Membrane fouling in the nanofiltration of landfill leachate and its impact on trace contaminant removal

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Abstract: Nanofiltration (NF) is an attractive option for the treatment of landfill leachate. However, membrane fouling can be a major obstacle in the implementation of this technology. In this study, bench-scale filtration experiments were carried out to study the fouling behaviour during the NF of a synthetic landfill leachate. The results indicate that calcium in combination with organic matter could play a major role in governing the fouling process. Membrane fouling depended on the calcium concentration in the feed solution. Moreover, the results also indicate a significant influence of membrane fouling on the retention of Bisphenol A (BPA). It was hypothesised that pore blocking and the presence of the fouling layer resulted in an enhanced sieving effect, which subsequently increased the retention of BPA. On the other hand, cake layer enhanced concentration polarisation could hinder BPA from back diffusing into the bulk solution, which would eventually result in a lower BPA retention.

Keywords: membrane fouling; landfill leachate; membrane filtration; nanofiltration; NF; trace contaminants; bisphenol A; BPA.
Introduction

Waste generation and hence its management have been part of human existence on earth for thousands of years. Landfilling, that is, disposal of the waste on or beneath the ground, has, for several reasons, been the most widespread method of waste management worldwide. Although alternative disposal technologies, such as incineration, are fully developed, to date, higher cost and limited capacities of those alternatives have led to an unbroken popularity of landfilling. In Australia, landfilling is the most common method of waste disposal and solid waste from almost all streams, that is, municipal, commercial and industrial, construction and demolition, as well as controlled waste, are disposed of in landfills (Newton et al., 2001). In 1996/1997, a total amount of 21.2 million tonnes of solid waste was sent to landfills, corresponding to a per capita disposal rate of more than 1.1 tonnes per annum. More than 95% of the total solid waste generated was received by landfills in some States and territories in 2001 (Newton et al., 2001). While there has been a considerable increase in recycling and waste diversion activities, this positive outcome has been offset by a steady increase in population.

Besides the emission of landfill gas, the release of leachate is the major route of interaction of a landfill with the environment and therefore is considered to pose the greatest potential for environmental harm (Christensen et al., 1989). Leachate is
Membrane fouling in the NF of landfill leachate and its impact

predominantly generated from precipitation onto the landfill surface, the moisture of the waste itself and, to a limited extent, groundwater (if the bottom of the landfill is not lined) or other water infiltration (Bilitewski et al., 1997). During the percolation through the body of the landfill, the infiltrated water is severely contaminated with a complex mixture of organic and inorganic contaminants. Therefore, leachate collection followed by an adequate treatment process is important for the protection of surface and subsurface watercourses and, depending on legislation, required in many countries (Anonymous, 1999).

According to Bilitewski et al. all contaminated water that has been in contact with waste is defined as leachate (Bilitewski et al., 1997). Its formation is the result of complex hydrodynamic and physico-chemical processes within the landfill body. The expected quantity and quality of the leachate depends on a number of factors, for example, climate, moisture content of the waste, landfill operation and landfill age. Within the landfill, water can be stored by the waste and due to biochemical processes water is mostly consumed since they mainly proceed under anaerobic conditions (Bilitewski et al., 1997; Melin et al., 2005). Guideline figures for leachate generation of 31–58% of the precipitation were reported for landfills with unconsolidated surface and 25–40% of the precipitation for landfills with compacted surface (Bilitewski et al., 1997).

Apart from the factors mentioned above, the characteristics of landfill leachate also depend on a number of other parameters, such as waste composition, the biochemical decomposition of the waste within the landfill, its pH range and the amount of water retained (Bilitewski et al., 1997). Thus, the leachate composition varies significantly among landfills. Leachate from municipal landfills typically contains 0.2–1.5% solutes, of which the largest portion (80–95 wt.%) consists of monovalent salts (Dahm et al., 1994). Furthermore, leachate may contain a large amount of inorganic nitrogen compounds, mainly as ammonia. A small portion (approximately up to 1 g/l) of the inorganic contents of leachate is made up by heavy metals. The remaining 5–20 wt.% are made up of organic compounds. Christensen et al. (1989) classified leachate pollutants from a typical landfill receiving municipal and commercial wastes (not industrial waste) into four groups:

1. common inorganic cations and anions
2. heavy metals
3. organic matter
4. specific organic compounds (originating from household or industrial chemicals, present in relatively low concentrations, usually less than 100 µg/l).

