Membrane Distillation for the Removal of Fluoride and Pesticides in Remote Areas in India

by

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Certificate of original authorship

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Journal articles published

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List of abbreviations

AGMD	Air gap membrane distillation
BB	Building blocks
BP	Biopolymers
BV	Bed volumes
CCD	Charge coupled device
CDI	Capacitive deionisation
CF	Concentration factor
CP	Concentration polarisation
DCMD	Direct contact membrane distillation
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EBCT	Empty bed contact time
ED	Electrodialysis
EDC	Endocrine disrupting chemicals
EDR	Reverse electrodialysis
EDX	Energy-dispersive x-ray spectroscopy
FE-SEM	Field emission scanning electron microscope
FO	Forward osmosis
GAC	Granulated activated carbon
GC-MS	Gas chromatography-mass spectrometry
HA	Humid acid
HPLC	High pressure liquid chromatography
IAP	Ion activity product
IC	Ion chromatography
LC-OCD	Liquid chromatography-organic carbon detection
MD	Membrane distillation
MED	Multiple-effect distillation
MEMD	Multi-effect membrane distillation
MGMD	Material gap membrane distillation
MP-AES	Microwave plasma-atomic emission spectrometry
MSF	Multi-stage flash
NF	Nanofiltration
NMI	National measurement institute
PAC	Powdered activated carbon

PEDCMD	Pressure enhanced direct contact membrane distillation
POE	Point-of-entry
POU	Point-of-use
PTFE	Polytetrafluorethylene
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
RR	Recovery ratio
RSSCT	Rapid small scale column test
SEM	Scanning electron microscope
SGMD	Sweep gas membrane distillation
SI	Saturation index
SIM	Selective ion mode
SPE	Solid phase extraction
SSS	Small-scale system
TDS	Total dissolved solids
TOC	Total organic carbon
TP	Temperature polarisation
TROCs	Trace organic compounds
TZW	Technologie Zentrum Wasser
UF	Ultrafiltration
VCF	Volume concentration factor
VE-DCMD	Vacuum enhanced direct contact membrane distillation
VMD	Vacuum membrane distillation
V-MEMD	Vacuum multi effect membrane distillation
WTP	Water treatment plant

List of symbols

A	Area
B_m	Membrane coefficient
c_{inf}	Concentration of the compound in the influent to the column
c_{f0}	Concentration in the feed solution at the beginning of the experiment
c_{fe}	Concentration in the feed solution at the end of the experiment
c_{eff}	Concentration in the effluent to the column
c_p	Concentration in the permeate at the end of the experiment
$\Delta H_{v,i}$	Latent heat of vaporization
ΔP	Delta P, partial pressure difference
Δt	Delta t, temperature difference
E^0	Oxidizing character
H	Global Heat Transfer Coefficient
$h_{w,f}$	Heat Transfer Coefficient in the Feed Boundary Layers
$h_{w,p}$	Heat Transfer Coefficient in the Permeate Boundary Layers
J	Flux [L/(m²·h)]
k_m	Thermal Conductivity of the Membrane
K_{OC}	Carbon-water partitioning coefficient
K_{SP}	Ion activity product
L_c	Concentrate Feed Volume
$L_{f,0}$	Initial Feed Volume
LogD	Distribution coefficient
LogP	Partition coefficient (octanol water partition coefficient)
m_f	Flow rate [L/min]
Nu	Nusselt number
Pr	Prandtl number
R_{ads}	Adsorptive removal
T_f	Feed temperature
T_{fb}	Fluid bulk temperature on the feed side
$T_{filtered}$	Filtration time
T_{fm}	Membrane surface temperature on the feed side
T_{pb}	Fluid bulk temperature on the permeate side
T_{pm}	Membrane surface temperature on the permeate side
T_p	Permeate temperature
v	velocity
vf0	Volume of the feed at the beginning of the experiment
vfe	Volume of the feed at the end of the experiment
vp	Volume of the permeate at the end of the experiment

List of illustrations

Abstract

The world's increasing population, economic development and climate change are driving the demand for more drinking water. In India, more than 100 million people live in areas of poor water quality. It has been reported that more than 33% of India's groundwater resources are unsuitable for consumption. Anthropogenic contaminants, such as microbial contaminants, nitrate, pesticides and industrial discharge, together with geogenic contaminants, such as fluoride, arsenic, iron and saline water, pose a threat to human health. In many rural areas neither a centralized system for drinking water production nor stable electric power supply exists. Decentralized small-scale water treatment systems with independent power supply could be implemented to produce safe drinking water for the communities. Recently, Membrane Distillation (MD) has been identified as a promising technology for drinking water production in situations with off-grid power supply. The objective of this research was to evaluate the application of MD for the production of drinking water in small-scale communities.

It was shown in this study that bulk salinity, as well as fluoride, nitrate and non-volatile pesticides were well removed from a synthetic brackish groundwater solution using a bench scale and a pilot scale MD unit. The application of a vacuum at the permeate side enhanced the permeate production up to 40%. An elevated scaling potential was identified in the presence of fluoride together with calcium. However, only minor traces of loosely deposited solids were observed in this study. The membrane was efficiently cleaned with flushing of Milli Q water.

Fluoride and nitrate were removed at rejection rates higher than 98-99% and 99% respectively in all experiments. The removal of pesticides was shown to be strongly depending on the vapour pressure and the LogD of the target compounds. A low vapour pressure and a low LogD were found to be favourable for a good rejection in MD.

Post-treatment with granulated activated carbon filtration after the MD was tested for removal of any remaining traces of pesticides to safeguard full compliance with drinking water standards. A 2 log unit removal for all selected pesticides was achieved up to 67,600 bed volumes.

The study demonstrates that membrane distillation is a promising alternative for small-scale water supply from brackish groundwater.

CHAPTER 1

INTRODUCTION

UTS

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1. Introduction

1.1. Background of research

1.1.1. Global fresh water demand

Approximately 2 billion people worldwide depend on groundwater supplies and 783 million people do not have access to clean water. With the ever growing population the numbers are subjected to increase significantly in the future (UNESCO 2012). 84% of the populations without access to an improved source of drinking water, such as a public tap, protected spring or a borehole, live in rural areas (WHO & UNICEF 2006). According to UNESCO (2006) 80% of all diseases and deaths in the developing world are due to water-related diseases. Therefore, there is a huge need for action to supply clean and safe drinking water all over the world, especially in developing and transitional countries as the infrastructure to treat and distribute water is absent or not yet established nationwide.

1.1.2. Fresh water supply for remote areas

For decentralized water supply, groundwater is almost always the preferred source as it is almost free of pathogenic organisms and turbidity in most cases. Smet and van Wijk (2002) estimate that the abstraction of groundwater for community water supplies is probably still to a great extent below its potential in many countries. To tap groundwater it is necessary to dig or drill a hole. The abstracted water then needs to be characterized to decide if treatment is necessary before distribution. If the water contains salt or other contamination that can be tasted such as iron, it is clear that treatment is necessary before consumption. However many types of contamination cannot be smelled or tasted directly. For example if the water is contaminated with fluoride, arsenic, heavy metals or trace organics (Kim *et al.* 2016). Without treatment of this water negative health effects will be notable in short or long term depending on the type of contamination and the concentration. Different types of small scale treatment systems will be introduced in Chapter 2.3.

1.1.3. Membrane distillation

Membrane distillation (MD) is a membrane technology for desalination purpose. The driving force is based on the vapour pressure gradient over a hydrophobic microporous membrane. Due to the hydrophobic characteristics of the membrane, only vapour can pass through the pores. It has been confirmed that the partial water vapour pressure is reduced only slightly with high salt concentrations (Martinetti, Childress & Cath 2009).

Therefore, the technology is well suited for highly saline water treatment up to 80 to 90% recovery, while reducing brine production significantly. Other low volatile water contaminants are also removed very efficiently by MD with a theoretical rejection of 100% (Wang & Thai-Shung 2015). Another interesting feature of MD is that it requires only low operating feed temperatures and therefore alternative energy sources can be used such as, solar energy or waste heat (Koschikowski *et al.* 2009). Furthermore the design of MD treatment plants makes it possible to build compact units that are suitable for small scale use. With the use of solar energy in the form of heat and electricity, MD small scale units can be used as standalone systems in remote areas where other treatment systems are challenged (Koschikowski *et al.* 2009). More details on MD can be found in Chapter 2.4.

1.2. Objective of this research

The main objective of this study is to investigate the removal of target contaminants from brackish synthetic groundwater by membrane distillation (MD). The results from this study target the application of a decentralized, off grid MD for drinking water production from brackish groundwater containing pesticides, fluoride and nitrate for the Indian context. In particular, the following topics are investigated:

1. Removal of fluoride and nitrate with DCMD as well as VE-DCMD

   This study investigates the fluoride removal capacity of MD using a low heating temperature setting. Specifically, the aspect of fouling and membrane cleaning and maintenance are studied in detail. Also the incorporation of a vacuum on the permeate side will be tested.
2. Removal of pesticides with DCMD

   This study is investigating the aspect of pesticide removal with MD. A detailed study on specific pesticides, namely phorate, parathion-methyl, dichlorvos, clofibric acid and atrazine is conducted in the context of the pesticide characteristics and the MD thermal operation and hydrophobic membrane permeate quality.
3. Removal of pesticides in an activated carbon filter

   This experiment is carried out as a possible post treatment option for the removal of pesticides that may be present after membrane distillation. Again, the above mentioned pesticides are examined.
4. Sustainable application of MD for groundwater treatment

In the final phase of this study, the application of MD is evaluated. The aspects of drinking water production, pesticide rejection, membrane scaling and fouling are discussed as part of the results.

1.3. Outline of this study

In the first part of this study, lab-scale experiments with brackish synthetic groundwater were conducted with regards to the system performance and flux pattern. The scaling and fouling behaviour was investigated as well as membrane maintenance. These experiments were followed by investigations with regards to fluoride, nitrate and pesticide removal by DCMD and VE-DCMD.

In the second part of the study, an activated carbon filter was tested as a possible post treatment option to membrane distillation as some pesticides may still occur in small quantities in the MD permeate. Further experiments with regards to pesticide removal were carried out using different feed temperatures such as 40 °C, 55°C and 70°C.

CHAPTER 2

LITERATURE REVIEW

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2. Literature review

2.1. Introduction

In India, groundwater is largely used for domestic purposes, namely by 80% of the rural population and 50% of the urban population. In many areas, groundwater serves as the only source of drinking water (Chakraborti, Das & Murrill 2011). Over-extraction of groundwater and river water for agricultural purposes leads to rapidly dropping water tables. Untreated sewage flowing in open drains and open landfills with no protection from leaching into the groundwater are the main man-made sources for water contamination (Central Pollution Control Board 2008). It has been reported that more than 33% of India's groundwater resources are unsuitable for consumption (Chakraborti, Das & Murrill 2011). Anthropogenic pollution such as microbial contaminants, nitrate, pesticides and industrial discharge, together with geogenic contaminants such as fluoride, arsenic, iron and saline water, pose a threat to human health.

2.2. Microbial and chemical contaminants in groundwater in India

2.2.1. Microbial contamination

It is estimated that currently only 10% of sewage generated in India's cities is treated prior to reaching groundwater or surface water resources (Chakraborti, Das & Murrill 2011; Nohar *et al.* 2016; Rajmohan & Amarasinghe 2016). The main problem resulting from this is the microbial contamination of drinking water with pathogenic bacteria, protozoa and viruses as well as elevated levels of nitrate.

Bacteria: Bacterial contamination can be removed largely through soil passage (Ayuso-Gabella *et al.* 2011; Tielemans 2007). Therefore, bacterial contamination applies mainly to surface water rather than groundwater. However, due to poor sanitation practice and infrastructure, bacterial contamination can also be found in shallow tube wells with a depth of around 10 m. With increasing depth, the contamination of bacteria decreases (Chakraborti, Das & Murrill 2011). Another source of bacterial contamination is the handling of the collected water in rural areas. Since many households have no direct fresh water access, water has to be collected on a daily basis and is stored in the house for use. This practice, in addition to the already contaminated collected water, increases the risk of microbiological growth, especially in hot climates. If water contaminated with bacteria is consumed, the most common consequence is diarrhoea caused by faecal coliform bacteria such as: *Escherichia Coli 0157:h7* or *Enterococci*. *Enterococci* are specifically a risk for people with a weak immune system, such as the elderly, young children and infants. *Legionella* is a bacterium found naturally in the environment. If it is aerosolized, for example, in a shower or in air conditioning and inhaled, legionnaires disease can be caused, a type of pneumonia (Water Technology 2015). *Salmonella* can also cause intestinal illness as well as typhoid and paratyphoid fever (Levantesi *et al.* 2012).

Viruses: Viruses present another major group of microbial contamination causing waterborne diseases such as hepatitis A, polio, meningitis, fever and gastroenteritis. Viruses are very small (10-100 nm) and often resistant to disinfection. UF filtration followed by disinfection has a good removal efficiency as viruses are often occurring in colloids with organic matter (ElHadidy, Peldszus & Van Dyke 2013). In India viruses pose a high threat to the population. Therefore the Indian Drinking Water Specification (BIS 2012 IS 10500:2012) states that the water should be free from viruses.

Protozoa: Contamination with *Gardia lamblia* and *Cryptosporidium* are one of the main microbial hazards in drinking water. Symptoms of infection are diarrhoea, abdominal cramps, headache and weight loss. The symptoms usually start 2 to 25 days after swallowing the cyst (Vermont Department of Health 2015).

Pathogens can be largely inactivated through disinfection with chlorination tablets, ozone, heat or UV-light, or removed with filtration technologies (UF/NF/RO). For drinking water application, it is advised to apply a multi-barrier approach to establish and maintain disinfection (Bennett 2008).

2.2.2. Pesticide contamination

The intensive use of pesticides in India has led to widespread contamination of the biotic as well as the abiotic environment in India (Yadav *et al.* 2015). Pesticides and their degradates were found in surface water and groundwater all over the world (Köck-Schulmeyer *et al.* 2014; Kolpin, Thurman & Linhart 2000; Lapworth & Gooddy 2006; Leistra & Boesten 1989). Like in many developing and emerging countries, pesticide contamination of groundwater sources has also been detected in India (Chakraborti, Das & Murrill 2011; Lari *et al.* 2014; Yadav *et al.* 2015). For example Lari *et al.* (2014 has found 0.25 µg/L of dichlorvos and 0.33 µg/L of phorate in the Yavatmal region. This is a serious issue as groundwater is one of the main source for drinking water in India, especially in remote areas that lack necessary infrastructure for proper water treatment (Chakraborti, Das & Murrill 2011). Pesticides are used in pest and weed control with a multitude of different mechanisms of action. They are contaminants of emerging concern due to a range of potential adverse effects on humans and environment (Schwarzenbach *et al.* 2010; Schwarzenbach *et al.* 2006).Globally, up to 3 million cases of acute, severe poisoning from pesticides are recorded. Suicidal pesticide poisoning causes the death of 230,000 to 325,000 people each year, with many more cases not being reported (Gunnell *et al.* 2007; WHO 1990). Pesticide poisoning is more frequent in developing countries than in industrialized countries, even though in developing countries only 25% of the pesticides worldwide are consumed. The increased risk for pesticide poisoning in developing and transitional countries has various reasons, such as the low level of protection of workers due to insufficient availability of protective equipment, improper application, condition and work practices, unsafe storage and disposal facilities, poor management, unqualified pesticide dealers and inadequate health centres (Yadav *et al.* 2015). Besides poisoning, a multitude of pesticides have been identified also as endocrine disrupting chemicals (EDC). Mnif *et al.* (2011) has compiled an overview of 105 substances and their effect on the hormone system of humans. The combined effects of pesticides are a major health risk to humans. In addition, wildlife is particularly vulnerable to the toxic and endocrine effects of pesticides.

In India, 76% of the used pesticides are accounted for as insecticides, 13% as fungicides and 10% as herbicides. In cotton and paddy cultivation, more than 50% of the pesticides are used. Depending on the climatic conditions and the agriculture in different states in India, the pesticide consumption can vary strongly from one state to another. Uttar Pradesh, Maharashtra and Andhra Pradesh are the states with the highest pesticide consumption (Yadav *et al.* 2015). Based on the precautionary principle, the European Drinking Water Directive (98/83/EC) has set a limit of 0.1 µg/L for single pesticides (with exception of aldrin, dieldrin, heptachlor and heptachlor epoxide where the limit for the single compound is 0.03 µg/L) and 0.5 µg/L for the sum of all active pesticides detected. India has set individual values for 18 substances in the Indian Standard Drinking Water Specification as shown in the Table below (Table 2.1). It can be seen that the European standards are much stricter and less compound specific than the Indian threshold values.

Table 2.1 Pesticide residue limits according to the Indian drinking water guidelines (BIS 2012)

Pesticide	**Limit [µg/L]**
Alachlor	20
Atrazine	2
Aldrin/Diedrin	0.03
Alpha HCH	0.01
Beta HCH	0.04
Butachlor	125
Chlorpyriphos	30
Delta HCH	0.04
2,4- Dichlorophenoxyacetic acid	30
DDT (*o, p* and *p, p* – Isomers of DDT, DDE and DDD)	1
Endosulfan (alpha, beta, and sulphate)	0.4
Ethion	3
Gamma - HCH (Lindane)	2
Isoproturon	9
Malathion	190
Methyl parathion	0.3
Monocrotophos	1
Phorate	2

In general, the mobility of pesticides and thus their risk of leachability into the groundwater have been correlated with a weak adsorption of the soil matrix quantified in terms of a small soil organic carbon-water partitioning coefficient (K_{OC}) (Arias-Estévez *et al.* 2008). Generally, pesticides with $K_{OC} \leqslant$1,000 are potentially leaching compounds whereas pesticides with $K_{OC} \geqslant$ 1,000 have also been found in the groundwater. This is mainly due to the fact that when the pesticides are polar, their behaviour does not follow that rule. Also the specific site and application along with the soil type and the climatic conditions play an important role on the fate of the pesticide in the environment (Arias-Estévez *et al.* 2008).

Another important chemical characteristic of pesticides that plays a role in their behaviour in the environment or in a treatment system is how hydrophilic or hydrophobic they are and hence, how prone they are to stay in the water phase or to adsorb at a different material or fluid. The partition coefficient (P) describes this behaviour using the logarithm of the ratio (LogP) of a compound in a polar (e.g. water) and non-polar solvent (e.g. octanol). It is therefore often also referred to as the octanol water partition coefficient. An extension of the LogP is the distribution coefficient LogD which also takes into account the ionic species of a specific compound at a defined pH. Therefore the LogD it is preferably used as an indicator of a compounds' solubility in water when the compound of interest is known to be ionized at a certain pH.

The before mentioned K_{OC} is related to the LogD (Xing & Glen 2002).

The LogD is calculated as following:

for acids

$$\log D = \log P - \log [1 + 10^{(pH-pK_a)}] \tag{2.1}$$

for bases

$$\log D = \log P - \log [1 + 10^{(pK_a-pH)}] \tag{2.2}$$

Where logP is the partition coefficient, and pK_a is the ionization constant (Xing & Glen 2002).

A LogD < 0 indicates that the compound is highly polar (hydrophilic) and therefore well soluble in water. If the LogD > 3 the compound is hydrophobic, which means it is not well soluble in water and prone to adsorption (Sangster 1997).

Common practices to remove pesticides from both drinking water and wastewater together with other trace organic compounds (TROCs) such as pharmaceuticals, personal care products and industrial chemicals, are adsorption e.g. on activated carbon (Kennedy *et al.* 2015; Mailler *et al.* 2015), oxidation using ozone, chlorine, H_2O_2 or UV and combinations of adsorption and oxidation (Broséus *et al.* 2009; Derco *et al.* 2015). Moreover dense membrane filtration systems such as RO and NF have been proven to remove pesticides effectively (Bonné *et al.* 2000; Plakas *et al.* 2006). One lab scale study in 2014 has proven that MD provides a barrier for TROCs (Wijekoon *et al.* 2014b). In Table 2.2 the advantages and disadvantages of different technologies for pesticide removal from drinking water are listed and evaluated.

Table 2.2 Pesticide removal in drinking water

Technology	Removal efficiency	Advantage	Disadvantage	Reference
Adsorption on activated carbon (GAC/PAC)	Highly depending on process conditions and water matrix (DOC), as well as selected carbon. e.g atrazine:	Relatively high removal efficiency for many pesticides	Selective removal depending on physio-chemical properties such as charge of compound or their molecular mass, competitive	(Humbert *et al.* 2008; Ormad *et al.* 2008; Snyder *et al.* 2007b)

Technology	Removal efficiency	Advantage	Disadvantage	Reference
	50-80% removal with 5 mg/L PAC and 4-5 h contact time 10% breakthrough at 20,000 to 50,000 BV at EBCT = 7.6 minutes		adsorption, removal of PAC after process, saturation of activated carbon, non destructive method	
Oxidation by chlorine	Highly depending on dosage and water matrix (NOM) 10-50% for triazines, Other pesticides ranging from 30 % to 100 % e.g atrazine <20% removal with 3 mg/L free chlorine and 24 h contact time	Simple application, long term disinfection with regards to bacteria	Very selective removal, formation of trihalo-methanes, formation of oxidation by-products, Low oxidizing character (E^0=1.36V)	(Ormad *et al.* 2008; Snyder *et al.* 2007b)
Ozonation	50% for triazines, 80 % for organophosphorous pesticides using 4.3 mg/L Ozone	High oxidizing character (E^0 = 2.8V)	Selective removal, formation of trihalo-methanes, bromate formation, formation of oxidation by-products	(Ormad *et al.* 2008)
Chemical precipitation with aluminium sulphate or ferric chloride	35 % e.g. atrazine <20% removal with aluminium sulphate or ferric chloride DDT 20% removal with aluminium sulphate or ferric chloride		Low removal rate, sludge generation	(Ormad *et al.* 2008; Snyder *et al.* 2007b)
UV and AOP (UV/H_2O_2)	Removal efficiency depending on chemical structure (aromatic compounds) e.g. atrazine main removal with	Effective process for many substances, removes also bacteria, uncomplicated process	formation of oxidation by-products, footprint of peroxide	(Snyder *et al.* 2007b)

Technology	Removal efficiency	Advantage	Disadvantage	Reference
	UV 60-70% removal with 1000 mJ/cm^2 and 1000 mJ/cm^2 with 5 mg/L H_2O_2			
Tight nano-filtration	Removal through size exclusion, electrostatic interactions and adsorption on membrane. Therefore the removal efficiency is mainly depending on molecular size, polarity, hydrophobicity/ hydrophilicity, and molecular weight cutoff of the selected membrane e.g. atrazine removal 50-80%	Successful large scale application for pesticide removal in WTP Méry-sur-Oise, Paris, France	It is not advised to use NF solely for pesticide removal, hydrophobic substances are not well retained, aging of membranes leads to reduced rejection	(Cyna *et al.* 2002; Plakas & Karabelas 2012a; Plakas *et al.* 2006; Snyder *et al.* 2007b)
Reverse Osmosis	Removal through size exclusion and electrostatic interactions >90% removal for most TROCs including pesticides	Successful large scale application for pesticide removal in Amsterdam, Leiduin WTP, Netherlands	Energy demand, pre-treatment of water, remineralisation	(Bonné *et al.* 2000; Snyder *et al.* 2007b)
Membrane Distillation	Strongly depending on vapour pressure and LogD, e.g. atrazine removal >95%	Very high removal rate of non-volatile compounds	Energy demand, remineralisation, only proven in lab scale	(Wijekoon *et al.* 2014a)

2.2.3. Nitrate contamination

Nitrate contamination in groundwater is mainly from agricultural runoff of nitrogen rich fertilizers or manure and the disposal of untreated or poorly treated wastewater containing human excretions. In India, 11 out of 29 states have nitrate contamination which exceeds the permissible level of 45 mg/L (Chakraborti, Das & Murrill 2011). Elevated nitrate intake can cause methemoglobinemia, whereby the oxygen uptake in the blood is reduced. This can cause serious damages to the brain and is in particular dangerous for infants (WHO 2015).

2.2.4. Fluoride contamination

In India, 20 out of the 29 states are reporting excessive levels of fluoride in raw drinking water. It can be found in groundwater due to geogenic contamination from deposits in solid rock (Chakraborti, Das & Murrill 2011). It is estimated that 66 million people in India are affected by fluoride contaminated water and 15 states have declared to be affected by fluorosis (Jagtap *et al.* 2012; Nemade, Rao & Alappat 2002). Fluorosis is a water-related disease originating from chronic high-level exposure to fluoride in drinking water and can be divided further into skeletal fluorosis and dental fluorosis. Dental fluorosis develops much earlier than skeletal fluorosis and can be identified by a change of colour of the teeth from white to brown. Skeletal fluorosis causes stiffness and pain in the joints and in severe cases the bone structure may change due to accumulation of fluoride in the bones. Common technologies for defluoridation of drinking water are: precipitation/coagulation, adsorption/ion exchange, electrodialysis and membrane technologies such as reverse osmosis and membrane distillation (Loganathan *et al.* 2013; Shen *et al.* 2015).

Chemical precipitation and coagulation was one of the earliest methods developed in the 1930's to remove fluoride with the addition of aluminium salts together with lime. The method is also called the Nalgonda process after a district in Telangana, India, because the technique was widely implemented in this area (Jadhav *et al.* 2015). Benefits of this application are the low initial costs and the easy and decentralized application. Drawbacks are the amount of chemicals needed and the large volume of sludge produced (He *et al.* 2015; Jadhav *et al.* 2015).

Adsorption is a conventional technique which is widely used for defluoridation. There are many adsorbent materials available, the most commonly used adsorbents are activated alumina and activated carbon (Loganathan *et al.* 2013). Other adsorbent materials have been reported in literature such as: metal oxides and hydroxides (Banat *et al.* 2007a), ion exchange resins and fibres (Cath, Adams & Childress 2005; McCutcheon, McGinnis & Elimelech 2005), zeolithes (Duong *et al.* 2016), carbon materials (Nghiem & Cath 2011), natural materials (Nemade, Rao & Alappat 2002), nanomaterials (Alklaibi & Lior 2005), and industrial by-products (Gryta 2008). Adsorption has its advantages in the decentralized application. It leads to efficient removal and a variety of alternative adsorbents are available. However, adsorption is only economic with low F^- and TOC (total organic carbon) concentrations and some of the adsorbents are expensive.

Reverse Osmosis (RO) has a very efficient fluoride removal of 90-97% (Banat *et al.* 2007b; Shen & Schäfer 2015). Drawbacks of RO are the expensive infrastructure (Gunko *et al.* 2006), the remineralisation of the permeate and the disposal of the brine.

The removal of fluoride with electrodialysis is a rather novel research field. It was initially developed for desalination of brackish water. Menkouchi Sahli *et al.* (2007) observed a removal efficiency of 96% for fluoride in fresh water. The advantage of electrodialysis is that there are no chemicals needed, however the application of electrodialysis is only economic if the water has a TDS below 4 mg/L (Fritzmann *et al.* 2007). Further, a remineralisation of certain ions is needed and the technology involves high capital cost.

