Comparison of sand and membrane filtration as non-chemical pre-treatment strategies for pesticide removal with nanofiltration/low pressure reverse osmosis membranes
Krzysztof P. Kowalski, Henrik T. Madsen and Erik G. Søgaard

ABSTRACT
Pilot plant investigations of sand and membrane filtration (microfiltration (MF)/ultrafiltration (UF)/nanofiltration (NF)/low pressure reverse osmosis (LPRO)) have been performed to treat groundwater polluted with pesticides. The results show that simple treatment, with use of aeration and sand filtration or MF/UF membranes, does not remove pesticides. However, by reducing the content of key foulants, the techniques can be used as a pre-treatment for nanofiltration and low pressure reverse osmosis that has proved to be capable of removing pesticides. It was found that a lower fouling potential could be obtained by using the membranes, but that sand filter was better at removing manganese and dissolved organic matter. The results indicate that combining aeration, sand filtration and membrane techniques might be a good option for pesticide removal without any addition of chemicals and minimized membrane maintenance.

INTRODUCTION
Membrane technologies are becoming increasingly popular due to improvements in their robustness and energy efficiency. Continuation of this trend might result in near future replacement of the well-known sand filtration technique with membrane separation. Especially in cases where advanced treatment might be necessary to solve current issues such as groundwater pollution with pesticides compounds the method will be useful. However, any new approach for the water treatment has to comply with existing legislation (Danish Ministry of the Environment 2007), and Danish law limits the usage of the physico-chemical processes used in waterworks, prioritizing only simple water treatment with use of aeration and sand filtration. This strategy results in abandonment of the difficult water sources, like those polluted with pesticides, and to use those where simple treatment can be applied instead. However, there is an increasing awareness of pesticide pollution of groundwater resources used for drinking water, where the pollution has been found to be stable over a period of many years (Søgaard et al. 2001; Thorling et al. 2010). Because of the enduring pollution, it is necessary to employ a method to remove the pesticide compounds if the groundwater is to be used for drinking water. Today granular activated carbon followed by UV (GAC UV) is the preferred method for removal of pesticides in Denmark, but the use of GAC suffers from problems mainly related to saturation and footprint size (Plakas & Karabelas 2012; Søgaard & Madsen 2013).

A promising technique for removal of pesticides is nanofiltration (NF) and low pressure reverse osmosis (LPRO), which does not result in complete demineralization and operates at lower pressures compared to reverse osmosis (Plakas & Karabelas 2012). The use of NF/LPRO membranes for removal of pesticides is also favorable since it allows for a treatment that does not involve the addition of chemicals, and it can be used in a decentralized drinking water system.
However, the concentrations of iron and manganese in groundwater are often high, and if they are not removed, they may precipitate and foul the NF/LPRO membrane. A pre-treatment method for iron removal could be to employ a tandem of aeration and sand filtration, which is used in the conventional treatment of groundwater. Here, ferrous iron is oxidized by help of oxygen from the air and filtrated as iron(III) oxides precipitates in the sand filter (Søgaard et al. 2011; Pacini et al. 2005).

Another possibility could be replacing sand filtration with low pressure membranes such as microfiltration and ultrafiltration (MF/UF). It has been shown in previous studies that a combination of aeration and microfiltration, where a polymeric polyethersulfone membrane with an absolute porosity 0.2 μm was used, might be adequate for iron removal; however, it required sufficient reaction time and pH adjusted to 8 with the help of sodium hydroxide (Ellis et al. 2000).

Another approach that has been studied is the usage of a chemical oxidant, like chlorine to enable fast and efficient iron oxidation prior to UF (Choo et al. 2009). The main issue with using MF/UF membranes for filtration of rich iron solutions is that it causes significant problems with fouling, because of the iron precipitation and formation of colloidal iron. This means that the MF/UF membranes require a regular and efficient cleaning process to avoid plugging of the membrane (Soffer et al. 2004; Korchef et al. 2009). For this reason, the use of ceramic membranes could be a good option. They have higher mechanical stability compared to polymeric membranes enabling the application of high backwash pressure for fouling removal (Hofs et al. 2011).

In this study we evaluate conventional and membrane processes for production of drinking water from groundwater, focusing on the pesticides removal. Following the Danish policy, especially its limitations, the treatment processes were performed without any chemical reagent enhancement.

