Occurrence and removal of endocrine disrupters in landfill leachate treatment plants

T. Wintgens, M. Gallenkemper and T. Melin

RWTH Aachen University, Department of Chemical Engineering, Turmstrasse 46, 52056 Aachen, Germany (E-mail: *Wintgens@ivt.rwth-aachen.de*)

Abstract Endocrine disrupting compounds can affect the hormone system in organisms. Industrial chemicals with estrogenic effects were detected in large quantities in landfill leachates. Membrane technology has proven to be an effective barrier to these substances and thus widely applied in the treatment of landfill leachate. The removal techniques under investigation are membrane bioreactors, nanofiltration, activated carbon adsorption, ozonation as well as reverse osmosis. Investigations were conducted at two different landfill leachate treatment plants with a variety of process configurations. The xenoestrogenic substances nonylphenol and bisphenol A were detected in high μg/L-ranges in raw landfill leachate. Membrane bioreactors (MBRs) were capable of removing more than 80% of the nonylphenol load. Final effluent concentrations range between 1–12 μg/L nonylphenol and 3–30 μg/L bisphenol A respectively. Reverse osmosis treatment proved to be less effective in nonylphenol and bisphenol A removal than MBRs with further polishing stages like nanofiltration and activated carbon adsorption.

Keywords Endocrine disrupter; landfill leachate; membrane bioreactor; nanofiltration; reverse osmosis; wastewater

Introduction

The European Commission defines landfill leachate as any liquid percolating through deposited waste and emitted from, or contained in a landfill (EC/31/1999). Generally, leachate composition depends on the characteristics of the deposited waste, on rainfall conditions, on landfill design, and on operation and age. Significant components are heavy metals, chemicals and soluble organic substances, such as the decomposition products of organic waste. The type and concentration of soluble organic substances vary with the age of the deposited waste and decline over time. Apart from the inorganic constituents of landfill leachate, a wide range of organic pollutants have been measured. Paxeus (2000) gives an overview on organic trace compounds detected in the μg/L-range in municipal landfill leachates. Among these substances are several compounds classified as potential endocrine disrupters. Endocrine disrupters can be defined as substances or mixtures that are able to disturb the hormonal balance of humans, animals and/or their descendants. Among estrogenic endocrine disrupters are industrial chemicals like nonylphenol (NP) and bisphenol A (BPA), which are classified as xenoestrogenic compounds.

Estrogenic contaminants in landfill leachate

Estrogenic substances were measured in landfill leachates in various investigations. Polyethoxylated and isomeric nonylphenol was detected in landfill leachate samples by Castillo and Barceló (2001). Yamamoto *et al*. (2000) measured bisphenol A concentrations between 0.3 and 17,200 μg/l in landfill leachates. In this study, the mean concentration was 269 μg/L. Estrogenic activity of landfill leachate was found in a bio-assay study utilising modified fish cell lines (Fent, 2001). In a comprehensive study on different environmental matrices in Germany, the highest concentrations of estrogenic compounds were measured in landfill leachate (Wenzel *et al*., 1998). The most extensive investigation on estrogenic

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potency in particular stages of a landfill leachate treatment plant was undertaken by Behnisch *et al.* (2001). Every process step of a plant with conventional biological and activated carbon treatment was analysed for overall estrogenic activity and several chemical components, e.g. nonylphenol, bisphenol A and estradiol. The plant achieved a reduction of 42% in terms of overall estrogenic activity and the plant discharge had a lower potency than the receiving water. Nonylphenol and bisphenol A occurred in considerably low concentrations (2.8 μg/L and 0.13 μg/L respectively) and could be reduced by 98%. The efficiency of membrane technology for endocrine disrupter removal from landfill leachate was not yet evaluated.