MD has been investigated as a possible alternative process for the removal of fluoride from brackish groundwater with hollow fiber direct contact membrane distillation (DCMD) (Hou *et al.* 2010a), whereas others have studied the removal of fluoride from brackish water with flat sheet DCMD (Boubakri *et al.* 2014). In both cases, large removal of fluoride was feasible, but for the application in hollow fibre DCMD the feed solution needed to be acidified in order to prevent scaling due to $CaCO_3$ formation (Hou *et al.* 2010a). Further, it was reported that after reaching a volume concentration factor of 4 a reduction of the flux was observed which could be attributed to deposits of CaF_2 on the membrane. Detailed scaling mechanisms with regards to the formation of CaF_2 were not discussed in these studies.

An overview on advantages and disadvantages of the different technologies for fluoride removal is given in Table 2.3.

Table 2.3 Advantages and disadvantages of defluoridation technologies (modified from Loganathan *et al.* (2013)

Technology	Advantages	Disadvantages	Source
Precipitation/coagulation, Nalgonda technique	Easy application, decentralized application, low initial costs	Large amount of chemicals, sludge volume	(He *et al.* 2015)
Adsorption/Ion exchange	Many different adsorbent materials can be used, decentralized	Only economic with low F^- concentrations, solution for regeneration/disposal of loaded adsorbent	(Jadhav *et al.* 2015; Loganathan *et al.* 2013; Nemade, Rao &

Technology	Advantages	Disadvantages	Source
	application, efficient removal	needed	Alappat 2002)
Reverse Osmosis	State of the art technology, good removal capacity	Scaling and fouling phenomena, expensive pressure driven process, brine, centralized treatment	(Banat *et al.* 2007b; Shen *et al.* 2015)
Electrodialysis	No chemicals, no waste, good removal	Only economic with low TDS water, remineralisation needed, high capital cost	(Chen *et al.* 2013; Menkouchi Sahli *et al.* 2007)
Membrane Distillation	Low brine production, No chemicals needed resistant to high salt concentrations, decentralized application	High thermal energy input	(Hou *et al.* 2010a)

2.2.5. Arsenic contamination

Arsenic contamination of groundwater is a geogenic contamination which occurs through the washing of local bedrock. It is also estimated that certain bacteria can promote the mobilization of arsenic from rock (Drahota *et al.* 2013). In India some of the main sources of arsenic, besides arsenic contaminated bedrock, are the Himalayan Mountains and the Tibetan Plateau. Rivers that originate from that region such as the Ganga River are expected to contain arsenic (Das *et al.* 2008). In India, 35 districts in 6 states are affected, namely: West Bengal, Bihar, Uttar Pradesh, Jharkhand, Assam and Manipur. It is estimated that the total number of people affected is 70.4 million (Chakraborti *et al.* 2009). Chronically long-term exposure to high levels of arsenic in drinking water causes firstly, skin irritation such as pigmentation changes, skin lesions and hard patches on the palms of the hands and soles of the feet and secondly, peripheral neuropathy, gastrointestinal symptoms, conjunctivitis, diabetes, renal system effects, enlarged liver, bone marrow depression, destruction of erythrocytes, high blood pressure, cardiovascular disease and cancer (WHO 2010).

2.2.6. Iron contamination

Elevated iron levels in groundwater are found in 12 states in India, particularly in Rajasthan, Orissa and Tripura (Mehta 2006). Drinking water containing less than

0.3 mg/L iron has no notable change in taste but at concentrations up to 1 mg/L the taste of the water changes to an unpleasant taste. Concentrations of 1 – 3 mg/L can be acceptable for drinking for some individuals, but people often refuse to drink water high in iron because of taste and discolouration (Chakraborti, Das & Murrill 2011). Adverse health effects only occur at much higher levels than 3 mg/L, therefore there is no health-based guideline value proposed by WHO (WHO 2008).

2.2.7. Salinization of groundwater

Another challenge for the water industry as well as the authorities and the public is the salinization of groundwater in coastal areas and inland. According to Freeze & Cherry (1979), groundwater is defined as brackish water when the total dissolved solids (TDS) range from 1,000 – 10,000 mg/L. TDS concentration below 1,000 mg/L is referred to as fresh water and above 10,000 mg/L as saline water. Solutions with a TDS concentration higher than 100,000 mg/L or which have nearly reached their saturation point are referred to as brine.

Salinization of groundwater in coastal areas can occur if the aquifer is hydraulically connected to the sea. When over-abstraction of the groundwater takes place, sea water intrudes into the fresh water. This process is called lateral sea water intrusion (Weert, Gun & Reckman 2009). Not only major coastal cities in India such as Chennai are affected by that phenomenon, but many coastal areas all over the world are also affected. With sea levels rising due to climate change, sea water intrusion is even increasing (Weert, Gun & Reckman 2009).

Inland salinization of groundwater and soil can have multiple origins. The simplest mechanism is a salt storage in the rock above the basement that can be mobilized through rainfall or irrigation and reach the groundwater. Secondly, inappropriate irrigation practices can lead to groundwater elevation and to water logging. Especially in arid and semi-arid areas water logging results in excessive evapotranspiration and accumulation of salts in the soil over time, which, eventually, leach into the groundwater. Irrigation with low quality water containing a high amount of salt can even lead to desertification (McFarlane & Williamson 2002; Singh 2009). Another reason for inland salinization of groundwater is saltwater upconing. This is a process where deep saline water underlying shallow fresh water in an aquifer, rises into the freshwater zone as a result of abstraction of water from the fresh water zone (Reilly & Goodman 1987). If the pumping rate fluctuates over a longer period, the mixing zone will grow and saline pollution increases (IWMI 2015).

It is estimated that 6.73 million ha are affected by soil salinity and alkalinity in India. This refers to about 5% of the arable land in India. About 25% of underground water is saline and/or sodic and unfit for irrigation or drinking (Singh 2009). The states affected by saline groundwater in India are listed in Table 2.4.

Table 2.4 Occurrence of Saline Groundwater in India (Central Pollution Control Board 2008)

Inland Salinity	State	Place of Occurrence
	Maharashtra	Amravati, Akola
	Bihar	Begusarai
	Haryana	Karnal
	Rajasthan	Barmer, Jaisalmer, Bharatpur, Jaipur, Nagaur, Jalore & Sirohi
	Uttar Pradesh	Mathura
Coastal Salinity	Andhra Pradesh	Visakhapatnam
	Orissa	Puri, Cuttak, Balasore
	West Bengal	Haldai & 24 Paragana
	Gujarat	Junagarah, Kachchh, Varahi, Banskanta & Surat

Technologies for desalination for drinking water production are either membrane based or thermal based. Membrane technologies include: reverse osmosis (RO), dense nanofiltration (NF) and electrodialysis (ED) or reverse electrodialysis (EDR). Thermal technologies include: multi-stage flash evaporation (MSF) and multiple-effect distillation (MED). The commonly used desalination technology is RO, followed by MSF (DesalData.com 2012). The percentages of the installed capacity are given in **Fehler! Verweisquelle konnte nicht gefunden werden.** (see p. 22).

2.3. Small scale water treatment technologies

Decentralized small scale water treatment systems are an important technology for developing and transition countries as centralized systems are often non-existing in rural areas. The requirements for such systems include low costs, low maintenance, safety, ease of use, independence of energy sources and sustainability (Peter-Varbanets *et al.* 2009). There are three main types of decentralized systems, namely point-of-use systems (POU), point-of-entry systems (POE) and small-scale systems (SSS). POU systems are small household units that treat only a minimum amount of about 2-8 L drinking water per person per day and sometimes also water for cooking for the family. POE systems treat all the water that is supplied to the household. The daily water supply normally ranges from 100-150 L per person. SSS refer to larger systems than POU and POE and can supply several families or a small village. The capacity of SSS's are variable, ranging from 1,000 to 10,000 L per day (Peter-Varbanets *et al.* 2009). In this work the focus is laid on small-scale membrane systems providing water for several families or small villages.

Membrane systems are attractive for SSS since the costs of membranes have decreased rapidly during the last decades and they can provide an absolute barrier for pathogens and other contaminants which were described in the previous chapters (Peter-Varbanets *et al.* 2009). Decentralized membrane systems can be based on microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) reverse osmosis (RO) or membrane distillation (MD). All of the mentioned membrane systems can be used for disinfection, however, due to the pore size of the membrane not all MD, MF and UF membranes are able to retain bacteria and viruses completely (Gryta 2002; Peter-Varbanets *et al.* 2009). RO and MD are suitable technologies when the treated water is saline or brackish (Peter-Varbanets *et al.* 2009). For the removal of pesticides NF, RO and MD are suitable (Bonné *et al.* 2000; Plakas & Karabelas 2012a; Wijekoon *et al.* 2014a). It has been shown that fluoride can be removed by RO and MD (Hou *et al.* 2010b; Shen *et al.* 2015). Successful studies on RO based (Shen *et al.* 2015) and MD based (Koschikowski *et al.* 2009) stand-alone SSS have been carried out. RO and MD seem to be the most favourable out of the mentioned membrane technologies for simultaneous desalination, and removal of fluoride and pesticides. However, the need for high pressure in the RO process comes along with cost- and maintenance-intensive pumps which are not needed for the MD process. The advantages and disadvantages are summarized in Table 2.5.

Table 2.5 Advantages and disadvantages of different membrane technologies for small scale applications

Technology	**Advantage**	**Disadvantage**	**Reference**
Microfiltration	Low pressure required, removal of pathogens (bacteria)	Not suited for desalination or fluoride removal, very low virus rejection, no micropollutant rejection	(Doulia *et al.* 2016; Matsushita *et al.* 2013; Snyder *et al.* 2007b)
Ultrafiltration	Low pressure required, removal	Not suited for desalination,	(ElHadidy, Peldszus & Van

	of pathogens (bacteria and viruses)	viruses only partially retained, not able to retain fluoride, no micropollutant rejection	Dyke 2013; Snyder *et al.* 2007b)
Nanofiltration	Good retention for many micropollutants (dense NF), bacteria and viruses	Partial desalination (multivalent ions only), only dense nanofiltration achieves sufficient fluoride retention, medium to high pressures required	(Jorba *et al.* 2014; Nghiem, Schaefer & Elimelech 2005; Nghiem, Schäfer & Elimelech 2004; Plakas & Karabelas 2009; Plakas & Karabelas 2012b; Plakas *et al.* 2006; Tahaikt *et al.* 2008)
Reverse Osmosis	Good retention of fluoride, micropollutants and viruses, suited for desalination	High pressures required, low water recovery, large amount of brine that needs to be disposed, not economic in small scale application	(Bonné *et al.* 2000; Drioli, Ali & Macedonio 2015; Shen & Schäfer 2014)
Membrane Distillation	Very high water recovery without significant flux decline, suited for desalination, good retention for many micropollutants, use of waste heat as energy source, suited for moderate size applications	Large thermal energy input, low flux, lack of commercially available membranes, limited number of commercial MD suppliers	(Al-Obaidani *et al.* 2008; B.B. Ashoor *et al.* 2016; Drioli, Ali & Macedonio 2015; Wijekoon *et al.* 2014b; Zuo *et al.* 2011)

2.4. Membrane Distillation

Membrane distillation (MD) is an emerging technology designed for desalination. MD is a thermally driven separation process where water vapour is transported through the pores of a hydrophobic microporous membrane. The vapour pressure difference of the hot feed and the cold permeate is the driving force which is a main advantage compared to conventional pressure-driven membrane processes (Wang & Thai-Shung 2015). Further, MD is less sensitive to high salinity waters and has a much higher recovery compared to RO, yielding in a significantly reduced brine production (Chen *et al.* 2013). Compared to other distillation processes MD operates at temperatures considerably below the boiling point around 40-80 °C. The principle of the MD process is illustrated in Figure 2.1.

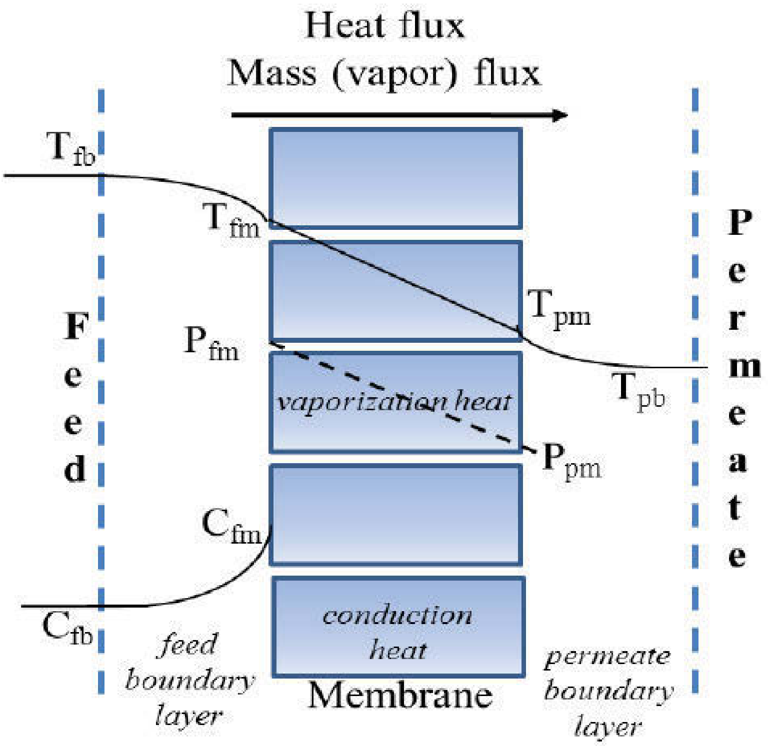


Figure 2.1 Illustration of the MD process displaying heat and mass transfer (Naidu 2014)

2.4.1. MD configuration

There are four main MD configurations: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD) and vacuum membrane distillation (VMD) (El-Bourawi *et al.* 2006). DCMD is the most frequent studied and also the simplest configuration where feed and permeate are directly separated by the hydrophobic membrane.

- Direct contact membrane distillation (DCMD): The hot feed solution and the cold distillate are in direct contact with the membrane.
- Air gap membrane distillation (AGMD): A thin air gap and a condensation surface is embedded on the permeate side of the module.
- Sweep gas membrane distillation (SGMD): A cold inert gas sweeps through the distillate channel and collects vapour molecules, which condense outside of the membrane module.
- Vacuum membrane distillation (VMD): Vacuum is applied at the permeate side of the membrane module.

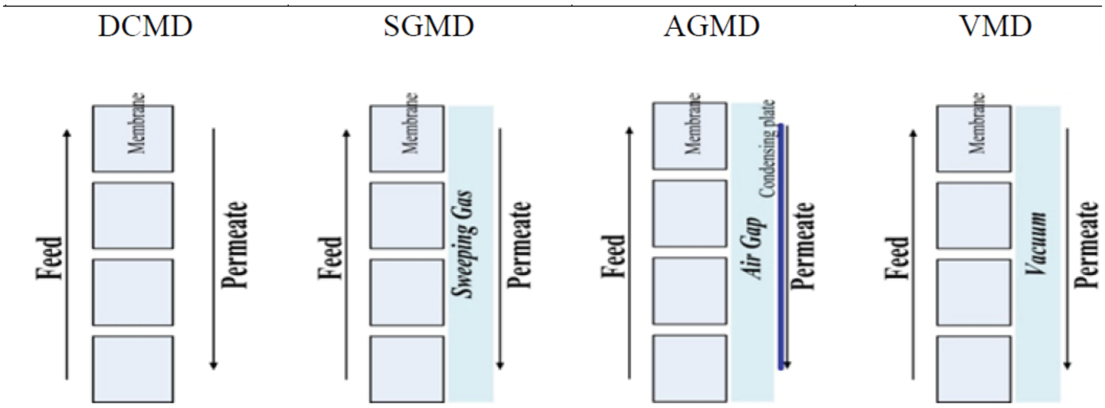


Figure 2.2 Membrane distillation configurations (Naidu 2014)

There are also new MD configurations being applied that are based on the above four main types of MD (Wang & Thai-Shung 2015).

- Multi-stage and multi-effect membrane distillation (MEMD): This concept is based on the multi-stage and multi-effect distillation. The main advantage is internal heat recovery which allows higher energy efficiency (Dotremont *et al.* 2010).
- Vacuum multi-effect membrane distillation (VMEMD): VMEMD shares a similar concept with the MEMD, but has additional vacuum enhancement (Camacho *et al.* 2013; Zhao *et al.* 2013).
- Hollow fibre multi-effect membrane distillation: A multi-effect AGMD hollow fibre module with internal heat recovery (Li *et al.* 2012).
- Material gap membrane distillation (MGMD): To increase the relatively low permeate flux in AGMD, the air gap could be filled with different materials like sponge and PP mesh (Francis *et al.* 2013).

Studies have also been conducted to enhance the flux in DCMD with the addition of hydraulic pressure on the feed side (pressure enhanced DCMD, PEDCMD) and with a vacuum on the permeate side (vacuum enhanced DCMD, VEDCMD). In comparison to VMD, the vacuum applied in VEDCMD is > 300 mbar absolute pressure, whereas in VMD the vacuum can be as low as 30-100 mbar absolute pressure. In VEDCMD the vacuum is not applied directly at the membrane, but at the headspace of permeate container. Therefore the membrane does not need any protection towards the vacuum as the effect is driven only indirectly by the pressure gradient across the membrane via the permeate solution (Cath, Adams & Childress 2004). Cath, Adams & Childress (2004) demonstrated with a PVDF membrane and a synthetic sea water solution (0.6 g/L NaCl) an increase of the flux with VEDCMD from 21 L/(m^2·h) to 26 L/(m^2·h) (95 kPa absolute pressure at permeate side, feed temperature 40 C°, permeate temperature 20°C, flow velocity 1.4 m/s). With this novel approach an increase of permeate flux of 23.8 % and even more was achieved.

MD offers various advantages such as theoretically 100% rejection of non-volatile compounds, relatively low operation temperatures, low operating pressure, resistant for high concentrated feed solutions and fewer requirements on membrane mechanical properties compared to other membrane technologies. The main drawbacks in MD are the lack of commercially available membranes and the high consumption of thermal energy. In addition, scaling and fouling are problems in MD as in any other membrane process (Wang & Thai-Shung 2015). However, the high energy consumption can be overcome by using solar energy for both thermal and electric energy generation (Ding *et al.* 2005; Koschikowski *et al.* 2009) or using low grade heat e.g. from a diesel generator operated in parallel for energy supply in remote areas.

2.4.2. Transfer mechanisms

2.4.2.1. Heat and Mass transfer

The transfer mechanisms in MD comprise the simultaneous heat and mass transfer from the hot feed to the cold permeate. The schematic diagram is displayed in Figure 2.1.

The mass transfer J is defined by the membrane coefficient B_m [kg/m^2/h] and the partial pressure difference across the membrane ΔP [Pa] as displayed in equation 2.3.

$$J = B\Delta P \tag{2.3}$$

The membrane coefficient B_m is dependent on the membrane geometry and can be determined by the Knudsen number (Kennedy *et al.*). It is the ratio of the mean free path, λ, of the travelling molecule to the pore size, *r* (Lawson & Lloyd 1997).

In MD the heat transfer occurs through lateral heat transfer and conduction heat transfer (Khayet & Matsuura 2011). The global heat transfer coefficient *H* of the MD process can be calculated as defined by Khayet & Matsuura (2011) as following:

$$\boldsymbol{h}_{w,f}\left(T_{fb} - T_{fm}\right) = \frac{k_m}{\delta}\left(T_{fb} - T_{fm}\right) + \sum_i J_i \,\boldsymbol{\Delta}\, H_{v,i} = \boldsymbol{h}_{w,p}\left(T_{pm} - T_{pb}\right) = H\left(T_{fb} - T_{pb}\right) \tag{2.4}$$

Where $h_{w,f}$ and $h_{w,p}$ are the heat transfer coefficient in the feed and permeate boundary layers, respectively. T_{fm} , T_{pm}, T_{fb} and T_{pb} are membrane surface temperatures and fluid bulk temperatures on the feed and permeate side. k_m is the thermal conductivity of the membrane. $\Delta H_{v,i}$, is the latent heat of vaporization, *H* is the global heat transfer coefficient in the MD process. Similar to the mass transfer coefficient, the MD heat transfer coefficient is usually estimated from the heat transfer empirical correlation of the Nusselt number (Nu) and the Prandtl number (Pr).

Polarization effect in MD

During the MD process a separation takes place between volatiles (water) and non-volatiles (salt). With increasing concentration of the feed solution, the concentration of salt near and at the membrane surface becomes higher than in the bulk feed. This concentration gradient is called concentration polarisation (CP) (El-Bourawi *et al.* 2006).

The second polarisation effect is the temperature polarisation (Sarkar *et al.* 2008). Due to the phase change of the solution at the permeation process the temperature at the membrane is reduced, creating a temperature difference (Lawson & Lloyd 1997). The extent of this phenomenon was defined by Schofield, Fane & Fell (1987) in the temperature polarization coefficient as displayed in equation 2.5.

$$\tau = \frac{T_1 - T_2}{T_f - T_p} \tag{2.5}$$

T_1 and T_2 are the temperatures on the membrane surface on the feed and permeate side (actual driving force) and T_f and T_p are the temperatures of the feed and permeate stream (overall driving force).

Both, concentration polarisation and temperature polarisation, implicate the MD process negatively by the loss of the driving force of the process. Mainly temperature polarisation has a big influence on the performance of the system since MD is a thermally driven process. By selecting appropriate operation parameters the effects of TP and CP can be reduced (Khayet & Mengual 2004).

2.4.3. MD in Drinking Water Production

Reverse osmosis together with multi stage flash evaporation are the most used technologies in seawater desalination, covering together almost 90% of the market (**Fehler! Verweisquelle konnte nicht gefunden werden.**) (DesalData.com 2012).

Table 2.6 Worldwide installed capacity by technology for seawater desalination (adapted from DesalData.com (2012))

Technology	**Installed capacity [m^3/d]**
RO	39.1
MSF	17.5
MED	5.2
ED	5.2
Hybrid	0.5
EDI	0.2
Other	0.2
Total	65.2

While RO is the state of the art technology for desalination on a large scale, the quantities of generated brine are a problem. In coastal areas the generated brine can be discharged into the sea increasing the local salt concentration, but in inland areas disposal management is challenging (Pérez-González *et al.* 2012). Further, RO desalination plants are built in large scale (up to 627'000 m^3/day Sorek plant, Israel) due to energy recovery, but there is also a need for fresh water in low-density population areas located in inland areas (Elimelech & Philipp 2011).

Emerging desalination technologies are membrane distillation, forward osmosis and capacitive deionisation.

Membrane Distillation (MD) demonstrated to be a promising alternative technology for standalone high saline water treatment in rural areas (Koschikowski *et al.* 2009; Wang & Thai-Shung 2015). Besides brine disposal the main issue in desalination is the thermal energy required. The energy challenge can be overcome by using waste heat or solar energy (see section 2.4.4).

Forward Osmosis (FO) uses the osmotic pressure of a draw solution to separate clean water from the feed solution. In a second step the draw solution is purified to drinking water. FO is less prone to fouling and scaling and can therefore treat water with high fouling and scaling risk. The application of FO is mainly applied to industrial processes but also in some cases to drinking water production (McCutcheon, McGinnis & Elimelech 2005) or pre-treatment for drinking water production (Cath, Adams & Childress 2005).

Capacitive Deionisation (CDI) is a novel technology which removes the positively and negatively charged ions found e.g. in seawater or brackish water by the electrostatic force of a negative and a positive electrode made of a porous conductive material such as porous carbon. This produces a particular advantage of a lower energy consumption than RO but the technology is not resistant to fouling and does not yet achieve high loading rates and is therefore not suitable for high saline water (Y. Gendel *et al.* 2014) (AlMarzooqi *et al.* 2014).

2.4.4. Challenges in MD application

One of the reasons why membrane distillation is not yet applied more to drinking water production is the leading market position of other technologies. Also there are still only few appropriate commercially available MD membranes available. Low flux in MD compared to other membrane technologies is an additional challenge. Consequently only few commercial systems by companies such as SolarSpring (Spin-off of the Fraunhofer Institute for Solar Energy System) in Germany, Memsys also in Germany and aquaver in the Netherlands with a VMEMD system, Keppel Serghes with their Memstill® system, further Deukun GmbH in Germany with a solar powered system and Aquastill from the Netherlands are supplied around the world (Drioli, Ali & Macedonio 2015; Wang & Thai-Shung 2015).

Another very important issue hindering the breakthrough of MD in its application is the relative high thermal energy input required. In Table 2.7 the specific energy demand for MSF, MED, RO and MD are compared. It can be seen that the electrical energy input for MD is very low compared to other technologies but the thermal energy input, which is dependent on boundary conditions and system size is considerably high (Table 2.7).

Table 2.7 Specific energy demand for the production of 1 m^3 of water, adapted after Al-Karaghouli & Kazmerski (2013) and (memsys 2014)

	Thermal energy [kWh/m^3]	**Electrical energy [kWh/m^3]**
MSF	190-282	2.5-5
MED	145-230	2.5-5
RO	-	2.5-6
MD	80-250 *	1-2.2

*depending on boundary conditions and system size

To support thermal energy input, waste heat energy could be used that has been generated by other processes. Alternatively, energy input could be supported by thermal solar energy. For example Koschikowski *et al.* (2009) have demonstrated that their MD unit developed at the Fraunhofer Institute for Solar Energy Systems for small scale application is capable to run energy self-sufficient using solar energy. Six compact units producing 100-500 L/day of drinking water from seawater were installed since 2004 in Gran Canary, Egypt, Jordan (Banat *et al.* 2007a), Morocco, Germany and Spain. Two large scale units producing up to 10 m^3/day were installed in 2005 and in 2006 in Jordan and Gran Canary (Banat *et al.* 2007b). All systems proved to be able to run for several years with minimum maintenance and energy self-sufficient. The specific thermal energy consumption was 100-200 kWh/m^3. Although no system was set up in India it was demonstrated that the system can be installed worldwide.

A holistic approach of providing drinking water with MD, electric energy and biogas for cooking was demonstrated in Bangladesh by Khan & Martin (2015). Biogas produced from agricultural and animal waste-fed digester drives a power generator while excess biogas is used for cooking and lighting. The waste heat drives a MD unit for drinking water production. The combined process can meet the daily electrical energy demand while providing cooking fuel and drinking water for one household. It is estimated that the pay back period for such a system is between 3 and 4 years.

