



The effect of water matrix, feed concentration and recovery on the rejection of pesticides using NF/RO membranes in water treatment



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ABSTRACT

In this study, we investigate the effect of feed concentration and recovery on the rejection of pesticides with NF/RO membranes. There is a discrepancy between laboratory studies carried out at relatively high pesticide concentrations and low recoveries and real-life conditions where filtration is carried out at lower pesticide concentrations and high recoveries, but this is often neglected when evaluating membrane rejection properties. Four commercially available polymeric thin film composite nanofiltration (NF) and reverse osmosis (RO) membranes were used to remove two phenoxy acid herbicides (2-methyl-4-chlorophenoxy acetic acid (MCPA) and 2-methyl-4-chlorophenoxy propionic acid, MCPP) and a pesticide transformation product (2,6-dichlorobenzamide, BAM) from three groundwaters of different geochemical origins in Denmark. To elucidate the prevailing rejection mechanisms, experimental data was compared to modelled rejections based on steric hindrance. Feed concentration of pesticides showed a considerable negative impact on the rejection of the charged phenoxy acids by negatively charged NF membranes, although for RO membranes the effect was negligible, showing that for NF membranes and charged pesticides, the rejection must be evaluated at actual concentrations. For all three pesticides, increasing recovery was found to lead to increased rejection values, which was ascribed to membrane pore blocking effects.

1. Introduction

Membrane separation by NF/RO membranes is a potential effective water treatment technology targeting pesticides and their metabolites [1–3]. Previous studies have shown that membrane rejection of pesticides is affected by a number of key pesticide solute characteristics including molecular weight, molecular size, geometry, polarity, charge and hydrophobicity [2,4,5] as well as membrane properties including molecular weight cut-off (MWCO), hydrophobicity and surface charge [6–8]. Together these factors determine the mechanism responsible for the rejection of different pesticides in terms of steric hindrance, electrostatic interactions, and membrane-solute interactions, which is often stated in terms of solution-diffusion [9,10]. A great deal of effort has been devoted to the development of reliable models using the aforementioned mechanisms predicting the performance of the membrane separation for removal of such compounds [3,11,12]. Feed water composition also plays a critical role in pesticides rejection since structure and charge of the membranes and solutes will depend on water pH, the ionic compositions of water as well as natural organic matter (NOM) existing in natural waters [13–15]. In a previous study

on removal of pesticides from groundwater, we found that steric hindrance was the main rejection mechanism for neutral pesticides and that the rejection increased with increasing ionic strength, which was correlated with a decreasing pore size of the membrane [3].

However, often experiments are carried out in solutions and concentrations different from those found in the environment. Due to the complexity and detection limit of analytical instruments for measurement of low concentrations of micropollutants in the real water resources, many researchers have preferred to use elevated spiked concentrations by assuming the feed concentration hypothesis which states that the efficiency of the membrane processes is not significantly correlated with the feed water concentration [16]. Nevertheless, depending on the intrinsic characteristics of targeted solutes and NF/RO membranes, various mechanisms might be applicable for pesticides rejection and as a result, pesticides concentration or water matrix might affect differently than expected. Further, in our previous studies on real groundwater, the effect of pesticide charge was not investigated. Charges on the pesticide molecules are expected to lead to increased rejection due to electrostatic repulsion at the membrane surface, but it is not known how this is affected by the water matrix and ionic strength

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of the groundwater. Finally, most studies do not take recovery into account. In real life settings, the membrane plant would be operating at recovery levels that are as high as possible and this will increase ionic strength and pesticide concentration between in and outlet of the membrane module, which could affect the overall recorded rejection.

In the present paper, four commercially available NF/RO membranes were employed to evaluate rejection of three frequently found pesticides in Danish groundwater wells, 2,6-dichlorobenzamide (BAM), a pesticide transformation product of the herbicide dichlobenil, and two charged phenoxy-acid herbicides; 2-methyl-4-chlorophenoxy acetic acid (MCPA) and 2-methyl-4-chlorophenoxy propionic acid (MCPP or Mecoprop). Denmark and several other countries rely partially or solely on groundwater for drinking water production, and contamination of reservoirs with BAM, MCPA and MCPP poses a serious threat to the future use of this resource without the need of advanced treatment at water works. As one example, BAM was measured in 16% of sampled Danish water wells and the legal threshold concentration of $0.1 \mu\text{g L}^{-1}$ was exceeded in 9.4% of cases in 2015, even though dichlobenil has been banned since 1997 [17,18]. It has also been detected in several other European countries such as Italy, the Netherlands, Belgium, Sweden and Finland and is known as the most detected pesticide transformation product in Europe [19].

