Removal of endocrine disrupting compounds with membrane processes in wastewater treatment and reuse

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Abstract Endocrine disrupting compounds can affect the hormone system in organisms and are the subject of environmental and human health concerns. The effluents of wastewater treatment plants contribute to the emission of estrogenically active substances into the environment. Membrane technology, which is an advanced wastewater treatment option, is the subject of this research. The removal techniques under investigation are membrane bioreactors, reverse osmosis, and nanofiltration. Eleven different nanofiltration membranes were tested in the laboratory set-up. The observed retention of NP and BPA ranged between 70% and 100%. The contact angle is an indicator for the hydrophobicity of a membrane, whose influence on the permeability and retention of NP was evident. Regarding the retention of BPA no dependency on the contact angle was observed. Results of the investigation of a full-scale landfill leachate treatment plant indicate a bisphenol A (BPA) removal of more than 98% with membrane bioreactors and reverse osmosis. The mass balance indicates that biological degradation is the most important removal process in the membrane bioreactor configuration.

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

Introduction

The occurrence of endocrine disrupting compounds (EDCs) in the environment has become more and more noted, sparking discussions between scientists, politicians, industry and environmental organisations on the significance of the effect of EDCs on wildlife and humans. Many articles have reported threats to health and reproductive biology in animal populations, e.g. reports of a stimulated vitellogenin synthesis in male fish (Sumpter, 1995), an increased uterus growth of rats (Bicknell *et al*., 1995) or changes in the gonads of alligators (Guillette *et al*., 1994). The effluents and sludges of municipal wastewater treatment plants (WWTPs) have been identified as input paths of EDCs into the aquatic and terrestrial environment (Körner *et al*., 2000; Ternes *et al*., 1999).

There are many different substances, which can disruptively interact with the human hormone system. The natural and synthetic estrogens, which belong to the most potent EDCs, are used in contraceptives. Among the more important compounds are estradiol and ethinylestradiol. Potentially endocrine disrupting industrial chemicals are, for example, nonylphenol (NP), bisphenol A (BPA), and tributyl-tin. Xenoestrogens like NP and BPA are not as estrogenically active as estradiol, but can be found in much higher concentrations in environmental compartments due to their widespread production (Körner *et al*., 2000). The European Commission has suggested that NP be included in a list of priority substances for pollution prevention policies in the water sector (EU, 1999, 2001).

Several endocrine disrupting substances, including NP and bisphenol A (Figure 1), have been found in sewage plant effluents and surface waters (Ahel *et al*., 1994). As conventional processes in municipal wastewater treatment plants are not able to eliminate EDCs below a no-effect level (Stumpf *et al*., 1996), advanced treatment processes need to be considered to minimise the discharge of those compounds. Therefore, the application of membrane

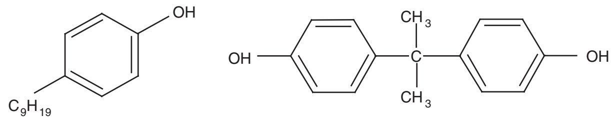

Figure 1 Structural formula of 4-nonylphenol and bisphenol A

technology is investigated here with the aim to evaluate the potential impact on increased endocrine disrupter removal.

The membrane processes under investigation include nanofiltration and a membrane bioreactor (MBR) configuration, which is already widely applied for the treatment of industrial and highly contaminated wastewater. The application of MBR concepts in municipal wastewater treatment is increasing in many countries, driven by high standards for discharge into sensitive areas and the potential of wastewater reclamation and recycling (Stephenson *et al.*, 2001). Generally the micro- and ultrafiltration membranes employed in membrane bioreactors for biomass retention do not display a barrier effect to EDCs. But compared to conventional secondary or tertiary systems a high EDC removal can be expected due to full particle retention promoting the removal of EDCs adsorbed to sludge flocs. Studies of Busch (2002) showed that MBRs were able to remove estrogenic steroid hormones significantly better than conventional wastewater treatment plants. Factors like high sludge ages and low organic loads could not yet be correlated to improved EDC degradation capacity, although biomass composition and starvation conditions might influence EDC removal in MBRs.

