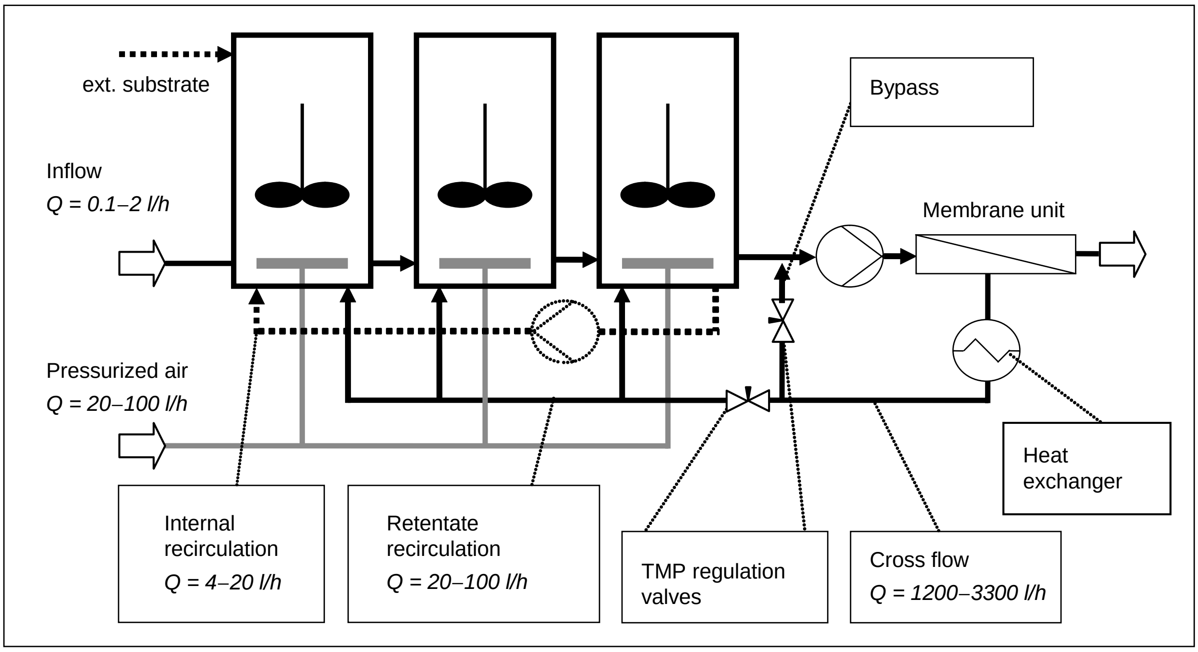

Fig. 1. Flow scheme of the pilot plant.

Table 1
Technological parameters of the MBR pilot plant.

Biological part		Membrane unit	
Influent flow	0.3–2.0 L/h	Manufacturer	Microdyn Nadir
Volume of the tanks	22, 17 and 14 L	Membrane material	PES
Sludge concentration	10–15 g/L	MWCO	70 kDa
Hydraulic retention time	70–170 h	Membrane area	0.1 m^2
Solids retention time	100 days	Cross flow velocity	0.6–1.9 m/s
Internal recirculation	1–5 L/h	TMP	2–4 bar

Table 2
Composition of influent water.

Parameter	N–NH$_4^+$	N–NO$_2^-$	N–NO$_3^-$	N$_{org}$	P$_T$	COD	BOD	pH	BPA
mg/L	1200	0.25	8.5	50	15	2200	100	8.5	2.1

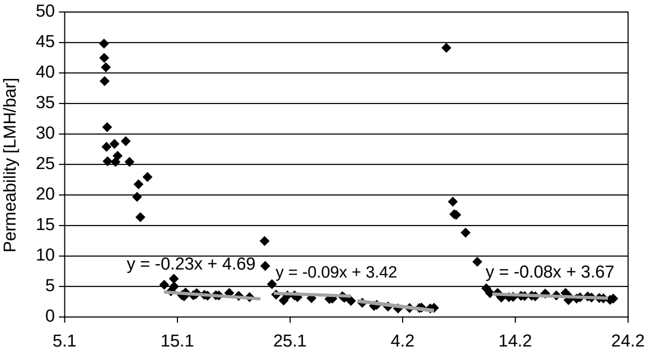

Fig. 2. Evaluation of regions with stable fouling.

