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Applicability and modelling of nanofiltration and reverse osmosis for remediation of groundwater polluted with pesticides and pesticide transformation products

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ABSTRACT

The main body of research on pesticide removal with membranes has looked at pesticides used for pest control, but during transport from surface to groundwater aquifers, pesticides are transformed. Therefore the real polluting compounds are often transformation products, and this vastly increases the total number of pollutants in need of treatment, which also creates a need for a simple way of predicting expected rejections to avoid the daunting task of investigating all these experimentally. In this study, the applicability of NF/LPRO/RO membranes for treatment of groundwater polluted with some of these key transformation products is assessed experimentally and compared to that of regular pesticides. Also, it was investigated whether the rejection could be modelled with a simple steric model. It was found that NF membranes capable of rejecting the regular pesticides did not give satisfactory rejections of the transformation products, mainly because of the reduced size of these. Further, the rejection could be described with a pore flow model, but different definitions of the molecular width were needed to describe rejection for NF and LPRO/RO membranes. With the model it was predicted that rejections over 90% can be obtained with an LPRO membrane for most pesticides and transformation products found in Danish groundwater.

1. Introduction

Pesticide pollution of surface and groundwater resources is an increasing problem in many parts of the world [1]. In Denmark almost the entire drinking water production is based on groundwater of which 44% has been found to be contaminated with pesticides [2], and it is estimated that between the years 1999 and 2009, pesticides have resulted in the abandonment of around 130 drinking water wells per year [3]. The research on pesticide removal is extensive, and traditionally the focus has been on the pesticides actually used for pest control, but for groundwater pollution this choice may be misguided. During percolation from surface to aquifer, pesticides are often transformed, and the compounds found in real groundwater are therefore different from the pesticides that dominate literature. These new compounds are called pesticide transformation products (PTPs), and for Danish groundwater they represent the largest part of the pesticide pollution [4].

Traditional Danish drinking water treatment consists of aeration and rapid sand filtration, which has been found to have no effect on pesticides and PTPs [5]. Therefore, activated carbon filtration is applied in cases where it has not been possible to find new unpolluted aquifers [6]. Activated carbon is generally an efficient method for removal of organic micropollutants, but it also suffers from a number of problems mainly related to saturation, foot print size and difficulties in removing small polar compounds [1]. An alternative to activated carbon is the use of nanofiltration (NF) and low pressure reverse osmosis (LPRO) membranes.

NF and LPRO membranes have been found to be an effective method for removal of pesticides, although the specific rejection of the pesticides is highly dependent on both membrane and pesticide characteristics [1,7,8]. In general size exclusion has been found to be the most important parameter determining rejection of pesticides, which has been seen from correlations between measured rejection values and molecular weight of the pesticides [1,9–11]. However, it has also been found that the rejection of pesticides is higher in real waters compared to distilled water [11], and that the presence of divalent ions (Ca^{2+}) [10,12] and specific types of organic matter [13] may impact the rejection. Other factors such as the dipole moment of the pesticides [14], relative hydrophilicity/

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hydrophobicity [15,16] and charge [17] have also been found to affect rejection, adding to the complexity. From an engineering point of view, it would very advantageous if rejections could be approximated reasonably well by assuming only steric effects because this would then only require knowledge of the size of the pesticides/PTPs and the pore size of the membrane; both of which are readily available. Studies have shown that under ideal conditions (laboratory grade water, low solute/membrane interaction, low solute dipole moment), steric models can be used to achieve acceptable results for rejection of organic molecules by NF membranes, even with simple models assuming cylindrical pores with the same pore size such as the steric hindrance pore model [18]. Recently Kiso et al. proposed a steric pore flow model based on geometrical parameters of the solutes to predict rejections, and found this model to be very successful compared to the use of molecular weight [19,20]. The model was however applied to hydrophilic alcohol compounds of relatively simple geometry that should not interact significantly with the membrane surface. Whether the same model can be used for pesticides/PTPs have not been investigated.

