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Ramatisa Ladeia Ramos

MEMBRANE DISTILLATION IN WATER TREATMENT AND RETENTION OF PHENOLIC COMPOUNDS: EVALUATION OF BENCH AND PILOT SCALE

Belo Horizonte
2023

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Tese de doutorado apresentada ao Programa de Pós-Graduação em Saneamento, Meio Ambiente e Recursos Hídricos da Universidade Federal de Minas Gerais como requisito parcial à obtenção do título de Doutor em Saneamento, Meio Ambiente e Recursos Hídricos.

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Orientadora: Dra. Míriam Cristina Santos Amaral Moravia

Coorientadora: Dra. Lucilaine Valéria de Sousa Santos

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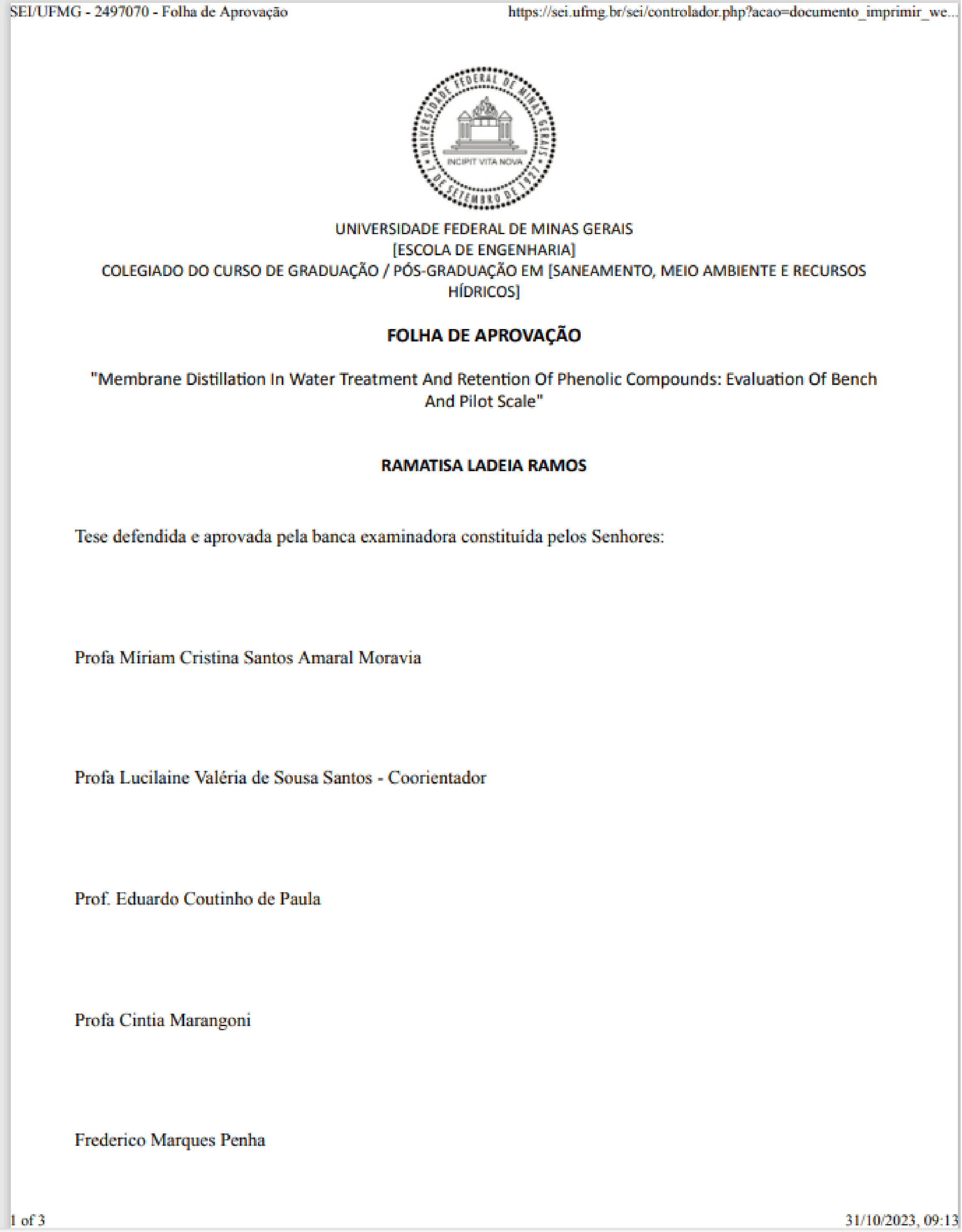