Electronic sensors were used for measurement of trans-membrane pressure (TMP), cross flow and return flow of retentate into activated sludge tank, permeate flow was measured by means of rotameter.

2.2. Landfill leachate

The landfill leachate serving as influent into the pilot plant was collected at the landfill in Alsdorf-Warden (Germany), its chemical composition can be seen in Table 2.

2.3. Chemical analyses

Samples of influent, permeate and activated sludge were withdrawn regularly and subjected to following analyses:

- COD, Nitrogen, Phosphorus – using cuvette tests LCK from Hach—Lange measured in the photometer LASA 100 from the same company,
- BOD$_5$ – using dilution and seeding method,
- BPA – before the measurement the samples were concentrated using the SPE method and subsequently analyzed by linear ion trap LC-MS/MS Thermo LXQ. The column used was Hypersil Gold 5µ, mobile phase water + methanol. Ionization was conducted by APCI (–), deuterated BPA-d16 served as internal standard.

3. Results

3.1. Relation between membrane permeability and operational parameters

Based on the data obtained at different operational conditions, measured permeabilities were plotted versus TPM, cross-flow velocity and concentration of biomass (suspended solids). The evaluation procedure is illustrated in Fig. 2: In the chart of permeabilities were found stable regions characterized by stable fouling rate (following regions of rapid decrease immediately after cleaning) and constant operational parameters. Trend lines of permeabilities in these regions were calculated, characterized by slope (fouling rate) and intercept (stable permeability).

Results are summarized in Table 3. The most evident trend is the dependency of fouling rate on the cross flow velocity. While at 1.7–1.8 m/s the fouling rate is usually below 0.4 LMH/bar/d, lower velocity lead to fouling rate above 1 LMH/bar/d. The role of biomass concentration does not seem to have significant influence on the filtration performance; this effect was also reported from other case studies [8]. On the other hand, trans-membrane pressure affects the level of the stable filtration plateau – 41 LMH/bar at 0.5 bar compared to 3–17 LMH/bar at pressures around 1 bar.

3.2. Nitrogen removal

Results on nitrogen removal are depicted in Fig. 3 and Fig. 4. The layout of aerated and anoxic tanks was changed several times to study its influence on nitrogen removal. In some periods, methanol was dosed into the anoxic tank to support the denitrification. The time schedule of the layout changes can be seen from Fig. 4.

Removal of ammonia (Fig. 3) was evaluated from the difference between influent and effluent concentration of ammonia nitrogen. It was working with approx. 90% efficiency before 15.2. (exchange of a part of the mixed liquor) and with over 99% efficiency after this date. However, a strong increase in concentration of nitrites in the effluent can be seen since the beginning of operation. A possible cause of this was the problem with aeration of the tank due to foaming problems. Although the use of antifoaming agent after 30.1. helped to increase dissolved oxygen (DO) concentration above 1 mg/L, the excessive concentration of nitrites was not suppressed, possibly because of the substrate inhibitory effect to nitrite oxidizing bacteria [9–11]. Thus, it was decided to solve the situation by replacement of 50% of mixed liquor by fresh activated sludge from the LLTP Alsdorf Warden diluted with tap water. This helped to decrease the concentration of nitrite nitrogen, but its concentration still remained over 200 mg/L in most cases. On the other

Table 3
Permeability versus TMP, cross flow and suspended solids.