2.4.5. Scaling and fouling phenomena in drinking water production

Although membrane distillation has many advantages scaling is still a problem as it also is for other membrane processes. Scaling is caused by the precipitation of sparingly soluble salts in the feed solution at high concentration levels, causing the formation of deposits on the membrane and in more severe cases also in the pores of the membrane - this is then called membrane wetting. The scale formation leads to a reduced hydrophobicity of the membrane surface which can cause the feed water to enter directly through the pores into the permeate and deteriorate distillate quality

(Duong *et al.* 2016). Furthermore, the layers of scale also negatively influence temperature and polarisation effects and the blocked pores significantly reduce the water flux (Nghiem & Cath 2011). With the presence of DOM (dissolved organic matter) the complexity of the fouling phenomena is increased, resulting in a cake formation on the membrane surface that causes an additional loss of hydrophobicity and a flux decline. The majority of DOM are high adsorptive humic substances which have their origin from chemical and biological degradation of microorganisms (Curcio *et al.* 2010).

In drinking water production from seawater or brackish water the main substances of concern are the formation of $CaSO_4$, $CaCO_3$, $Mg(OH)_2$ and DOM (Duong *et al.* 2016; Gryta 2008; Nghiem & Cath 2011).

Recently there have been many publications focusing on scaling and/or fouling in membrane distillation as this topic is still a novel area. Fouling in MD differs from other low pressure membrane processes and research needs to be undertaken to understand these processes better. A recent study by Duong *et al.* (2016) on seawater desalination with AGMD showed that operating temperatures strongly influenced the water flux and therefore also membrane scaling. Cleaning of membranes that were scaled at commonly used feed temperatures of 60°C (60°C/50°C feed/coolant temperature) was more difficult and repetitive cleaning with vinegar lead to performance deterioration, compared to lower feed and coolant temperatures of 35°C/25°C.

Also the flow rate plays a significant role in the formation of scaling structure. With low flow rates the scaling formation on the surface of the membrane was observed to be more compact in comparison to higher flow rates influencing also the transmembrane flow rate. A retarded scaling formation was observed at flow rates above 0.6 L/min and below 80°C (Gryta 2008).

With the formation of scaling on the membrane not only the chemistry of the solution has to be taken into account but also the morphological and physico-chemical properties of the membrane are important as they control the nucleation mechanisms (Curcio *et al.* 2010).

Mitigation of the formation of scaling layers could be reached in one study by Chen *et al.* (2013) through gas bubbling on the membrane surface during the concentration process. Under these conditions the flux was enhanced with simultaneous delay of flux decline. Also the use of antiscalants such as polyphosphates could effectively reduce the formation of $CaCO_3$ layer on the membrane surface due to the adsorption of antiscalant on the crystal surface and the blocking of crystal growth (Gryta 2012).

Reduce HCO_3^- ions with pretreatment for example by ion exchange water softening, boiling or the removal of the ions by acidifying the feed to pH 4 or less. Also precipitation of $CaCO_3$ with lime or soda ash is possible requiring time for settling of solids (Tijing *et al.* 2015).

2.5. Conclusions

As illustrated in the previous chapter microbial and chemical contaminants in saline groundwater sources, which have to be utilized due to increasing water stress e.g. in India and other water scarce countries, are posing threats to human health. MD can be seen as an alternative to well-established technologies such as RO to provide high quality drinking water. However, the optimum boundary conditions are still to be identified. Although MD is not yet widely applied in drinking water production due to drawbacks such as high (thermal) energy demand and low flux it is a suitable technology for drinking water production in a small scale systems. The required thermal energy demand can be provided from solar thermal energy or waste heat coming for example from an off-grid diesel generator. Vacuum enhanced MD studied in this thesis is an important research area as it helps to overcome low flux problem by enhancing the permeate production.

CHAPTER 3

MATERIAL AND METHODS

UNIVERSITY OF TECHNOLOGY, SYDNEY

Faculty for Engineering & Information Technology

3. Material and Methods

3.1. Chemicals and solutions

3.1.1. Feed solutions fluoride experiments

Four main synthetic feed solutions containing 5 mg/L of F^-, represented as Solution A, B, C and D were used in this study as presented in Table 3.1. The detailed chemical concentration for all compounds can be found in Table 2.3. Solution A was used to evaluate the performance of CaF_2 under MD operation. The influence of F^- in a mixed solution representing F^- contaminated groundwater was studied using Solution B. The impact of organics in F^- contaminated groundwater was tested using Solution C. And finally, the removal of nitrate was examined using Solution D.

All chemicals used were of analytical reagent grade (Sigma Aldrich). The organics spiked in Solution C was in the form of Suwannee River Humic Acid Standard II supplied by the International Humic Substances Society (Minnesota, USA).

Table 3.1 Chemical composition of the F^- based feed solutions representing groundwater.

Parameter	Unit	Solution A	Solution B	Solution C	Solution D
Organic compounds					
Humic acids	mg/L	0	0	10	10
Inorganic compounds					
Sodium	mg/L	0	1181	0	1181
Calcium	mg/L	150	150	150	150
Magnesium	mg/L	0	150	0	150
Chloride	mg/L	257	2440	257	2440
Sulphate	mg/L	0	100	0	100
Fluoride	mg/L	5	5	5	5
Nitrate	mg/L	0	0	0	89
Kalium	mg/L	0	0	0	56
TDS (calculated)	mg/L	412	4026	422	4181

Table 3.2 Concentration of investigated substances

Concentration		Name
mg/L	**mMol/l**	
1,180	51.33	Na^+ as NaCl
2440	68.83	Cl^- as NaCl
150	7.5	Ca^{2+} as $CaCl_2 \cdot 2\ H_2O$
150	12.35	Mg^{2+} as $MgCl_2 \cdot 6\ H_2O$
100	2.08	SO_4^{2-} as Na_2SO_4
5	0.26	F^- as NaF
20	1.4	NO_3-N as KNO_3
5-10	-	DOC as Suwanee River Humic Acid Standard II
0.2		Of each pesticide

3.1.2. Feed solutions pesticide experiments

Four main synthetic feed solutions A, B, C and D containing 200 µg/L of each pesticide were used as presented in Table 3.3. To study the removal performance of the pesticides without the influence of any salts or other organic contaminants during MD operation Solution A was utilized. The influence of humic acid was evaluated by solution B. The impact of inorganics in a synthetic groundwater solution was studied with Solution C. The combined influence of humic acid and salts was then tested with solution D. For the RSSCT experiment Milli Q water with 50 µg/L of each pesticide was used.

All chemicals utilized for the experiments were of analytical reagent grade (Sigma Aldrich). The organics spiked in Solution B and C was in the form of Suwannee River Humic Acid Standard II supplied by the International Humic Substances Society (Minnesota, USA).

The experiments regarding different feed temperatures were conducted with solution C.

Table 3.3 Chemical composition of feed solutions for pesticide experiments

Parameter	Unit	Solution A	Solution B	Solution C	Solution D
Organic compounds					
Atrazine	µg/L	200	200	200	200
Clofibric acid	µg/L	200	200	200	200
Dichlorvos	µg/L	200	200	200	200
Phorate	µg/L	200	200	200	200
Parathion-methyl	µg/L	200	200	200	200
Humic acids	mg/L	0	5	0	5
Inorganic compounds					
Sodium	mg/L	0	0	1181	1181
Calcium	mg/L	0	0	150	150
Magnesium	mg/L	0	0	150	150
Chloride	mg/L	0	0	2449	2449
Sulphate	mg/L	0	0	100	100
TDS (calculated)	mg/L	1	6	4031	4036

3.1.2.1. Cleaning solutions

For cleaning of the MD unit two cleaning solution were utilized: Citric acid and sodium hydroxide (NaOH) at 0.1 M. The solutions were applied for the removal of deposits that may have built up during an experiment as well as for the membrane cleaning experiments.

3.1.3. Selected pesticides

The pesticides investigated in this study (Table 3.4) were selected based on:

A) Characteristics - range of LogD, polarity and vapour pressure.

A LogD < 0 indicates that the compound is highly polar (hydrophilic) and therefore well soluble in water. If the LogD > 3 the compound is hydrophobic (Sangster 1997), which means it is not well soluble in water and prone to adsorb in the MD system and particularly on the hydrophobic membrane.

In addition, the polarity of the compounds which is related to the LogD plays a major role in the behaviour of the compounds in the environment. If a compound is polar, it tends to have a good solubility in water and is therefore prone to leak into the groundwater.

Moreover the specific vapour pressure is an indicator for the volatility of a compound. It is considered to be a very important parameter in MD, since only volatiles can pass through the membrane. A high vapour pressure indicates the possibility of a reduced rejection.

Pesticides were selected within a range of different logD values ranging from -1.06 to 3.67 and a range of vapour pressure ranging from 1.45 to 1.27 x 10^{-5}.

B) Occurrence and toxicity

In India, most pesticides (>75%) are used as insecticides compared to the rest of the world where more herbicides, which have a lower acute ore immediate toxicity than insecticides, are being used. Therefore higher levels of acute risk are found in India (Yadav *et al.* 2015). In 2015 India accounted for almost 3% of the total pesticide consumption in the world and 67% of the total consumption is used in agriculture and horticulture (Yadav *et al.* 2015).

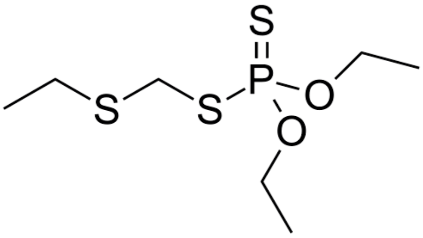
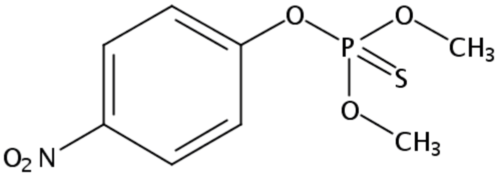
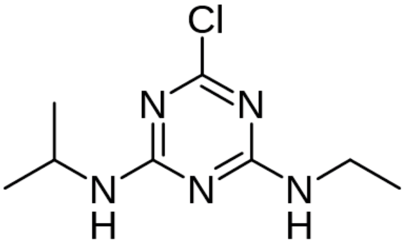
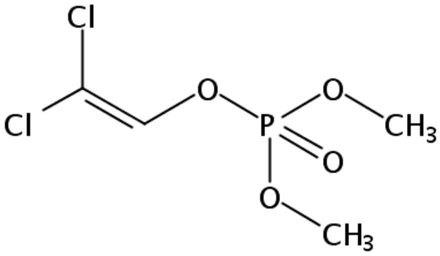
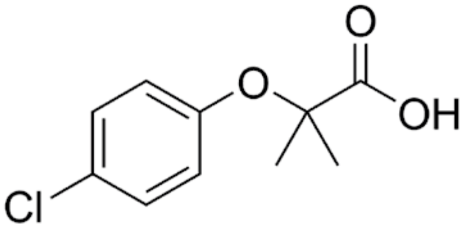
A literature review on the chemical properties, occurrence and distribution of 27 pesticides was conducted. Out of the studied 27 pesticides, 5 pesticides were selected for this study, taking into account the occurrence, toxicity and the widespread use in India and further considering that in India mostly insecticides are used. The selected pesticides are phorate, parathion-methyl, atrazine, dichlorvos and clofibric acid.

Phorate, Parathion-Methyl and Dichlorvos are amongst the most used pesticides in India (Bhushan, Bhardwaj & Misra 2013). Atrazine was selected because it is one of the most commonly used herbicides worldwide although it was banned in the EU in 2004 due to its persistent groundwater contamination. Three out of the five selected compounds are insecticides. The detailed physiochemical properties are listed in Table 3.4 and in Table 3.5 the chemical structures of the selected pesticides are shown.

Table 3.4 Physiochemical properties of the selected compounds (data from Scifinder Scholar, log D calculated by ACD Lab I software)

Name	Use	Log D at pH 7	Vapour pressure 25ºC [mmHg]	Water solubility pH 7 25ºC [mg/L]	K_{OC} pH 7	Molecular weight [g/Mol]	pK_H 25 °C
Phorate	Insecticide	3.67	2.60×10^{-3}	50	2’360	260.38	4.75
Parathion Methyl	Insecticide	2.82	2.4×10^{-4}	37	816	263.21	5.65
Atrazine	Herbicide	2.64	1.27×10^{-5}	69	647	215.68	7.28
Dichlorvos	Insecticide	1.07	1.45	57’000	91.5	220.98	5.13
Clofibric Acid	Herbicide	-1.06	1.03×10^{-4}	100’000	1	214.65	9.54

Table 3.5 Chemical structure of selected pesticides

Name	Chemical structure	Charge at pH 7
Phorate **CAS: 298-02-2**		none
Parathion Methyl **CAS: 298-00-0**		none
Atrazine **CAS: 1912-24-9**		none
Dichlorvos **CAS: 62-73-7**		none
Clofibric Acid **CAS: 882-09-7**		negative

3.2. Experimental setup

Two MD units were employed to carry out the described experiments. Firstly a bench scale DCMD unit was used for most experiments with regards to fluoride removal and pesticide behaviour as well as VE-DCMD experiments. Secondly a flexible pilot scale DCMD unit was utilized to repeat some of the pesticide experiments and to test different feed temperatures. And thirdly, for the post treatment, a rapid small scale column test (RSSCT) was carried out using activated carbon and a feed solution with spiked pesticides.

3.2.1. Bench scale DCMD unit

The experimental setup of DCMD and VE-DCMD is shown in Figure 3.1 and in Figure 3.2. The water in the permeate tank was chilled by an external cooler and connected to the membrane module. A balance was used on the permeate side to quantify the permeate volume. The water in the feed tank was continuously heated up and pumped to the membrane module. The membrane in the test cell separated the feed and permeate solutions. The experiments were conducted in counter-current mode. Temperature sensors were placed at the inlet and the outlet of both, permeate and feed tanks. The volumetric flow of the feed and permeate were measured by flow meters. Experiments were carried out using 1.5 L of feed solution. In VE-DCMD a vacuum pump, which was connected to the permeate tank was being used, whereas in the DCMD setup the vacuum pump was not operated.

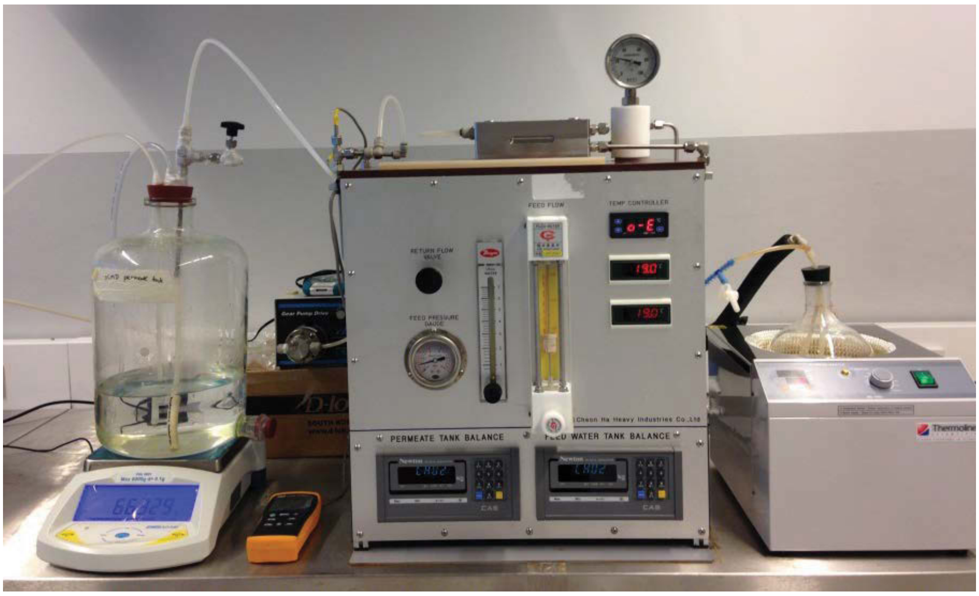


Figure 3.1 DCMD bench scale setup

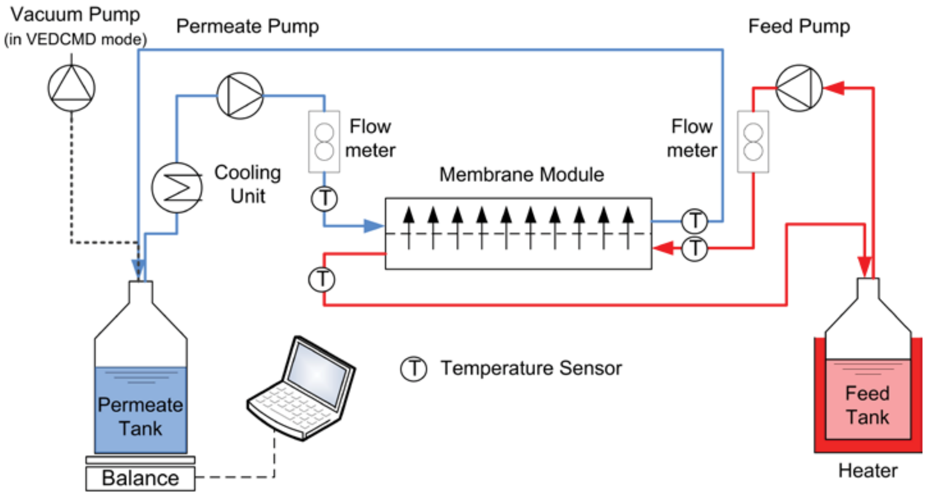


Figure 3.2 Schematic setup of bench scale VE-DCMD/DCMD

3.2.2. Pilot DCMD unit

The pilot DCMD unit (Convergence, The Netherlands) (Figure 3.3 and Figure 3.4) was employed for repetition of pesticide experiments and to test different feed temperatures (40°C, 55°C and 70°C). The setup of this unit also consisted of the major components as the bench scale DCMD unit. But additionally it had a heat exchanger to help maintain stable temperatures and all parameters (temperature, pressure, pH, scale weight, volume flow, permeate conductivity, time) were automatically recorded by a computer. The membrane test cell was made from plexiglass so that processes in the test cell during an experiment could be observed easily (Figure 3.5). Experiments were carried out using 5 L of feed solution.

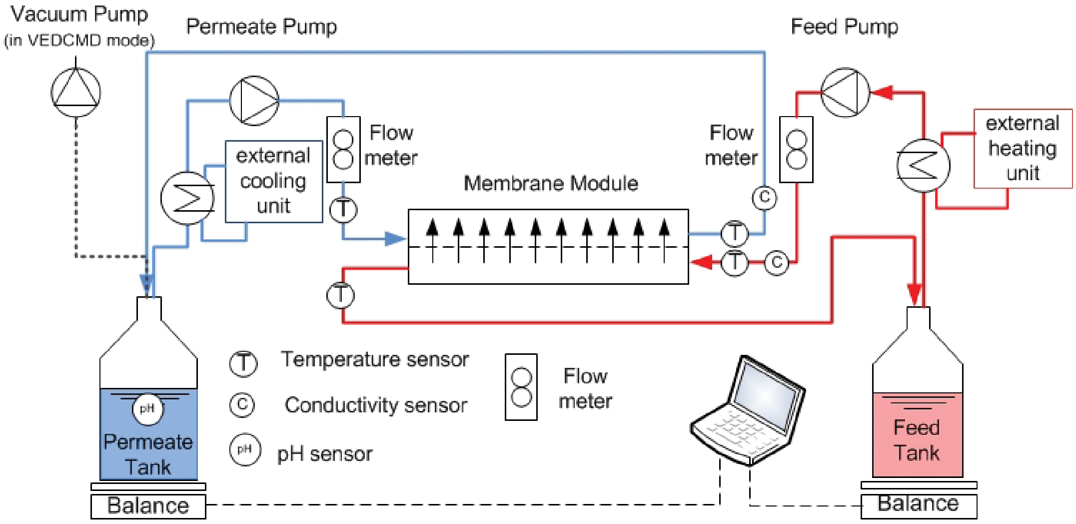


Figure 3.3 Schematic setup of the pilot DCMD

Figure 3.4 Pilot DCMD unit

Figure 3.5 Membrane test cell viewed from the permeate side

3.2.2.1. Membrane

A polytetrafluoroethylene (PTFE) membrane was used for the experiments. It was supplied by General Electrics (GE), USA. The porosity, average pore size and thickness of the membrane were 70-80%, 0.2 µm and 179 µm, respectively according to the manufacturer. The effective membrane area was 0.0168 m^2 (0.21 m x 0.08 m).

3.2.3. Rapid small scale column test

A rapid small scale column test (RSSCT) was carried out as a post treatment to MD to remove possible traces of pesticides and other organic material. The setup and down scaling procedure were according to Crittenden et al. (2005) and consisted of a glass column (Götec Labortechnik, Bickenbach, Germany; type: SuperVarioPrep glass column 300-10 „SC“). filled with granulated activated carbon (Filtrasorb 400, Chemviron carbon, 125 – 250 µm) and 3 mm diameter glass beads on top (Figure 3.6). At the outlet there was an 80-120 µm PTFE filter plate (Götec Labortechnik, Germany;) to prevent the carbon to be washed out of the column. Two 20 L glass flasks contained the feed solution that was continuously pumped with a peristaltic pump (Ismatec MCP Standard) to the column (Figure 3.7). The daily flow volume was 19.8 L/day. All tubing consisted of Teflon except the part in the peristaltic pump consisted of Tygon® (approx. 20 cm). The schematic setup is shown in Figure 3.8.

For downsizing purposes the commercial granulated activated carbon was crushed using an automated ball mill (M301 Retsch, Germany) and then fractioned using different sieves (315 µm, 250 µm, 125 µm and 100 µm). The fraction ranging from 125 to 250 µm was then selected for the experiment. The activated carbon was washed 20 times using nanopure grade water to remove excess dust from the particles. Then, the activated carbon was dried under a slight vacuum at 105 °C. A light microscope (BX41 Olympus, USA) was used to determine the mean diameter of 190.3 µm. Process conditions equivalent to 10 min empty bed contact time (EBCT) and a volume feed flow of 2 m/h in large scale were used for the experiment. The actual EBCT in the RSSCT was 0.36 min and the volume flow was 10.5 m/h. The daily feed volume amounted to 19.81 L. The activated carbon was filled into the column up to 6.34 cm. The inner diameter of the column was 10 mm. The pesticide concentration in the feed was 50 µg/L for each compound spiked and was prepared daily from a pesticide stock solution containing 100 mg/L of each pesticide. To maintain a stable pH of 7 a 0.1 mM potassium buffer solution was added to the feed. The pump was calibrated daily. A total of 67'600 bed volumes was achieved during 17 days of operation. The parameters for the RSSCT experiment are shown in Table 3.6.

The adsorptive removal (R_{ads}) in the GAC column was calculated as following:

$$R_{ads} = 1 - \frac{c_{inf}}{c_{eff}} \tag{3.1}$$

where c_{inf} is the concentration of the compound in the influent to the column (treated MD water) and c_{eff} is the concentration of the compound in the effluent of the column.

To evaluate the performance of the GAC filtration the typical unit bed volume (BV) is used. The bed volume is calculated as the quotient from the filtration time ($t_{filtered}$) and the empty bed contact time (EBCT) of the GAC filter.

$$BV = \frac{t_{filtered}}{EBCT} \tag{3.2}$$

Table 3.6 Parameters for RSSCT

Parameter	Unit	Value
EBCT (large scale)	min	10
EBCT (small scale)	min	0.36
Selected carbon particle fraction (after grinding)	µm	125 - 250
Volumetric flow rate	mL/min	13.75
Inner diameter of column	cm	1
Height filling activated carbon	cm	6.34
Pesticide concentration feed	µg/L	50

3.2.3.1. Activated carbon

The activated carbon F400 (mesh size 12x40) selected for this study was supplied by Chemviron Carbon the Netherlands, and is typically used for the purification of drinking water. The particular high inner surface area of 940 m^2/g as well as the high micropore volume of 0.34 cm^3/g and low mesopore volume of 0.16 cm^3/g are well suited for the removal of small molecules (Summers, Knappe & Snoeyink 2011). The carbon is made from an agglomerated material blend. Further details can be found in Annex 3.

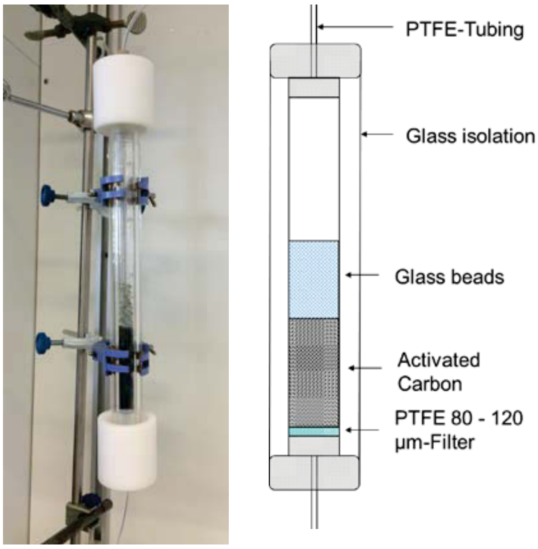


Figure 3.6 Small scale column with activated carbon and glass beads

Figure 3.7 Feed tanks (20L each)

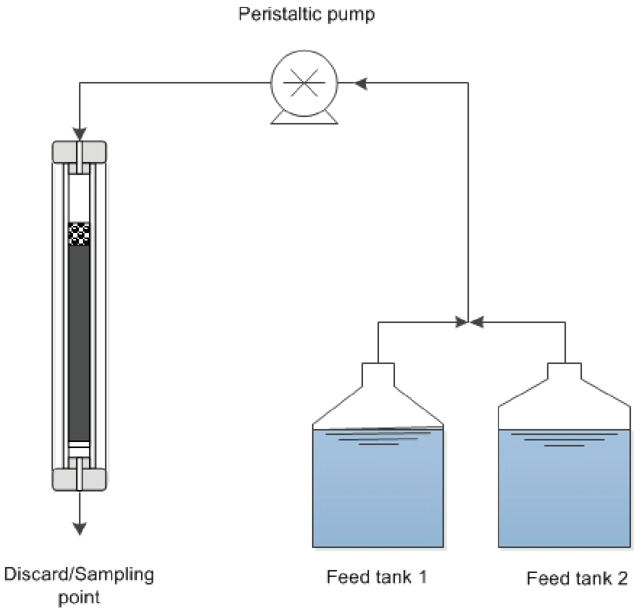


Figure 3.8 Setup of rapid small-scale column test

3.3. Experimental protocols

3.3.1. Optimum operation conditions for MD

3.3.1.1. Feed velocity

Five different flow rates were tested to evaluate the most favourable system conditions. The tested flow rates were the following: 0.4 , 0.6 , 0.8 , 1.0 and 1.2 L/min for 30 min each. The flow rates were tested at a fixed feed temperature of 55 ± 0.5°C and permeate temperature of 25 ± 0.5°C. The permeate generation was recorded with a balance in 5 min intervals for 30 min. The average flux [L/(m²·h)] was calculated following equation 2.3 by using the permeate weight reading as volumetric value, assuming that 1,000 g ≙ 1 L.