Membrane processes for landfill leachate treatment

Membrane processes play a key role in the treatment of water and wastewater due to their reliable barrier effect and modular plant design (Rautenbach and Voßenkaul, 2001). Various pressure-driven membrane processes have been investigated and applied for landfill leachate treatment (Rautenbach *et al.*, 1997). In most applications different processes are combined to achieve a suitable effluent quality, which is generally defined in terms of organic, e.g. chemical oxygen demand (COD) as well as in terms of inorganic parameters (ammonia, conductivity, trace metals). With respect to membrane processes, reverse osmosis was combined with nanofiltration to achieve a minimisation of concentrate (Rautenbach and Linn, 1996). But pure reverse osmosis with high-pressure stages for concentrate treatment is applied as well (Rautenbach *et al.*, 2000). The combination with biological processes led to the invention of membrane bioreactors, where membranes are utilised to retain the biomass in the system (Krauth, 1996). The application with micro- or ultrafiltration membranes is now the most common one for wastewater treatment (Stephenson *et al.*, 2001) but in landfill leachate treatment nanofiltration membranes were tested as well (Rautenbach and Mellis, 1994). Nanofiltration was also investigated in combination with other physico-chemical pre-treatment processes to reduce the fouling potential (Trebouet *et al.*, 2001). With respect to endocrine disrupter removal, nanofiltration and reverse osmosis membranes were found to have a high potential (Nghiem and Schäfer, 2001). Gallenkemper *et al.* (2002) investigated the retention of nonylphenol and bisphenol A with nanofiltration membranes.

Methods

Within the presented studies different process options for municipal landfill leachate treatment were analysed with regard to the removal of estrogenically active nonylphenol and bisphenol A. The analysis was not extended to different nonylphenol compounds like nonylphenolethoxylates or nonylphenolcarboxylates because nonylphenol was assumed to be the most refractory and estrogenically active compound under the anaerobic conditions prevailing in landfills. Sampling and measurement campaigns were conducted at two different landfill leachate treatment plants (A and B) in Germany.

The major investigation was conducted at a landfill site, where different process configurations are used to treat particular portions of the raw leachate taken from a municipal landfill (Figure 1). One process train consists of a membrane bioreactor configuration with granulated activated carbon adsorption (GAC) as final treatment stage. Alternatively a small fraction of the membrane bioreactor effluent can be fed to a pilot-scale hybrid process which combines nanofiltration and powdered activated carbon adsorption (PAC) (Meier *et al.*, 2001). The second major process train treats the raw leachate exclusively by reverse osmosis membranes. There is a separate concentrate treatment stage in this train, which processes the retentate of the first stage and increases the overall water recovery (Peters, 1998).