In the present study, the effect of charged pesticides, pesticide feed concentration, groundwater type and recovery on the rejection of pesticides for NF/RO membranes were experimentally investigated. Adsorption was measured in order to determine the actual steady-state rejection values. Previously a pore flow model has been used to describe the rejection of neutral pesticides [3,11], and the same model was employed in this study to investigate its applicability to describe rejection of charged phenoxy acid pesticides. The influence of pesticide concentration was investigated by measuring rejection for feed concentrations ranging from the environmentally relevant concentration of $1 \mu\text{g/L}$ to 10mg/L . Moreover, the effect of water matrix was evaluated by measuring rejection in three different groundwater samples spanning a range from soft to very hard groundwater. Finally, the effect of recovery on pesticide rejection was investigated by measuring the rejection of the three pesticides in one of the groundwater samples at recoveries from 10% to 90%.

2. Materials and methods

2.1. Water matrices

The ultra-pure Milli-Q water was produced in the laboratory using Synergy UV water purification system. The groundwater samples used in the study were collected from the clean water reservoirs of three waterworks from different regional supply areas; Varde (Lerpøtvej Waterworks, DIN Forsyning, South-West Jutland), Kolding (Trudsbro Waterwork, TREFOR, South-East Jutland), and Hvidovre (Hvidovre Waterworks, DIN Forsyning, East Zealand) in Denmark, see Table 1. After collection, the water was stored overnight in a refrigerator at 4.0°C before being treated by membrane separation the next day. Analysis of the water characteristics was done by an external accredited analytical laboratory (Eurofins Miljø A/S).

2.2. Pesticides


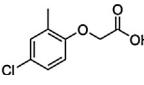
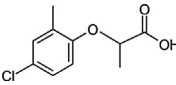
BAM (purity 99.9%), MCPA (purity 95%) and MCPP (purity 99.6%) were all purchased from Sigma-Aldrich. The chemical structure and properties of these pesticides are listed in Table 2.

Molecular geometry of the pesticides was approximated by a rectangular parallelepiped shape and examined using Gaussian software by a model described by Madsen and Søgaard [3]. The other values were extracted from the literature.

Table 1
Characterization of the water samples from the selected geographical regions in Denmark.

	Unit	Varde	Kolding	Hvidovre
pH		7.7	8.0	8.1
Conductivity	(mS/m)	37	50	130
Hardness	(°dH)	6.9	12	29
Calcium (Ca^{2+})	(mg/L)	37	72	160
Magnesium (Mg^{2+})	(mg/L)	7.4	7.0	28
Potassium (K^+)	(mg/L)	2.4	2.6	6.1
Sodium (Na^+)	(mg/L)	22	30	71
Nitrate (NO_3^-)	(mg/L)	9.4	0.92	3.7
Chloride (Cl^-)	(mg/L)	37	41	170
Sulphate (SO_4^{2-})	(mg/L)	57	17	130
Bicarbonate (HCO_3^-)	(mg/L)	67.1	230	416
NVOC	(mg/L)	0.4	1.2	2.2
Total-P	(mg/L)	0	0.033	< 0.01

Table 2
The chemical structure and properties of targeted pesticides in this study.

	BAM	MCPA	MCPP
Chemical structure			
Molecular weight (Da)	190.028	200.62	214.65
Length (Å)	9.299	12.843	12.847
Height (Å)	9.133	8.434	8.402
Width (Å)	5.909	4.191	5.460
MWd (Å)	3.673	2.973	3.387
pK _a	13–14 [20]	3.07 [21]	3.19 [22]
log K _{ow}	0.77 [23]	2.73 [21]	2.56 [22]
Water solubility (mg/L)	2730	630	880

2.3. Membranes and characterization

In this study, the performance of four commercially available flat-sheet NF/RO membranes was evaluated (Table 3); NF270 (Dow Chemicals) and NF99HF (Alfa Laval) NF membranes, XLE a low pressure reverse osmosis (LPRO) membrane (Dow Chemicals), and BW30 (Dow Chemicals) an RO membrane. All the membranes were polyamide thin-film composite (TFC) membranes. Characterization was performed by determination of pure water permeability, hydrophobicity/hydrophilicity using contact angle measurements, and membrane surface charge using zeta potential measurements.