3.3.1.2. Heating temperature

For evaluation of the optimum feed temperature the DCMD system was run for 30 min at the following feed temperatures: 45, 50, 55 and 60 °C. The permeate temperature was kept stable at 25 ± 0.5°C for all experiments and the feed flow was 0.8 L/min corresponding to a cross flow velocity of 0.04 m/s (Reynolds number = 618).

3.3.1.3. Vacuum pressure

In this study the incorporation of a vacuum on the permeate side at a low feed temperature of 55 °C was tested. The vacuum pressure tested varied from 1,000 to 200 mbar absolute pressure. The vacuum was added to the permeate tank as described in Chapter 3.2.1 and shown in Figure 3.2.

3.3.2. Performance measurement methods

3.3.2.1. Permeate flux

The permeate flux was documented using a balance connected to a computer. The permeate generation was recorded in 5 min intervals. The average flux [L/(m²·h)] was calculated following equation 2.3 by using the permeate weight reading as volumetric value, assuming that 1,000 g ≙ 1 L. At the beginning of an experiment 2 L of Milli Q were used as cooling solution. The water quality was analysed before and after the experiment.

3.3.2.2. Recovery Ratio

The recovery ratio (RR) is used as an indication on how much permeate is produced in relation to the feed water flow and is given as percentage. It can be used to evaluate the cost effectiveness of an MD design and is defined by dividing the normalized distillate flow rate J x A [L/(m²·h)] by the feed flow rate m_f [L/min] and multiplied by 100. Where J is the permeate flux and A is the membrane area (Guillén-Burrieza *et al.* 2012). A RR of 4.4 % was estimated for a single pass MD (Saffarini *et al.* 2012). For the experiments and the calculation of the RR an average distillate flow rate was collected during 30 min of operation with Mili Q water.

$$RR = \frac{J * A}{m_f * 100\%} \tag{3.3}$$

3.3.3. Membrane cleaning

Membrane cleaning on the used MD membrane was carried out by cutting the membrane (0.0168 m^2) into two pieces. The membrane pieces were placed in petri dishes containing Milli Q water and 0.1 M NaOH and 0.1 HCl respectively, and stirred for 2h on a shaker.

3.3.4. Calculation of volume concentration factor (VCF) and water recovery

The volume concentration factor (VCF) is defined as the ratio of initial feed volume ($L_{f,0}$) to concentrate feed volume (L_c): VCF = $L_{f,0}/L_c$ (Naidu, Jeong & Vigneswaran 2015).

The DCMD was operated up to a VCF of 4 to achieve 75% water recovery.

The VEDCMD experiments were operated up to a VCF of 3 to achieve 67% water recovery.

3.3.4.1. Pesticide experiments

Experiments with the different feed solutions were carried out with a bench scale DCMD system as described in Chapter 3.2.1. The experiments regarding different feed temperatures were executed using the pilot DCMD unit as described in Chapter 3.2.2. Solution A (Milli Q water) was used to study the removal performance of the pesticides without influence of any salts or other trace or bulk organics compounds during MD operation. The influence of organic compound was evaluated using solution B containing humic acid. The impact of inorganics in a synthetic brackish groundwater solution was studied using solution C. The combined influence of humic acid and salts was then tested with solution D.

The average pesticide rejection R was defined as following:

$$R = \left(\frac{\frac{C_{f0}+C_{fe}}{2} - C_P}{\frac{C_{f0}+C_{fe}}{2}} \right) * 100\ [\%] \tag{3.4}$$

The pH was adjusted to 7 using caustic soda or hydrochloric acid. Pre-conditioning of the system was applied by circulating the spiked feed solution for 24 h in the system prior to the experiment to minimize adsorptive losses to the system during the experiment.

Pesticides that did not accumulate in the feed and permeate solution were categorized as losses. Losses of pesticides in MD operation were attributed to their tendency to either evaporate or adsorb onto the hydrophobic MD membrane (Naidu et al, 2017; Wijekoon et al., 2014a). Losses of pesticides during the DCMD operation was calculated by mass balancing of each pesticide compound in the initial feed, final feed/concentrate and permeate as following:

$$C_{f0} * V_{f0} = (C_p * V_p) + (C_{fe} * V_{fe}) + losses \tag{3.5}$$

3.3.5. Calculation of saturation index

In this study the saturation index (SI) was calculated using the PHREEQC interactive software (USGS, version 3.3.5.10806). It is defined as follows:

$$SI = log_{10} \frac{IAP}{K_{SP}} \tag{3.6}$$

where IAP is the ion activity product and K_{SP} is the solubility product constant which are both without unit.

If the SI > 0, the solution is oversaturated with regards to this solid and it may precipitate, if the SI < 0, the solution is unsaturated and the solid can dissolve in the solution. At SI = 0 the solution is in equilibrium (Davis & Ashenberg 1989).

Experimentally the F precipitation was evaluated by initial and final feed mass balancing.

3.4. Analyses

3.4.1. Organic analysis

3.4.1.1. Liquid chromatography-organic carbon detection (LC-OCD)

For the analysis of dissolved organic carbon (DOC) and detailed organic fraction of polysaccharides/biopolymers (BP), humic acid (HA), building blocks (BB), low molecular acids and low molecular neutrals (LMW) a liquid chromatography organic carbon detector (LC-OCD model 8, DOC Labor, Germany) was used. The size exclusion column in the LC-OCD separates the fractions according to their molecular size and subsequently the substances are detected by an UV detector at 254 nm and an organic carbon detector (OCD). Based on the retention time the peaks can be attributed to the organic fractions and the concentrations can be calculated by software programme (Huber *et al.* 2011).

Prior to analysis the samples were diluted to less than 5 mg/L DOC and filtered with a 0.45 µm filter to remove any solids that would damage the system.

3.4.1.2. Gas chromatography mass spectrometry (GC-MS)

Pesticides were analyzed using a GC-MS/MS equipped with an auto sampler (7890A, 5977A, Agilent Technologies, Germany) and a DB-35ms 30 m x 0.25 mm capillary column with a 0.25 µm film (Agilent Technologies, Germany). Helium was used as carrier gas at a constant flow of 1 mL/min. The injection of 1µl sample was in splitless mode at 240°C. The liner was a cyclo double taper liner without glass wool (Restek, USA). The temperature program was adapted from Štajnbaher & Zupančič-Kralj (2003) and consisted of the following oven temperature: initial temperature at 55°C, held for 2 min, 25 °C/min ramp to 130 °C, then 1 °C/min to 185 °C. Followed by 20°C/min to 300°C and held for 5 min. The total program time was 70.75 min.

Quantification of pesticides was done with internal deuterated standards (dichlorvos d6, atrazine d5 and clofibric acid d4 from Toronto Research Chemicals, Canada and phorate d10 and parathion-methyl d6 by Augusta Laborbedarf GmbH, Germany). The quantitation was done in selective ion mode (SIM). The identification ions are presented in Table 3.7.

Table 3.7 Parameters for determination of pesticides by GC-MS

Pesticide	Quantitiation ion (m/z)	Identification ion 1 (m/z)	Identification ion 2 (m/z)	Retention Time [min]	LOD [µg/L]
Dichlorvos d6	115	191		9.4	
Dichlorvos	109	185	220	9.6	15
Phorate d10	75	271		32.6	
Phorate	260	97	231	33.4	21
Atrazine d5	178	221		40.4	
Atrazine	173	200	215	40.8	17
Parathion-Methyl d6	115	269.25		54.4	
Parathion Methyl	109	125	263	54.8	24

Samples were also analysed by the National Measuring Institute (NMI) and Technologie Zentrum Wasser (TZW), in Karlsruhe Germany, to confirm the findings.

The TZW used an on column injection for LC/MS-MS (HPLC: 1260 Infinity from Agilent Technologies; MS: API 5500 tandem mass spectrometer from AB Sciex). Injection volume for pharathion-methyl was 40 µL and for atrazine and dichlorvos 2 ml. The column used was UltraAromax from Restek, USA. The eluent was run as a gradient with HPLC water and methanol with 0.1% formic acid.

The NMI is a certified commercial lab. The samples were analysed using GC-MS, details on the method used were not disclosed.

3.4.1.3. Sample preparation for GC-MS

The extraction of the pesticides from water samples was done with solid phase extraction (SPE). Octadecyl (C18) columns with 500 mg substrate and 6 ml volume were obtained by J.T. Baker. First the cartridges were conditioned with 3 ml methanol, 3 ml acetonitrile and 6 ml deionizes water at pH 7. Then the samples with spiked deuterated standards were loaded onto the cartridges at around 10 mL/min. The pH of the sample was 7. After loading, the cartridges were flushed with 3 ml deionized water to remove any salts from the cartridges. After flushing, the cartridges were immediately eluted with 3 ml methanol and 3 ml acetonitrile. The eluate was evaporated by a gentle

nitrogen stream at 50°C until the volume was 1 ml. Finally the sample was measured immediately by GC-MS.
With this procedure it was possible to determine traces of pesticides in ng/L range. The recovery of the deuterated standards was between 70 and 120%.

3.4.2. Inorganic analysis

3.4.2.1. Microwave plasma-atomic emission spectrometry (MP-AES)

For the analysis of Ca^{2+} and Mg^{2+} a microwave plasma atomic emission spectrometer was used (4200 MP-AES, Agilent, USA). The light emission from the plasma is detected by the charge coupled device (CCD) detector which makes it possible to quantify ions in low ppb concentrations.

Prior to analysis the samples were filtered with 0.45 µm filter to remove any solids that would damage the system. Calibration curves were created for the ions of interest using Ca^{2+} and Mg^{2+} calibration standard (0.0, 0.25, 5.0, and 10.0 mg/L). Dilution of the samples was done to stay within the calibration range. The sample concentration was calculated by the software according to the calibration curve.

3.4.2.2. Ion chromatography (IC)

Ion Chromatography (790 Personal IC, Metrohm, Switzerland) was used for the analysis of fluoride and nitrate. The chromatographic separation in the column is based on the affinity of the ions to the ion exchange raisins in the column. A mobile phase is employed to transport the sample through the system. The ions can be identified according to their specific retention time. The quantification is done by an external calibration curve.

Prior to analysis the samples were filtered with 0.45 µm filter to remove any solids that would damage the system. Dilution of the samples was done to stay within the calibration range.

3.4.2.3. Total dissolved solids (TDS)

The pH and conductivity were measured directly in the sample with a combined handheld device (HQ30d HACH, Germany) using a pH and a conductivity sonde. The TDS was calculated by the device from the measured conductivity of the sample water.

3.4.3. Membrane characterisation

3.4.3.1. Contact angle measurement

Hydrophobicity of the membrane surface was determined by the membrane contact angle. The membrane contact angle was measured with a goniometer (Theta Lite, Biolin Scientific, Sweden) using the standard sessile drop optical method integrated with the image-processing software (OneAttention, Laplace). Membrane pieces attached to microscope slides were placed on the goniometer platform, and ultrapure water droplets (5–8 µL) were dispensed on the membrane surface. A real-time camera captured the image of the droplet, and the contact angle value was acquired by the computer software. At least 3 measurements were made for each membrane sample and the average value was reported in this study

3.4.3.2. Field emission scanning electron microscope (FE-SEM) coupled to energy-dispersive x-ray spectroscopy (EDX)

The morphology and composition of the membrane surfaces were captured with a field emission scanning electron microscope, FE-SEM (Zeiss Supra 55VP), coupled with Bruker XFlash silicon drift detector energy-dispersive x-ray spectroscopy (EDX) detector for element characterisation. SEM imaging was carried out at a voltage of 15 kV.

Table 3.8 Summary of experimental analyses used in this study

Classification	Target compound	Method used	Objective	Measured in
Organic	DOC and detailed organic fraction	LC-OCD	Quantification of organic carbon concentration and detailed fraction	Initial feed, final feed, initial permeate, final permeate
	Phorate, Atrazine, Clofibric Acid, Parathion-Methyl, Dichlorvos	GC-MS	Quantification of pesticides	Initial feed, final feed, initial permeate, final permeate
Inorganic	Ca^{2+}, Mg^{2+}	MP-AES	Quantification of Ca^{2+}, Mg^{2+}	Initial feed, final feed, initial permeate, final permeate
	Fluoride, Nitrate	Ion Chromatography	Quantification of F^- and Nitrate in the as total N	Initial feed, final feed, initial permeate, final permeate
Membrane characterisation	Hydrophobicity of membrane	Contact angle	Characterisation of the membrane surface and indications of scaling	Selected membrane surfaces
	Membrane structure and chemical composition	SEM-EDX	Qualitative indication of chemical composition of deposits on the membrane surface	Selected membrane surfaces

CHAPTER 4

RESULTS AND DISCUSSION

UNIVERSITY OF TECHNOLOGY, SYDNEY

Faculty for Engineering & Information Technology

4. Results and discussions

In this chapter results regarding the studied parameters are being discussed.

The following aspects have been studied:

1. Optimum operating parameters for MD
2. Removal of fluoride from an brackish groundwater solution as well as aspects of scaling and fouling
3. Application of vacuum
4. Removal of selected pesticides

4.1. Optimum operating parameters for MD

To conduct experiments at optimum operation conditions with regards to permeate flux, initial tests were carried out with the bench scale DCMD system. The permeate flux is influenced by different factors, mainly the feed temperature but also the feed flow rate (El-Bourawi *et al.* 2006; Lawson & Lloyd 1997).

It is acknowledged that the feed temperature is the main factor influencing the permeate flux (Lawson & Lloyd 1997). The increase of the vapour pressure (Antoine equation) along with the temperature has an exponential effect on the permeate flux therefore, the temperature difference Δt of feed and permeate cannot (only) be used as a comparing parameter (Gunko *et al.* 2006). For example, it was shown that with the same Δt the flux was more than double at higher feed temperatures compared to the same solution at lower temperatures (Alklaibi & Lior 2005). Membrane distillation is therefore carried out at feed temperatures ranging from 60°C to 80°C (Alkhudhiri, Darwish & Hilal 2012).

Usually a high feed velocity is recommended because the boundary layer and polarization effect are being reduced and the heat and mass transfer is increased in the feed channel resulting in a higher permeate flux (Phattaranawik, Jiraratananon & Fane 2003). Also a turbulent flow can help in reducing deposits on the membrane surface. On the other hand a too high flow rate will cause unstable experimental conditions in which the temperature of the feed solution is hard to control and the membrane is exposed to stress conditions and may cause failure, such as membrane wetting (Naidu, Jeong & Vigneswaran 2014; Zhang *et al.* 2010).

As already explained in Chapter 2.4.1 there are several ways to enhance the permeate flux by the addition of vacuum or pressure. In this study the VEDCMD configuration is tested where a vacuum is added to headspace of the permeate container. This configuration was shown to be a very simple but highly effective configuration, even with as low feed temperatures as 40°C (Cath, Adams & Childress 2004).

It has been explained previously that the increase of flux due to the application of vacuum can be partially or fully attributed to the decreased air pressure inside the membrane pores, decreased temperature polarization, decreased membrane conductivity heat loss and increased pressure difference across the membrane. (Rao *et al.* 2015; Schofield, Fane & Fell 1990).

Different flow rates and temperatures were tested with Milli Q water to evaluate the performance of the DCMD bench scale system. Based on the results, the optimum conditions were selected for the following experiments. The following chapters describe how the parameters were evaluated. In Chapter 4.1.1 the effect of feed velocity is studied, in Chapter 4.1.2 the influence of the feed temperature is tested and then in Chapter 4.1.3 the incorporation of vacuum on the permeate side of the system is evaluated.

4.1.1. Effect of feed flow

Different flow rates of 0.4 , 0.6 , 0.8 , 1.0 and 1.2 L/min were tested at a set feed and permeate temperature of 55 ± 0.5°C and 25 ± 0.5°C respectively. It could be shown that with increasing flow rate, the flux is also increasing linear (Figure 4.1). This findings are in line with Phattaranawik, Jiraratananon & Fane (2003) where it has been stated that a high flow rate reduces the boundary layer and the polarization effect and increases therefore the permeate production.

To assess the effect of the feed velocity from another perspective, the recovery ratio (RR) was calculated. It can be seen from Figure 4.1 that the RR is declining with increasing flow rate. This is due to the reduced time of residency in the module with high flow rates and therefore lower heat recovery (Guillén-Burrieza *et al.* 2015).

For the determination of the optimum flow rate a trade-off between heat recovery and distillate production has to be made. During the experiments in this study a flow rate of 0.8 L/min showed the most stable results with regards to temperature and permeate flux together with a RR of 1.5 % and a permeate flux of 12.6 L/($m^2 \cdot h$) and was therefore chosen as the most suitable value. The flow rate of 0.8 L/min corresponds to a cross flow velocity of 0.04 m/s (Reynolds number = 618, laminar flow).

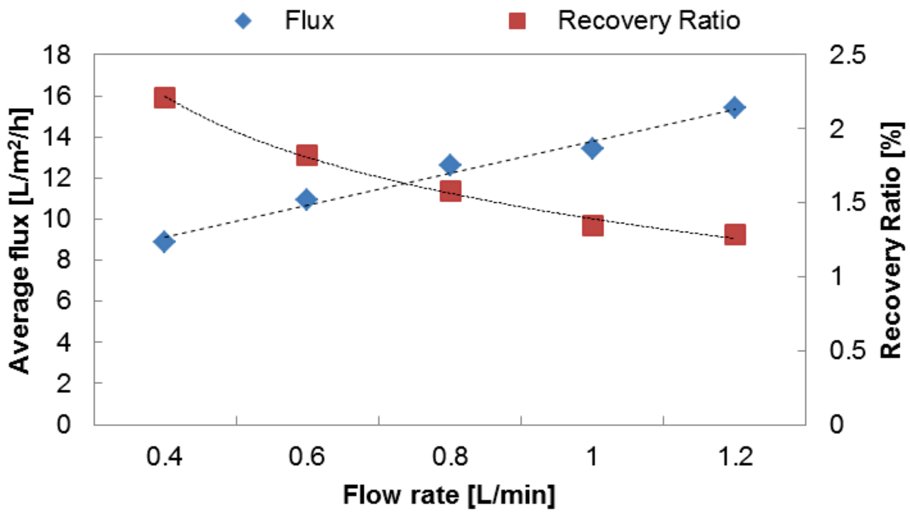


Figure 4.1 Flux and RR at different flow rates (T_f = 55°C, T_p = 25 °C)

4.1.2. Effect of feed temperature

The effect of feed temperature was tested using different low feed temperatures at 45°C, 50°C, 55°C and 60°C. The permeate temperature was 25 ± 0.5°C for all experiments and the feed flow was 0.8 L/min which corresponds to a cross flow velocity of 0.04 m/s (Reynolds number = 618).

The results showed that the flux increases linearly with increasing feed temperature although the vapour pressure is expected to increase exponentially (Antoine equation). It is concluded that in the tested small temperature range of 45 to 60°C the exponential trend is not well visible but expected that with higher feed temperatures this trend would become noticeable.

By increasing the feed temperature from 45°C to 60°C the flux was increased by 127 % from 6.5 to 14.9 L/(m²·h). At 55°C the MD system was running most stable at a relative high flux of 12.6 L/(m²·h) along with moderate feed temperature was observed. Based on these findings 55 ± 0.5°C was selected as experimental temperature. The results for the average flux at different feed temperatures are plotted in Figure 4.2.

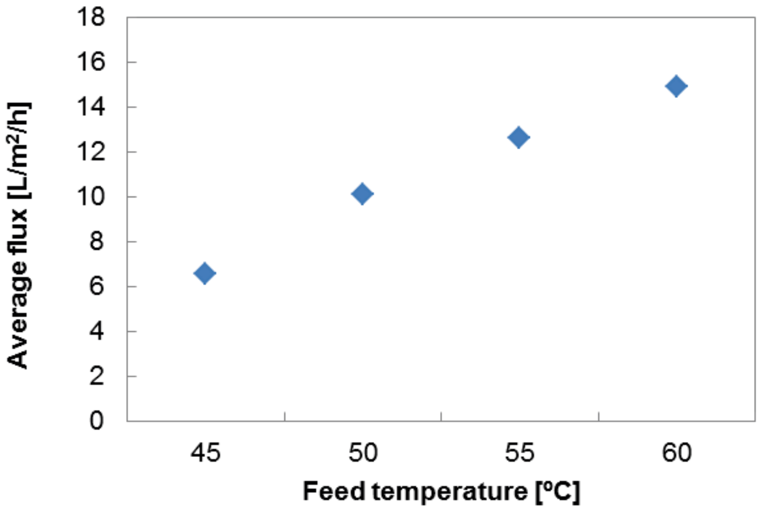


Figure 4.2 Flux at different feed temperatures, (T_p = 25 ± 0.5 °C, m_f 0.8 L/min, cross flow velocity = 0.04 m/s)

4.1.3. Effect of vacuum incorporation

In this study the incorporation of vacuum on the headspace of the permeate side increased the permeate production up to 140%. In Table 4.1 the average flux for the different vacuum settings are listed and in Figure 4.3 the values are plotted. It can be seen that with additional vacuum, the permeate flux is increased linear. Other studies also reported a linear increase of the flux with decreasing absolute pressure (Cath, Adams & Childress 2004; Schofield, Fane & Fell 1990).

Overall, the presence of a vacuum increased the flux by 40% from the conventional setting of DCMD (1000 mbar, 11.9 LMH). The most stable setting was at 300 mbar. Therefore the experiments conducted with VEDCMD were carried out at 300 mbar absolute pressure.

Table 4.1 Tested vacuum settings

Vacuum [mbar]	Average water flux [L/(m²·h)]	Flux increase [%]
1000	11.9	100
800	13.4	113
600	14.4	121
300	16.9	143
200	17.2	141

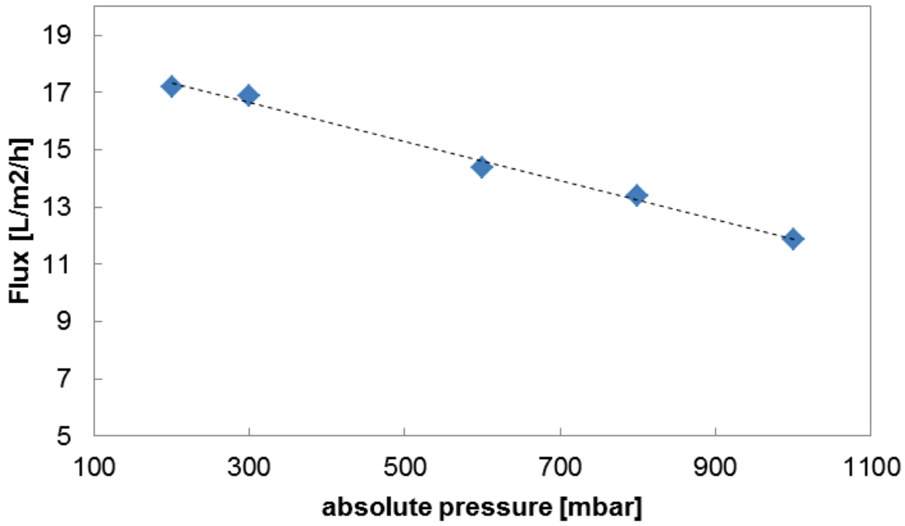


Figure 4.3 Average flux at different system pressures, (T_f = 55 ± 0.5°C, T_p = 25 ± 0.5°C, m_f 0.8 L/min, cross flow velocity = 0.04 m/s)

4.1.4. Summary of results

The study of different flow rates and different feed temperature for the energy efficient use of DCMD revealed that although it is recommended to use high flow rates, not the highest possible value must be chosen, but also the RR must be taken into account. Regarding the feed temperature, also low temperatures such as 55°C have been demonstrated to deliver an acceptable permeate flux of around 12 L/(m²·h) at a flow rate of 0.8 L/min corresponding to a cross flow velocity of 0.04 m/s (Reynolds number = 618) and a permeate temperature of 25°C. The particular advantage in using VEDCMD could be demonstrated with an enhanced permeate flux of 40% even with low feed temperatures. Based on this evaluation, the below parameters are chosen for the further study (Table 4.2).

Table 4.2 Operating parameters used in the study

Setting	Optimum condition
Flow rate	0.8 L/min
Cross flow velocity	0.04 m/s
Reynolds number	618
Feed temperature	55 ± 0.5°C
Permeate temperature	25 ± 0.5°C
Vacuum	300 mbar
Feed volume	1.5 L
Membrane area	168 cm^2
Volume concentration factor	4

4.2. Removal of fluoride and nitrate in MD

Small communities in remote areas especially in India, China, and Africa lack the necessary infrastructures and utilities for elaborate water treatment technologies. Invariably, these small communities rely on groundwater as a main source of drinking water (Amini *et al.* 2008; Bhatnagar, Kumar & Sillanpää 2011). Given the importance of groundwater as a drinking water source, the presence of excessive concentrations of fluoride (F^-) in groundwater is of increasing concern as described in Chapter 2.2.4.

This has led to the focus on the application of membrane processes for small-scale drinking water production (Peter-Varbanets *et al.* 2009). In recent times, membrane distillation (MD) has gained wide attention as an alternative water treatment technology with the capability of treating solutions with high salinity (Alkhudhiri, Darwish & Hilal 2012; Naidu *et al.* 2014). The application of stand-alone solar driven membrane distillation has been tested and regarded as extremely advantageous (Alkhudhiri, Darwish & Hilal 2012; Banat *et al.* 2007a; Ding *et al.* 2005; Koschikowski *et al.* 2009; Qtaishat & Banat 2013). Further, few studies have started to study the removal of fluoride in membrane distillation and have achieved high rejection rates (98-99%) (Boubakri *et al.* 2014; Hou *et al.* 2010a). Hou *et al.* (2010a) reported the formation of CaF_2 deposits on the membrane surface which led to a decline of permeate production, also the precipitation of $CaCO_3$ was observed with natural groundwater.

More detailed evaluation must be carried out on this aspect, especially in terms of the intensity of the inorganic precipitation and its potential reversibility with membrane cleaning. Further, apart from the inorganic constituents, the influence of the organic substances present in groundwater must be studied in determining the suitability of MD for groundwater treatment.

The advantages of VEDCMD have been highlighted in previous literature (Cath, Adams & Childress 2004; Naidu *et al.* 2016). Cath et al. (2004) demonstrated up to 84% flux increment with VEDCMD (550 mbar permeate pressure) compared to DCMD (1080 mbar permeate pressure). Similarly, Naidu et al. (2016) observed up to 58% flux increase with a VEDCMD (with 300 mbar permeate pressure) compared to DCMD. Hence, the application of VEDCMD would be advantageous in increasing the water production rate of small-scale drinking water from groundwater. However, the aspect of fouling on the membrane with VEDCMD for groundwater application has to be evaluated so far.

Therefore, this study aims to evaluate the suitability of MD for producing high quality potable water from F contaminated groundwater. For this purpose, a bench scale DCMD system was used to assess the F removal and precipitation in synthetic groundwater and in the presence of organics experimentally. Additionally, modelling was used to complement scaling and fouling studies with model groundwater solutions.

