PURIFICATION OF LANDFILL LEACHATES BY MEANS OF COMBINED BIOLOGICAL AND MEMBRANE SEPARATION TREATMENT

B. Mayr[a], S. Novak[b*], P. Horvat[b], F. Gaisch[c], M. Narodoslawsky[c], A. Moser[d]

[a]A.S.A. Abfall Service Holding GmbH. Straβganger Str. 293, A-8053 Graz, Austria

[b]Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, HR-41000 Zagreb, Croatia

[c]Technical University of Graz, Institute for Chemical Engineering, Infeldgasse 25, A-8010 Graz, Austria

[d]Technical University of Graz, Institute for Biotechnology, Petersgasse 12/I, A-8010 Graz, Austria

* Author to whom all correspondence should be addressed

Summary

The pilot plant combined of two bioreactors (aerobic and anaerobic one), together with microfiltration and reverse osmosis units was used to conduct the purification of leachates from two sanitary landfills.

One leachate was heavily loaded and it contained about 6 $kg \cdot m^{-3}$ of ammonium-nitrogen and organic matter expressed as COD in a quantity of 30 $kg \cdot m^{-3}$. After the careful adaptation of the culture high efficiency of ammonium-nitrogen and COD removal was achieved in the steady state (more then 95 % and 85 % respectively). The productivity of ammonium-nitrogen removal was more then 1 $kg \cdot m^{-3} \cdot d^{-1}$, and neither additional carbon source nor pH correction was necessary.

The second leachate had lower level of COD and ammonium-nitrogen (5.5 and 1.5 $kg \cdot m^{-3}$ respectively). Nevertheless, because of the lower C:N ratio and low COD biodegradability additional carbon source was necessary for efficient nitrogen removal.

After the biological treatment and microfiltration both permeates were treated further by two step reverse osmosis giving in both cases the purified water which could be used for technical purposes.

Key words:

landfil leachates, nitrification, denitrification, chemical oxygen demand (COD)

Introduction

The concept of "ecological process engineering" has the intention to embed technology into biosphere by using the whole range of biodiversity in a holistic and low-invasive way in order to achieve benefit for human mankind[1-3]. The primary goal of this concept is to restructure the whole technology including "the end of the pipe technology" into the ecologically sustainable activity[2,4]. The "ecological process engineering" concept has been applied in great extent to develop the new process[5] for the purification of landfill leachates - fluids which are produced as a result of the microbial anaerobic degradation and compression of solid waste on landfills[6]. Landfill leachates are characterized by both high organic and high ammonium concentration[5,6]. The load of organic compounds in waste water, expressed as chemical oxygen demand (COD), has been treated successfully by biological oxidation since beginning of this century in the activated sludge process[7]. A removal of ammonium and organic nitrogen compounds by the combined aerobic and anaerobic biological treatment (so called nitrification/denitrification process) was developed more recently and since then has been widely integrated in biological treatment processes[5,7].

In this work the biological treatment was conducted in two bioreactors. One bioreactor was the nitrification tank which maintained aerobic conditions for oxidation of ammonium to nitrate in a two step reaction carried on by the two chemolithotrophic microorganisms[7]:

$$NH_4^+ + 3/2\ O_2 \xrightarrow{\text{Fehler!}} NO_2^- + H_2O + 2H^+ \qquad (1)$$

$$NO_2^- + 1/2\ O_2 \xrightarrow{\text{Fehler!}} NO_3^- \qquad (2)$$

In the aerobic reactor part of the organic load is oxydized as well.

The second bioreactor was an anaerobic plug flow reactor where facultative anaerobes in the absence of oxygen performed the nitrate respiration - oxidation of dissolved organic substances accompanied by reduction of nitrate to elemental nitrogen[7] expressed qualitatively by equation:

$$NO_3^- + \text{organic substances} \xrightarrow{\text{Fehler!}} N_2 + CO_2 + H_2O \quad (3)$$

The culture could be adapted to use the organic waste as an electron donor for the above reaction, but if the C:N ratio of the waste water is too small, then use of an additional carbon source is usually necessary[7].