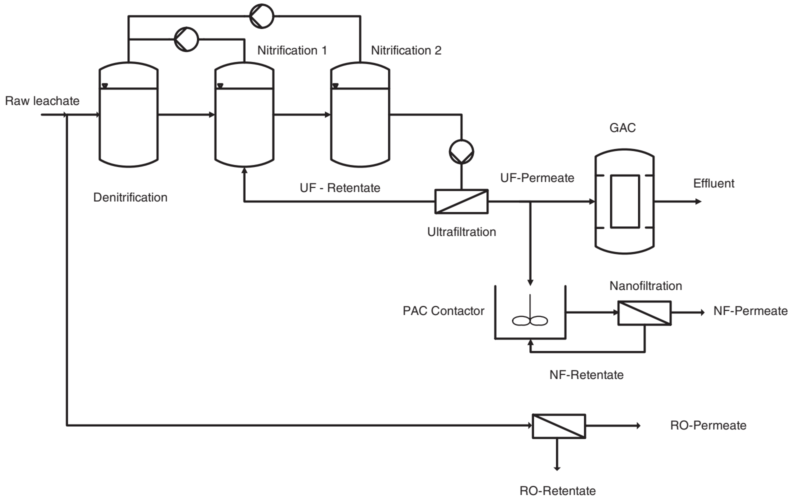

Figure 1 Landfill leachate treatment plant A with different treatment processes

The membrane bioreactor configuration consists of three activated sludge tanks and an external ultrafiltration unit. This process train treats an average feed flow of 7 m^3/h landfill leachate. The membrane bioreactor configuration works with denitrification and a two-stage nitrification and is able to decrease the ammonia concentration from 1,163 mg/L to about 7 mg/L, which is a main process objective. The bioreactors have a gross volume of 180 m^3 each and operate under 3.5 bar total pressure with internal re-circulations. Oxygen transfer is a major challenge in this process, owing to high operation temperatures (up to 40°C) and high suspended solids concentrations as well as on the grounds of the wide range of dissolved compounds which decrease the oxygen solubility. Activated sludge from the nitrification reactors is re-circulated to the denitrification tank. The total suspended solids concentration within the bioreactors is kept at about 25 g/L by discontinuous excess sludge removal. The ultrafiltration stage is equipped with tubular modules in six parallel racks and operated in cross-flow mode. The cross-flow velocity is kept at about 5 m/s and the trans-membrane pressure difference is around 6 bar. A total membrane area of 120 m^2 is installed. Samples were taken at various monitoring points, from the raw influent, activated sludge, ultrafiltration permeate to the final effluent after passing the activated carbon units. Permeate from the pilot-scale hybrid process was sampled as well. The samples were analysed in order to measure NP and BPA concentrations. The alternative process route for landfill leachate treatment from the same site with reverse osmosis plant was installed since the capacity of the plant had to be increased because of higher feed water flows. The reverse osmosis plant is equipped with flat sheet modules and operates with 60 bar transmembrane pressure, whereas the second stage for concentrate treatment utilises 120 bar. Feed and permeate samples were collected from these treatment processes as well.

The second landfill leachate treatment plant (Plant B) under investigation employs a membrane bioreactor configuration with an additional nanofiltration stage for final effluent treatment. In order to minimise nanofiltration concentrate disposal the retentate is treated by an advanced oxidation process, which uses ozone to break down refractory organic compounds rejected by the nanofiltration membranes. The upgraded retentate is re-circulated to the membrane bioreactor. The plant flowsheet is given in Figure 2. The second plant treats 2 m^3/h landfill leachate. Both denitrification and nitrification are combined in a loop-type reactor. The absolute pressure is 3.5 bar and the suspended solid concentration is around 22 g/L. The transmembrane pressure in the nanofiltration stage is increasing with membrane age from 10 bar to 25 bar. The addition of 0.2–0.5 kgO_3/kgCOD in the oxidation

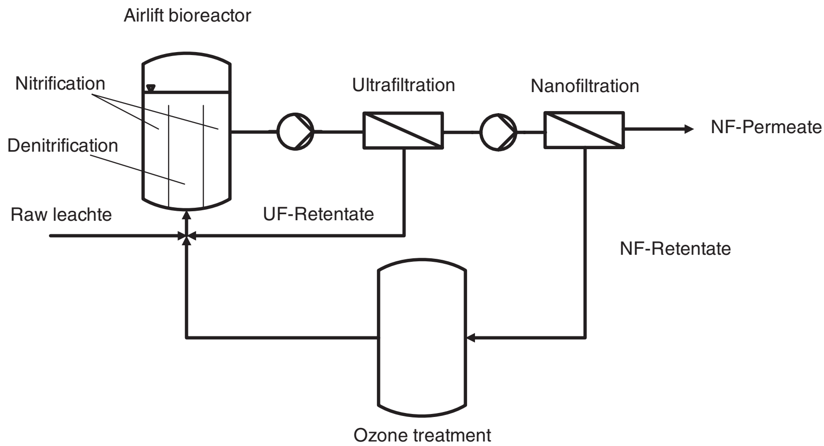

Figure 2 Landfill leachate plant B with nanofiltration and ozone treatment

stage allows a considerable COD reduction and utilises the breakdown of refractory compounds, which can be more easily degraded in the bioreactor after ozonation. Samples were taken at different monitoring points within the process, starting with the raw influent, activated sludge, ultrafiltration permeate, the nanofiltration permeate and concentrate before and after ozone treatment.

Sample preparation

All samples were immediately stabilised by addition of $NaN_{3.}$ Within two hours, they had been carried to the laboratory, where they were kept refrigerated in brown glass bottles. The samples were prepared and analysed within 72 hours. Sample processing and analysis for measurement of nonylphenol and bisphenol A was performed according to Meesters and Schröder (2002) and basically consists of an *in-situ* derivatisation step and liquid-liquid extraction prior to the GC-MS measurements.