In addition to Table 3.1 and Table 3.2 the actual ionic concentration and the calculated TDS of solution A to D are shown in the table below for easier reference (Table 4.2).

Table 4.2 Ionic concentration of solutions A to D

Solution	Cations [mg/L]	Anions [mg/L]	Organic [mg/L]	TDS [mg/L]
A	150 Ca^{2+}	131.25 Cl^-	-	292.3
	6.053 Na^+	5 F^-		
B	150 Ca^{2+}	1868.6 Cl^-	-	3,463.6
	150 Mg^{2+}	5 F^-		
	1190 Na^+	100 SO_4^{2-}		
C	150 Ca^{2+}	1868.6 Cl^-	10	3,463.6
	150 Mg^{2+}	5 F^-		
	1190 Na^+	100 SO_4^{2-}		
D	150 Ca^{2+}	1868.6 Cl^-	-	3,607.9
	150 Mg^{2+}	5 F^-		
	1190 Na^+	100 SO_4^{2-}		
	55.7 K^+	88.6 NO_3^-		

4.2.1. Permeate flux

Average initial fluxes in the range of 12.1 ± 0.5 L/(m²·h) to 13.3 ± 0.2 L/(m²·h) were achieved for all feed solutions A to C (Table 3.1). In the experimental duration of 5 h, minimal flux decline (3-5%) was observed for CaF_2 (Solution A with scaling potential from 150 mg/L of Ca and 5 mg/L of F) up to 4 times VCF achieving 75% water recovery. The model solution representing groundwater (Solution B with high TDS, mainly from NaCl plus other inorganics incl. sulfate and fluoride) led to a flux decline of 15-17% which was related to the effect of concentration polarization due to the presence of inorganic ions at higher concentration levels (100 - 150 mg/L of Ca^{2+}, Mg^{2+} and SO_4^{2-}) as well as bulk salinity (Figure 4.2). In comparison to a solution containing only 3 g/L NaCl a similar flux reduction of 14-16% was observed. The results indicate that the bulk salinity is the dominant factor influencing the MD flux reduction. The effect of concentration polarization due to the increased ion concentration at the membrane compared to the bulk feed is a well-known phenomenon in MD operation and can lead to a reduction of flux (El-Bourawi *et al.* 2006; Lawson & Lloyd 1997) (Chapter 0).

A slightly higher flux decline (22-23%) was observed with the additional presence of organics (humic substances) in the groundwater solution (Solution C = Solution A plus moderate organics). At this MD operating condition, the low concentration levels of F$^-$ (5 mg/L) had minimal influence on the MD flux trend (Solution A).

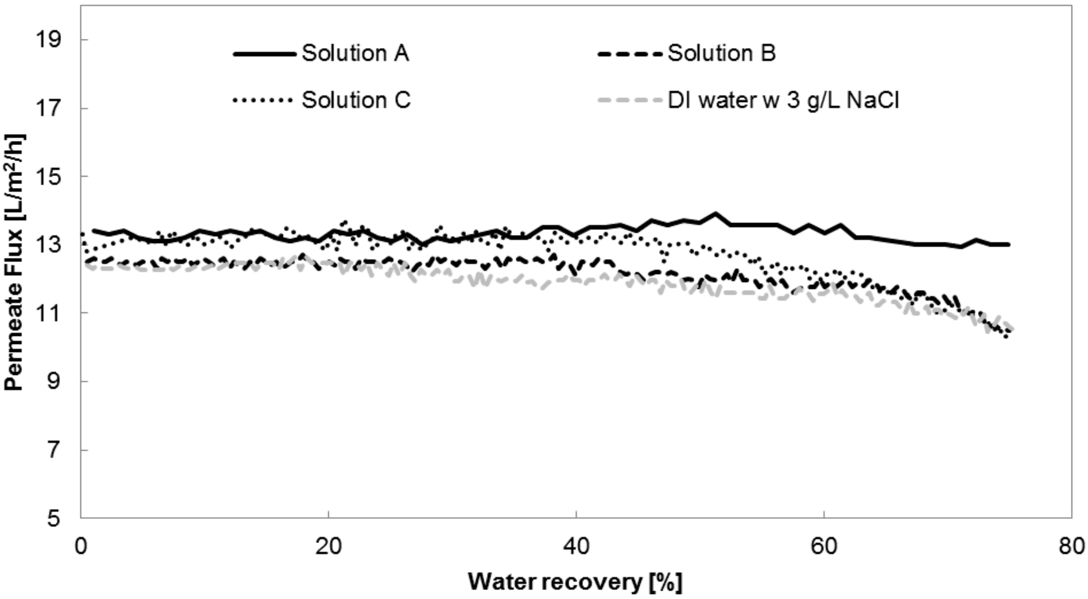


Figure 4.2 Permeate flux in DCMD with different F based feed solutions (A, B, C) representing groundwater and a solution containing only 3 g/L NaCl ($T_{f=}$ 55 ± 0.5° C, and T_p =25 ± 0.5 °C).

4.2.2. Permeate quality and fluoride rejection

In all experiments, a high quality permeate was obtained with low TDS values. For instance, the TDS of the groundwater feed solution (Solution B) increased from 3,500 to 14,500 mg/L at the end of the MD operation, while the permeate TDS remained in the range of 3.0 - 4.3 mg/L. Similarly, while the CaF_2 feed solution TDS increased from 436 to 1,728 mg/L, the permeate TDS was maintained in the low ranges of 4.8 - 6.0 mg/L. This confirmed that salt penetration and possible pore wetting through the membrane did not occur during these experiments.

Furthermore, 96 - 99% F$^-$ rejection was achieved, resulting in a concentration of the permeate with less than 1.5 mg/L F which was within the acceptable levels of WHO recommendations (WHO 2011). These results indicated the capacity of DCMD operation to treat F$^-$ containing groundwater and, produce high quality drinking water.

4.2.3. Influence of nitrate

The effect of a possible Nitrate contamination was studied using solution D (synthetic groundwater solution with addition of nitrate).

In this study nitrate was removed with DCMD to 99.8 % as a single substance as well as in the synthetic groundwater solution. So far no detailed studies have been carried out with regards to the removal of nitrate from brackish groundwater with DCMD.

The presence of 89 mg/L nitrate did have a comparable influence on the membrane as ultra-pure water by itself. The contact angle originally of 137 ± 5º was reduced to 135 ± 3º. When Nitrate was added in the mentioned concentration of 89 mg/L to the synthetic groundwater solution, no further influence on the contact angle was observed in comparison to experiments of the synthetic groundwater solution without nitrate. The measured contact angle was 133º for the standard synthetic groundwater solution containing nitrate and fluoride.

4.2.4. Membrane morphology and element characteristics (SEM-EDX)

The SEM images of the used MD membranes with different feed solutions were evaluated. The MD membrane used with solution A (CaF_2) and solution B (groundwater) showed some evidence of inorganic deposits across the membrane surface (Figure 4.2.1 a & b). At high magnification of the membrane treating the groundwater feed solution, cubic and needle shapes were detected, which could be related to the presence of NaCl and inorganic salts or $CaCO_3$ (Antony *et al.* 2011; Gryta 2009) (Figure 4.2.1 b). In line with this, the EDX element spectrum of the membrane used for treating the CaF_2 (Solution A) showed the presence of only F^-, Cl^- and traces of Ca^{2+} and (Figure 4.2.1 a). Meanwhile, the groundwater feed solution (Solution B) showed the presence of a broad spectrum of inorganic, namely of Na^+, Mg^{2+}, Ca^{2+}, S^{2-} as well as F^- and Cl^- (Figure 4.2.1 b). It is possible that formation of $CaCO_3$ and gypsum at the membrane surface occurred.

The F^- detected by the EDX analysis could not be entirely related to the precipitation from the feed solution since F^- is also present in the membrane material itself to a high degree. Instead, the fluoride precipitation was determined from the mass balance of the fluoride in the initial and final feed solution.

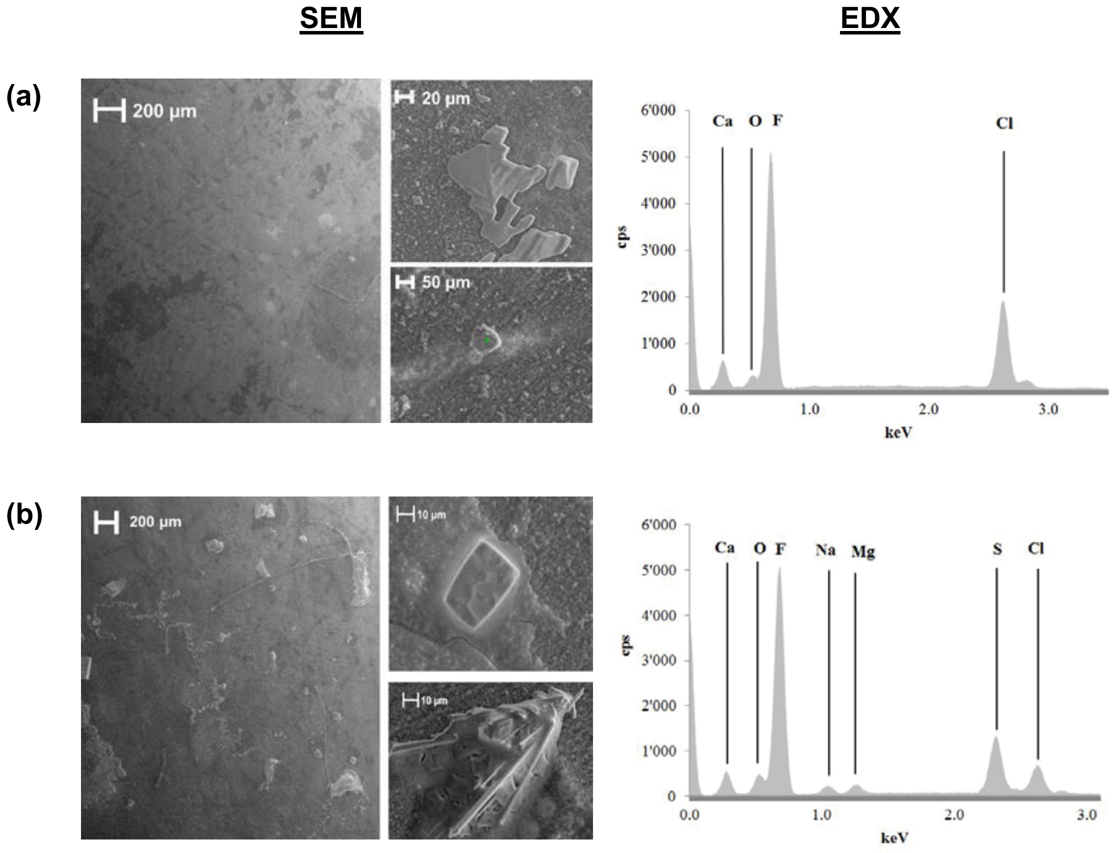


Figure 4.2.1 Membrane SEM images and EDX inorganic element spectra of used MD membranes with (a) Solution A (CaF_2) and (b) Solution B (groundwater).

4.2.5. Fluorite precipitation

The saturation index (SI) is an indicator that describes the precipitation tendency of a particular salt. A positive SI value indicates that precipitation would occur (Davis & Ashenberg 1989). In this study the SI of CaF_2 was evaluated using the PHREEQC software as a function of feed concentration factor (CF) at (i) different feed solution temperatures at fixed pH 7 for solutions A and B (Figure 4.2.2) and (ii) different feed solution pH values at fixed feed temperature of 55 °C for solution B (Figure 4.2.3).

As expected, the model projected a correlation of increased SI value with feed concentration increment (from CF 1 to 10) (Figure 4.2.2 and 5.4). This is because, as the CaF_2 solution concentration increases, it becomes more saturated, increasing salt precipitation tendency. This is especially prevalent due to the low solubility limit of CaF_2 at a K_{SP} of 3.9×10^{-11} or 16 mg/L at 25°C.

Further, the model prediction showed a higher SI value for feed solution A, containing only CaF_2 compared to the mixed groundwater solution B containing CaF_2 with other inorganics including NaCl (Figure 4.2.2). A previous study related this to the tendency of CaF_2 forming sodium fluoride complexes in the presence of NaCl, increasing the induction time for CaF_2 precipitation (Tropper & Manning 2007).

Increasing the temperature from 55 °C to 70 °C showed only a minor effect in reducing the SI value of CaF_2 (Figure 4.2.2). The SI showed the highest value at low temperature of 30 °C. On the other hand, at 55 °C, reducing the pH (from pH 7 to pH 5 and below) was effective in lowering the SI value of CaF_2, indicating that acidification of the feed solution would minimise CaF_2 salt precipitation (Figure 4.2.3).

The CaF_2 precipitation in DCMD experiment at 55 ºC was evaluated by measuring the initial and final F^- concentration in the feed, and calculating the F^- mass balance of both solutions A (CaF_2) and solution B (groundwater) as shown in Table 4.1.4. A 15% lower F precipitation was observed in the groundwater solution compared to the CaF_2 solution (A) which was similar to the precipitation pattern predicted from the model simulation.

Another substance of concern in membrane distillation is the formation of $CaSO_4$. In Figure 4.2.4. the SI of $CaSO_4$ and CaF_2 is shown at pH 7 with a feed temperature of 55°C. The SI of $CaSO_4$ remains negative up to concentration factor of 10. At the concentration factor of 4, which was achieved during the experiments, the SI is still less than -1 which means that the solubility product of $CaSO_4$ is a factor 10 lower at this concentration. It can therefore be concluded that $CaSO_4$ is not subjected to precipitation at the selected experimental settings. Nevertheless, due to concentration polarisation or local oversaturation minor formation of $CaSO_4$ deposits at the membrane surface are possible. A minor sulfate peak was observed in the EDX of Solution B (Figure 4.2.1) suggesting a possible gypsum deposition.

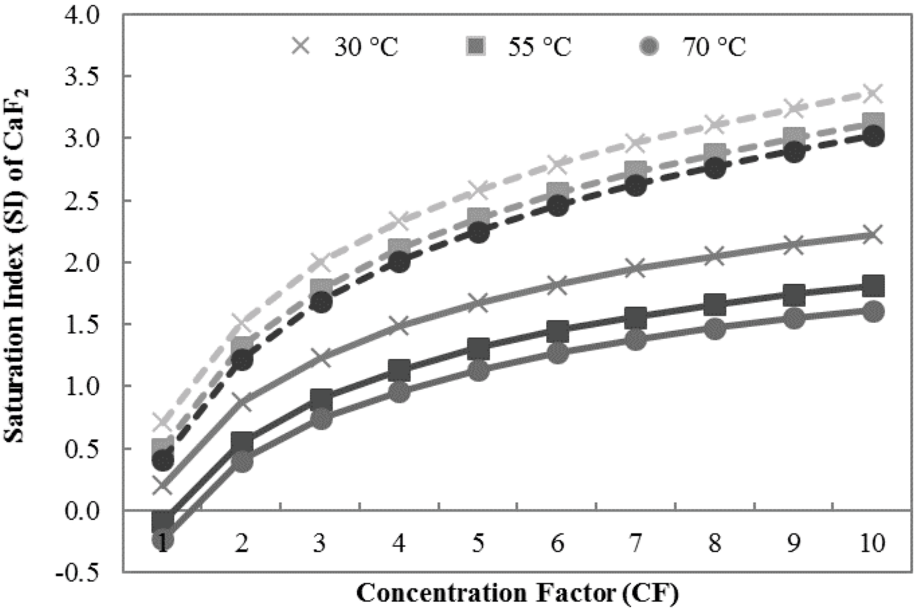


Figure 4.2.2 Model simulation of SI variation of CaF_2 as a function of CF with Solutions A and B (Solution A: - - - - and Solution B: ——) at different solution temperatures and constant pH 7.

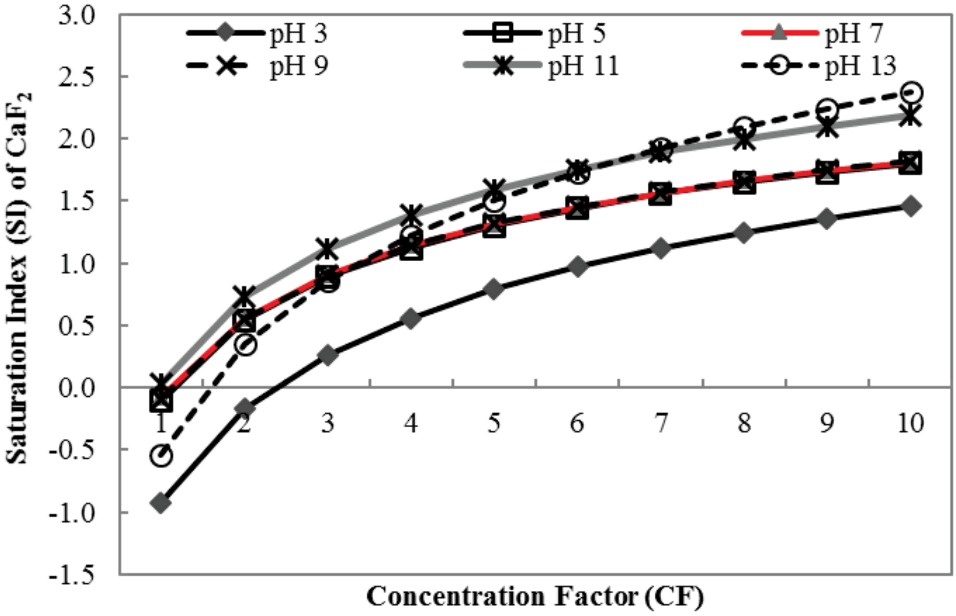


Figure 4.2.3 Model simulation of SI variation of CaF_2 as a function of CF with Solution B at different solution pH values and constant temperature of 55 °C.

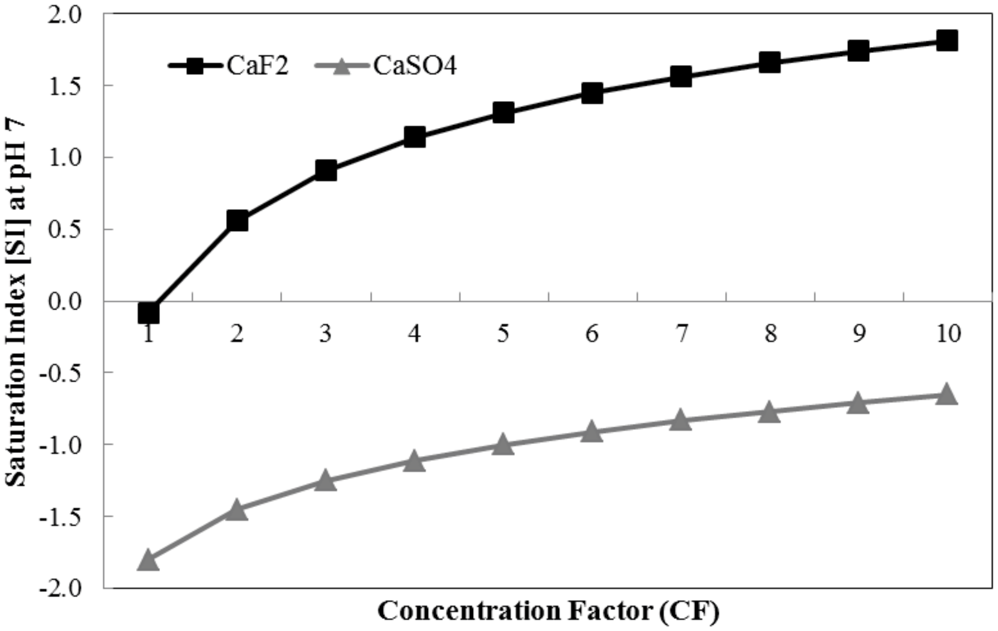


Figure 4.2.4 Model simulation of SI variation of CaF2 and CaSO4 as a function of CF with Solution B at different solution pH values and constant temperature of 55 °C.

4.2.6. Contact angle measurement

The membrane contact angle was measured to evaluate the hydrophobicity of the membrane at the end of the DCMD operation with the different feed solutions (4 times of VCF, 75% water recovery) (Table 4.1.4). The contact angle of the virgin membrane was 137 ± 5°. The contact angle of the used MD membrane with feed solution A (CaF_2) showed only a 10-12% reduction (120 ± 7°), whereas solution B (model groundwater) remained almost unchanged (135 ± 6°) compared to the virgin membrane (137 ± 5°). Meanwhile, based on the feed and permeate solution concentration mass balance, it was estimated that around 50-70% F^- precipitation occurred during the DCMD operation with both these feed solutions. The results suggested that with the selected DCMD operating conditions, the F^- precipitation and deposition onto the MD membrane by these feed solutions only minimally influenced the membrane hydrophobicity.

Comparatively, the used MD membrane with solution C (containing addition of organics) exhibited a significantly higher membrane hydrophobicity reduction (37-40%) although the fluoride precipitation (13-15%) was much lower. The results suggest that the inorganic precipitation and deposition onto the MD membrane at this concentration level influenced only marginally the membrane hydrophobicity. On the other hand, organics play a more significant role in reducing the MD membrane hydrophobicity, although it did not significantly reduce the membrane flux (Figure 4.2). A similar observation was made in another MD study on organic fouling by Naidu et al. (2014, 2015). The study highlighted that fouling was predominantly caused by adsorption of organics onto the MD membrane, which led to the loss of membrane hydrophobicity while maintaining a stable permeate in terms of conductivity and flux pattern.

Table 4.1.4 Membrane contact angle of used MD membrane and F^- precipitation with different F^- based feed solutions.

Membrane	Feed solution	Membrane contact angle (º)	F precipitation (%)
Virgin		137 ± 5	-
Used	Solution A	120 ± 7	67-70
	Solution B	135 ± 6	51-53
	Solution C	86 ± 8	13-15

4.2.7. Organic analysis

In order to obtain a better understanding of the influence of organics in Solution C on the MD membrane hydrophobicity condition, detailed characterisation of the organic contents in the initial and final feed and permeate solution were analysed using LC-OCD (Figure 4.2.5). The total DOC of the initial and final permeate solution was 0.6 mg/L and 0.5 mg/L indicating a 99% rejection of organics was achieved Table 4.1.5. Meanwhile, the concentration of the initial feed solution was 8.6 mg/L, predominantly containing humic substances. The concentration of the final feed solution (at VCF 4, 75% water recovery) was 29.6 mg/L, which was 14% lower than the expected value at 4 times concentration factor of the initial feed solution (Table 4.1.5).

The lower organic contents in the final feed solution could be assumed to have deposited onto the MD membrane. This could also be confirmed by the observation of the brownish layer on the used MD membrane with Solution C. Although the presence of organics in Solution C resulted in only a minor additional permeate flux decline (almost similar flux decline pattern in solution B and C), the deposition of organics on the MD membrane reduced the membrane hydrophobicity by 37-40%.

Table 4.1.5 Organic composition of initial and final feed and permeate in treating Solution C with DCMD.

Solution	Total DOC (mg/L)	BP (mg/L)	HS (mg/L)	BB (mg/L)	LMW neutrals (mg/L)	LMW acids (mg/L)

Initial feed	8.6	-	4.9	1.1	0.4	1.7
Final feed	29.6	-	20.8	2.7	0.6	3.2
Initial permeate	0.6	-	0.1	0.2	0.1	0.2
Final permeate	0.5	-	0.3	0.2	<0.1	<0.1

BP=biopolymer, HS=humic substance, BB= building blocks, LMW=low molecular weight organics

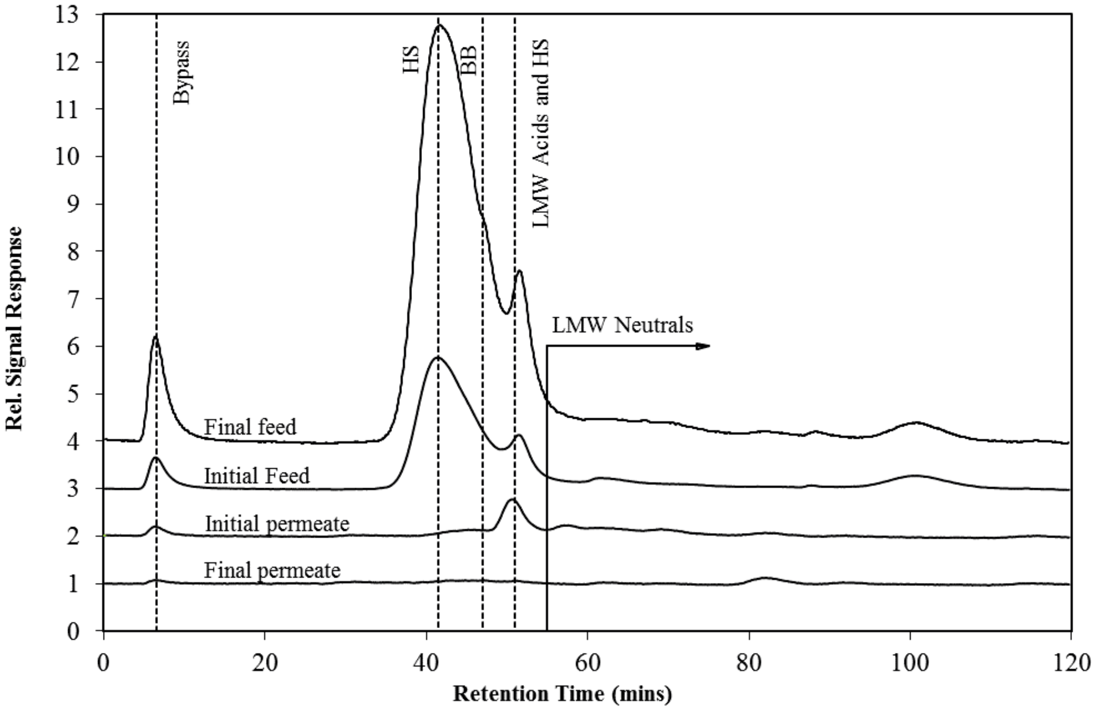


Figure 4.2.5 LC-OCD chromatograms of initial and final feed and permeate in treating Solution C with DCMD (*BP=biopolymer, HS=humic substance, BB= building blocks, LMW=low molecular weight organics*).

4.2.8. Restoring hydrophobicity of used MD membrane

The capacity to restore the reduced membrane hydrophobicity of the MD membrane used with organics was evaluated by cleaning with water (Milli Q) and chemical solution (0.1 M NaOH). The hydrophobicity of the membranes was mostly restored to the original condition upon membrane cleaning with Milli Q washing by 88-90% and with chemical cleaning by 96-98% based on the contact angle measurement (Table 4.1.). The results indicated that chemical cleaning the organically fouled MD membrane was effective in restoring the MD membrane hydrophobicity mostly to its original condition. Alternatively, granular activated carbon (GAC) and powdered activated carbon (PAC) would be an effective pre-treatment in reducing the organic contents in the feed solutions (Jeong, Naidu & Vigneswaran 2013; Naidu *et al.* 2013) prior to MD treatment and thus extend the operation period without membrane cleaning.