The molecular weight cut-off (MWCO) of the membranes was reported by the manufacturers. The pure water permeability was determined using a dead-end filtration setup from the slope of Milli-Q water permeate flux versus applied pressure (2–20 bar) curves. The contact angle was measured using the conventional sessile drop method with distilled water using a KRUSS DSA100 instrument. A membrane disc was immersed in Milli-Q water overnight before drying in a desiccator for the measurements. For determination of all contact angles, the average was taken of at least five different measurements on different spots. Zeta potential was determined by Anton Paar SURPASS streaming potential analyzer in a 1.0 mM KCl solution at pH 5.3 and pH 8.0.

2.4. Membrane filtration

A dead-end filtration set-up using a Sterlitech Cell (HP4750, Sterlitech Corporation, USA) equipped with a magnetic stirring bar was used for membrane filtration experiments [14]. For each test, a fresh 50-mm diameter membrane disc (effective surface area of 14.6cm^2)

Table 3
Characteristics of the membranes used in this study.

	NF270	NF99HF	XLE	BW30
Molecular weight cut-off (MWCO) (Da)	200–400	> 200	> 100	> 100
Pure water permeability ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)	15.2 ± 0.7	13.7 ± 0.5	5.7 ± 0.6	2.9 ± 0.2
Contact angle ($^{\circ}$)	17.5 ± 3.7	20.7 ± 3.2	75.8 ± 4.5	79.4 ± 5.7
Zeta potential (mV) at pH 5.3	–52	–50	–26	–21
Zeta potential (mV) at pH 8.0	–74	–77	–50	–38

was used. At first, the fresh membrane disc was rinsed with deionized water for 3 min to remove the preservative layer from the membrane active layer. Afterwards, the membrane disc was placed in the Sterli-tech cell and exposed to Milli-Q water at 15 bar for 2 h in order to compact the membrane. Then, pure water flux was determined using Milli-Q water for 1 h at 10 bar.

For experiments with pesticides, 200 mL pesticide solution was transferred to the cell and stirred for 1 h without pressure to allow the membrane surface to equilibrate with the feed solution in terms of adsorption of pesticides. After this preconditioning, filtration was initiated at 10 bar and terminated at 50% recovery. Finally, the membrane cell and membrane were rinsed with deionized water and pure water flux was determined again to investigate possible decline in flux due to pesticide adsorption on the membrane surface during saturation and filtration steps. All the experiments were conducted at ambient temperature, 22 °C.

Rejection of pesticides, R , was calculated using Eq. (1):

$$R(\%) = \left(1 - \frac{C_p}{\frac{1}{2}(C_f + C_c)}\right) \times 100 \quad (1)$$

C_p , C_f , and C_c are concentrations of pesticides in permeate, feed and concentrate, respectively.

In addition, permeate flux, J , was determined using Eq. (2):

$$J = \frac{V_p}{A \times t} \quad (2)$$

where, V_p is the volume of permeated water, A is active membrane surface area, and t is the time of filtration.

When a fresh membrane is used for removal of pesticides, some pesticides solutes tend to adsorb onto the surface of the membrane resulting in higher initial rejection values [14]. The adsorption continues until the adsorption sites on the membranes are saturated by the pesticides and a steady-state rejection value is achieved. Thus, adsorption was also taken into consideration by calculation of the percentage of adsorbed pesticides ($A\%$) using the following mass balance for pesticide solutes:

$$A(\%) = \left(1 - \frac{C_p V_p + C_c V_c}{C_f V_f}\right) \times 100 \quad (3)$$

where, V_f , V_p , and V_c represent respectively volume of feed, permeate and concentrate.

Pure water flux decline ($FD\%$), which could be a measure to evaluate the effect of adsorbed compounds on the flux, was also determined using Milli-Q water flux before and after filtration as follows:

$$FD(\%) = \left(\frac{J_b - J_a}{J_b}\right) \times 100 \quad (4)$$

where J_b and J_a represent pure water flux before and after filtration of feed water polluted by pesticides.