TMP [bar]	Cross flow [m/s]	Suspended solids [g/L]	Fouling rate [LMH/bar/d]	Stable permeability [LMH/bar]
0.5	1.5	10.3	2.13	41.20
	1.7	8.4	0.24	12.17
		10.7	0.23	4.69
0.9		7.1	0.35	10.57
	1.8	8.9	0.33	12.41
		10.7	0.08	3.67
	1.2	7.2	1.99	7.14
1.0		10.4	0.09	3.42
	1.8	12.6	0.73	7.47
		13.8	0.13	3.67
	0.8	8.4	0.99	4.26
1.15	1.3	10.2	2.41	16.62
	1.80	9.6	0.21	2.85

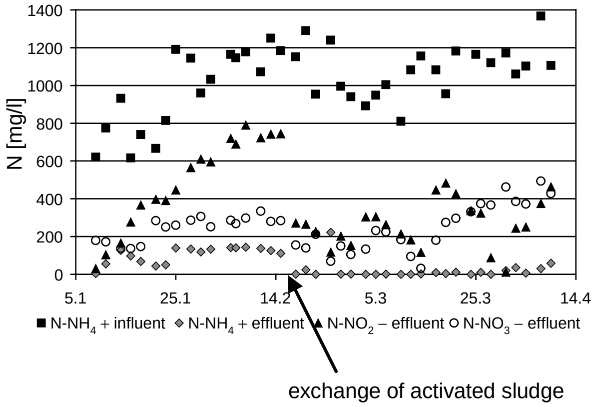

Fig. 3. Nitrification.

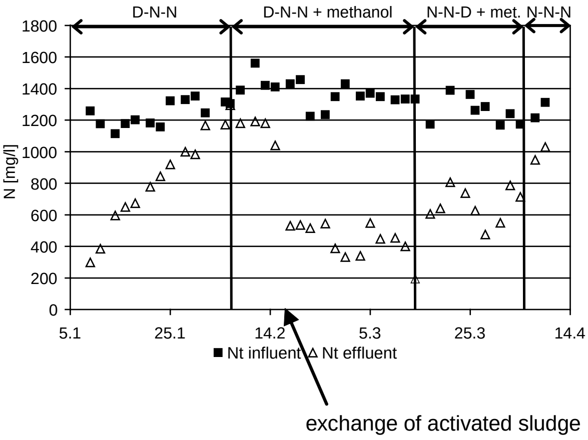

Fig. 4. Denitrification. Different layouts of activated sludge tank are indicated.

hand, production of excessive amounts of nitrites can also originate from denitrification, where they act as intermediate as well. Their release was reported in processes with shortage of organic matter [10–12] which was true in the beginning of the experiment – before dosing of methanol. Therefore it cannot be concluded, whether the excessive nitrites come from nitrification or denitrification. The graph in Fig. 4 illustrates the removal of nitrate nitrogen by denitrification. Its function can be evaluated from the difference between total nitrogen in the influent and effluent from the biological tank, since nitrogen can be only removed by conversion of NO_3^- (or NO_2^-) to nitrogen gas (neglecting the assimilation in new biomass). In the initial period the effluent concentration of nitrogen increased until it reached the influent level. Despite the presence of anoxic regions in the activated sludge tank, no significant denitrification activity was expected, since no external substrate was added. The dosing of methanol to the denitrification tank was started on 7th February, nevertheless it did not lead to any removal of nitrogen, probably because of the inhibitory effect of nitrites. After the exchange of a part of the activated sludge an immediate drop of the concentration of nitrogen was observed to approx. 30% of the initial concentration and remaining relatively stable till the end of the measurement. Slightly lower efficiency of nitrogen removal was reached in the post-denitrification layout (13th March to 4th April), presumably because the organic matter in the landfill leachate was no more available for denitrifaction.

The dose of external carbon was set to COD:N_{influent} ratio = 3. The removal of 50–75% of nitrogen is thus in compliance with experience from other sites (consumption in anoxic reactors is reported between COD:N = 4–6) [12].

Table 4
Concentration of BPA in influent, filtrate of mixed liquor and removal efficiency.