The nitrifying bacteria are slow growing chemolithotrophs[7] so keeping the high biomass concentration is crucial for maintaining the high volumetric rate of the continuous process. This could be done by immobilization of the bacterial cells in the packed bed[8] or fluid bed[9-13] reactors, or biomass should be separated by sedimentation[7] or ultrafiltration[14] and then recycled back to bioreactors.

In this work the pilot plant combined of the aerobic and anaerobic reactor was used to conduct the purification of leachates from two sanitary landfills in order to evaluate the necessary process parameters for the scale up as well as to establish the protocol for the start up of a large scale plant and the maintenance of the steady state of the continuous process. For biomass recyclation, for the first time according to the available literature, microfiltration instead of the ultrafiltration was applied in the process.

For complete purification the permeate from the microfiltration unit was treated further by the two step reverse osmosis to remove ionic and low molecular weight pollutants and intermediates. As a result, in both cases a purified water was obtained which could be used for technical purposes on the landfill.

Materials and methods

Equipment

The detailed description of the pilot plant equipment was given elsewhere[14]. Main parts of the equipment (Fig. 1) were: the denitrification tank - an anaerobic plug flow reactor with working volume of 0.155 m^{-3}, the nitrification tank - an aerobic air sparged reactor with working volume of 470 m^{-3}, and the cross-flow microfiltration unit for biomass separation, with ceramic elements of 0.5 μm cutting edge. The leachate was fed into the denitrification tank as the first one in a series of two bioreactors. Ammonium from the leachate was passing through this tank mostly uneffected and then it was flown further to the nitrification tank (NT) where it was oxidized to nitrate by chemolithotrophs (reaction equations 1 and 2). Part of the liquid from this tank was recycled back continuously to the denitrification tank (DN) where it was mixed with the organic load (COD) from the inlet fluid which was used to carry on the reduction of nitrate to elemental nitrogen (reaction equation 3). The equipment was provided with several recirculation loops. The first loop was for the culture recirculation from nitrification to denitrification tank. The culture from the nitrification tank was also circulated through the microfiltration unit. The concentrate was pumped back to the nitrification tank, and the permeate was collected in the permeate tank. Part of the permeate was recycled back to the denitrification tank to maintain the nitrite reduction and the constant liquid level in the whole reactor system. The rest that was coming out through the exhaust pipe was treated further by the two step reverse osmosis. The culture in the nitrification tank was aerated permanently, and air flow rate was adjusted manually according to readings of the flow indicator. The experiment was conducted under atmospheric pressure.

Activated sludge

The activated sludge was obtained from a municipal waste water treatment plant.

Additives

The main intention was to run the process with the least amount of additives possible. During the start-up period the technical grade sulfuric acid (96 %) was used for the pH correction of the culture in biological

treatment, but no pH correction was performed during the steady state. Phosphorus salts in the form of dihydrogen-ortho-phosphate, polyphosphate or hexameta-phosphate were added in excess to prevent the phosphorus limitation. Acepol 83E from Carl Becker, Bilbrookdeich, was used for the foam control. When neccessary a technical grade acetic acid (20 or 80 %) was used as an additional carbon source,

Analysis

Samples of leachate, microfiltration permeate, as well as samples from both bioreactors were analysed regularly. The conductivity was measured with conductometer WTW LF 196, and pH with Orion 420A pH-meter. The Merck kits were used for colorimetric determination of ammonium-, nitrate- and nitrite-nitrogen (Spectroquant 14752, Spectroquant 14773, and Spectroquant 14776 respectively). The tube tests COD 15000 and COD 1500 of Macherey-Nagel were used to measure the COD colorimetricaly after the two hours digestion on 148 ^{o}C. For all colorimetric measurements the Hewlett Pacard 8352A spectrophotometer was used. The phosphate concentration in the permeate was checked out occasionally with the Aquamerck 14661 semiquantitative quick test.

The biomass concentration in both bioreactors was estimated indirectly by the dry weight (DW) and the ash free dry weight (AFDW) measurements of the whole sample. For a DW measurement 50 mL of the well mixed sample from the reactor was dried on 110^{o}C till constant weight. The AFDW was evaluated by subtraction of the ash content which was determined by incineration of the same dried sample at 600^{o}C through 12 h. Other analysis were done by specialized company.