2.5. Analytical methods

Concentrations of the pesticides in feed, permeate and concentrate samples were measured using HPLC/MS-MS (Thermo Scientific Dionex UltiMate 3000/TSQ Vantage) method equipped with an ACQUITY UPLC BEH C18, 1.7 μ m, column. 60% methanol and 40% ammonium

acetate 5 mM, pH 3, was used as the eluent mixture with a flow rate of 0.35 L/min with a column temperature of 40 °C and the injection volume was 4 μ L. The limit of detection by this method was 10 μ g/L and for those solutions with lower concentrations, solid phase extraction (SPE) technique was used to concentrate pesticides solutes in the water solution.

SPE was carried out by employing CHROMABOND HR-X 200 mg/3 mL cartridge, and the procedure was as follows: the SPE-column was equilibrated with 2 mL methanol and washed with 1 mL Milli-Q water. 80 mL of the aqueous sample was then loaded to the SPE column, which was then washed with 1 mL Milli-Q water and allowed to dry. Afterward, the SPE-column was eluted with 2 mL acetonitrile which was collected in a glass tube. Finally, the sample was evaporated to dryness in a gentle stream of N_2 at 30 °C and redissolved in 0.5 mL ammonium acetate 5 mM, transferred to a UPLC vial and stored at 4 °C until analysis.

2.6. Modelling with steric hindrance model

In order to elucidate the mechanism controlling rejection of pesticides, the steric pore model flow described by Kiso et al. [11] was employed similar to our previous work [3]. To this end, non-spherical geometric parameters of the pesticide molecules (length and molecular width) were used to calculate the steric partition factor and then estimate the pore radius of the membranes that subsequently used for calculation of the rejection values. Afterward, the calculated values were compared to the measured values to see if the steric hindrance model gave a good fit to the experimental data.

3. Results and discussion

3.1. Pesticide rejection in pure water

The rejection values of pesticides in Milli-Q water at 50% recovery are shown in Fig. 1. All the experiments for this section were carried out at initial pesticide concentrations of 1 mg/L. Both the RO and LPRO

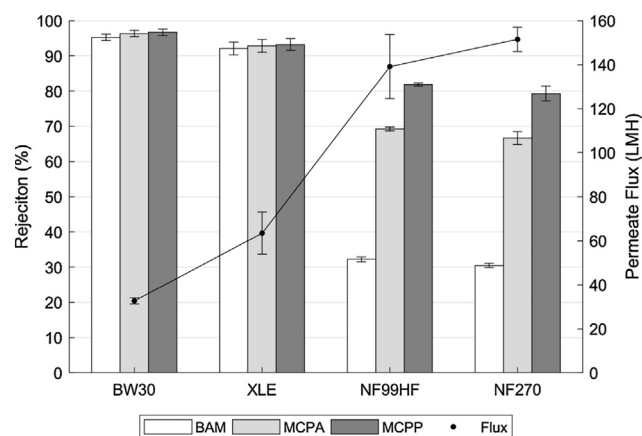


Fig. 1. Pesticides rejection and permeate flux data for Milli-Q water samples using membrane filtration. Error bars represent the deviation of triplicated results calculated using 95% confidence interval.