Nanofiltration membranes are expected to remove EDCs like bisphenol A or nonylphenol based on size exclusion due to their potential molecular-weight-cut-off in the order of 200 g/mol. The application of nanofiltration in wastewater treatment is not yet applied in full scale systems but investigated in the context of wastewater reuse for artificial aquifer recharge purposes. The ability of nanofiltration (NF) to impact on a wide range of parameters like organic contaminants, pathogens, conductivity and heavy metals might offer some potential as a polishing step in wastewater treatment plant effluent recycling applications. Schäfer *et al*. (2003) have demonstrated the capability and limitations of nanofiltration and reverse osmosis (RO) membranes to remove estrogenic trace contaminants.

Methods

Investigation of nanofiltration membranes

The experiments included a membrane screening (flux, retention) and contact angle measurements of eleven different membranes. The membrane screening was conducted in a pilot-scale test cell set-up shown in Figure 2. Each cell has a membrane area of about 50 cm^2 and the cross-flow in each radial-cell is 6 L/min. The pressure was adjusted close to the maximum pressure of each membrane and the temperature was always 20°C. Before taking 0.5 L-samples the concentrate and permeate was recycled for at least two hours to reach an adsorption equilibrium. The sample was stabilised by addition of NaN_3 and kept refrigerated. After enrichment in methyl chloride the samples were analysed by GC-FID. The measurements of the contact angle are performed by a drop-shape-analyser.

Investigation of full-scale membrane processes

The presented studies were conducted at a full-scale landfill leachate treatment plant, which is operated by the AWA Entsorgung GmbH in Warden close to Aachen. The process scheme includes a membrane bioreactor configuration and a parallel reverse osmosis installation. Landfill leachate has generally been identified as being highly contaminated

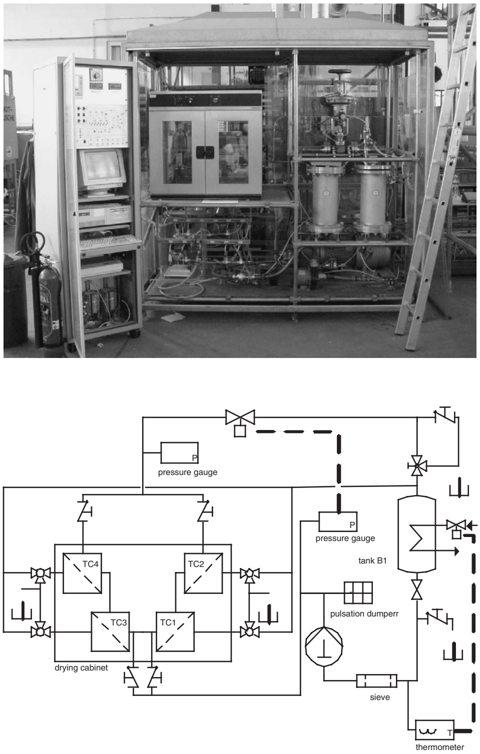

Figure 2 Photo and scheme of the pilot-scale test cell set-up

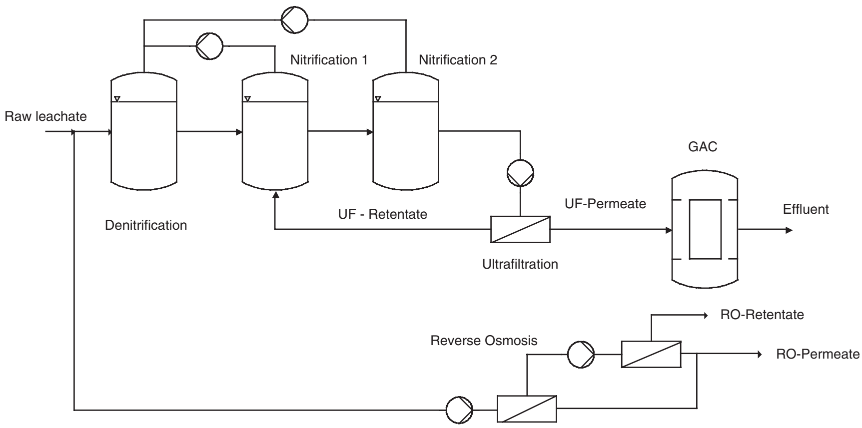

Figure 3 Membrane bioreactor configuration at a landfill leachate treatment plant

by organics including endocrine disrupting compounds by Paxeus (2000), Wenzel *et al.* (1998) and Behnisch *et al.* (2001).