Date	Influent µg/L	Liquid phase of activated sludge µg/L	Permeate	
			µg/L	% removal
14.11.2007	2100	70	70	96.67
11.1.2008	2100	1.9	1,9	99.91
15.1.2008	1735	3.5	1.7	99.90
22.1.2008	2010	0.4	<0.1	>99.99
28.1.2008	2720	2	<0.1	>99.99
5.2.2008	2155	9	4.5	99.79
12.2.2008	2200	0.6	<0.1	>99.99
19.2.2008	2040	0.6	<0.1	>99.99
26.2.2008	2240	3.5	<0.1	>99.99
18.3.2008	2135	<0.1	<0.1	>99.99
25.3.2008	2052	<0.1	<0.1	>99.99
1.4.2008	2175	0.8	0.4	99.98
8.4.2008	2140	<0.1	<0.1	>99.99

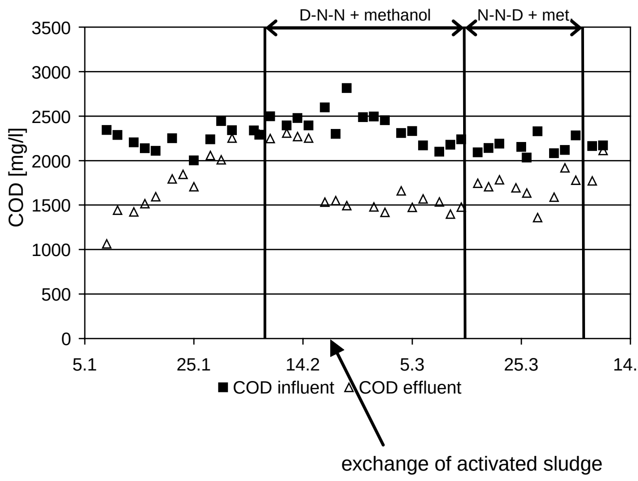

Fig. 5. COD removal during the 4th phase.

3.3. COD

Results on COD removal are shown in Fig. 5. Deterioration prior to the sludge exchange was likely connected with a high concentration of nitrites in mixed liquor resulting in inhibition of heterotrophic microorganisms (discussed above). The exchange of the biomass led to an improvement of COD degradation, reaching 30–40% in the D-N-N layout and 20–30% in the N-N-D layout. Higher effluent concentration of COD in the post-denitrification period was probably caused by the presence of residues of external substrate, since the mixed liquor from the last compartment is led to the filtration unit.

Biological oxygen demand (BOD_5) of the influent and effluent samples was measured approximately once every month. The results proved very poor degradability of the landfill leachate (BOD_5:COD ratio <0.05). Average concentrations were 73 and 6.3 mg/L in influent and effluent respectively, meaning 91% removal efficiency. The effluent values are comparable to other activated sludge applications; relatively poor removal efficiency was thus caused rather by low BOD in the influent.

3.4. Removal of bisphenol A

The concentration of bisphenol A (BPA) was measured in samples of influent wastewater, permeate and the liquid phase of the mixed liquor once a week (results in Table 4). The average concentration in the influent was 2100 µg/L, the effluent value were in most cases below the detection limit (0.1 µg/L) and the elimination efficiency above 99.99%. Concentration in the liquid phase of activated sludge is usually higher than those in permeate, although the cut-off level of the membrane (70 kDa) and molecular mass of BPA (219 Da) are incomparable. However, it is necessary to take into consideration that the pore size of the standard filter for suspended solid separation (0.45 µm) is greater than that of the membrane installed in the pilot plant. Thus, BPA associated with part of the colloidal material was measured in the filtrate from mixed liquor.

Regarding the processes involved in BPA elimination, sorption on activated sludge and biological degradation have to be considered in this case. The share of BPA removed with excess sludge was calculated using data from the literature. Its share was calculated to be less than 1% depending of sludge withdrawal and concentration of BPA in the bulk liquid [5, 7, 13].