Results and discussion

Two leachates, named A and B respectively were treated in this work. The leachate A from the particular sanitary landfill of A.S.A. Süd was characterized by high COD and high ammonium concentration. To adapt the culture on this heavily loaded leachate the process was started up with a very low volumetric load rate of the leachate (Fig. 2). During the adaptation period which lasted first 17 days the volumetric load rate was gradually increased according to the culture response with a special care

to enable the slow growing nitrifying autotrophs to prevail in the culture. After the 17th day the steady state was maintained and monitored over next 23 days. Only exceptions were two accidents on the 21st/22nd day when aeration was interupted and the 29th/30th day when electricity for the whole plant went off. During the steady state the concentration of ammonium-nitrogen in the inlet leachate was fluctuating in the range of 5.5 and 6.2 $kg \cdot m^{-3}$ and pH between 8.1 and 8.8 respectively.

The process equipment was not provided with any means of temperature control, therefore temperature was sensitive to climate conditions. The experiment was conducted through May and June, 1993. Several pumps that were operating in the plant at high flow rates were always generating some heat which kept process temperature somewhat higher then ambient temperature. The lowest process temperature recorded was 30°C and the highest was 43°C. The most of the time the temperature was in the range of 36-38 °C.

The aeration of the nitrification tank has been gradually increased during the start up period and up to the 21st day when maximum of the 12 m^3/h was reached. The aeration rate has been increased according to the readings of the oxygen electrode (not shown). During the steady state the culture conditions were mostly in the range of oxygen limitation (DO probe readings were mostly below 0.5 mg/L). In the steady state the air/leachate ratio was in a range of 2.1 - 2.7 m^3 of air per liter of leachate indicating a low oxygen transfer efficiency of the aeration system in the nitrification tank.

The biomass concentration was evaluated indirectly in both bioreactors by DW and AFDW measurements presented on Fig. 3. Two phases of the process could be clearly recognized: the start up phase with significant growth, and steady state phase in which growth was negligible. In the start up phase the biomass productivity calculated on the AFDW basis was 0.53 $kg \cdot m^{-3} \cdot d^{-1}$, for the denitrification tank, 0.45 $kg \cdot m^{-3} \cdot d^{-1}$, for nitrification tank, and 0.47 $kg \cdot m^{-3} \cdot d^{-1}$, calculated on the total working volume of the plant. It should be noted that in this experiment the whole biomass was recycled, therefore a biomass residence time was infinite.

In Fig. 4 data on concentrations of ammonium-, and nitrite-nitrogen as well as COD level in the microfiltration permeate outlet are presented. The nitrate-nitrogen was not detectable in the microfiltration permeate

throughout the whole experiment (data not shown). The most of the time the outlet ammonium concentration was also below the sensitivity of the analytical method. Only exceptions were when the two aforementioned accidents occurred.

On 22nd day the compressor of the aeration system went off but other elements of the plant including the leachate pump were active. Without aeration nitrification process was stopped and with undisturbed feeding of the leachate the ammonium concentration increased. Ammonium accumulated in the plant during 15 - 20 hours and later, when aeration was reestablished, respective peak in nitrite concentration was observed. However, after three days the process was completely stabilized. On 29th day, all electricity went off. Therefore all the pumps were stopped. The damage was far less pronounced than on the 22nd day, because the leachate pump was not working and so ammonium was not fed into the system. However, small increase of ammonium concentration was observed most probably due to the needed readaptation of the culture when plant was restarted again.

As was said previously, throughout the whole experiment no nitrate-nitrogen was detected in any occasion. Because the nitrite was always detectable we believe that during the adaptation period *Nitrosomonas sp.* (which oxidize ammonium to nitrite) overgrew *Nitrobacter sp.* (which oxidize nitrite to nitrate). This hypotheses was confirmed further with small experiment when portion of the culture was withdrawn from the nitrification tank and aerated further batchwise. No decrease of nitrite or occurrence of nitrate were detected during 48 hours of this experiment. However, if oxidation of nitrite to nitrate is avoided in the nitrification process, then oxygen requirements, according to stoichiometry, would be decreased by 25 %. Interestingly, an attempt to conduct the process without nitrite oxidation step in the immobilized system was tried recently, but was reported failure[13].