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"Membrane Distillation In Water Treatment And Retention Of Phenolic Compounds: Evaluation Of Bench And Pilot Scale"

RAMATISA LADEIA RAMOS

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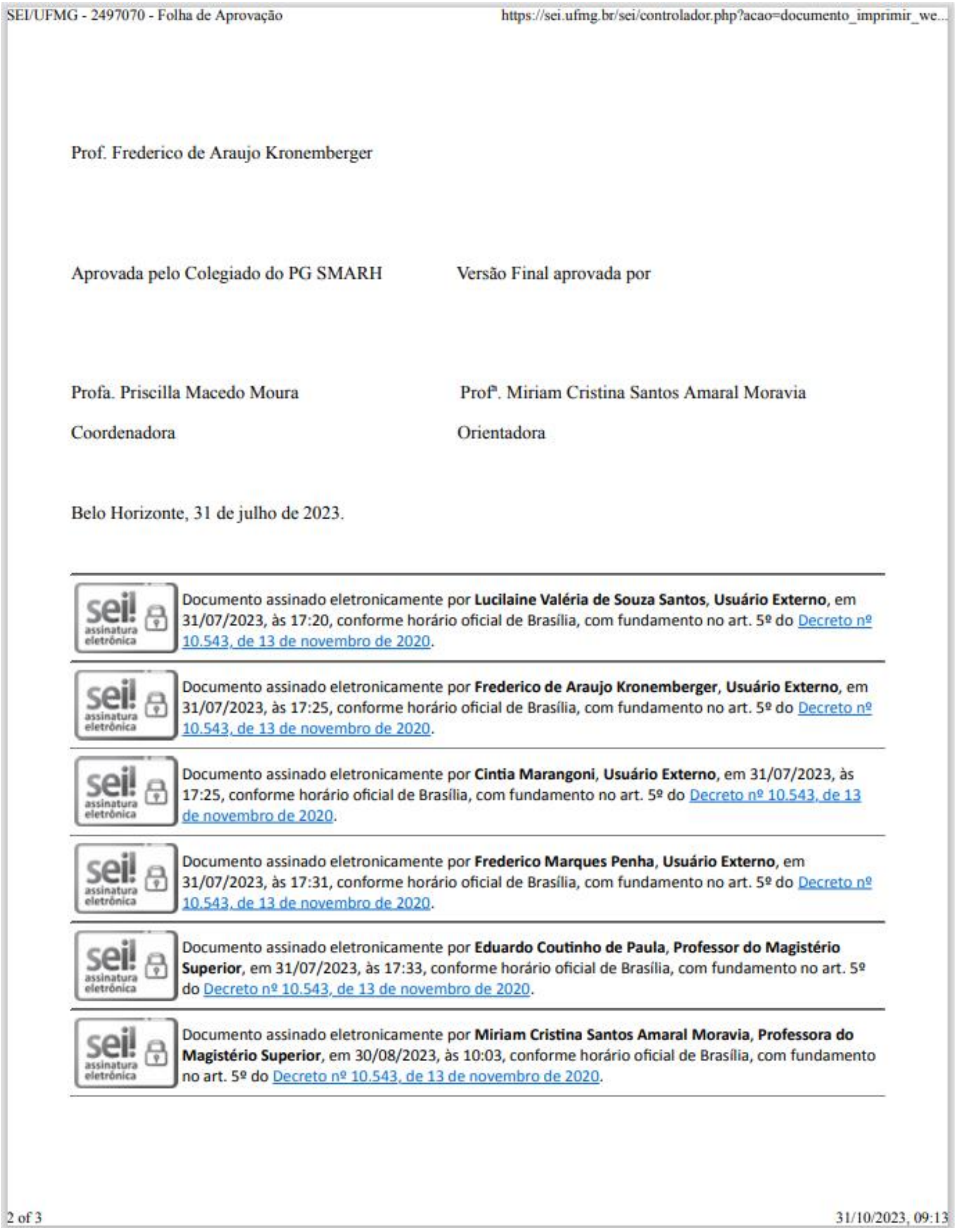