The remaining >99% was removed biologically. Kinetics of biological degradation of BPA is assumed to follow the first order reaction equation:

$$\frac{dC}{dt} = -kC$$

where k is the first order reaction constant [/h]. After the correction on the amount of BPA sorbed on activated sludge, the values were between k = 0.17–2.5/ h.(values related to sludge concentration k = 0.022–0.25 L/g/ h) These results are comparable to those obtained by Urase *et al.* [13] (k = 0.01–0.08 L /g/h with non-acclimated sludge) and Zhao *et al.* [5] (k = 0.4 L/g/h, sludge acclimated to BPA).

4. Conclusions

After the stabilisation of biological processes nitrification efficiency was 90–99% (elimination of ammonia nitrogen from 1200 mg/L to 10–150 mg/L), denitrification was only possible after addition external substrate (methanol), with the efficiency around 50%. High release of nitrites was observed in most phases, resulting in comparable concentrations of $N–NO_2^-$ and $N–NO_3^-$ in the effluent. It was not proven where nitrification or denitrification process is responsible for formation of nitrites. Because of the low biodegradability of the landfill leachate (BOD:COD 0.05), overall COD removal was less than 30% in most cases, while BOD removal was 91%.

Removal of BPA was highly efficient – from initial concentration in the influent of 2000 µg/L to less than 1 µg/L in the effluent. Corresponding rate constants were calculated between k = 0.022–0.25 L/g/h.

The membrane permeabilities varied from 3.5 to 40 LMH/bar depending on the operational conditions (cross-flow velocity, trans-membrane pressure and biomass concentration). From these parameters, cross flow velocity had decisive effect on fouling rate.

References

[1] N. Paxéus, Organic compounds in municipal landfill leachates. Water Sci. Technol., 42 (7–8) (2000) 323–333.

[2] H. Doedens, U. Theilen, Sickerwasserentsorgung und-reinigung. Entsorgungpraxis-Spezial, 4 (1990) 2–10.

[3] P. Ilies, D.S. Mavinic, The effect of decreased ambient temperature on the biological nitrification and denitrification of a high ammonia landfill leachate. Water Res., 35 (8) (2001) 2065–2072.

[4] T. Yamamotoet al., Bisphenol A in hazardous waste landfill leachates. Chemosphere, 42 (2001), 415–418.

[5] J. Zhao et al., Sorption and degradation of bisphenol A by aerobic activated sludge. *J. Hazard. Mat.*, 155 (1–2) (2008) 305–311.

[6] S. Lyko, T. Wintgens, T. Metlin, Estrogenic trace contaminants in wastewater—possibilities of membrane bioreactor technology. *Desalination*, 178 (1–3) (2005) 149–159.

[7] T. Wintgens, Modellierung von Membranbioreaktoren für die Abwasserbehandlung unter Berücksichtigung endokrin wirksamer Substanze. Verlagshaus Mainz, Aachen, 2005.

[8] S. Rosenberger et al., The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge process—six case studies of different European research groups. J. Membr. Sci., 263 (2005) 113–126.

[9] I. Jubany et al., Respirometric calibration and validation of a biological nitrite oxidation model including biomass growth and substrate inhibition. Water Res., 39 (2005) 4574–4584.

[10] S.-Y. Weon et al., Nitrite inhibition of aerobic growth of *Acinetobacter* sp. Water Res., 36 (2002) 4471–4476.

[11] C. Glass, J. Silverstein, Denitrification kinetics of high nitrate concentration water: pH effect on inhibition and nitrite accumulation. Water Res., 32 (1998) 831–839.

[12] M. Henze, P. Harremoës, J. la Cour Jansen, E. Arvin, Wastewater Treatment, Biological and Chemical Processes, Third edition, Springer-Verlag, Berlin, 2002.

[13] T. Urase, T. Kikuta, Separate estimation of adsorption and degradation of pharmaceutical substances and estrogens in the activated sludge process. Water Res., 39 (2005) 1289–1300.

[14] J. Chen, X. Huang, D. Lee, Bisphenol A removal by a membrane bioreactor. Proc. Biochem., 43(2008) 451–456.