Obviously the culture in the denitrification tank adapted well for nitrite reduction because nitrite was never detected at the outlet of the denitrification tank. Furthermore, the culture in the denitrification tank was well adapted on organic load in the leachate as well, thus there was no need for an additional carbon source throughout the experiment.

The COD in the microfiltration permeate was unexpectedly low (Fig. 4). The biological part of the plant (nitrification-denitrification-microfiltration) removed most of ammonium-nitrogen and organic substances from the leachate. In the steady state phase the ammonium removal efficiency was higher than 95% and efficiency for COD removal was mostly higher than 85% (Fig. 5). The analysis in Table 1 show that in addition to ammonium and COD, good efficiencies of sulfide and organic halogenides (AOX) removal were achieved. Main parameters of the biological treatment are summarized in Table 2. The microfiltration permeate was purified further by reverse osmosis which removed most of the impurities that remained after the biological treatment (Table 1).

A similar experimental strategy was used for the leachate B which came from other landfill. This leachate had lower levels of COD and ammonium-nitrogen (Table 3). However, because of the lower C:N ratio and low biodegradability of the organic load additional carbon source was necessary for efficient nitrogen removal. Relativly low levels of COD and ammonium-nitrogen as well as high removal efficiencies allowed much shorter hydraulic residence times (Table 4) then with leachate A.

Presented results were used for the scale-up and further improvement (mainly in the aeration system) of the leachate treatment plant at an A.S.A. Süd landfill with capacity of 100 $m^3 \cdot d^{-1}$. The scale-up procedure was done related to the strategy which was introduced recently[15,16]. The start-up of the plant is scheduled for spring 1994.

ACKNOWLEDGMENTS

The authors are grateful to ASA Süd for generous permission to conduct the research and publish the results of these experiments.

References

1. *Moser, A.,* Acta biotechnologica **12** (1992) 69

2. *Moser, A.,* Eco-principles for Restructuring Technology in Direction of Ecologic Process Engineering, in Sixth European Congress on

Biotechnology, Firenze 13-17 June, 1993., Book of Abstracts TH074

3. *Narodoslawsky, M.,* Ecologic Process Engineering - a New Dimension of biotechnology, in Sixth European Congress on Biotechnology, Firenze 13-17 June, 1993., Book of Abstracts TH073

4. *Hell, F., Moser, A.,* The Biological Denitrification of Drinking Water as a case study of ecological process engineering, in Sixth European Congress on Biotechnology, Firenze 13-17 June, 1993., Book of Abstracts TH079

5. *Mayr, B.,* Die Sickerewasserproblematik auf Deponien: Versuch einer Lösung in Zusammenarbeit mit Forschung und Wissenschaft, in Handbuch der Umweltechnik, 7. Internationalen Kongreβ-Messe für Umwelttechnik, Wien 19.-22. Oktober 1993., 114

6. *Küster, E., Niese, G.,* Dumping of Refuse and Sludges, in Rehm, H.-J. and Reed, G. (Ed.), Biotechnology, Vol. 8, pp. 349-362, VCH Winheim, 1986

7. *Verstraete, W., van Vaerenbergh,E.,* Aerobic activated sludge, in Rehm, H.-J. and Reed, G. (Ed.), Biotechnology, Vol. 8, pp. 43-112, VCH Winheim, 1986

8. *Atanasoff-Kardjalieff, K., Strohmeier, A.,* Oesterreichische Wasserwirtschaft **45** (1993) 71

9. *de Gooijer, C. D., Wijffels, R. H., Tramper, J.,* A Dynamic Model for the Growth of Immobilized Nitrifying Bacteria; Biofilm Development, in Sixth European Congress on Biotechnology, Firenze 13-17 June, 1993., Book of Abstracts MO181

10. *de Gooijer, C. D., Wijffels, R. H., Tramper, J.,* Biotechnol. Bioeng. **38** (1991) 224

11. *Wijffels, R. H., de Gooijer, C. D., Kortekaas, S., Tramper, J.* Biotechnol. Bioeng. **38** (1991) 232

12. *Csikor, Z., Mihaltz, P., Czako, L., Hollo, J.,* Fluidized Bed Nitrification-Denitrification, in Sixth European Congress on

Biotechnology, Firenze 13-17 June, 1993., Book of Abstracts MO185.