In particular, the occurrence of these specific organic compounds of the last group at trace level has attracted many intensive research efforts in the last decade. These studies revealed that an extensive range of organic compounds such as plasticisers (phthalates), pesticides, pharmaceuticals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, flame retardants can be found ubiquitously in landfill leachate (Behnisch et al., 2001; Paxeus, 2000; Yamamoto and Yasuhara, 1999). This, once again, underlines the necessity of sufficient treatment of the leachate to avoid negative environmental impact.

Most Australian landfills currently have an onsite pretreatment process to reduce ammonia prior to sewer disposal as trade waste. However, as landfills are being located further away from metropolitan areas and sewage treatment plants, it would be more
cost-effective to have direct leachate disposal after being treated by advanced treatment processes, which can meet the very stringent discharge regulations required. In fact, this has been proven to be an effective approach in Europe, particularly in Germany. Amongst several technologies currently available for the treatment of landfill leachate, Nanofiltration (NF) has emerged as an attractive option since complementary combinations with pre/post-treatment can be more cost-effective than the reverse osmosis applications that are most commonly used at present (Melin et al., 2005). However, NF is not suitable as a single process in landfill leachate treatment since it has a low rejection for nitrogen compounds (Trebouet et al., 2001) and can be subjected to severe fouling. Hence, combined processes are used in full-scale applications. These basically contain a biological treatment (conventional nitrification/denitrification or sequencing batch reactor combined with sedimentation tank or ultrafiltration membrane for sludge retention) followed by the NF stage. However, it must be pointed out that for landfill leachate even a very comprehensive pretreatment will not be able to completely eliminate potential fouling causing constituents. Thus, fouling will always be a part of membrane applications in the treatment of polluted water.

Membrane fouling can be defined as irreversible flux decline (and thus loss of performance), which can only be removed by physical and chemical cleaning. Fouling in NF is a very important factor due to its negative impact on the competitiveness of the process. Generally fouling can be categorised as organic, inorganic, particulate and biological fouling (Schäfer et al., 2005). Depending on the pretreatment, organic and inorganic fouling probably exhibit the most significant impact on the application of NF for landfill leachate treatment, for which the fouling potential has been found to be high, reflected by the fouling index ranging between 3.5 and 5.4 (Trebouet et al., 1999). Due to the high concentrations of organic matter in landfill leachate, organic fouling is expected to play a major role in membrane filtration (Scott et al., 2005). Despite the high fouling propensity of leachate, the effects of membrane fouling on retention in the NF process of landfill leachate have, to date, been largely overlooked. In fact, several studies investigating the NF of groundwater and secondary effluent have revealed some considerable effects of membrane fouling on the retention of organic contaminants (Xu et al., 2006). These authors attributed the differences in the retention between virgin and (organically) fouled NF membranes to the changed membrane characteristics. Nghiem et al. (2002) reported a decrease in the retention of the trace organic compound estrone when the feed water contained natural organic matter compared to pure Milli-Q water. In other more recent studies, some observable effects of organic matter on the retention of several herbicides (Plakas et al., 2006) and on the membrane characteristics (Xu et al., 2006) have been reported. Furthermore, Plakas et al. (2006) suggested that the extent of membrane fouling as well as the structure of the foulants and solutes might have an influence on retention. Calcium was shown to affect retention of herbicides differently depending on whether it was applied alone or in conjunction with organic matter. While most of these findings to some degree demonstrate the importance of the feed water constituents in membrane filtration processes, the underlying mechanisms governing membrane fouling and especially the influence of fouling on trace organic retention remain unclear.

In this study, the effects of natural organic matter in combination with calcium on the fouling behaviour of NF membranes were investigated using a synthetic landfill leachate. Bisphenol A (BPA), which is found ubiquitously in landfill leachate and is also one of the most significant endocrine active substances, was selected as a model trace organic
Membrane fouling in the NF of landfill leachate and its impact

Membrane filtration experiments were conducted under accelerated fouling conditions, thus, enabling a detailed examination of the fouling behaviour during landfill leachate NF processes. The influence of fouling on the retention of BPA and possible mechanisms were also delineated and discussed.

2 Materials and methods

2.1 Analytical reagents and chemicals

All chemicals used in this investigation were of analytical grade and supplied by APS Australia, Auburn, NSW, Australia unless otherwise stated. Chemical solutions and feed waters were prepared with deionised (DI) water (Milli-Q Ultra Pure Water System, Millipore, North Ryde, NSW, Australia). Adjustments of the pH value were carried out using 1 M sodium hydroxide (NaOH) or 1 M hydrochloric acid (HCl), respectively. A stock solution (1 g/l) of BPA (Sigma Aldrich, Castle Hill, NSW, Australia) was prepared in pure methanol (High-Performance Liquid Chromatography (HPLC) grade). It was stored in the freezer at −18°C and used within 1 month.