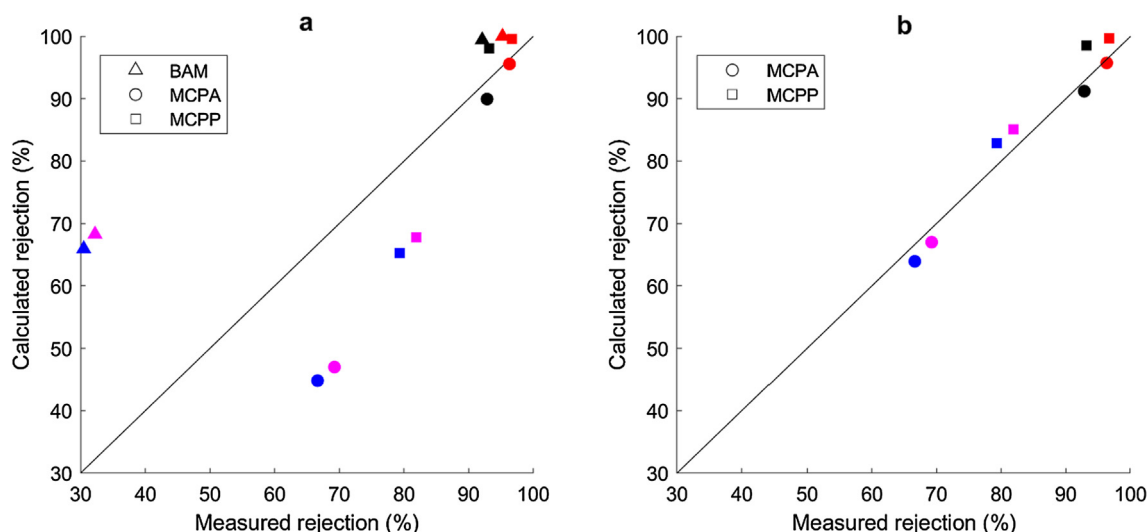


Fig. 2. Fit for measured rejection values modelled by purely steric model (a) All the pesticides. (b) Phenoxo acids (BAM is excluded from the dataset). Rejection values for different membranes are shown with colors; Red = BW30, black = XLE, magenta = NF99HF, blue = NF270.

Table 4

The percentage of pesticides adsorption on the surface of the membranes for pesticide concentrations of 1, 5 and 10 mg/L in Milli-Q water.

Membrane	Pesticide	Adsorption (%) for feed water of 1 mg/L	Adsorption (%) for feed water of 5 mg/L	Adsorption (%) for feed water of 10 mg/L
BW30	BAM	6.9 ± 1.0	7.1 ± 1.5	8.4 ± 1.5
	MCPA	11.5 ± 0.1	11.8 ± 0.7	13.2 ± 0.9
	MCPA	10.2 ± 0.8	11.3 ± 0.6	11.8 ± 1.1
XLE	BAM	4.3 ± 1.5	3.8 ± 0.7	5.3 ± 0.3
	MCPA	7.2 ± 1.1	7.7 ± 1.9	8.3 ± 0.9
	MCPA	6.4 ± 1.3	6.7 ± 0.5	7.1 ± 1.9
NF99HF	BAM	2.3 ± 1.0	3.4 ± 1.6	6.6 ± 2.5
	MCPA	2.0 ± 0.5	3.3 ± 1.4	5.4 ± 1.1
	MCPA	2.2 ± 0.7	4.2 ± 1.6	5.8 ± 0.7
NF270	BAM	2.7 ± 0.6	2.9 ± 1.8	4.9 ± 1.9
	MCPA	1.6 ± 0.4	2.9 ± 1.7	3.8 ± 1.1
	MCPA	0.3 ± 0.3	3.6 ± 0.2	4.6 ± 0.9

membrane, BW30, and XLE, were found to reject all three pesticides at a level > 92%. The two NF membranes, NF99HF and NF270, achieved similar and noticeably lower rejections ranging from 30% to 82%, depending on the pesticide compound. The observed rejection values are correlated to the MWCO of the selected membranes. NF membranes have larger pore sizes resulting in higher MWCO values compared to relatively dense RO membranes, indicating that the overall mechanism of rejection might be size exclusion [1,24,25].

The distinction between rejection values of these pesticides is more pronounced in the case of NF membranes where the MWCO of the membranes is greater than the molecular weight of pesticides (Table 3). Van der Bruggen et al. [4] and Braeken et al. [26] had shown that when the molecular weight of solutes was lower than MWCO of the NF membranes, size exclusion could not be the only descriptor for rejection of compounds and the other characteristics such as charge and hydrophobicity should also be taken into account.

As shown in Fig. 2-a, steric hindrance alone cannot explain the observed rejection. A good fit to the model would require the modelled and observed rejection values to lie on the indicated line. Based on the size parameters, the model expects a higher rejection of BAM. This is because BAM has a higher MWd value compared to the phenoxo acids (Table 2), which have a more linear structure that can more easily fit through a cylindrical pore. For neutral pesticides, NF99HF, XLE, and BW30 membranes have previously been found to give a good fit to the steric hindrance model [3] and this finding, therefore, indicated that

electrostatic charge of phenoxo acids might play an important role and contribute to higher rejection values compared to what steric hindrance model suggests. This consideration is confirmed by what was inferred in another study where as a result of looking into various feed pH values, the rejection of the undissociated form of MCPP was found to be lower than that of the dissociated form [27].