The initial experiments investigated the fate of pesticides during sand filtration and ceramic MF/UF membranes. These experiments were performed to assess whether the current technologies were capable of affecting the pesticides. The main investigations then focused on the use of sand filtration and microfiltration/ultrafiltration as pre-treatment techniques for pesticide removal with NF/LPRO. The two techniques were compared with respect to removal efficiency of compounds responsible for inorganic, organic, particulate and biological fouling. Thus, permeates were examined not only for mineral and organic matter content, but also turbidity, particle size and bacteria removal were determined. Moreover, the unified membrane fouling index (UMFI) (Huang et al. 2008) was measured for each permeate since fouling indexes are a typical way of classifying the fouling potential of a given water source.

### MATERIALS AND METHODS

#### Water characterization

The experiments were performed with use of natural groundwater that was acquired from an abandoned drinking water well in Vognsbloparken, Esbjerg, Denmark. Composition of the groundwater can be seen in Table 1. For investigation of manganese and pesticides, the raw groundwater was spiked with manganese(II) ions in form of MnSO$_4$$\cdot$H$_2$O, Sigma Aldrich and a mixture of pesticides that contained atrazine (Pestanal, Fluka), atrazine-d$_5$ (Pestanal, Fluka), bentazon (Pestanal, Fluka), 2,6-dichlorobenzamide (BAM) (Pestanal, Fluka) and desethyl-desisopropyl-atrazin (DEIA) (Pestanal, Fluka). All pesticides were purchased at Sigma-Aldrich. Methanol and acetonitrile (HPLC grade) and acetone were purchased from VWR. Demineralized water was produced in house with a Silex II ion exchanger from SILHORKO.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.6–6.8</td>
</tr>
<tr>
<td>Turbidity [NTU]</td>
<td>3.0–4.0</td>
</tr>
<tr>
<td>$O_2$ [mg/L]</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Fe total [mg/L]</td>
<td>3.5–4.2</td>
</tr>
<tr>
<td>Fe(II) [% of total Fe]</td>
<td>90–100</td>
</tr>
<tr>
<td>Ca [mg/L]</td>
<td>35</td>
</tr>
<tr>
<td>Mg [mg/L]</td>
<td>3.6</td>
</tr>
<tr>
<td>Cl$^-$ [mg/L]</td>
<td>35</td>
</tr>
<tr>
<td>SO$_{4}^-$ [mg/L]</td>
<td>2</td>
</tr>
<tr>
<td>UV [Abs at 254 nm]</td>
<td>0.35 ± 0.05</td>
</tr>
</tbody>
</table>

Table 1: Composition of raw groundwater taken from pilot plant for membrane filtration.
Aeration and sand filtration method

For the investigation of the aeration and sand filtration process, a pilot plant installed at the well site was used. The plant is shown in Figure 1. Aeration was performed with MicroDrop Aqua aeration unit containing open walled cylindrical plastic tubes that like a drizzling filter increases water–air contact surface. For sand filtration a pressurized filter (1 m³ of quartz sand 0.2–1 mm) was used.

Two procedures were used: continuous flow of groundwater through the system and recirculation of a groundwater batch. The first procedure was used to evaluate the iron and spiked manganese (reaching a concentration of 1.2 mg/L in feed water) removal and turbidity lowering, while the second procedure was used to evaluate the effect on pesticides. In the recirculation procedure 120 L of groundwater was collected in a holding tank where it was spiked with pesticides to obtain a concentration of 2 μg/L. This concentration value was chosen to avoid the pesticides having an effect on the microorganisms in the sand filter, and to avoid saturation. If the pesticides adsorb to the sand filter, saturation may be reached quickly by use of higher concentrations and hereby hide the adsorption effect. Also concentrations in this range are close to what is found in real polluted groundwater. The spiked solution was then allowed to recirculate for 15 minutes for homogenization. Before each experiment, water was allowed to run through the system for 30 minutes to obtain fresh groundwater. Triplicate samples of 1 L were taken at three places: before aeration, after aeration and after sand filter. For each sample pH and dissolved oxygen (DO) was measured.

Aeration and MF/UF method

MF/UF membrane filtration was carried out with four silicon carbide ceramic MF/UF membranes with reported pore sizes: 3, 1, 0.1 and 0.04 μm from CoMeTas (now LiqTech) – system shown in Figure 1. The membranes differ in surface area and geometry; i.e. membranes with pores sizes of 3 and 1 μm membrane had area of 0.09 m².
and 31 channels and those with pores sizes of 0.1 and 0.04 μm had an area of 0.05 m² and 19 channels.