2.2 NF membrane

A commercially available NF membrane, namely NF-270 (FilmTec Corp., Minneapolis, MN, USA), was used in this study. The membrane was received as flat sheet and was stored under dry conditions at room temperature. According to the manufacturer, the membrane is thin-film composite with a polyamide active layer on a microporous polysulfone supporting layer.

2.3 Membrane filtration set-up and protocol

A laboratory-scale cross-flow NF set-up (Figure 1) was used in this study. The NF/RO filtration unit comprises a stainless steel plate-and-frame membrane cell with an effective surface area of 7.7 cm × 3.0 cm, a 15 l stainless steel feed tank and a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN, USA). Retentate flow rate was monitored by a rotameter. Feed pressure and cross-flow velocity were controlled by means of a bypass valve and a back pressure regulator.

Figure 1 Schematic diagram of the laboratory-scale cross-flow NF test unit
Prior to every membrane filtration test two consecutive pretreatment steps were carried out. Firstly, a membrane compaction was performed at a feed pressure of 130 kPa for 1 hr using DI water in the feed tank. Then a fouling cocktail containing NaHCO₃, NaCl and humic acid was added to make up concentrations of 1 mM, 20 mM and 20 mg/l in the feed water (total volume = 7 l), respectively. Depending on the experiment, the concentration of CaCl₂ was set to 0, 0.5, 1 or 4 mmol/l in the feed solution. Subsequently, the fouling layer was established on the membrane surface by running the system at a pressure of 1000 kPa for 18 hr. Throughout the experiment, the permeate was recycled back to the feed tank after passing through a digital flow meter (Optiflow 1000, J&W Humonics, Folsom, CA, USA), connected to a PC, to monitor the flow rate. All experiments were run at a cross-flow rate of 30.4 cm/s and a constant temperature of the feed solution of 20 (± 0.5)°C, controlled by a circulating heater/chiller (Neslab RTE 7, Newington, NH, USA). A digital pH meter (Model 744, Metrohm, Herisau, Switzerland) was used for the measurements of pH.

After the fouling development, the permeate flow rate was set to 3.7 ml/min followed by the addition of BPA to make up a concentration of 750 µg/l in the feed solution. Samples of feed and permeate (approximately 1.5 ml) were collected at specified intervals.

2.4 Analytical technique

A Shimadzu HPLC (Rydalmere, NSW, Australia) system was used to analyse the organic contaminant BPA. The solvent delivery system included two HPLC pumps, a degaser and a gradient mixer. A reversed phase column (Discovery ® C18 with particle size, length and diameter of 5 µm, 250 mm and 4.6 mm, respectively) supplied by Supelco (Castle Hill, NSW, Australia) was used. The UV wavelength was set at 280 nm. Premixed mobile phase was prepared using HPLC grade Acetonitrile (ACN) and an aqueous buffer solution (DI water containing 25 mmol/l of KH₂PO₄): Eluent A (80% ACN/20% aqueous buffer solution) and eluent B (20% ACN/80% aqueous buffer solution). Further details of this analysis method are available elsewhere (Nghiem et al., 2005).

3 Results and discussion

3.1 Landfill leachate characterisation

A literature review was conducted to examine the typical compositions of the major constituents in landfill leachate. The results are summarised in Table 1, which clearly highlights the elevated salt concentrations and dissolved organic matter as the major constituents in landfill leachate. Furthermore, it is interesting to note that all parameters are subject to large variations, approximately 3 orders of magnitude or more. As a result of this literature review study, a model synthetic landfill leachate was selected to present the characteristics typical to those of real leachate (Table 1).
Membrane fouling in the NF of landfill leachate and its impact

Table 1  Concentrations of salts and dissolved organic carbon in typical landfill leachate and composition of the synthetic leachate solution used in this study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Real landfill leachate</th>
<th>Synthetic leachate</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mg/l)</td>
<td>HA content as part of DOC (%)</td>
<td>mg/l</td>
<td>mg/l</td>
</tr>
<tr>
<td>Sodium</td>
<td>2770</td>
<td>Xu et al. (2006)</td>
<td>483</td>
</tr>
<tr>
<td>0–8000</td>
<td></td>
<td>Scott et al. (2005)</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>38</td>
<td>Xu et al. (2006)</td>
<td>0, 20, 40, 160\textsuperscript{a}</td>
</tr>
<tr>
<td>4–7200</td>
<td></td>
<td>Scott et al. (2005)</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>34–11,375</td>
<td>Scott et al. (2005)</td>
<td>780</td>
</tr>
<tr>
<td>DOC</td>
<td>649</td>
<td>Xu et al. (2006)</td>
<td>6\textsuperscript{b}</td>
</tr>
<tr>
<td>78–663</td>
<td></td>
<td>Choi and Lee (2006)</td>
<td></td>
</tr>
<tr>
<td>Average (n = 5) = 388</td>
<td></td>
<td>Nanny and Ratasuk (2002)</td>
<td></td>
</tr>
<tr>
<td>57–138</td>
<td></td>
<td>Artiola-Fortuny and Fuller (1982) and Castagnoli et al. (1990)</td>
<td></td>
</tr>
<tr>
<td>Average (n = 3) = 89</td>
<td></td>
<td>Christensen et al. (1998)</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Depending on the experiment.