It is interesting to note that, by excluding BAM from the dataset a better fit was achieved (Fig. 2-b). This shows that the difference between the rejection of MCPA and MCPP was primarily due to the difference in molecular size and the charge impact was similar for both phenoxo acids. This is in accordance with their pK_a which is almost the same for both solutes (Table 2).

Even though the charge effect is most pronounced for the two NF membranes, it is also worth noting that although the model seemingly gave a better match for RO membranes, looking into calculated rejection values for BAM revealed that again the charged solutes affected the estimated membranes pore size and consequently higher rejection values for BAM were calculated.

3.2. Adsorption of pesticides

The percentage of pesticides adsorption onto the surface of the membranes is listed in Table 4. As can be seen, the extent of pesticides adsorbed on the RO membranes was greater than NF membranes. This is correlated with the relative membrane and pesticide hydrophobicity, which in other studies [5,8,28–30], have been shown to govern the amount of adsorbed compounds on the NF/RO membranes. The XLE and BW30 membranes are more hydrophobic than the NF membranes and the hydrophobic pesticides, therefore, adsorb more strongly on relatively hydrophobic RO membranes than hydrophilic NF membranes. Also, the more hydrophobic pesticides, MCPA and MCPP (log K_{ow} > 2) tend to adsorb more than BAM.

For the NF membranes, BAM and the phenoxo acids adsorb to a similar extent, which may be explained by the electrostatic repulsion. Both NF membranes are characterized by a negative charge and repel the negatively charged phenoxo acids. Consequently, these species cannot readily approach the membrane surface resulting in a tendency to minimize the adsorption of these compounds. A similar observation has been made in other studies in which it is pointed out that the adsorption does not significantly occur for charged organic compounds and in return, the adsorption for electrostatically neutral compounds is higher [8,10,31].

Furthermore, in an attempt to examine whether observed values

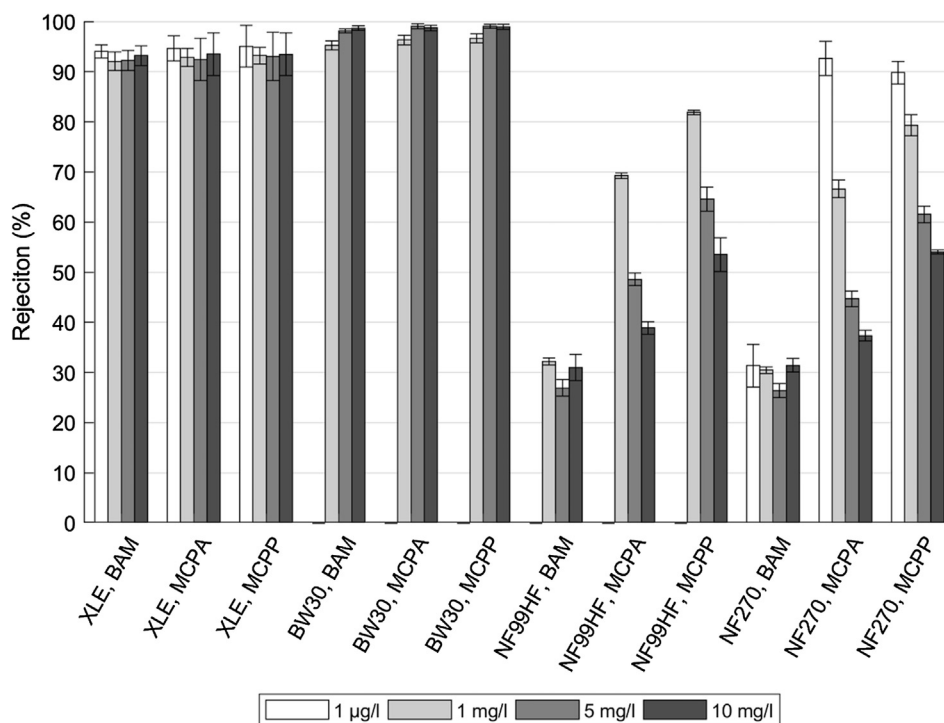


Fig. 3. Rejection values at different pesticides concentrations in Milli-Q water.

were actual (steady-state) rejection values, follow-up experiments were completed by using the same membrane disc for filtration of polluted feed water of 1 mg/L in three batches. It was found that the rejection did not change notably over three consecutive filtration experiments, showing that the adsorption sites on the membranes were sufficiently saturated with pesticide to remove this as a factor that could influence the observed rejection. Detailed description and data on the follow-up study are provided as supplementary material Table S1.