13. *Zastrutzki, M., Feuerhake, E., Jördening, H.-J.,* High rate Nitrification-Denitrification with Immobilized Systems, in Sixth European Congress on Biotechnology, Firenze 13-17 June, 1993., Book of Abstracts MO185

14. *Lang, D.,* Deponiesickerwasser Versuche zur biologischen Vorbehandlung, TU Graz, Austria, Diploma work, 1992

15. *Mayr, B., Nagy, E., Horvat, P., Moser, A.,* Chem. Biochem Eng. Q. **7** 31 (1993)

16. *Mayr, B., Nagy, E., Horvat, P., Moser, A.,* Biotechnol. Bioeng. 43 (1994) in press

Nomenclature

AFDW - ash free dry weight concentration [$kg \cdot m^{-3}$]
B - volumetric loading rate of COD or ammonium-nitrogen [$kg \cdot m^{-3} \cdot d^{-1}$]
COD - chemical oxygen demand [$kg \cdot m^{-3}$]
DW - dry weight concentration [$kg \cdot m^{-3}$]
E - efficiency of the whole plant [-]
NH_4-N - ammonium-nitrogen concentration in the microfiltration permeate [$kg \cdot m^{-3}$]
NO_2-N - nitrite-nitrogen concentration in the microfiltration permeate [$kg \cdot m^{-3}$]
NO_3-N - nitrate-nitrogen concentration in the microfiltration permeate [$kg \cdot m^{-3}$]
Q_{in} - inlet flow rate of the leachate [$m^3 \cdot d^{-1}$]
V_{DN} - working volume of denitrification tank [0.155 m^3]
V_{NT} - working volume of nitrification tank [0.47 m^3]
V_{PL} - total working volume of bioreactors ($V_{DN}+V_{NT}$)

Indices

AFDW - on ash free dry weight basis
COD - regarding COD
DN - regarding denitrification tank
DW - on dry weight basis
MFP - microfiltration permeate

N - regarding ammonium-nitrogen
NT - regarding nitrification tank
PL - regarding whole plant (total working volume)

List of Tables

Table 1 Analysis of the leachate A, its microfiltration permeate after the biological treatment, and the permeate of the second step of the reverse osmosis

Parameter	Unit	Leachate	Microfiltration permeate	Reverse osmosis permeate
pH	-	8.4	8.6	8.6
El. conductivity	mS m^{-1}	3137	1455	4.7
COD	kg m^{-3}	30.26	3.000	0.006
AOX (as Cl)	kg m^{-3}	$18x10^{-3}$	$1.4x10^{-3}$	$0.02x10^{-3}$
Lead	kg m^{-3}	$3.3x10^{-5}$	$1.9x10^{-5}$	$0.6x10^{-5}$
Chromium	kg m^{-3}	$6.5x10^{-3}$	$4.7x10^{-3}$	$< 0.05x10^{-3}$
Nickel	kg m^{-3}	8.4	$x10^{-3}$	$4.9x10^{-3}$ $1.3x10^{-3}$
Zinc	kg m^{-3}	$1.4x10^{-3}$	$0.8x10^{-3}$	$0.26x10^{-3}$
Ammonium-N	kg m^{-3}	6.145	0.007	< 0.0001
Nitrate-N	kg m^{-3}	0.013	0.010	< 0.0005
Nitrite-N	kg m^{-3}	0.001	0.130	< 0.0003
Phosphate (tot.)	kg m^{-3}	0.215	0.120	< 0.0001
Sulfide-S	kg m^{-3}	0.042	0.005	NT[a]
Chloride	kg m^{-3}	3.800	3.500	0.0005