For experimental purposes 100 L of aerated groundwater was collected at the pilot plant and transported to the membrane filtration unit. Pesticide removal was investigated by spiking pesticide mixture to the feed water to obtain a concentration of 2 μg/L, and the filtration was performed for each membrane separately with a transmembrane pressure between 200 and 300 mbar in a recirculated cross-flow mode. Two samples of 400 mL were taken from the feed, retentate and the permeate. Flow and pressure were measured for each stream, and was used to monitor the degree of fouling on the membranes. To clean the membranes, a 3 bar back flush was used. To evaluate the efficiency of the filtration, particle size distribution was determined before and after filtration.

**Nanofiltration method**

Nanofiltration and low pressure osmoses were investigated with a DDS Lab-Unit 20 equipped with two commercial membranes: NF 99 HF from Alfa Laval, Nakskov, Denmark and NF90 from Dow chemicals. The NF99HF is a classic NF membrane that shows selective removal of divalent ions, whereas the NF90 membrane is characterized as a tight NF membrane, which might also be classified as a LPRO membrane. The nanofiltration experiments were conducted by first recirculating distilled water through the system for 30 minutes at 10 bars to clean and compress the membranes. Then the distilled water was replaced by 4 L of pesticide solution with 1 mg/L concentration. Concentrations of 1 mg/L were chosen to avoid solid phase extraction as a preanalytical method and thereby increase the variance of the results. The use of pesticide concentrations of this value is standard in membrane filtration experiments and is not expected to influence the true rejection. Before samples were collected, the filtration system was allowed to run for 1 hour to ensure that adsorption to membranes and equipment would not influence the results. After 1 hour of recirculation triplicate samples were extracted over a 10 minute period and transferred directly to vials for analysis. The filtration was run at 25 °C, 10 bars, flow of 8 L/min and a total membrane area of 59 cm². Because only small samples were extracted, the recovery was low and the concentration of the solution would not affect rejection.

**Analytical methods**

From the primary sample were taken 40 mL for sample digestion together with nitric acid in an autoclave (30 minutes at 120 °C). The prepared samples were analyzed by use of inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Perkin Elmer Optima 3000 DV) for content of Fe, Mn, Ca and Mg all with a detection limit of 0.1 mg/L.

Pesticides were analyzed with a solid phase extraction (SPE) high-performance liquid chromatography/electrospray ionization mass spectrometry (HPLC/ESI-MS) method. The procedure for the solid phase extraction was: activation of column with 6 mL methanol, equilibration with 6 mL of demineralized water, application of 500 mL of sample on column, elution of interferences with 6 mL demineralized water, vacuum drying of column for 30 minutes, elution of analytes with 10 mL acetone, evaporation of acetone at 70 °C and dissolution in 0.5 mL acetonitrile spiked with 0.1 mg/L internal standard (atrazine-d₅). For solid phase extraction, TELOS ENV 200 mg/6 mL was used. The HPLC method was specific for each pesticide. For atrazine, BAM and bentazon an eluent of methanol (A) and 5 mM ammonium acetate pH 3, adjusted with formic acid (B) was used, while for DEIA the pH was set to 6.5. For atrazine, BAM and DEIA an eluent mixture of 70/30 A/B was used, while for bentazon a 65/35 mixture was used. A ZORBAX Eclipse Plus C18, 3.5 μm, column was used. On the ESI-MS, the nebulizer pressure was set at 40 psi, the nebulizer flow at 9 L/min and the dry temperature at 350 °C.

pH was measured by Meter Lab PHM 250 pH meter (Radiometer Analytical) and oxygen with OxyMeter (Oxymeter Handy MK II) in the freshly collected samples. The Merck photometric methods were implemented to determine the following: iron speciation (Fe(II) and Fe total) with method no. 1.00796.0001, chloride ions with method no. 1.14730.0001 and sulphate with method no. 1.14548.0001. Turbidity was measured with the compact AQUALYTIC® infrared turbidity meter.