3.3. Influence of feed concentration on pesticides rejection

Fig. 3 shows the rejection values measured for different pesticide feed concentrations. No significant effect was seen for the XLE membrane performance, while an increase in rejection was seen for the BW30 membrane. For the NF membranes rejection decreased significantly with concentration for the phenoxy acids whereas no significant correlation was seen for BAM.

The rejection values of BAM for the RO and NF membranes show that the generally accepted hypothesis that rejection can be evaluated at elevated concentrations is reasonable.

However, in the case of NF membranes filtrating charged molecules, the hypothesis does not hold. Here lower feed concentrations lead to higher rejection values. As the feed concentration rose from 1 µg/L to 10 mg/L the rejection by NF270 dramatically declined from 92.6% to 37.3% and 89.8% to 54.0% for MCPA and MCPP, respectively. Adsorption could not explain the observed behavior as the membranes had been pre-saturated with pesticides and were stable over successive filtration runs, see Section 3.2. Instead, we invoke a charge shielding hypothesis to explain the observed results. An increase in the concentration of pesticide in the feed water will lead to an increase in adsorption on the membrane surface and increase the pesticide concentration in the electric double layer. Consequently, this increased presence of pesticide molecules at the membrane surface might shield the NF membranes surface charge and inhibit electrostatic repulsion between NF membranes and charged compounds, MCPA and MCPP, and thus result in a decrease of the phenoxy acids rejection. Therefore, by increasing feed concentration the electrostatic repulsive effect is

decreased leading to considerably lower rejections.

This charge shielding effect was also investigated using steric hindrance model, and it was seen that for feed concentration of 5 mg/L and particularly 10 mg/L, the model provided a perfect fit for charged molecules (The supplementary material Figure S1). It proves that unlike lower concentration of 1 µg/L for which charge repulsion stimulated rejection of phenoxy acids by NF270 membrane, since at higher concentration of 10 mg/L the membrane surface charge was shielded and therefore the strength of charge repulsion decreased, the membrane performance could be mainly explained by steric hindrance for charged solutes.

3.4. Influence of ionic strength on pesticides rejection

To study the effect of water matrix on the membrane performance, the groundwater samples from three different locations in Denmark were spiked with 1 mg/L of the targeted pesticides and the experiments were carried out using the XLE membrane.

By using different water matrices as the feed, it was seen that in a stronger ionic environment a slight enhancement from 93.5% to 95.8% for BAM, 94% to 95.9% for MCPA and 94% to 95.8% for MCPP is attainable in Varde water and Hvidovre water, respectively. The increase is not significant, but there was a definitive trend going towards increased rejection. This rise in the rejection values in real water matrices could be due to pore blocking effect caused by the other ions present in real groundwater samples (Table 1). Such compounds might block the membrane pores leading to a shortage of passageway for both water and pesticides molecules. As a result, the rejection of the pesticides would increase while a decline in the water permeate flux would be found. The same explanation has been proposed elsewhere [3,16,24]. In addition, the electrostatic interaction between negatively charged phenoxy acids (MCPA and MCPP) and cations (Ca^{2+} , Mg^{2+} , and Na^{+}) in real groundwater samples might contribute to the formation of complexes of higher molecular size justifying higher observed rejection values. However, in our earlier study, an increase in apparent size of negatively charged pesticides (Atrazine and Bentazon) as a result of interaction with water matrices could not be proved, and only pore

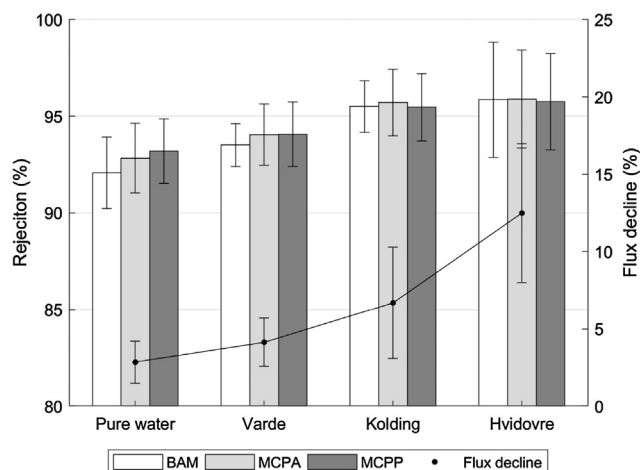


Fig. 4. Rejection and permeate flux decline values of XLE for pure water and groundwater samples from three different locations in Denmark.