Table 4.1.6 Membrane contact angle of used MD membrane with Solution C and washed MD membrane and percentage value restoration compared to virgin membrane.

Membrane	**Solution**	**Membrane contact angle [°]**	**Hydrophobicity restoration to original condition (%)**
Virgin (Original)		137 ± 5	
Used	Solution C	86 ± 8	
Washed	Milli Q	122 ± 6	88 - 90
	0.1 M NaOH	133 ± 4	96 - 98

4.2.9. Conclusions

This study evaluated the performance of DCMD for treating F^- contaminated groundwater solution. The results of this study demonstrated that MD is a suitable alternative treatment option with high rejection rate of F^- (98 - 99%) for all F^- related experiments. At a moderate feed temperature of 55 ºC, up to 75% water recovery was achieved with synthetic groundwater with only 15-17% permeate flux decline. F^- precipitation does not occur if only slightly exceeding the SI. However, the performance of MD decreased at elevated concentrations of potential scalants which suggests that the scaling potential of the feed water has to be well assessed prior the application of MD.

Organic water contamination lead to a brownish discolouration of the membrane as well as to a strong reduction of the membrane hydrophobicity. Washing with Milli Q water was also efficient for organic deposition, reaching an 88 - 90% restoration of the original condition. Washing with 0.1 M NaOH even reached a 96 to 98% of the original membrane condition.

4.3. Impact of vacuum application

The VEDCMD (application of vacuum on the permeate side of DCMD) was beneficial in increasing the permeate flux. In Chapter 4.1.3, a permeate flux enhancement of up to 42% with Milli Q water was achieved in VEDCMD (at 300 mbar permeate pressure) compared to the DCMD (at 1,000 mbar permeate pressure) at the same feed temperature of 55 ºC (Table 4.2.1). Previous studies also observed a significant flux enhancement with VEDCMD (Cath, Adams & Childress 2004; Naidu *et al.* 2016).

Table 4.2.1 Permeate fluxes of DCMD and VEDCMD (feed and permeate solution = Milli Q water, 55 ± 0.5 °C, and T_p =25 ± 0.5 °C).

Permeate pressure (mbar)*	**Average water flux (L/(m²·h))**
1000 (no vacuum)	11.9
800	13.4
600	14.4
300	16.9

**Measured as absolute pressure*

4.3.1. Flux pattern and fluoride rejection by VEDCMD

At 75% water recovery, a similar flux decline was observed for both DCMD and VEDCMD with Solution A (3-5% flux decline), while a slightly higher flux decline was observed with VEDCMD (18-20%) with Solution B (Table 4.2.2). This could be associated with the higher polarization effect due to the different transport mechanisms in VEDCMD compared to DCMD (Naidu *et al.* 2016). Also local scaling of gypsum could be of minor importance.

In terms of F^- rejection, the VEDCMD achieved high rejection of F^- in synthetic groundwater (98-99% rejection) similar to the DCMD (Table 4.2.2). At the same time, similar F^- precipitation was observed for both DCMD and VEDCMD. The results indicated that VEDCMD was effective to increase the permeate flux while maintaining the similar F^- rejection and inorganic precipitation as DCMD. Nevertheless, a more detailed study should be carried out to understand the flux decline pattern of VEDCMD in terms of transport mechanism.

Table 4.2.2 Comparison of flux decline ratio, F^- precipitation and rejection rate in treating Solution A and B with DCMD and VEDCMD (300 mbar) at 75% water recovery (VCF of 4).

MD configuration	Feed Solution	Flux decline [%]	F^- precipitation [%]	F^- rejection rate [%]
DCMD	Solution A	3-5	67	99 - 99
	Solution B	15-17	52	98 - 99
VEDCMD	Solution A	3-5	66	98 - 99
	Solution B	18-20	58	98 - 99

4.3.2. Continuous VEDCMD operation with groundwater solution

A continuous operation of VEDCMD (300 mbar permeate pressure) was carried out with F^- contaminated groundwater (Solution B), which was concentrated up to VCF 3 (67% water recovery) to minimize permeate flux decline that mostly occurred more prevalently after VCF 3 in DCMD at 75% water recovery (Figure 4.2). The operation was carried out for three runs, with intermediate membrane washing with Milli Q water, at the end of each run (Figure 4.2.6). The approach of continuous VEDCMD operation at 67% water recovery and intermediate membrane washing was effective in maintaining a stable flux.

At the same time, at the end of the third run with VEDCMD, the hydrophobicity of the used VEDCMD membrane was measured in terms of contact angle measurement (Table 4.2.3) The used VEDCMD membrane showed only slightly reduced contact angle by 8% compared to the virgin membrane and this was mostly restored to its original condition with Milli Q membrane washing and fully restored with chemical washing (0.1 M NaOH and 0.1 M HCl). Further, the SEM image of the washed MD membrane (Figure 4.2.7) showed a clear membrane surface (without any deposits) compared to the SEM image of the used membranes (Figure 4.2.1).

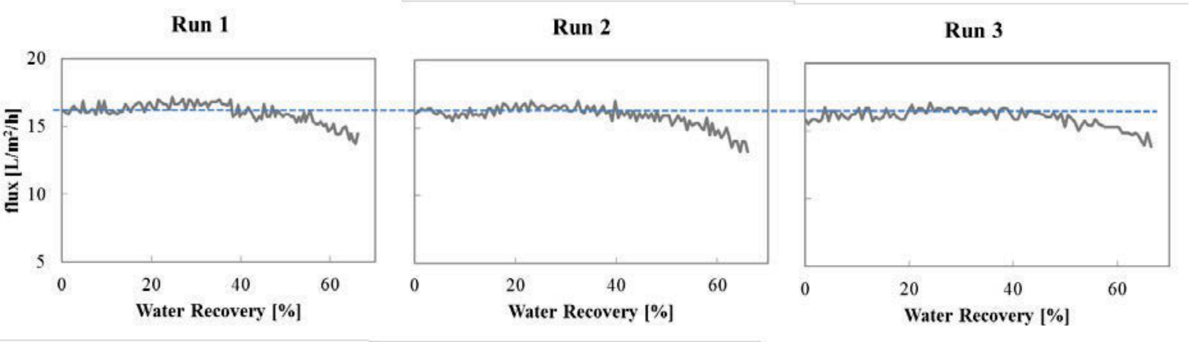


Figure 4.2.6 Permeate flux pattern with continuous VEDCMD operation for 3 runs with intermediate membrane cleaning with water at the end of each run (Solution B, T_{f} = 55 ± 0.5 °C, and T_p =25 ± 0.5 °C, permeate vacuum = 300 mbar).

Table 4.2.3 Membrane contact angles of used VEDCMD membranes (after three continuous runs) and after membrane cleaning.

Membrane type	Membrane contact angle (°)	Hydrophobicity restoration to original condition (%)
Virgin (Original)	137 ± 5	-
Used	129 ± 3	90 - 92
Milli Q washed	132 ± 5	94 - 96
0.1 M NaOH washed	135 ± 4	97 - 99
0.1 M HCL wash	131 ± 3	94 - 95

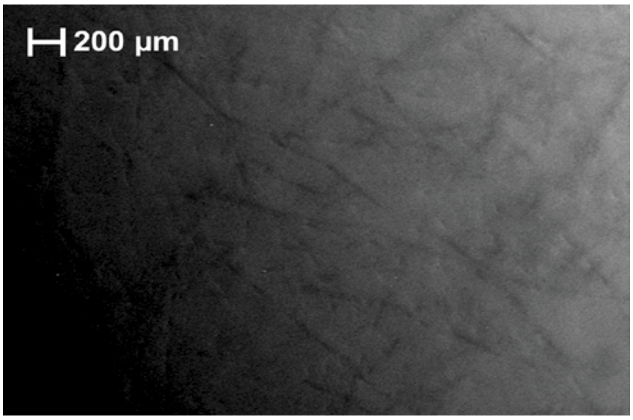


Figure 4.2.7 SEM image of the used VEDCMD membrane upon cleaning with Milli Q water.

4.3.3. Conclusions

The DCMD permeate flux was effectively enhanced by incorporating vacuum on the permeate side (VEDCMD). A 42% permeate flux increment was observed with 300 mbar permeate pressure compared to DCMD. Nevertheless, a further study should be carried out to analyse the transport mechanism in VEDCMD that attributed to higher flux decline (18-20%) compared to DCMD (15-17%) at 75% water recovery with F^- containing groundwater. A possible reason for the higher flux decline might go in hand with the higher flux achieved and therefore enhanced concentration polarisation leading to local oversaturation and scaling. The approach of treating F^- contaminated groundwater in VEDCMD with intermediate membrane cleaning at 67% water recovery, was effective in maintaining a stable permeate flux and a high F^- rejection of 98-99% in a continuous operation mode.

4.4. Removal of pesticides in MD

The removal of trace organic contaminants from drinking- or wastewater with membrane distillation is a novel field of research. To date, only very few studies have been published in this area. A feasibility study for the removal of 29 trace organic contaminants, including six pesticides, from Milli Q water and bioreactor effluent was carried out by Wijekoon *et al.* (2014b). The follow up study combined a thermophilic bioreactor system with membrane distillation to treat wastewater continuously (Wijekoon *et al.* 2014c). In both studies the feed temperature was only 40°C and the permeate temperature was 14 - 20°C. The rejection of the studied substances was more than 50% and in combination with the bioreactor the removal for all substances was more than 95%. The authors found that the volatility of the studied substances had more influence on the rejection rate than the hydrophobicity.

Granulated activated carbon is widely used as a treatment option for the removal of DOC and trace organic contaminants in wastewater as well as in drinking water (Matilainen, Vieno & Tuhkanen 2006; Snyder *et al.* 2007a; Summers, Knappe & Snoeyink 2011).

In the following study the removal of five pesticides from brackish groundwater was investigated in detail with the DCMD bench scale system. Four different feed solutions (A, B, C, D, see Table 3.3) containing the pesticides were tested in duplicates after the system was pre-conditioned with the feed solution for 24 h prior to each experiment by circulating the feed water in the feed side of the MD unit without operating the filtration.

With the MD pilot system different feed temperatures were studied regarding the rejection of the substances. A synthetic groundwater solution was used for these experiments (solution C). The tested feed temperatures were 40°C, 55°C and 70°C.

Further, a granulated activated carbon filter was tested as a potential MD post-treatment option to remove possible traces of pesticides before the water is supplied to the end user.

4.4.1. Preparatory pesticide removal experiments

In an initial experiment only three pesticides (atrazine, phorate and cypermethrin) with a concentration of 12.5 µg/L each were investigated. The pH was adjusted to 7 before the start of the experiment. The experiment was first carried out using only Milli Q water and secondly with the addition of 3 g/L of NaCl. In both runs the concentration factor was 4 (75 % water recovery).

The selected pesticides showed good rejection rates above 95 % in both experiments as shown in Figure 4.2.8. The concentration of each pesticide in the permeate was below 0.4 µg/L. Also the distillate TDS in the second experiment remained low. Pesticide measurements were performed by the National Measurement Institute (NMI).

Although the rejection of the substances is very high, a great loss was observed in the mass balance due to adsorption in the MD unit and on the membrane of the partially highly hydrophobic substances (Figure 4.2.9). Out of the studied substances atrazine has the lowest LogD. It is therefore less likely to adsorb on the membrane or the MD unit and could be concentrated in the feed solution. Due to the high hydrophobicity of cypermethrin the whole amount of the spiked substance was adsorbed in the MD system and the membrane. Therefore, further studies with cypermethrin were discontinued. The results showed that the addition of NaCl did not have an influence of the rejection of the selected substances.

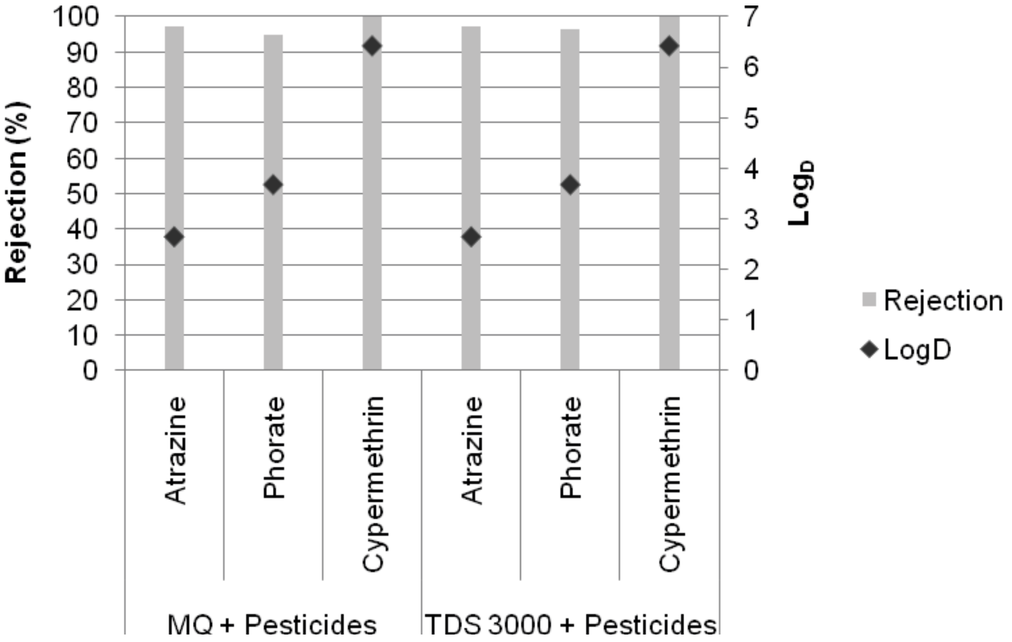


Figure 4.2.8 Rejection rates and LogD of investigated pesticide

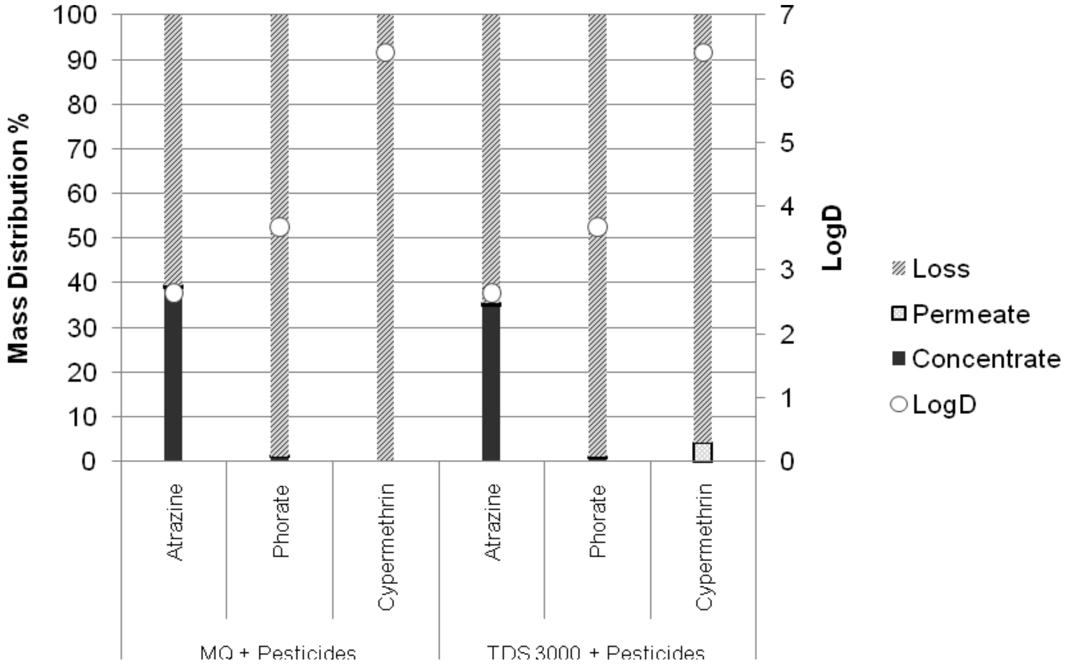


Figure 4.2.9 Mass distribution and logD of investigated pesticides

4.4.2. System pre-conditioning

In order to prevent adsorption in the MD system, a system pre-conditioning was studied in detail. The feed solution was prepared and stirred for 24 h and then circulated in the system for 48 h. Samples were taken after 24 h of stirring, 24 h of system circulation and 48 h of system circulation. The results are presented in Figure 4.2.10. It was clearly shown that with increasing contact time in the MD system the concentration of the compounds are reduced. The percentage of adsorption is directly related to the LogD of the substances as given in Figure 4.2.11. This finding is in line with the definition of LogD which describes the hydrophobicity of a compound and therefore the affinity of a non-hydrophilic compound to adsorb on a surface when the substance is solved in an aqueous solution. It is estimated that a large amount of pesticides is adsorbed onto the membrane due to its highly hydrophobic property. As a result of these tests it was decided, to pre-condition the system for 24 h with the feed solution prior to each experiment to minimize the contribution of adsorption during the rejection tests.

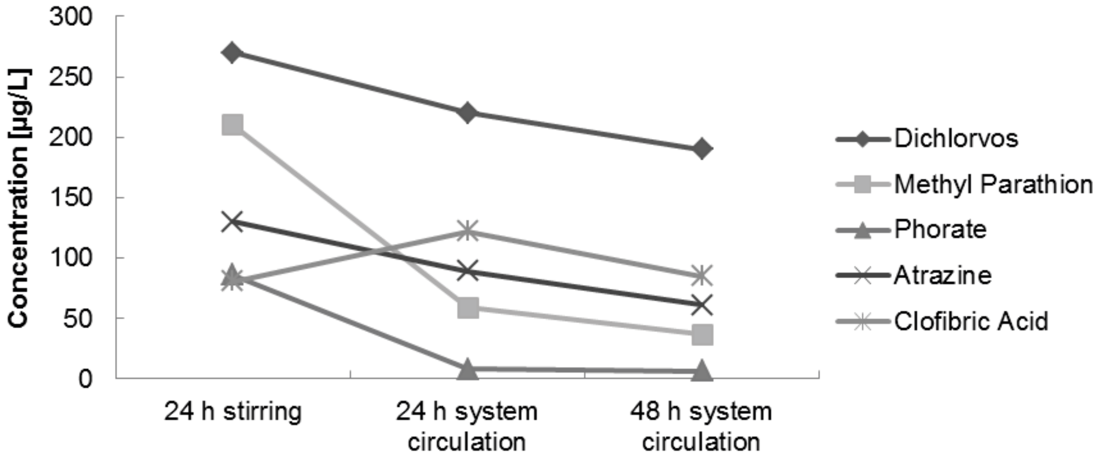


Figure 4.2.10 System pre-conditioning with 200 µg/L of each pesticide in Milli Q water.

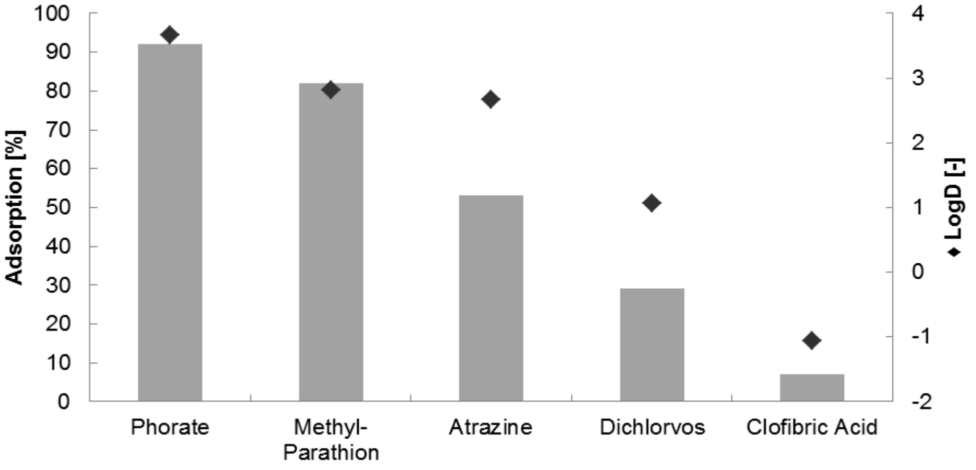


Figure 4.2.11 Adsorption of tested substances in the MD and membrane system in comparison to LogD after 48h of circulation

4.4.3. Permeate flux

Average initial permeate fluxes in the range of 12.3 ± 0.3 L/(m²·h) to 14.9 ± 1.0 L/(m²·h) were achieved for all feed solutions A to D at 55 ± 0.5°C feed temperature. At a lower feed temperature of 40°C the flux was dramatically reduced 3.9 ± 0.1 L/(m²·h) and at 70°C the flux was, as expected, high at 34.9 ± 0.3 L/(m²·h). The permeate temperature was kept stable at 25 ± 0.5°C for all experiments.

Table 4.2.4 Average permeate flux and average contact angle for each solution carried out in duplicates

Solution	Average flux	Flux reduction [%]	Average contact angle [°]
A at 55°C	12.3 ± 0.3	10 - 13	135 ± 4
B at 55°C	14.1 ± 0.6	14 -16	121 ± 6
C at 55°C	14.9 ± 1	15 - 17	129 ± 6
D at 55°C	14.7 ± 0.75	18 - 20	86 ± 7
C at 40°C	3.9 ± 0.1	N/A*	-
C at 70°C	34.9 ± 0.3	N/A*	-

* high variability of flux values does not allow deriving a clear trend

For solution A (Milli Q with 200 µg/L of each selected pesticide) a flux decline of 10 - 13% was observed, compared to previous studies, this flux decline is more than expected. This could be due to the adsorption of pesticides onto the membrane and blocking of membrane pores. Compared to solution A the flux reduction for solution B (5 mg/L humic acid (HA) with 200 µg/L of each selected pesticide) was slightly higher at 14 - 16%. This could be due to the formation of a slight organic fouling by humic acid. A visually detectable brownish discolouration of the membrane was observed to support this assumption. With solution C (synthetic groundwater solution with 200 µg/L of each selected pesticide) the sampe flux reduction was observed as in the previous fluoride study (Chapter 4.2.1). Therefore, it can be concluded that the addition of pesticides did not have an influence on the permeate flux reduction. As shown in the previous chapters the flux changes are attributed to effects from temperature, salinity and concencentration polarisation in the synthetic groundwater solution containing potential scaling causing ions at higher concentration levels (100 - 150 mg/L of Ca^{2+}, Mg^{2+} and SO_4^{2-}) as well as NaCl. With solution D (solution C with humic acid) the highest flux reduction of 18-20% after reaching 50% water recovery was observed. The brownish discolouration of the membrane indicating organic fouling by HA was clearly visible and accounted to the flux reduction (Figure 4.2.13).

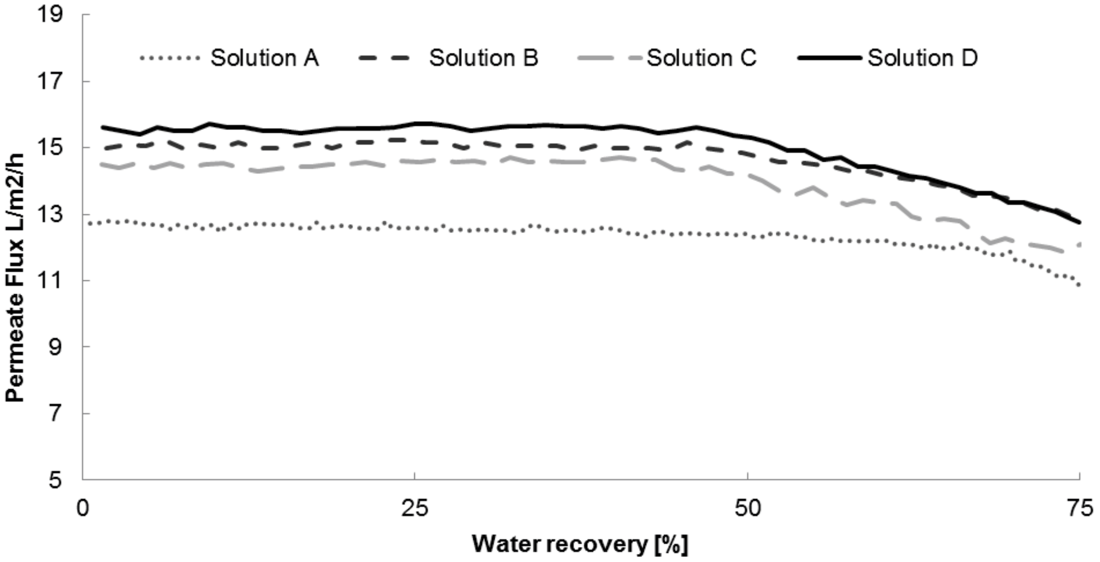


Figure 4.2.12 Permeate Flux of solution A to D, at 55 ± 0.5 °C feet temperature and 25 ± 0.5 °C permeate temperature.

Figure 4.2.13 Fouled membrane with solution D containing 5 mg/L humic acid, 200 µg/L of each pesticide and the synthetic groundwater model solution.

4.4.4. Contact angle measurement

Regarding the contact angle measurement, the experiment with solution A had similar results as observed in previous rest runs with Milli Q water (135 ± 4°). The addition of pesticides therefore had no detectable influence on the contact angle. With solution C the contact angle was reduced to 129 ± 6° which is higher compared to solution B at 121° ± 6 and can be explained with the adsorption of humic acid on the membrane leading to fouling and loss of hydrophobicity. With solution D this trend is observed even more, where the formation of inorganic deposits together with humic acid on the membrane leads to a dramatic loss of hydrophobicity and a contact angle of 86 ± 7°. This observation was made also previously and is discussed in Chapter 4.2.6.

4.4.5. Permeate quality and pesticide rejection

The average rejection rates for the spiked pesticides in solution A (Milli Q water) with system pre-conditioning are presented in Table 4.2.5, Figure 4.2.14 and Figure 4.2.15. The results show that both parameters, vapour pressure and LogD, are the key parameters for a high rejection rate in membrane distillation. Atrazine and parathion-methyl have similar LogD values. With regards to the vapour pressure there is a difference of 1 Log unit, resulting in a 20-25% higher rejection for atrazine compared to parathion-methyl. Also clofibric acid has a 20-25% higher rejection compared to parathion-methyl. This can be explained in terms of their LogD values. The vapour pressure for clofibric acid and parathion-methyl are similar, whereas clofibric acid is highly soluble in water and parathion-methyl is not. LogD and vapour pressure have an additive effect on the rejection of compounds. This can be seen when comparing the rejection of clofibric acid and phorate where the LogD differs significantly and additionally the vapour pressure has a difference of one log unit, resulting in a total rejection difference of 55-60%. A second example is the case of phorate and parathion-methyl where the LogD differs only to a minor degree while the vapour pressure has a difference of one log unit, resulting in a difference in rejection of 30-40%. The mass distribution of the solution A experiments can be seen in Figure 4.2.16.