Particle size was determined by help of a PhotoCor dynamic light scattering (DLS) instrument that was used to gather light scattering data. Bacteria count was performed according to the Danish Standard 2251:1983, where collected sterile samples were cultivated for 7 days with agar (DS 2251:1983 1983:01-01).
Unified membrane fouling index

To obtain an overall indication of the effectiveness of sand filtration and MF/UF membranes for reducing the fouling potential, the UMFI, based on Hermia’s model (Huang et al. 2008), was applied. In this model fouling is often assumed to be purely due to cake filtration, in which case the UMFI can be obtained from the slope of a linear relationship between experimentally obtained specific flux, $J_s$, and cumulative permeate volume, $V_s$:

$$\frac{1}{J_s} = 1 + (\text{UMFI}) V_s$$

where $J_s$ is dimensionless normalized specific flux, equal to $1/TMP$ and $TMP$ is normalized transmembrane pressure $TMP_t/TMP_0$; $V_s$ is the permeate throughput defined as the cumulative volume of permeate per membrane surface area (L/m²).

The model was applied for constant pressure (2 bar) dead-end filtration test using a 0.04 my cellulose filter with area of 0.00096 m².

RESULTS AND DISCUSSION

Removal of pesticides

Based on the pore size of sand filters and MF/UF membranes, it is not expected to be able to remove pesticides. However, several factors could influence the fate of pesticides through these processes and hereby affect the level of pesticides. It is possible that some of the pesticides are removed together with the iron oxides. This could happen through adsorption to the iron oxide colloids, which would lead to co-precipitation of the pesticides. Another possibility is that the enhanced aeration by help of the MicroDrop system could lead to stripping off some of the pesticides, especially the smaller ones such as DEIA and BAM, similar to that known to occur for smaller chlorinated solvents. Finally, it could be possible that the microorganisms in the sand filter would be able to metabolize some of the pesticides.

As seen in Figure 2, no change in pesticide concentration was observed during aeration, sand filtration or the MF/UF membranes. The observed differences are explained by the combined variance of the sampling, SPE and instrumental procedure. Neither sand filtration nor MF/UF processes can as such be expected to affect pesticide concentrations. Instead the two polymeric membranes were found to be capable of removing the pesticides. For the two larger pesticides, atrazine and bentazon, the NF membrane is sufficient, whereas to remove the two smaller pesticides, BAM and DEIA, a tight NF or LPRO membrane is necessary. The results show that in a removal procedure of pesticides in water, sand filtration and/or MF/UF membranes are better used as pre-treatment techniques for the NF/LPRO processes.

Pre-treatment of groundwater

To evaluate the suitability of the four ceramic membranes and the sand filtration process as pre-treatment techniques for subsequent NF/LPRO process, they were compared on
their ability to reduce inorganic, organic, particulate and biological fouling potentials. Properties of groundwater samples collected before and after the different processes are presented in Figure 3. For filtration purposes aerated groundwater was used, where DO content was higher (9.5 mg/L) resulting in differences between values of some factors from raw groundwater presented in Table 1.

With respect to the inorganic fouling potential, the sand filter and the ceramic membranes were evaluated on their ability to remove iron and manganese. Concerning the removal of iron, the sand filter is found to outperform the two MF membranes, while the UF membranes are able to remove slightly more iron than the sand filter. None of the membranes were found to remove manganese, but the sand filter was found to reduce it from 1.2 to 0.06 mg/L. This points at a difference in the removal mechanism for the two pre-treatment methods. Membrane filtration operates in the principle of size exclusion, and as such it was anticipated that iron removal efficiency would be correlated with membrane pore size. Unexpectedly, MF with 3 μm pore size was found to give higher iron removal than MF with 1 μm pore size. This finding was confirmed in several repeated experiments with two different membrane units of the same type. It is possible that the pore size reported by the producer was not correct, which would explain why the 3 μm membrane was found to be consistently better on all parameters compared to the 1 μm membrane. Other possible explanations could also be internal pore blocking of the 3 my membrane or difference in the pore size distribution of the two membranes. The specific underlying reason was not investigated in this study. Removal of iron and manganese in a sand filter is based on precipitations rather than size exclusion. Sand filtration enables autocatalytic processes involving precipitated iron hydroxides on the sand media surfaces, which results in much faster iron oxidation and precipitation compared to its rate of oxidation in an aerated water solution of iron(II) (Davison & Seed 1983; Geroni & Sapsford 2011). Furthermore, the effect of naturally occurring iron and manganese oxidizing bacteria cannot be neglected. For example by help of the iron oxidizing bacteria Gallionella ferruginea that was also found to grew uninhibited and perform biological iron oxidation in partly oxygen-saturated natural water in circum-neutral pH range (Søgaard et al. 2001; Pacini et al. 2005; de Vet et al. 2011). The fact that a large part of the oxidation of iron and manganese occurs in the sand filter, gives the
sand filter an advantage over membrane filtration, that require pre-oxidation and particulate matter formation to occur prior to filtration (Ellis et al. 2000).