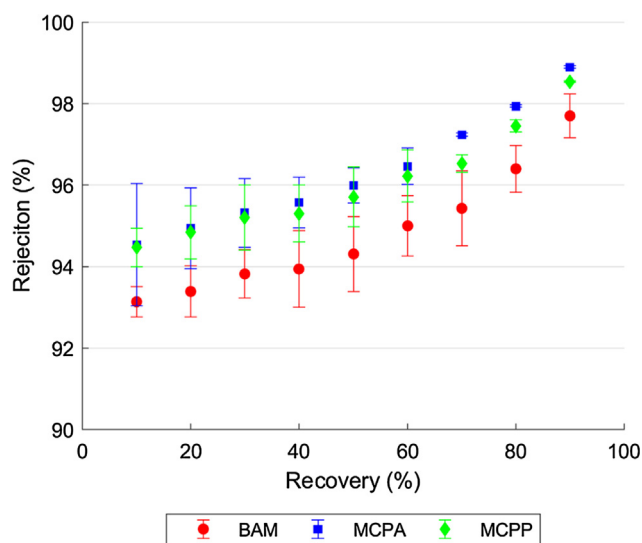


Fig. 5. Rejection values by increasing recovery (permeate volumes) using XLE for a water sample from Varde.

blocking could evidently explain such higher rejections [3].

The pore blocking phenomenon could also be validated by looking into the pure water permeate flux decline after the filtration process. The flux decline after using spiked pure water as feed was around 3% while for the Hvidovre water with the highest concentration of ions, was 12.5%. This result is suggestive of having pores of the membrane blocked by the ions and thus a decline in the flux of water molecules capable of passing through the membrane pores (Fig. 4).

3.5. Effect of feed recovery on pesticides rejection

The previously reported results were obtained by collecting 50% of the volume of the feed as the permeate. In this section, the effect of permeate volume or recovery come under examination. For this purpose, 250 mL of spiked Varde water with pesticides concentration of 1 mg/L was used together with the XLE membrane.

It was observed that rejection values correlated directly with feed water recovery (Fig. 5) for all three pesticides. Rejection rose from approximately 93% to 98% for BAM, 94.5% to 98.5% for MCPP and 94.5% to 99% for MCPA when recovery increased from 10% up to 90%. This finding is in accord with the aforementioned arguments regarding ionic strength effect on the rejection values. Because as more clean

water passes across the membrane to permeate side in a dead-end filtration, the feed becomes more concentrated resulting in a solution of increased ionic strength exposed to the membrane. Similarly, the concentration of pesticides also increases in the feed when higher recoveries are achieved. However, in the present study, it was observed that increased pesticides concentration could not make a difference in the rejection of targeted pesticides by XLE membrane. Then, as previously argued, this direct effect of recovery might be mainly due to the concentrated ionic content of feed/concentrate mixture in this study. Nevertheless, for charged solutes and NF membranes it is possible that the increased pesticide concentration would lead to decreased rejection at higher recoveries.

4. Conclusions

The main findings of this study are as follows:

- The feed concentration hypothesis is only valid for neutral pesticides but breaks down for charged pesticides being partially rejected by electrostatic repulsion (NF membranes). Here rejection must be determined at environmentally relevant concentrations. If elevated concentrations are used, a membrane may be wrongfully dismissed for having too low rejection.
- Recovery increases rejection for the XLE membrane, independent on the type of pesticide and should, therefore, be stated in membrane studies on pesticide rejection.
- The primary reason for the increase in rejection with recovery is increased ionic strength, which leads to an increase in rejection through pore blocking.
- If a mixture of neutral and charged compounds are used, the purely steric hindrance model cannot be used to describe the performance of the membrane and charge interactions also play a critical role. Therefore, a more comprehensive model will be required to fully encompass all pesticides, which will then point to the need for further work.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.01.047>.

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