The membrane bioreactor configuration consists of three activated sludge tanks and an external ultrafiltration unit (Figure 3). This process train treats an average feed flow of 7 m^3/h landfill leachate. The membrane bioreactor configuration includes a denitrification and a two-stage nitrification. The bioreactors have a gross volume of 180 m^3 each and are operated under 3.5 bar total pressure with internal re-circulations. The principle of pressurised membrane bioreactors is described by Krauth (1996). 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 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 and ultra-filtration permeate to the final effluent after passing the granular activated carbon units (GAC).

The reverse osmosis unit was installed in parallel to the MBR configuration to increase the overall plant capacity. The raw leachate is pre-filtered and fed to flat sheet RO modules operated under 60bar trans-membrane pressure. Out of an average feed of 5 m^3/h about 80% are recovered in the first RO stage. The retentate of the first stage is treated in a second high-pressure stage with a transmembrane pressure of 120 bar to recover 50% of the feed. Different process options for landfill leachate treatment with reverse osmosis were discussed by Rautenbach *et al*. (1996). The permeate of the second stage is mixed with the permeate of the first stage and discharged along with the effluent of the activated carbon filters into the municipal sewer system. The effluent from the plant is consequently diluted and treated in a municipal wastewater treatment plant prior to discharge into the environment.

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 h. Sample processing and analysis for measurement of bisphenol A was performed according to Meesters *et al*. (2002) and basically consists of an in-situ derivatisation step and liquid-liquid-extraction prior to the GC-MS measurement.

Results and discussions

Removal of xenoestrogenes with nanofiltration membranes

The results of the membrane screening are shown in Figure 4. The retention of the two compounds by the different membranes varies considerably. Especially the variance in the retention ratio for both compounds is noticeable, considering the fact that both substances have a similar molecular weight and size. It should be noted that the results given are average values from at least three measurements that did not indicate reproducibility problems.

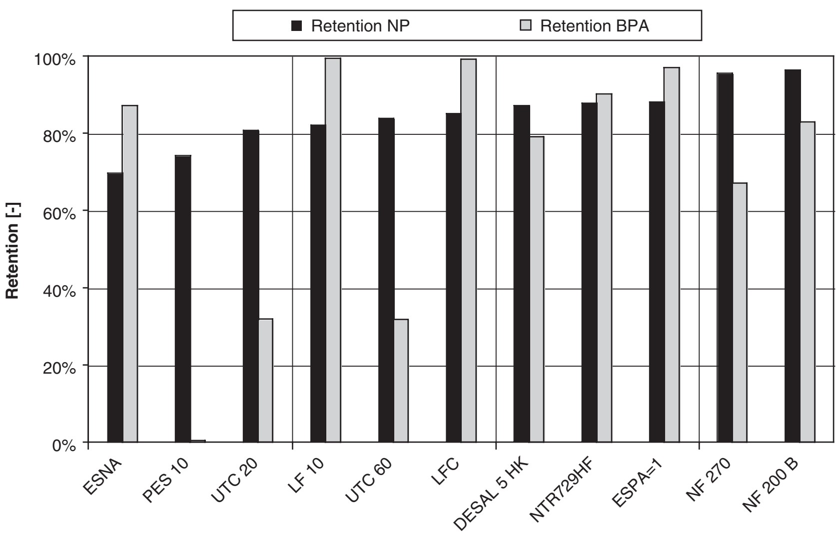

Figure 4 Membrane screening

The retention of all membranes for nonylphenol lies above 70%. In the case of bisphenol A only three membranes have a retention below 70%. PES 10 does not show any retention for BPA. To investigate a possible connection between retention and wetting properties (hydrophilicity) of the membranes, the contact angles were measured and correlated with the retention and permeability of the different membranes (Figure 5).