Results and discussion

Results for the first plant are summarised in Figure 3. Considerably high concentrations, ranging up to milligrams of NP and BPA per litre, were measured in the raw landfill leachate. The concentration of NP within the bioreactor is slightly higher than in the feed stream but a significant drop of more than one order of magnitude was observed after the ultrafiltration. The activated sludge was centrifuged and the analysis of the supernatant showed a significantly higher NP concentration than the ultrafiltration permeate, 252 μg/L in comparison to 28 μg/L respectively. While the molecular mass of nonylphenol (M_{NP} = 220 g/mol) should not allow a retention by ultrafiltration membranes, this difference can be explained by a shift in molecular weight cut-off (MWCO) of the membranes due to gel layer formation and a tendency of nonylphenol to associate with macromolecular compounds like humic acids which are abundantly present in leachates. The final activated carbon adsorption was able to remove half of the remaining micropollutants. This relatively small reduction might depend on the total operation time of the granular activated carbon (GAC) columns.

Combining data on xenoestrogene concentrations and the hydraulic characteristics of the plant, a NP mass balance was derived as is illustrated in Figure 4. It is obvious that most of the nonylphenol load is reduced in the membrane bioreactor. The considerable elimination in the membrane bioreactor might rest on biodegradation, on adsorption on sludge and on air stripping. Ahel (1997) showed that nonylphenol strongly accumulates on

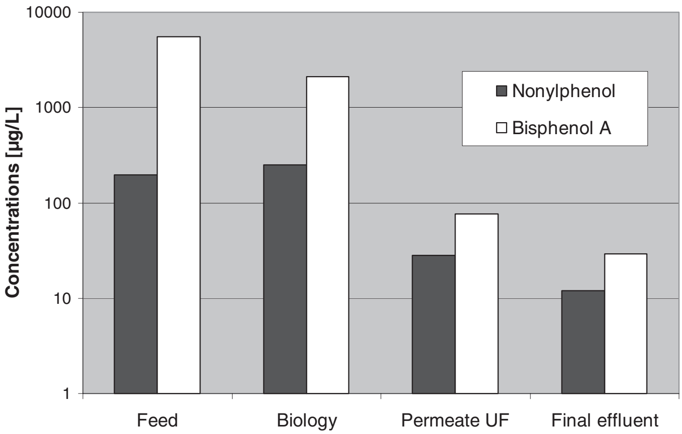

Figure 3 Bisphenol A and nonylphenol concentrations in landfill leachate treatment plant A

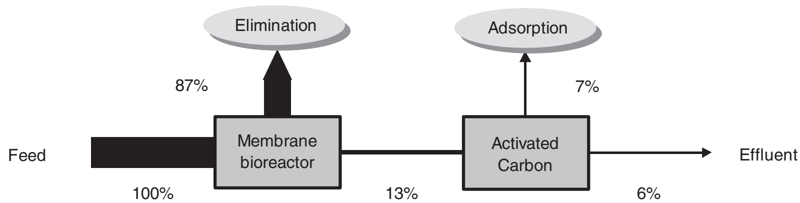

Figure 4 Mass balance of NP in landfill leachate treatment plant A

activated sludge and considerable quantities might leave the system with excess sludge. The determination of sludge concentrations is a subject of ongoing research. The granular activated carbon unit accounts for a further reduction by about 50% with respect to the ultrafiltration permeate.

Bispenol A removal with different process configurations

Removal rates found for bisphenol A with different process configurations in plant A are listed in Table 1. It becomes obvious that the removal rates for bisphenol A are generally higher than for nonylphenol but the membrane bioreactor still carries the bulk load in terms of elimination. The hybrid process with nanofiltration and powdered activated carbon leads to the highest overall removal.

Results from plant B

The sampling and measurement program at plant B had similar results in terms of nonylphenol and bisphenol A occurrence as well as fate within the plant. Figure 5 indicates that concentrations found at particular sample points are of a lower order of magnitude than in plant A.

Table 1 Bisphenol A removal rates with different process configurations

Process configuration	Removal rate
Membrane bioreactor	95.3%
Membrane bioreactor plus granular activated carbon adsorption	96.8%
Membrane bioreactor plus nanofiltration with powdered activated carbon adsorption	97.8%
Reverse osmosis membranes	94.2%