[a] not tested

Table 2 Efficiency parameters of the biological treatment*

Parameter	Unit	tank	Nitrification	tank	Denitrification	Plant
volumetric load of COD	kg $m^{-3} \cdot d^{-1}$		7.73		24.43	5.81
volumetric load of nitrogen compounds[a]	kg $m^{-3} \cdot d^{-1}$		1.28		3.89	0.965
specific load of COD (on DW bases)	kg $kg^{-1} \cdot d^{-1}$		0.309		1.062	0.237
specific load of COD (on AFDW bases)	kg $kg^{-1} \cdot d^{-1}$		0.600		2.036	0.422
specific load of nitrogen[a] (on DW bases)	kg $kg^{-1} \cdot d^{-1}$		0.512		0.169	0.039
specific load of nitrogen[a] (on AFDW bases)	kg $kg^{-1} \cdot d^{-1}$	0.098		0.322	0.070	
hydraulic residence time	h		2.24		0.74	140
nitrogen[a] conversion efficiency	%		-		-	95-98
COD removal efficiency	%		-		-	80-88

[a] NH_4-N for NT and total volume and NO_x- N for DN

Table 3 Analysis of the leachate B, its microfiltration permeate after the biological treatment, and the permeate of the second step of the reverse osmosis

Parameter	Unit	Leachate	Microfiltration permeate	Reverse osmosis permeate
pH	-	8.4	8.3	8.6
El. conductivity	mS m^{-1}	1737	855	4.7
COD	kg m^{-3}	5.200	1.600	0.006
BOD_5	kg m^{-3}	2.200	NT	NT
AOX (as Cl)	kg m^{-3}	$13x10^{-3}$	$6.3x10^{-3}$	$0.64x10^{-3}$
Ammonium-N	kg m^{-3}	1.470	0.013	< 0.0005
Nitrate-N	kg m^{-3}	0.004	0.026	NT[a]
Nitrite-N	kg m^{-3}	0.005	0.0226	NT[a]
Phosphate (tot.)	kg m^{-3}	0.016	0.007	NT[a]

[a] not tested

Table 4 Efficiency parameters of the biological treatment of the leachate B

Parameter	Unit	Nitrification tank	Denitrification tank	Plant
volumetric load of COD[a]	kg $m^{-3} \cdot d^{-1}$	4.825	14.631	3.629
volumetric load of nitrogen compounds[b]	kg $m^{-3} \cdot d^{-1}$	1.007	3.054	0.75
specific load of COD[a] (on DW bases)	kg $kg^{-1} \cdot d^{-1}$	-	-	0.190
specific load of COD[a] (on AFDW bases)	kg $kg^{-1} \cdot d^{-1}$	-	-	0.320
specific load of nitrogen[b] (on DW bases)	kg $kg^{-1} \cdot d^{-1}$	-	-	0.040
specific load of nitrogen[b] (on AFDW bases)	kg $kg^{-1} \cdot d^{-1}$	-	-	0.067
hydraulic residence time	h	1.469	0.484	49.992
nitrogen[b] conversion efficiency	%	-	-	90-98
COD[a] removal efficiency	%	-	-	65-81

[a] including COD of the additional carbon source

[b] NH_4-N for NT and total volume and NO_x- N for DN

Figures captions

Figure 1 The scheme of the pilot plant equipment: nitrification tank (NT), denitrification tank (DN), microfiltration unit (MF), buffer tank for microfiltration permeate (MFP), and reverse osmosis unit (RO); marks 1 through 5 designate pumps for: leachate inlet (1), additional carbon source (2), recirculation from NT to DN (3), microfiltration (4), recirculation of microfiltration permeate to DN (5); and (6) is an air compressor

Figure 2 Volumetric loading rates of COD and ammonium-nitrogen during the biological treatment of the leachate A

Figure 3 Concentrations of dry weight (DW) and ash free dry weight (AFDW) in nitrification (NT) and denitrification (DN) tank during the biological treatment of the leachate A

Figure 4 Concentration of ammonium-nitrogen, nitrite-nitrogen and COD level in the microfiltration permeate of the biological treatment of the leachate A

Figure 5 Overall reduction efficiencies of ammonium-nitrogen ($E_{N/PL}$) and COD ($E_{COD/PL}$) during the biological treatment of the leachate A