NP-retention and water permeability, respectively the wetting properties, of the membranes seem to correlate. The permeability increase with decreasing contact angle is not unexpected in the light of the solution-diffusion-model, because one would expect the water solubility to be higher in a hydrophilic than in a hydrophobic membrane. Looking at nonylphenol retention

$$R_{\mathrm{NP}} = \frac{c_{feed} - c_{permeate}}{c_{feed}} = 1 - \frac{c_{permeate}}{c_{feed}} \underset{\rho_{\mathrm{W}} = \mathrm{const.}}{=} 1 - \frac{\dot{m}_{NP,\ permeate}}{\dot{m}_{H_2O,\ permeate}} \cdot \frac{\dot{m}_{H_2O,\ feed}}{\dot{m}_{NP,\ feed}}$$

one could attribute the observed increased retention simply to increased water flux, resulting in a stronger dilution of nonylphenol. However, increased water flux may also be caused by other factors and some of the highest permeability figures are not accompanied by correspondingly high NP retention. A closer look at Figure 5 shows an even stronger effect of contact angle on NP-passage than on permeability. This could be caused by a decrease of NP-solubility in the membrane with increasing hydrophilicity. In the case of bisphenol A, which showed a much higher variation in retention behaviour, no relation to the contact angle could be observed. This may be caused by the more polar character of BPA, compared to nonylphenol.

Removal of bispenol A in landfill leachate treatment

In this study, bisphenol A (CAS 80057) is taken as an indicator for the behaviour of xenoestrogenic compounds in the plant. The analysis of nonylphenol behaviour in landfill leachate treatment is discussed in more detail elsewhere (Wintgens *et al.*, 2003). Results of a sampling campaign are summarised in Figure 6, where the mean values of five samples and the minimum and maximum levels are given for each sampling point. Considerably high concentrations, ranging up to milligrams of BPA per litre, were measured in the raw landfill leachate, comparable to results obtained by Yamamoto *et al.* (2000). The high concentrations of bisphenol A might be explained by leaching effects from polycarbonate