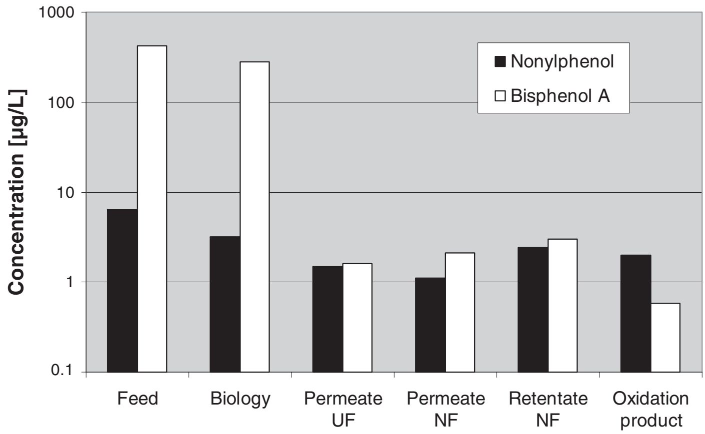

Figure 5 Nonylphenol and bisphenol A concentrations in plant B

Again the membrane bioreactor, which has a similar configuration as in plant A, contributes predominantly to the overall removal. An obvious contradiction in the given data was that the bisphenol A concentration in the nanofiltration permeate was slightly higher than in the nanofiltration feed, while the nanofiltration retentate concentration clearly shows that a bisphenol A retention occurs. Data reconciliation indicates that the measured UF permeate concentrations are too low to fulfil mass balance requirements. Apart from this mistake the presented data seem to be consistent.

To illustrate the effect of nanofiltration and ozonation mass balance data for nonylphenol is presented in Figure 6 on the basis of the given concentrations and volumetric flow rates within the plant. The huge elimination within the membrane bioreactor, in this case 80.8% in comparison to 85% at plant A, might be attributed again to biodegradation, adsorption on sludge and to vaporisation. The slightly lower removal might be explained in terms of a shorter hydraulic retention time and sludge age, and respectively a higher sludge loading rate, than in plant A. Nanofiltration removes another 9.4% of the input nonylphenol load, i.e. significantly more than granular activated carbon filtration in the case of plant A. But owing to the low effect of the ozonation stage, 7.8% of the nonylphenol re-circulates to the membrane bioreactor. This contrasts with the high efficiency of the COD removal, which usually consists, in a reduction from 3,500–5,200 mg/L in the nanofiltration retentate down to 1,500–3,000 mg/L.

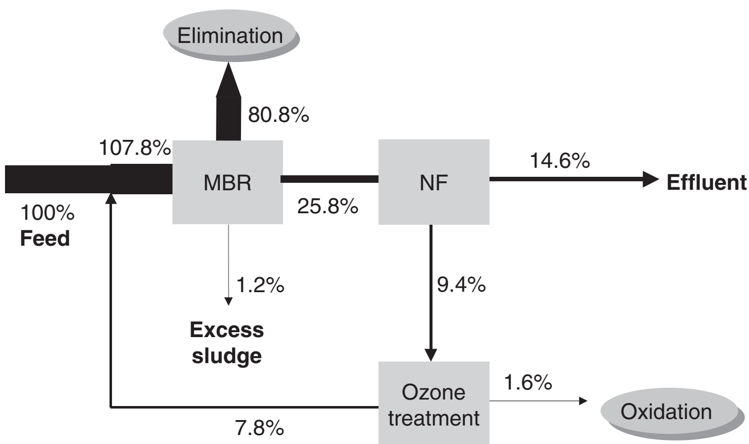

Figure 6 Mass balance of NP in landfill leachate treatment plant B

Conclusions

The presented study underlines the importance of considering landfill leachate treatment in the context of endocrine disrupter discharge minimisation. The xenoestrogenic substances nonylphenol and bisphenol A were measured in considerably high concentrations up to the mg/L-range in raw landfill leachate. In both plants under investigation membrane bioreactor configurations were capable of removing more than 80% of the incoming load. A strong accumulation of these substances on the activated sludge is usually expected (Ahel, 1987). This assumption must be verified in the ongoing investigation. The contribution of excess sludge withdrawal to contaminant removal is however limited in such applications because of the low volumes discharged. Further polishing steps, such as granular activated carbon adsorption and nanofiltration or a combination of both unit operations, were able to reduce the concentration levels significantly though not tremendously. The reverse osmosis treatment as an alternative process created somewhat lower removal rates, indicating the limited barrier effect of dense polymer membranes with respect to low molecular weight organics, such as nonylphenol and bisphenol A.

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