\textsuperscript{b}20 mg/l HA added to feed water.

3.2 Physico-chemical properties of BPA

Important physico-chemical and toxicological properties of BPA are presented in Table 2. BPA has a moderately high octanol-water partitioning coefficient (log $K_{ow}$) which indicates the hydrophobicity of the compound leading to an instant adsorption to hydrophobic materials. BPA is a weak acid with the two phenolic groups having a pKa value of 10.1. This means that at the pH value present during the experiments (approximately 8), the functional groups are not dissociated so the compound remains neutral.

Table 2  Physico-chemical and toxicological characteristics of BPA

<table>
<thead>
<tr>
<th>Formula</th>
<th>$C_{15}H_{16}O_2$</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW (g/mol)</td>
<td>228</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Solubility in water (mg/l)</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>pKa</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>Log $K_{ow}$</td>
<td>3.32</td>
<td></td>
</tr>
</tbody>
</table>
3.3 Influence of the calcium concentration on the flux

A clear impact of the feed water calcium concentration on the flux was found in this study. Figure 2 shows the normalised flux profiles over time during the fouling layer development phase (18 hr) for 4 different calcium concentrations in the feed water. All curves show a relatively similar profile with an initial steep drop followed by a delayed flux decline over time.

Figure 2  Influence of feed solution calcium concentration on permeate flux. The feed solution contained 750 µg/l of BPA, 1 mM of NaHCO₃, 20 mM of NaCl, 20 mg/l of humic acid and variable calcium concentrations, pH = 8

As expected, the flux decline over time was the lowest when no calcium was present. It dropped to 52% of the initial value after 18 hr, which can be attributed solely to organic fouling due to the humic acid in the feed solution (see Figure 3). Organic fouling is caused by the adsorption or deposition of organic matter to or on the membrane surface, gel formation or pore blocking (Schäfer et al., 2005). All of these mechanisms can occur at the same time. As a result, it may not be possible to determine the actual extent to which each mechanism contributes to the fouling process.

Fouling increased as calcium was introduced to the feed water. The result reported here is consistent with several previous studies, which have demonstrated an increase in membrane fouling in the presence of calcium (and other multivalent cations) (Hong and Elimelech, 1997; Seidel and Elimelech, 2002; Teixeira and Rosa, 2006). Intermolecular bridging between organic foulants and the membrane may be caused by cations (Seidel and Elimelech, 2002). Furthermore, positively charged calcium ions can form complexes with the functional groups of the humic acid (solute–solute interaction), resulting in a reduction of the interchain repulsion between the macromolecules of the humic acid and can lead to the formation of small and coiled macromolecules. In addition, the calcium ions partly neutralise the negative charge of the membrane causing an increase in interaction between the membrane and the humic acid molecules (Teixeira and Rosa, 2006).

In this study, a steep decrease of the curves for 0.5 and 1 mM of calcium was observed at the beginning of the run which was possibly caused by pore blocking. In contrast, the flux decreased more slowly in the absence of calcium. The flux decline
over time slows down for all curves with the progress of the experiment and after approximately 500 min all curves run relatively parallel. It is assumed that more gentle increase of fouling is attributed to a second fouling mechanism, namely the formation and compaction of the cake layer on the membrane surface after the pores have been blocked.

Figure 3 Permeate flux after 18 hr of fouling layer development depending on calcium concentration in the feed water for a NF-270 membrane. The feed water contained 750 µg/l of BPA, 1 mM of NaHCO₃, 20 mM of NaCl, 20 mg/l of humic acid and variable calcium concentrations, pH = 8

The overall extent of flux decline with time was dependant on calcium concentration as follows: 0.5 mM > 1 mM > 4 mM > 0 mM. Thus, 0.5 mM appears to be a critical concentration for fouling at the conditions given in this study. This is consistent with a previous study by Nghiem et al. who reported a peak in membrane fouling in the ultrafiltration of grey water at a similar calcium concentration (Nghiem et al., 2006). It is hypothesised that a high calcium concentration may lead to the formation of large and compact aggregates (or flocs) that are bigger than the pores. Thus, they cannot penetrate into the membrane and cause pore blocking. Additionally, the cake layer formed may be more porous. This causes less hydraulic resistance and, consequently, a flux decline which is less severe. In contrast, at lower calcium concentrations, smaller aggregates are formed which has been shown for colloidal systems (Nghiem et al., 2006). This results in a dense cake layer and/or pore blocking (Waite et al., 1999).