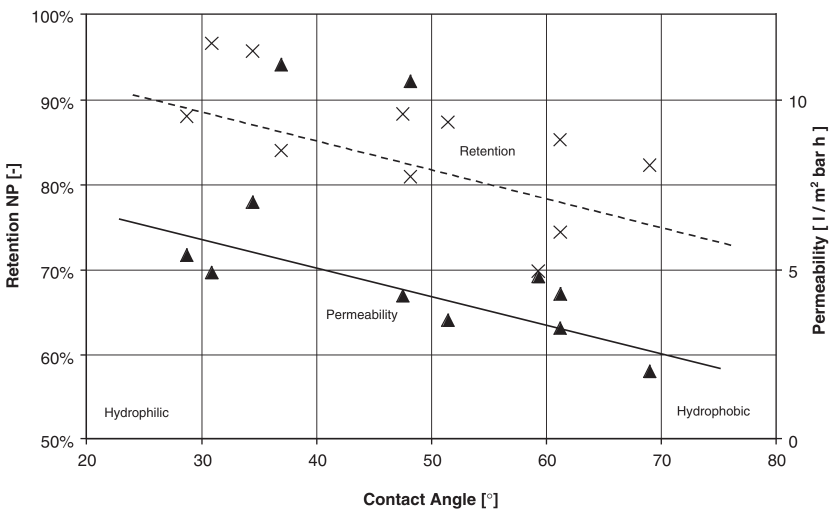

Figure 5 Influence of the contact angle

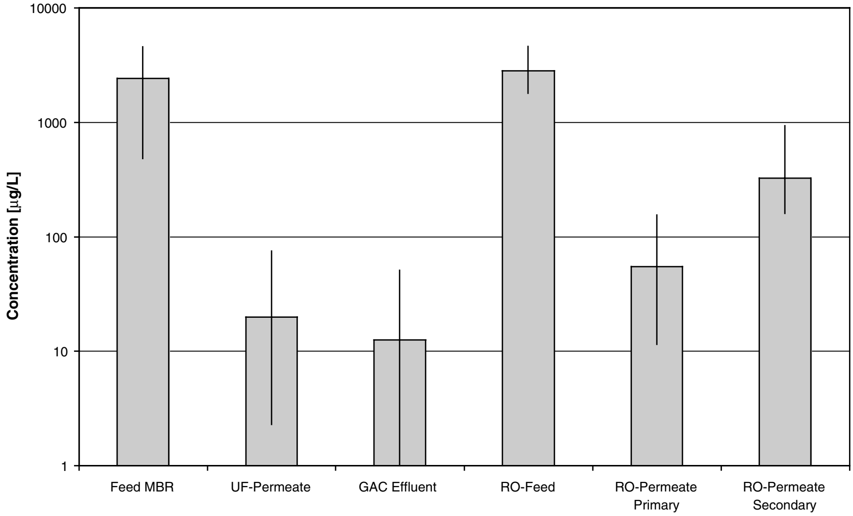

Figure 6 Bisphenol A concentrations in landfill leachate treatment plant

plastics abundant in the deposited waste which were described by Yamamoto *et al*. (1998). The conditions encountered in the landfill in terms of alkaline pH, mesophilic temperature and high ionic strength might promote the leaching process. There is a 99% BPA-removal in the MBR plus additional polishing by the granular activated carbon system, which is higher than the removal observed in conventional wastewater treatment systems, e.g. 91% BPA removal in a municipal wastewater treatment plant reported by Körner *et al*. (2000). The removal in the first RO stage is only slightly lower than that of the biological treatment, whereas high pollutant concentration in the RO retentate lead to high BPA concentrations in the permeate of the second RO stage.

A special sampling was conducted to investigate the phase distribution of bisphenol A in the activated sludge system of the MBR (Table 1).

The results indicate that the concentration in the liquid phase of the activated sludge is higher than in the permeate which might be due to the association of BPA with macromolecular substances retained by the membranes. The adsorption on sludge is evident but does not lead to a significant output of bisphenol A on the sludge path due to the low excess sludge removal. Mass balancing shows that both permeate and excess sludge removal contribute less than 1% of the influx of BPA into the system. Due to the low vapour pressure and high solubility of BPA, which is reported to be 8.70×10^{-10} mm-Hg-3.39×10^{-7} mmHg and 120 mg/L–300 mg/L respectively, volatilisation can be neglected (Staples *et al*., 1998). Biological degradation is assumed to be the major removal mechanism of bisphenol A. The removal rates observed are comparable to data published by Busch (2002). The concentrations of BPA in the plant effluent and sludge are somewhat higher than in municipal wastewater and sludge as reported in the literature (Wenzel *et al*., 1998; Körner *et al*., 2000).

Table 1 Bisphenol A concentration in the MBR system

Sampling point	Bisphenol A concentration
Liquid phase of the activated sludge	14.6 µg/L
Ultrafiltration permeate	10.1 µg/L
Solid phase of the activated sludge	14.0 mg/kg

Conclusions

The presented results show that membrane processes can significantly contribute to the removal of endocrine disrupting compounds like estrogenically active industrial chemicals bisphenol A and nonylphenol from aqueous streams. The processes investigated include membrane bioreactors with ultrafiltration membranes for biomass retention and dense polymer membranes applied in nanofiltration and reverse osmosis. All treatment options could generally achieve a high removal ranging from 70–99% of the target compounds based on different removal mechanism being either size exclusion in NF and RO or biological removal in MBRs. BPA seems to be removed most effectively by biodegradation in a system with high sludge age and complete retention of solids. RO is slightly less effective and the results for NF require further study. In the case of nonylphenol, NF yields consistent retention values well above 90 percent. The presented research comprises both small and full-scale applications complementing each other.

Within the ongoing research activities membrane bioreactor concepts and nanofiltration will be applied in municipal wastewater treatment. As xenoestrogenic compounds like nonylphenol and bisphenol A are probably not the most critical EDCs in municipal wastewater the focus will be shifted to estrogenic steroid hormones like 17-β-estradiol, estrone, and 17-α-ethinylestradiol.

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