In this study we attempted to evaluate the applicability of membrane filtration for treatment of groundwater polluted with not only pesticides, but also PTPs. This was done by selecting two pesticides: atrazine and bentazon and two PTPs: BAM and DEIA. DEIA is a transformation product of atrazine and the pesticide/PTP pair could as such be used to directly investigate the effect of the transformation process on the applicability of the membranes. BAM and bentazon represented pollutants for which the expected rejection was important to determine. The possibility of using a purely steric model to calculate the rejections was investigated by applying the model of Kiso et al. [19]. To verify the use of the model, the fitted pore sizes were subsequently used to calculate rejection values of two other pesticides, prometryn and isoproturon, that has been investigated in a separate study. Furthermore, to give an evaluation of the overall applicability of the investigated membranes to treat any polluted groundwater, predictions were made on the rejection of the remaining pesticides and PTPs included in the Danish groundwater monitoring program. Finally, the effect of groundwater on the rejection was investigated by comparing the results from the model with measurements of streaming potential and pesticide/ion-pair formation.

2. Experimental work

2.1. Materials and methods

2.1.1. Pesticides

Two pesticides and two PTPs were used in the experiments: atrazine, bentazon, 2,6-dichlorobenzamide (BAM) and desethyl-desisopropyl-atrazine (DEIA): BAM and DEIA are PTPs of the pesticides dichlobenil and atrazine. All were purchased at Sigma–Aldrich (Pestanal, Fluka).

The pesticides and PTPs were chosen based on their occurrence in Danish groundwater samples. BAM and DEIA are the two main polluting compounds, with BAM being found in 18.8–20.2% and DEIA in 11.0–16.1% of the groundwater analyses [4]. Of the pesticides still in use, bentazon is the one found in the largest amount of groundwater samples, 3.4–4.9% [4]. Atrazine was banned for use in 1994, but it is still found in 5.2% of the groundwater samples [2]. It is also one of the most studied pesticides in literature. In an overview of membrane/pesticide studies presented by Karabelas and Plakas [21], atrazine accounted for 23.9% of the total sum of pesticides used in the experiments. Given its widespread use in scientific work, atrazine is used to link this study to former studies.

Data for the four compounds are presented in Table 1. The amount of data on these compounds is scarce, and the values often originate from isolated studies that have not been confirmed, which lead to some contradictory values. Based on the log $K_{o/w}$ values for bentazon and BAM, bentazon would be expected to have the highest aqueous solubility, but the reported solubilities give BAM the highest aqueous solubility. The p*K*a values are also often reported for protonated species, without that being properly indicated. The applicability of these data may as such be questioned. The geometric parameters have been determined with the method described in Section 2.4. Width and height are defined here as the side lengths of the rectangle enclosing the molecule perpendicular to its length axis with height being taken as the longest side.

2.1.2. Groundwater samples

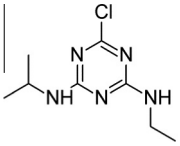
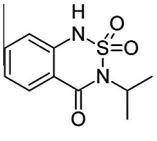
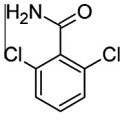
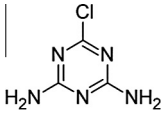
Groundwater was acquired from two waterworks: Astrup (south-west Jutland, Esbjerg, Denmark) and Hvidovre (East Zealand, Copenhagen, Denmark). These two groundwaters represent minimum and maximum values of hardness and total ionic concentration that can be encountered in Denmark, as seen from the compositions listed in Table 2. Both waters are also characterised by a low content of organics, which may be considered a best case scenario since it lowers the effect that NOM might have on the measured rejections.

Demineralised water was produced in house with a Silex II ion exchanger from SILHORKO, and used as a reference water type.

2.1.3. Membranes

Five different membranes were used in the experiments: NF90, XLE, BW30 (Dow Chemicals), NF99 and NF99HF (Alfa Laval). NF90 has been used in previous studies [12,13,27], and is classified as a tight NF membrane. XLE is characterised as an extra low energy reverse osmosis membrane, and BW30 as a loose reverse osmosis membrane. The two Alfa Laval membranes are NF membranes

Table 1
Properties of the pesticides used in this study.

	Atrazine	Bentazon	BAM	DEIA
Chemical structure				
Formula	$C_8H_{14}ClN_5$	$C_{10}H_{12}N_2O_3S$	$C_7H_5Cl_2NO$	$C_3H_4ClN_5$
Molecular weight (Da)	215.69	240.28	190.028	145.55
Length (Å)	13.76	11.98	9.200	8.595
Width (Å)	6.267	7.493	5.784	3.950
Height (Å)	8.752	8.378	9.042	8.060
Log K_{ow}	2.68 [13]	−0.46 [22]	0.77 [23]	−0.1 [24]
Aqueous solubility (mg/L) 20 °C	33 [22]	570 [22]	2730 [25]	66 [24]
p*K*a	1.7 [12]	3.3 [22]	13–14 [26]	–