The presence of 5 mg/L humic acid (solution B) seemed to slightly influence the rejection rate of clofibric acid and dichlorvos, but considering the error, no clear statement can be made. The error appears to be too high to deduct a clear trend. More detailed studies would be required to clearly identify the influence of background bulk organics on the rejection of trace organics. The mass distribution can be seen in Figure 4.2.17.

With regards to solution C (the synthetic groundwater solution) dichlorvos was not rejected. Also with solution D the rejection for dichlorvos was significantly reduced. The reduced rejection cannot only be explained with the high vapour pressure, but also with a high loss of the substance in these two experiments (mass balance shown in Figure 4.2.18 and Figure 4.2.19).

Generally, it can be seen from Figure 4.2.14 and Figure 4.2.15 that with increasing LogD values the rejection is reduced with exception of dichlorvos which has, compared to the other substances, a very high vapour pressure. It is assumed that this substance passes as a vapour through the membrane. Dichlorvos was further detected in the permeate in high concentrations of 40-60 µg/L supporting this assumption.

The results suggest that the vapour pressure and the LogD have both an influence on the rejection rate and that the effects can intensify each other. A low vapour pressure and a low LogD are thus favourable for a good rejection in membrane distillation.

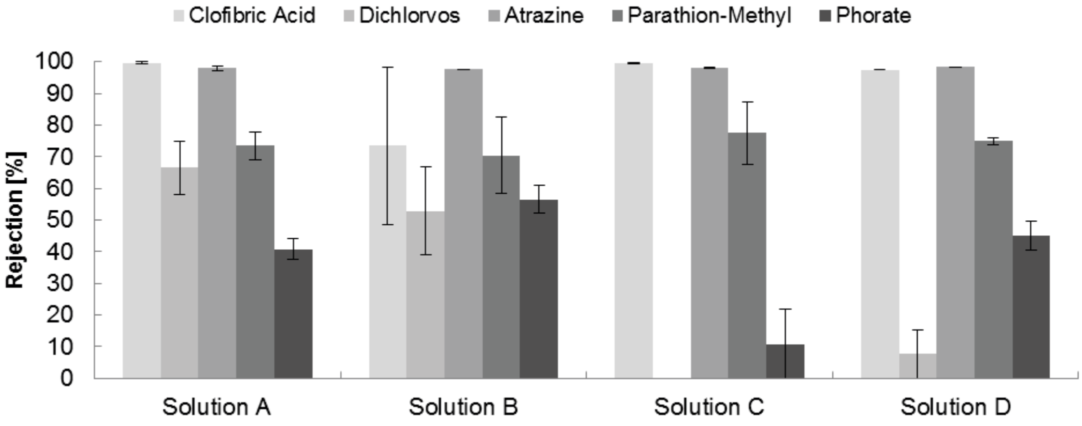


Figure 4.2.14 Rejection rates for solution A to D (error bars represent the standard deviation)

Figure 4.2.15 shows more clearly that for each compound a visible trend can be derived. The average rejection for clofibric acid was between 97 and 99 %, not considering the results from the experiments with solution C since the error margin was too high to clearly derive a result.

Dichlorvos and phorate had an average rejection of 10-60 % and 10-50% respectively. The reduced rejection rates are due to the high volatility of dichlorvos and the high hydrophobicity of phorate. It is assumed that phorate first accumulates on the hydrophobic membrane and is then partly released and thus more likely to be transported through the membrane.

For atrazine the rejection remained above 97 % during all experiments. For parathion-methyl the rejection was between 60 and 80 %. Atrazine and parathion-methyl have a similar LogD but the vapour pressure of atrazine is 10 times lower. As a result the rejection is around 20 to 35 % higher.

Wijekoon *et al.* (2014b) compared the rejection rates of 29 substances with the Henry's law constant (pK_H = -Log (vapour pressure [atm] x molecular weight [g/mol] / water solubility [mg/L])), stating that compounds with a $pK_H > 9$ (classified as non-volatile) were highly removed by MD (95-99.9%) and substances having a $pK_H < 9$ (partially volatile) were removed at lower rejection rates ranging from 54 to 73%.

In the present study only clofibric acid had a pK_H > 9 and was, as expected, retained well in the system. Atrazine, which was also studied by Wijekoon *et al.* (2014b) was also retained well in this study and in the study of Wijekoon, having a pK_H of 7.3. Parathion-methyl and dichlorvos have a similar pK_H of 5.6 and 5.1 respectively, but the rejection in the MD system was different. Parathion-methyl had rejection rates of more than 70% and dichlorvos was always rejected to less than 70%, mostly only around 10-50%. Phorate having the lowest pK_H of 4.7 was not well rejected in the system, but slightly better than dichlorvos (10-65%).

It is important to note that vapour pressure and water solubility data are mostly only available at 25°C, hence the actual pK_H values at the experimental temperatures (55°C) can deviate from the calculated values. It would be important to include the vapour pressure at the experimental temperature, especially at high temperatures, to obtain a reliable constant. The rule stated by Wijekoon *et al.* (2014c) could not be confirmed as clearly in this study, although a trend can be acknowledged.

The pK_H values of the tested substances can be found in Table 3.4.

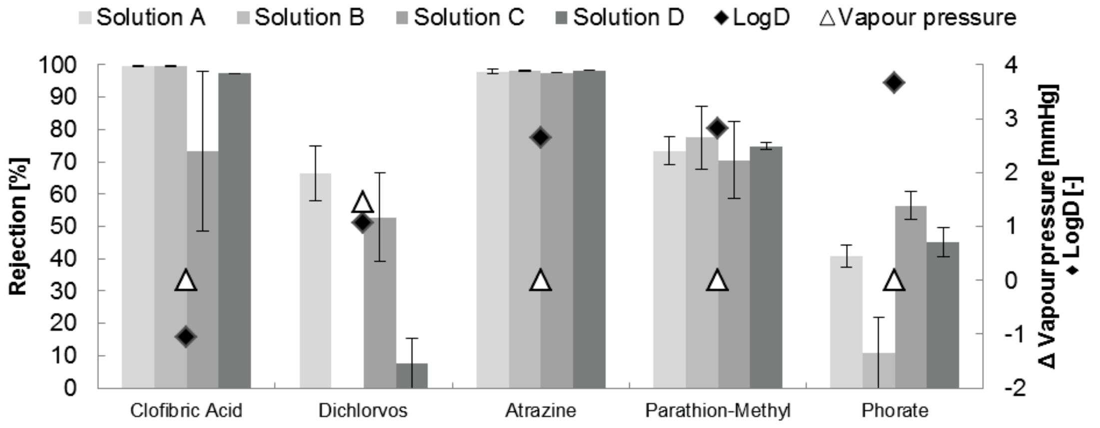


Figure 4.2.15 Rejection rates for each compound (error bars represent the standard deviation)

Table 4.2.5 Average rejection for all tested substances

Name	LogD at pH 7	Vapour pressure 25ºC [mmHg]	Average Rejection sol. A [%]	Average Rejection sol. B [%]	Average Rejection sol. C [%]	Average Rejection sol. D [%]
Phorate	3.67	2.60 x 10^{-3}	40.9 ± 3	56.5 ± 4	10.9 ± 11	45.1 ± 5
Parathion-methyl	2.82	2.4 x 10^{-4}	73.5 ± 4	70.5 ± 12	77.5 ± 10	74.8 ± 1
Atrazine	2.64	1.27 x 10^{-5}	98.0 ± 1	97.6 ± 0	98.0 ± 0.2	98.4 ± 0.1
Dichlorvos	1.07	1.45	66.5 ± 9	52.9 ± 14	N/A	7.7 ± 8
Clofibric acid	-1.06	1.03 x 10^{-4}	99.4 ± 0.3	73.4 ± 25	99.6 ± 0.2	97.4 ± 0

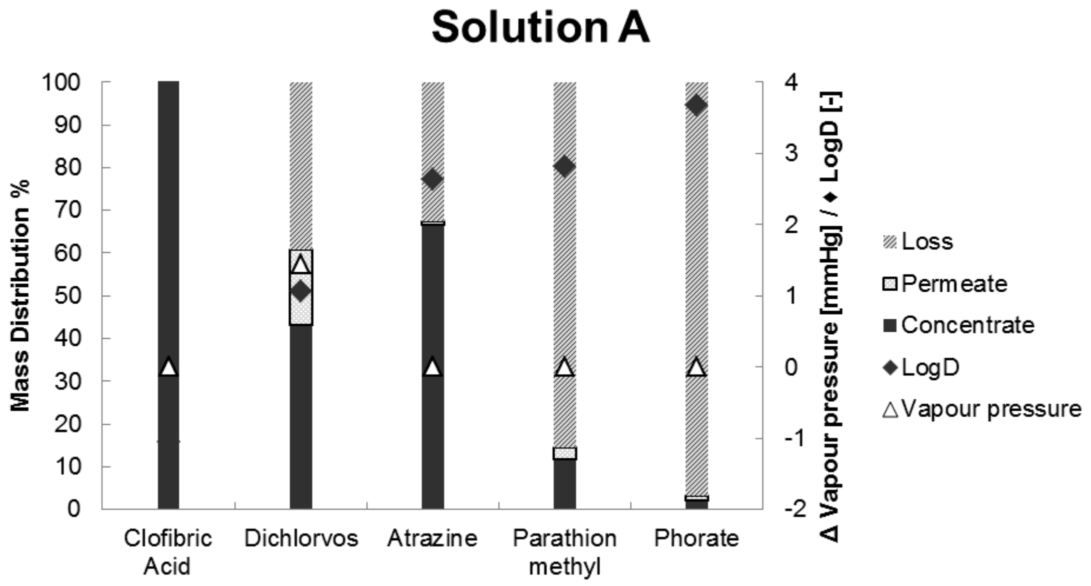


Figure 4.2.16 Mass distribution of pesticides in solution A

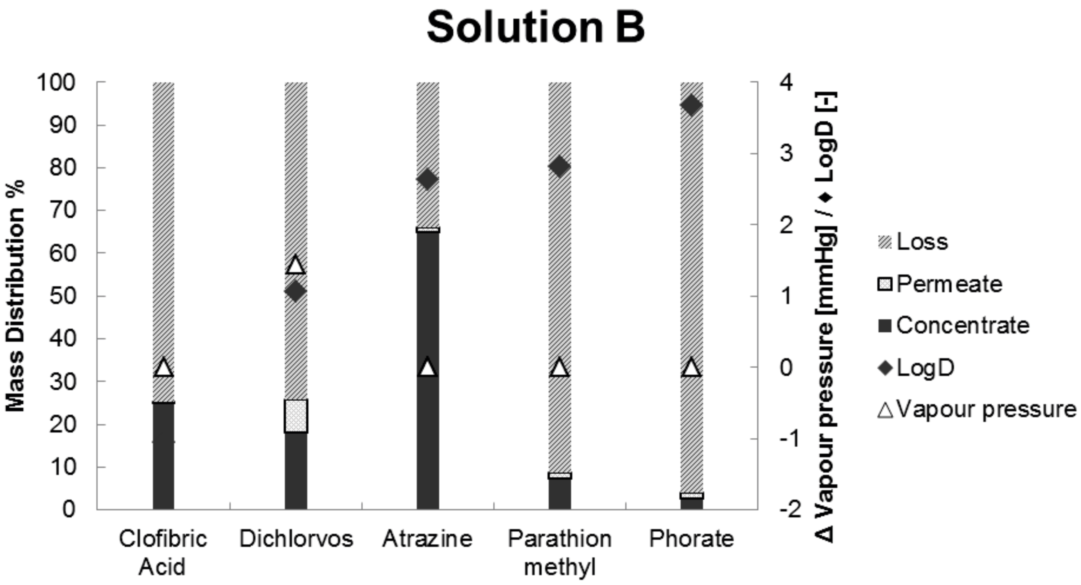


Figure 4.2.17 Mass distribution of pesticides in solution B

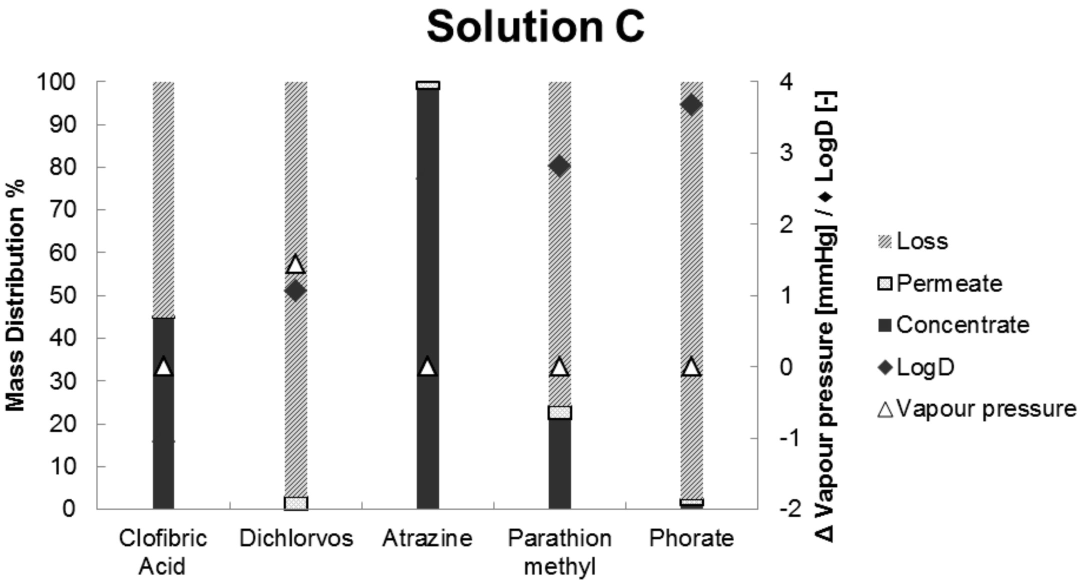


Figure 4.2.18 Mass distribution of pesticides in solution C

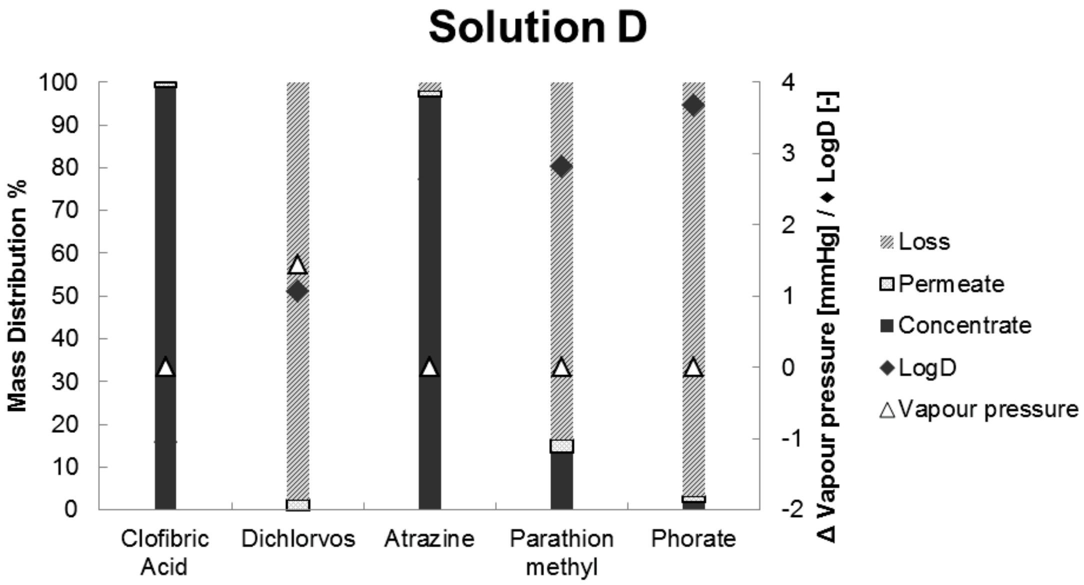


Figure 4.2.19 Mass distribution of pesticides in solution D

4.4.6. Permeate quality and pesticide rejection at 40°C and 70°C

The experiments regarding rejection at lower and higher temperatures than 55°C were conducted with solution C using the pilot MD system as described in Chapter 3.2.2. Experiments at 55°C were repeated first to study the comparability to the results from the bench scale MD system.

The calculated rejection rates for the pilot system are generally higher as the rejection rates obtained in the bench scale system. Further, higher losses were observed in the pilot system (see Annex 2). One reason could be that the bigger inner surface of the pilot system leads to more adsorption. But also the material of the tubing of the system could account for the higher adsorption. The tubing in the bench scale system was PFTE whereas in the pilot system it was polyurethane, less inert on one hand in terms of the adsorptive characteristics but also with regards to an observed slight release of PUR monomers into the liquid.

Nevertheless a clear trend regarding the rejection at 40°C and 70°C feed temperature could be derived from the obtained results.

As it can be seen from Figure 4.2.12 and Table 4.2.6 that a reduced rejection at higher feed temperatures was observed. This is especially evident for the case of dichlorvos, which has the highest vapour pressure and thus behaved as expected. Also for atrazine and parathion-methyl this tendency was observed but to a much smaller degree. In the case of phorate this phenomena was not observed for the 40 °C experiment which however had a high error margin and must thus be seen as less robust.

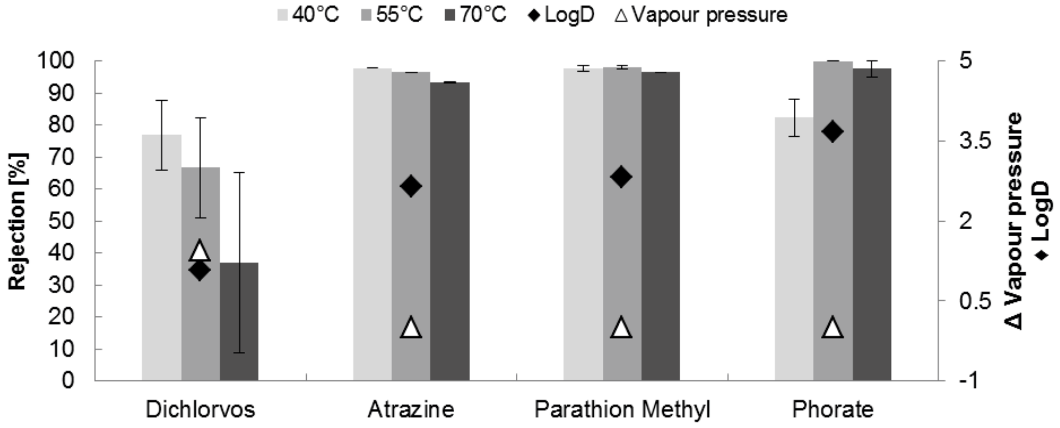


Figure 4.2.12 Rejection rates of solution C at 40, 55 and 70°C feed temperature (error bars represent the standard deviation)

Table 4.2.6 Rejection rates for solution C at 40, 55 and 70°C

Name	LogD at pH 7	Vapour pressure 25ºC [mmHg]	Average Rejection sol. C 40 °C [%]	Average Rejection sol. C 55°C [%]	Average Rejection sol. C 70°C [%]
Phorate	3.67	2.60×10^{-3}	82.3 ± 6	100 ± 0	97.5 ± 2.5
Parathion-methyl	2.82	2.4×10^{-4}	97.7 ± 0.8	96.4 ± 0	76.5 ± 0.1
Atrazine	2.64	1.27×10^{-5}	97.8 ± 0	96.4 ± 0	93.3 ± 0.3
Dichlorvos	1.07	1.45	67.9 ± 11	66.7 ± 16	36.8 ± 28

4.4.7. Rapid small scale column test

As it was shown in the previous chapters traces of pesticides can still be found in the permeate after MD treatment at moderate feed temperatures. Therefore a rapid small scale column test was studied as a possible post treatment option to remove any remaining pesticides before supplying the product water to the end user.

The RSSCT was operated for during 17 days reaching 67,600 bed volumes. In a large scale application this would correspond to a column operated during 15 months, having an inner diameter of 10 cm and a height of 34 cm (volume = 2,670 cm^3) containing approx. 1 kg of activated carbon. With an EBCT of 10 min and a linear velocity of 2 m/h this column would treat 377 L/day. The experiment was stopped when Atrazine started to slowly breakthrough. It must be noted that a GAC column treating the MD permeate largely benefits from the prior desalination and bulk organics retention which eliminate negative effects from the adsorption of the trace compounds to the activated carbon.

After 12,000 bed volumes traces of dichlorvos were firstly detected in the treated water, remaining constant at a concentration of 15 to 25 ng/L, still equivalent to a 3 log removal. As dichlorvos has the highest vapour pressure and the lowest logD, it has the lowest adsorption affinity to the carbon material.

After 63,000 bed volumes all substances started to become detected in the GAC filtrate at elevated ng/L concentrations (2 log removal). Especially atrazine was found in higher concentrations. This might be linked to competitive adsorption. However, a 2 log removal was still maintained during the whole time of the experiment for all substances and the product water would have been compliant with the Indian drinking water guidelines.

All tested substances are neutral at pH 7.

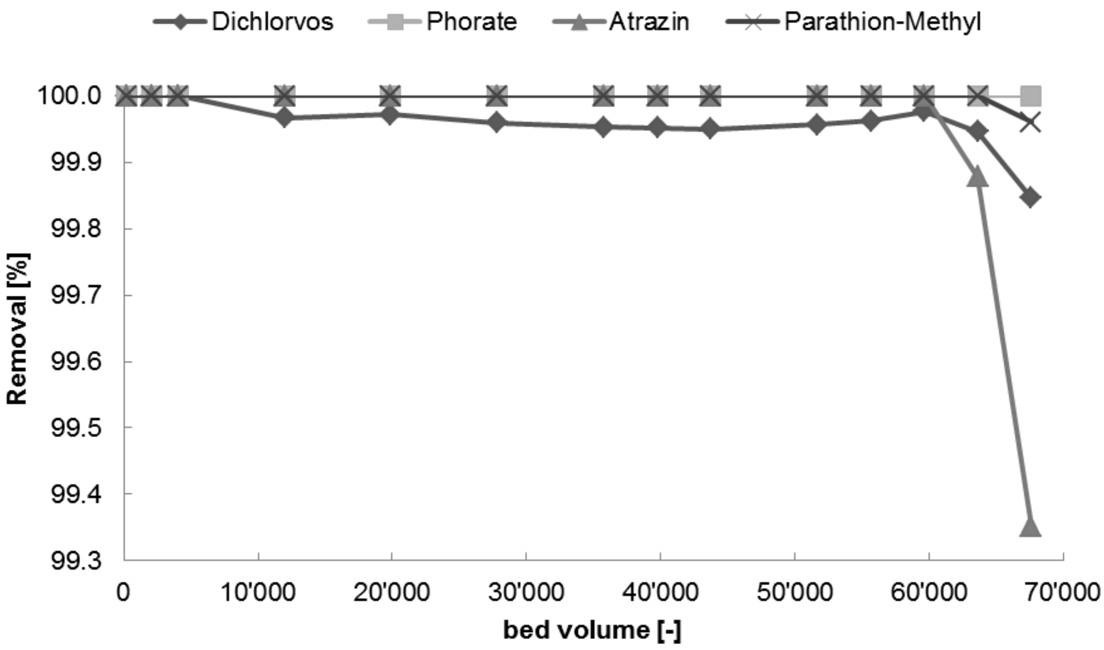


Figure 4.2.20 Removal of selected pesticides in RSSCT (F400, Chemviron Carbon, EBCT = 10 min equivalent in full scale)

4.4.8. Conclusions

In summary it can be concluded that non-volatile and weak adsorptive substances are well rejected in membrane distillation. Also the bulk salinity and humic acid have negligible effect on the rejection rate. However special care has to be given for the operation with solutions containing high amounts of inorganic substances that can lead to scaling and subsequently wetting of the membrane which would result in leaking of feed solution into the permeate. Highly volatile (dichlorvos) and highly adsorptive (phorate) substances are rejected to a lower degree (10-65 % and 10-50 % rejection respectively). The influence of the volatility seems to be more relevant than the adsorptivity. This is valid at least for the studied short operation period. Long term piloting could be used to study the relationship of these two effects further.

Constants such as the Henry's law constant pK_H can be considered for an initial assessment whether a substance is retained well by MD or not. However lab experiments are regarded as indispensable since the compound properties are often only available for standard conditions i.e. 25 °C, and the experimental temperature plays a big role.

It is advisable to use an activated carbon filter, as a post treatment to membrane distillation to polish the distillate and prevent leaking of possibly harmful micropollutants into the produced drinking water. It was shown in this study that substances were well retained with a GAC filter with 10 min contact time for a period of about 15 months. A 2 log removal was obtained for all substances during the whole time of the experiment and the requirements of the Indian drinking water guidelines were met. Yet, not all substances were retained perfectly in the filter for example, dichlorvos was found in very low traces already after three days of operation in the GAC filtrate. While also being rejected at a lower rate due to its high volatility, dichlorvos thus represents a group of possibly harmful substances that are not well retained in the combined MD / activated carbon system. Therefore before considering such a combined system, it is crucial to analyse and evaluate carefully the contaminants present in the raw water to be treated. Nevertheless under the conditions of the present case, the removal for dichlorvos in the activated carbon filter amounted still to 3 log units up to 63,600 BV (470 days of operation in large scale). Up to 67'600 BV (15 months of operation in large scale) all substances showed a 2 log removal. MD followed by GAC can thus be regarded as an efficient treatment for pesticide contaminated groundwater if the aforementioned design criteria are taken into consideration.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Faculty for Engineering & Information Technology

5. Conclusions and recommendations

In this final chapter the main outcomes of this study are summarized and recommendations for the application of MD for drinking water supply are given.

5.1. Conclusions

5.1.1. Fluoride removal

Fluoride is an important and widely present contaminant in groundwater in India and other parts of the world. In this study it was shown that fluoride can be effectively removed in MD to 98-99%. It was shown that possible formation of fluoride based scaling was loosely deposited on the membrane surface and could be removed efficiently with Milli Q water flushing. If high inorganic concentrations are expected, slight acidification of the feed solution could help to contain scaling.

5.1.2. Pesticide removal

It was further demonstrated that non-volatile and weak adsorptive pesticides in trace concentrations are well rejected in membrane distillation. Bulk salinity and bulk organics such as humic acid had a negligible effect on the rejection rate. Vapour pressure and LogD of the target compounds such as pesticides are the key parameters for an initial estimation of the rejection in MD. The pK_H can give a first indication of the behaviours of substances in MD. However, lab scale experiments need to be carried out for a final evaluation on the compound behaviour under the specific conditions of MD.

5.1.3. Application of a GAC post treatment

The application of a GAC filtration as a final polishing step was shown to be very efficient. The MD permeate is already of a very high quality in terms of bulk salinity and organics minimizing competitive adsorption and therefore a high number of bed volumes could be reached before a slight breakthrough was detected at 67,600 bed volumes (equivalent to 15 months of application in a full scale plant).