3.4 **Influence of fouling on the retention of organic contaminants**

Similar to the fouling studies, retention tests with varying calcium concentrations were carried out. In Figure 4, BPA concentrations in the feed solution and the permeate as well as the retention of BPA throughout the experiment are shown for a calcium concentration of 4 mM. The concentration of BPA in the feed water slowly decreases in the course of the run from approximately 750–700 µg/l. The permeate concentration increases sharply in the beginning of the test starting at approximately 75 µg/l. The curve starts to stabilise
from ca. 70 min and reaches 490 µg/l at 120 min. After that only a very slight increase of the permeate BPA concentration was observed. Accordingly, the retention shows a sharp decrease in the beginning of the test, starting at 90% and reaching an almost stable level of approximately 30% after 10 hr.

**Figure 4** Concentrations of BPA in feed water and permeate and retention of BPA for a calcium concentration of 4 mM in the feed water for a NF-270 membrane. The feed water contained 750 µg/l of BPA, 1 mM of NaHCO₃, 20 mM of NaCl, 20 mg/l of humic acid, pH = 8

An initial drop of the retention of BPA was observed for all calcium concentrations (data shown for 4 mM of calcium only), however, the extent was different which eventually leads to quite significant differences in retention of BPA as shown in Figure 5. Adsorption of BPA to the membrane surface and possibly the humic acid is responsible for the high retention in the beginning of the test which is consistent with previous studies where a significant adsorption of hydrophobic, neutral compounds onto NF membranes was found (Kimura et al., 2003). Nghiem et al. observed a similar initial drop of BPA retention stabilising at approximately 45% retention when running a feed water solution containing 10 mM of NOM through a NF-270 membrane (Nghiem et al., 2005). The low BPA retention for both 0 and 4 mM of calcium correlates with less fouling compared to 0.5 and 1 mM as described above. This effect may be attributed to limited pore blocking occurring when no calcium is present, thereby resulting in a less dense fouling layer. At a concentration of 4 mM of calcium, large compact aggregates are presumably formed that are too large to block pores and also form a fairly porous cake layer on the membrane surface. An additional effect, the prevention of back diffusion of solute into the bulk solution, has been previously described (Ng and Elimelech, 2004). This results in a higher concentration of the solute at the membrane surface, which eventually leads to a lower retention. For 0.5 and 1 mM of calcium, respectively, small, coiled macromolecules are formed that can cause pore blocking (Seidel and Elimelech, 2002). Besides an increase in fouling, a simultaneous increase in retention of BPA at these calcium concentrations was observed. Furthermore, the formation of the dense cake layer may induce an additional sieving, which can result in a higher retention. Both of these mechanisms are thought to occur at the same time and cannot easily be separated.
Figure 5  Retention of BPA by NF-270 membrane after 420 min (7 hr) of membrane retention test. The feed water contained 750 µg/l of BPA, 1 mM of NaHCO₃, 20 mM of NaCl, 20 mg/l of humic acid and variable calcium concentrations, pH = 8

4 Conclusions

The results reported here demonstrate a considerable effect of the feed water calcium concentration on membrane fouling. Fouling was most severe at 0.5 mM, whereas at no calcium or at a higher concentration (e.g. 4 mM) membrane fouling was considerably lower. Two major fouling mechanisms, pore blocking and cake layer formation, are assumed to take place. Both can be caused by solute–solute interactions (bridging and complexation) and solute–membrane interactions (bridging and charge neutralisation). The study also showed a significant influence of fouling on the retention of BPA. Low rejection coincided with low fouling at 0 mM and 4 mM of calcium, respectively. Retention increased commensurate with the extent of fouling. However, the highest retention (at 1 mM of calcium) was not observed when fouling was most severe (at 0.5 mM of calcium). It was hypothesised that pore blocking, which induced an enhanced sieving effect, resulted in an increase in the retention of BPA. On the other hand, the cake enhanced concentration polarisation, which hindered back diffusion into the bulk solution, could eventually result in a lower BPA retention.

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Membrane fouling in the NF of landfill leachate and its impact