The fouling potential of organic matter was evaluated by measuring the UV absorption at 254 nm. Here the sand filter was found to result in a higher removal level compared to all four membranes, which were found to give equal removals. The fact that the membranes give the same content of organic matter in their permeates indicates that the organic compounds that permeates are smaller than the pore size of the membranes. The removal of natural organic matter (NOM) in the sand filter could be because of biological activity, where microorganisms are capable of metabolizing part of the organic matter. Moreover, the diverse efficiency of iron removal could have impacted organic matter removal, as it was suggested in other studies indicating that the precipitated iron can play a part in removing NOM from water by sorption (Choo et al. 2005).

The two ceramic UF membranes were found to give the highest reduction in turbidity, while the sand filter gave a slightly higher reduction compared to the MF membranes. When comparing the average particle size, it is seen that the smallest particles are found in the sand filter permeate. The difference between turbidity and particle size performance, even though the fact that the both factors refer to particulate matter, might be caused by the fact that the DLS device measures average particle size and not their quantity. Moreover, iron removal efficiency corresponds to the particle size found in permeates, which suggest that the colloidal iron was an important part of particle size results.

To assess the biological fouling potential, the number of colony forming units (CFUs) was measured before and after filtration. The membranes gave higher reductions in the number of CFUs compared to the sand filter, but none of them were found to completely remove the microorganisms in the groundwater. This is a clear indication that the labelled pore sizes of these membranes may not be correct, or that the pore size distribution is relatively large since membranes with pore sizes below 0.2 μm should ensure a complete removal of CFUs (Bobbitt & Betts 1992; Hagen 1998; Hofs et al. 2011). In a previous study, the pore size of the used 0.04 μm membrane was determined with porometry to be 0.96 μm (Hofs et al. 2011). In general though, membranes will be better than sand filters at reducing biological fouling. The sand filter is in part a biological process, and microorganisms from the sand filter may detach from the sand filter, and end up in the permeate.

The UMFI ranged from 0.07 m⁻¹ for the 0.04 μm permeate to 1.0 m⁻¹ for the sand filter permeate. The UMFI was obtained for permeates from experiments with a Mn-spiked solution. The difference between UMFI values seems to be correlated to the CFU counts and the turbidity, which indicates that biological and particulate fouling are the main causes of the measured UMFI values.

The UMFI values may be considered as the overall indicator of the fouling potential, and based on these values, the 0.04 μm should be considered as the best pre-treatment method. However, this view may be too simplified. The analyses show that the sand filter and the membranes both have strengths and weaknesses. The sand filter is good at removing iron, manganese and organic matter, but ineffective in removal of particulate and biological matter. The membranes can obtain high removals of iron, particles and microorganisms, but dissolved matter and particles below the pore size of the membranes will not be removed. This should be considered when choosing a pre-treatment strategy. If the groundwater is low in organic matter and manganese, aeration and a UF membrane system will be sufficient, but if the content of dissolved organic matter and manganese is high, a combination of aeration, sand filtration and UF membranes may be the best choice for a pre-treatment strategy.

**CONCLUSIONS**

Aeration and sand filtration/MF/UF membranes were found to be unable of removing pesticides from polluted groundwater, and these techniques should instead be used as pre-treatment methods for subsequent NF/LPRO treatments. Sand filtration was found to be effective at removing iron, manganese and dissolved organic matter, whereas its effect on particulate and biological matter was found to be limited. Ceramic UF membranes were found to be effective at removing iron, particulate and biological matter, but unable to remove manganese and dissolved organic matter.
The results indicate that the main cause of fouling in groundwater might be iron, biological and particulate matter that was found to be correlated with the UMFI of sand filtrated permeate.

The lowest UMFI was obtained by the use of the UF membrane with the smallest pore size (0.04 μm) used in this study, and is the most promising pre-treatment technique. However, in cases with high concentrations of dissolved organic matter and manganese, a serial combination of aeration, sand filtration and ultrafiltration may be the best choice.

REFERENCES


Danish Ministry of the Environment 2007 Executive order no. 1451, Executive order for water extraction and waterworks.


First received 23 September 2013; accepted in revised form 20 January 2014. Available online 31 January 2014