5.1.4. Application of vacuum for performance enhancement

To improve the performance of the permeate production a slight vacuum of 300 mbar absolute pressure was applied at the permeate side. This measure showed an increase of the permeate flux of 42% compared to the DCMD experiments. However, there was an indication of a slightly higher flux decrease with increasing water recovery. Due to the higher flux achieved it is possible that local oversaturation from concentration polarisation took place and caused some scaling. A more detailed study should be carried out to analyse the transport mechanism in VEDCMD that attributed to higher flux decline compared to DCMD in more detail.

5.2. Recommendations

One of the main factors that would determine the suitability of MD application as a small standalone DCMD unit in rural areas is the level of operation and maintenance required. In this regard washing without chemicals would be favourable. It was shown that washing with Milli Q water can reach nearly as good results as washing with caustic soda or hydrochloric acid solution. Therefore, it is assumed that the maintenance of the system by periodic flushing with permeate stored will be sufficient with for the removal of moderate scaling. For the removal of potential fouling, it could be necessary to clean the system chemically, e.g. with caustic soda, on demand. Detailed studies for deployment in the field would be required to identify the optimum O&M procedures.

It is advisable to use an activated carbon filter as post treatment to membrane distillation to prevent the leaking of possibly harmful micropollutants into the produced drinking water. Optimum and robust designs for the field application should further tested prior potential deployment.

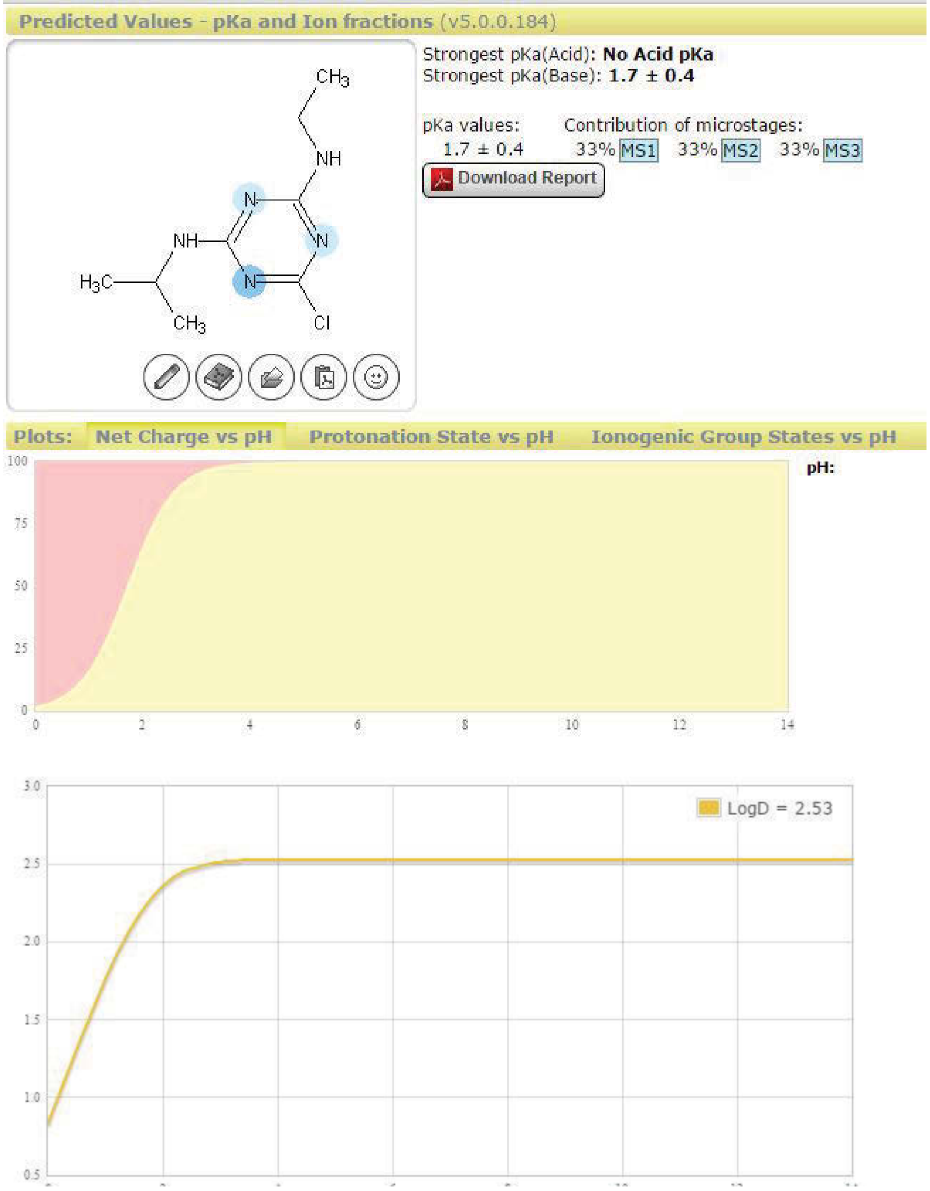
The particular advantage of a coupled MD/GAC system is the simultaneous removal of inorganic as well as organic contamination from a contaminated groundwater sources. Presently, only RO could be applied for comparable removal efficiencies for both substance groups. The incorporation of solar energy was studied previously (Banat *et al.* 2007a, 2007b; Koschikowski *et al.* 2009) and is advisable for rural applications. Optimum combinations with power supply e.g. from solar thermal or waste heat produced by a diesel generator etc. would require further detailed investigation.

Appendix

A1 Speciation and log D of selected ionic micropollutants

Atrazine

1912-24-9



Predicted Values - pKa and Ion fractions (v5.0.0.184)

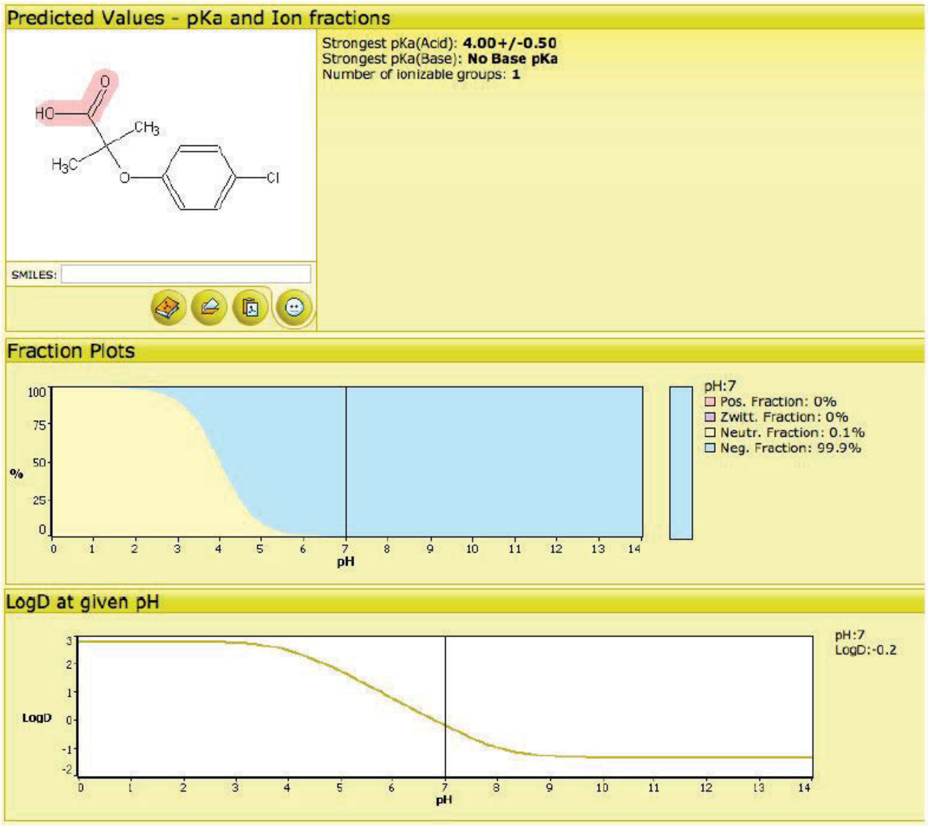
Strongest pKa(Acid): **No Acid pKa**
Strongest pKa(Base): **1.7 ± 0.4**

pKa values: 1.7 ± 0.4

Contribution of microstages: 33% MS1 33% MS2 33% MS3

Clofibric Acid

882-09-7



Predicted Values - pKa and Ion fractions

Strongest pKa(Acid): **4.00+/-0.50**
Strongest pKa(Base): **No Base pKa**
Number of ionizable groups: **1**

SMILES:

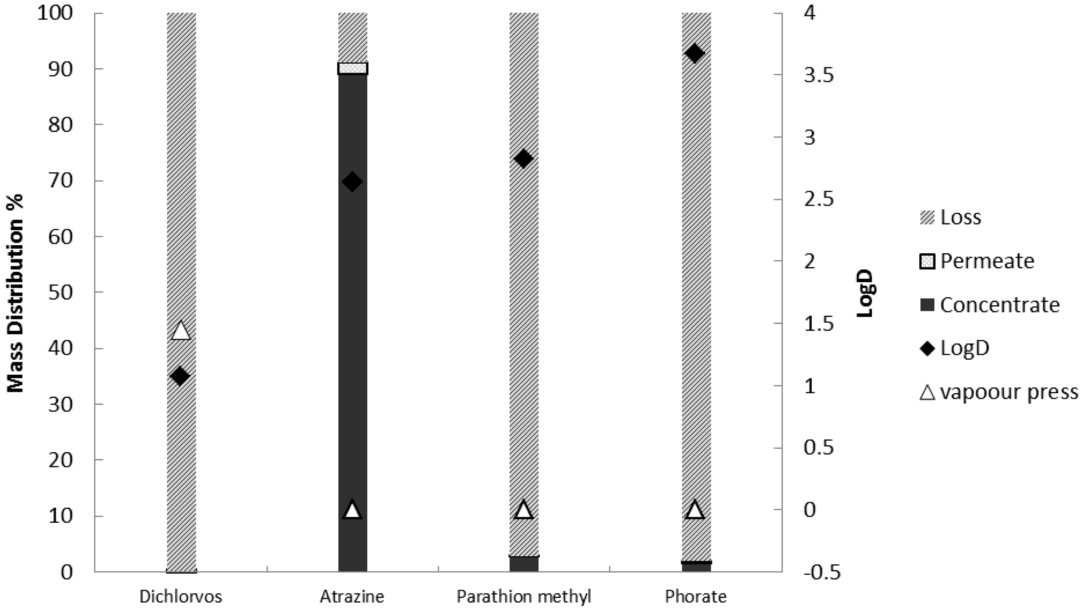
Fraction Plots

pH:7
☐ Pos. Fraction: 0%
☐ Zwitt. Fraction: 0%
☐ Neutr. Fraction: 0.1%
☐ Neg. Fraction: 99.9%

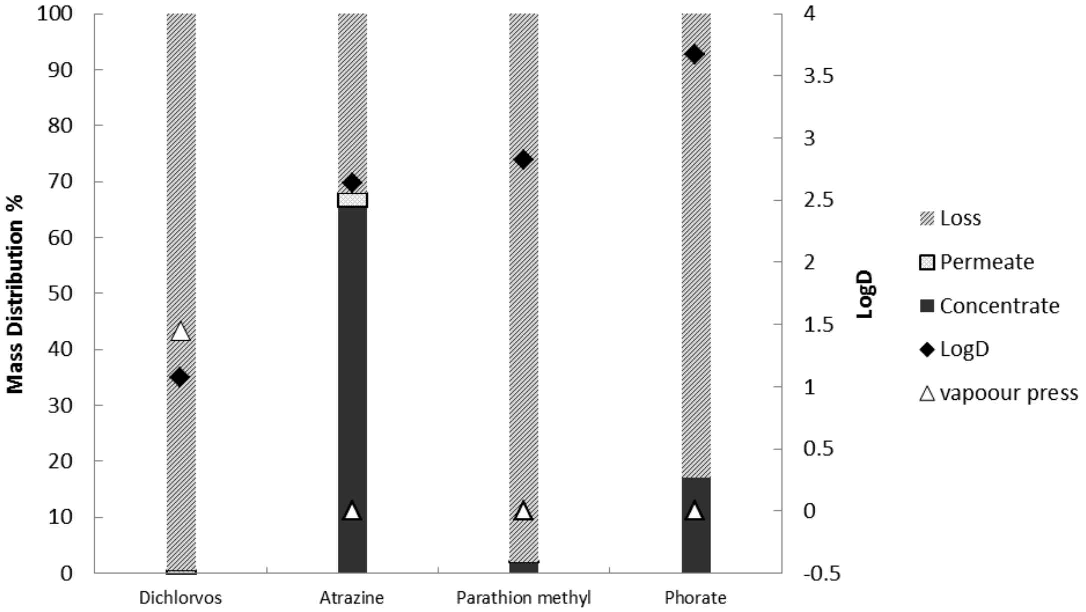
LogD at given pH

pH:7
LogD:-0.2

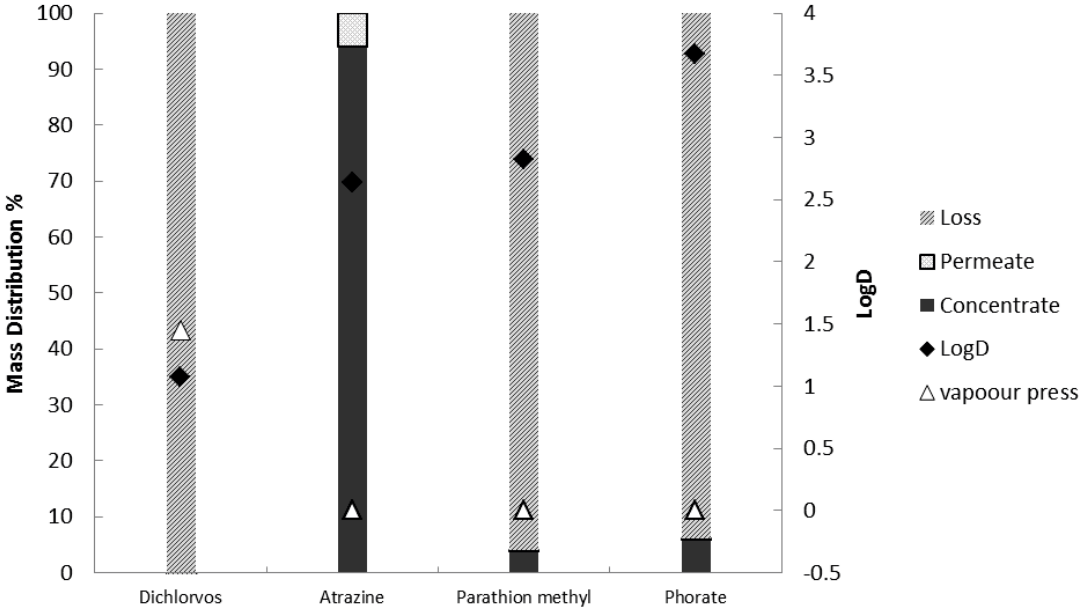
A2 Mass distribution pesticide experiments at different temperatures discussed in Chapter 4.4.6



Mass distribution at 40°C feed temperature



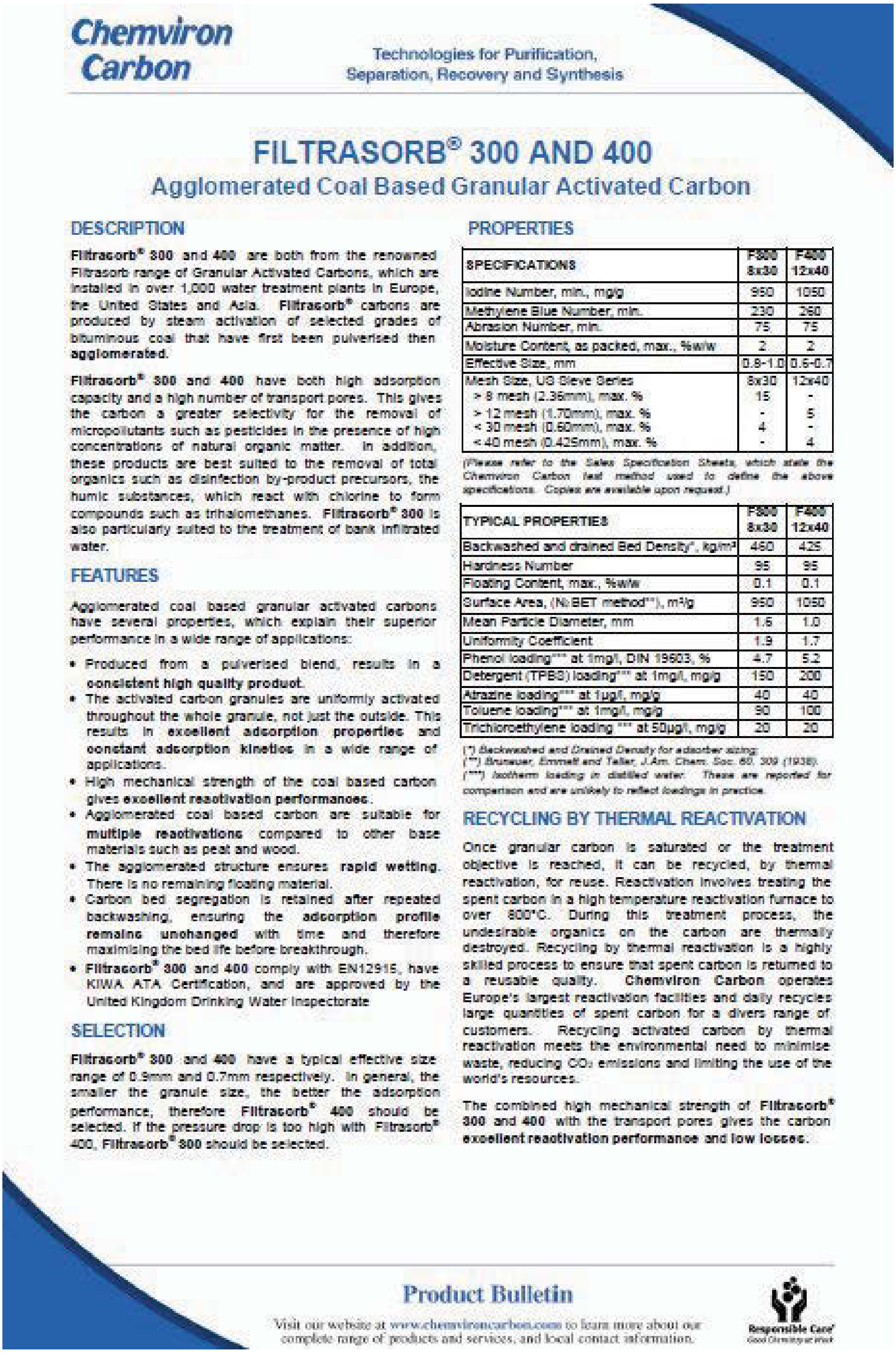
Mass distribution at 55°C feed temperature



Mass distribution at 70°C feed temperature

A3 Chemviron Carbon Activated Carbon Datasheet

In this study the Filtrasorb® 400 (F400) carbon by Chemviron Carbon was used.



Chemviron Carbon

Technologies for Purification, Separation, Recovery and Synthesis

FILTRASORB® 300 AND 400

Agglomerated Coal Based Granular Activated Carbon

DESCRIPTION

Filtrasorb® 300 and **400** are both from the renowned Filtrasorb range of Granular Activated Carbons, which are installed in over 1,000 water treatment plants in Europe, the United States and Asia. **Filtrasorb®** carbons are produced by steam activation of selected grades of bituminous coal that have first been pulverised then **agglomerated.**

Filtrasorb® 300 and **400** have both high adsorption capacity and a high number of transport pores. This gives the carbon a greater selectivity for the removal of micropollutants such as pesticides in the presence of high concentrations of natural organic matter. In addition, these products are best suited to the removal of total organics such as disinfection by-product precursors, the humic substances, which react with chlorine to form compounds such as trihalomethanes. **Filtrasorb® 300** is also particularly suited to the treatment of bank infiltrated water.

FEATURES

Agglomerated coal based granular activated carbons have several properties, which explain their superior performance in a wide range of applications:

- Produced from a pulverised blend, results in a **consistent high quality product.**
- The activated carbon granules are uniformly activated throughout the whole granule, not just the outside. This results in **excellent adsorption properties** and **constant adsorption kinetics** in a wide range of applications.
- High mechanical strength of the coal based carbon gives **excellent reactivation performances**.
- Agglomerated coal based carbon are suitable for **multiple reactivations** compared to other base materials such as peat and wood.
- The agglomerated structure ensures **rapid wetting.** There is no remaining floating material.
- Carbon bed segregation is retained after repeated backwashing, ensuring the **adsorption profile remains unchanged** with time and therefore maximising the bed life before breakthrough.
- **Filtrasorb® 300** and **400** comply with EN12915, have KIWA ATA Certification, and are approved by the United Kingdom Drinking Water Inspectorate

SELECTION

Filtrasorb® 300 and **400** have a typical effective size range of 0.9mm and 0.7mm respectively. In general, the smaller the granule size, the better the adsorption performance, therefore **Filtrasorb® 400** should be selected. If the pressure drop is too high with Filtrasorb® 400, **Filtrasorb® 300** should be selected.

PROPERTIES

SPECIFICATIONS	**F300 8x30**	**F400 12x40**
Iodine Number, min., mg/g	950	1050
Methylene Blue Number, min.	230	260
Abrasion Number, min.	75	75
Moisture Content, as packed, max., %w/w	2	2
Effective Size, mm	0.8-1.0	0.6-0.7
Mesh Size, US Sieve Series	8x30	12x40
> 8 mesh (2.36mm), max. %	15	-
> 12 mesh (1.70mm), max. %	-	5
< 30 mesh (0.60mm), max. %	4	-
< 40 mesh (0.425mm), max. %	-	4

(Please refer to the Sales Specification Sheets, which state the Chemviron Carbon test method used to define the above specifications. Copies are available upon request.)

TYPICAL PROPERTIES	**F300 8x30**	**F400 12x40**
Backwashed and drained Bed Density*, kg/m³	460	425
Hardness Number	95	95
Floating Content, max., %w/w	0.1	0.1
Surface Area, (N_2 BET method**), m²/g	950	1050
Mean Particle Diameter, mm	1.6	1.0
Uniformity Coefficient	1.9	1.7
Phenol loading*** at 1mg/l, DIN 19603, %	4.7	5.2
Detergent (TPBS) loading*** at 1mg/l, mg/g	150	200
Atrazine loading*** at 1µg/l, mg/g	40	40
Toluene loading*** at 1mg/l, mg/g	90	100
Trichloroethylene loading *** at 50µg/l, mg/g	20	20

(*) Backwashed and Drained Density for adsorber sizing.
(**) Brunauer, Emmett and Teller, J.Am. Chem. Soc. 60, 309 (1938).
(***) Isotherm loading in distilled water. These are reported for comparison and are unlikely to reflect loadings in practice.

RECYCLING BY THERMAL REACTIVATION

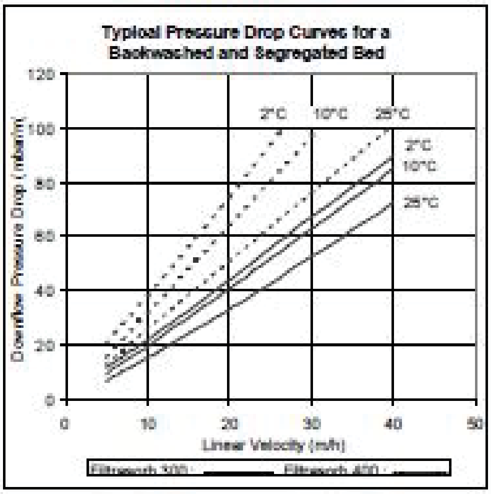
Once granular carbon is saturated or the treatment objective is reached, it can be recycled, by thermal reactivation, for reuse. Reactivation involves treating the spent carbon in a high temperature reactivation furnace to over 800°C. During this treatment process, the undesirable organics on the carbon are thermally destroyed. Recycling by thermal reactivation is a highly skilled process to ensure that spent carbon is returned to a reusable quality. **Chemviron Carbon** operates Europe's largest reactivation facilities and daily recycles large quantities of spent carbon for a divers range of customers. Recycling activated carbon by thermal reactivation meets the environmental need to minimise waste, reducing CO_2 emissions and limiting the use of the world's resources.

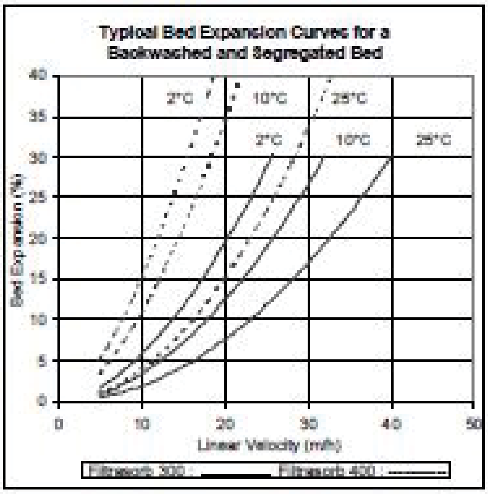
The combined high mechanical strength of **Filtrasorb® 300** and **400** with the transport pores gives the carbon **excellent reactivation performance and low losses.**

Product Bulletin

Visit our website at www.chemvironcarbon.com to learn more about our complete range of products and services, and local contact information.

Responsible Care® Good Chemistry at Work


Typical Pressure Drop Curves for a Backwashed and Segregated Bed


Typical Bed Expansion Curves for a Backwashed and Segregated Bed

DESIGN INFORMATION

The following are typical design parameters for **Filtrasorb® 300 and 400** installed for the treatment of surface water.

• Empty bed contact time	10-30min.
• Bed depth	1-3m
• Linear velocity	5-20m/h
• Backwash bed expansion	20%

PACKAGING

- 25kg bags
- Big bags
- Bulk tanker

SAFETY MESSAGE

Wet activated carbon preferentially removes oxygen from air. In closed or partially closed containers and vessels, oxygen depletion may reach hazardous levels. If workers are to enter a vessel containing carbon, appropriate sampling and work procedures for potentially low-oxygen spaces should be followed.

QUALITY

Each of our worldwide operations has achieved **ISO9002** certification for their quality management system related to activated carbon. **Chemviron Carbon** guarantees the quality and consistency of every **Filtrasorb® 300 and 400** shipment and all specifications are guaranteed against representative sampling.

CHEMVIRON CARBON

Chemviron Carbon, the European operation of Calgon Carbon Corporation, is a global manufacturer, supplier, and developer of granular activated carbon, innovative treatment systems, value added technologies, and services for optimising production processes and safely purifying the environment.

With over 60 years of experience, facilities around the world, and a world-class team of over 1,000 employees, Calgon Carbon Corporation can provide the solutions to your most difficult purification challenges.

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