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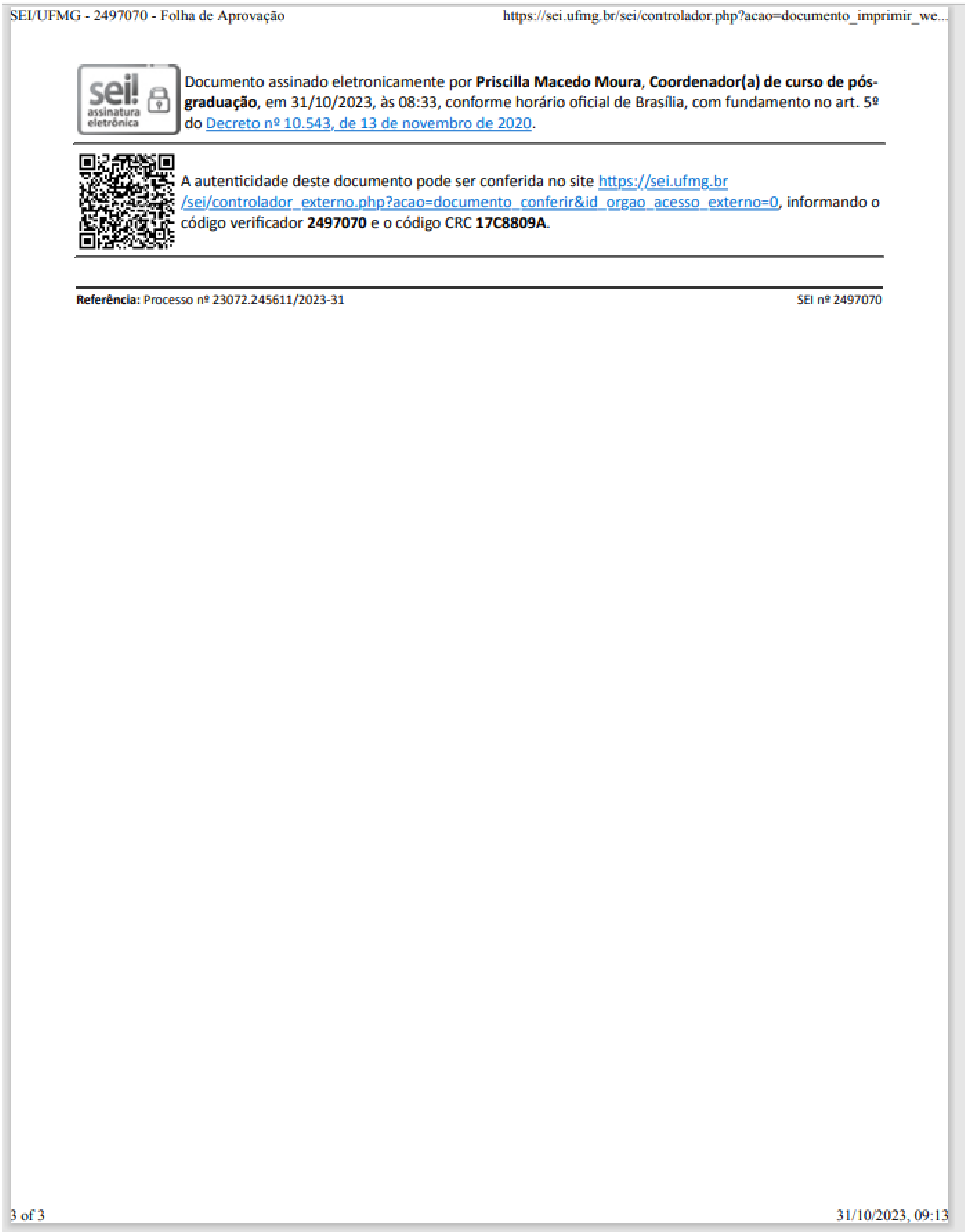

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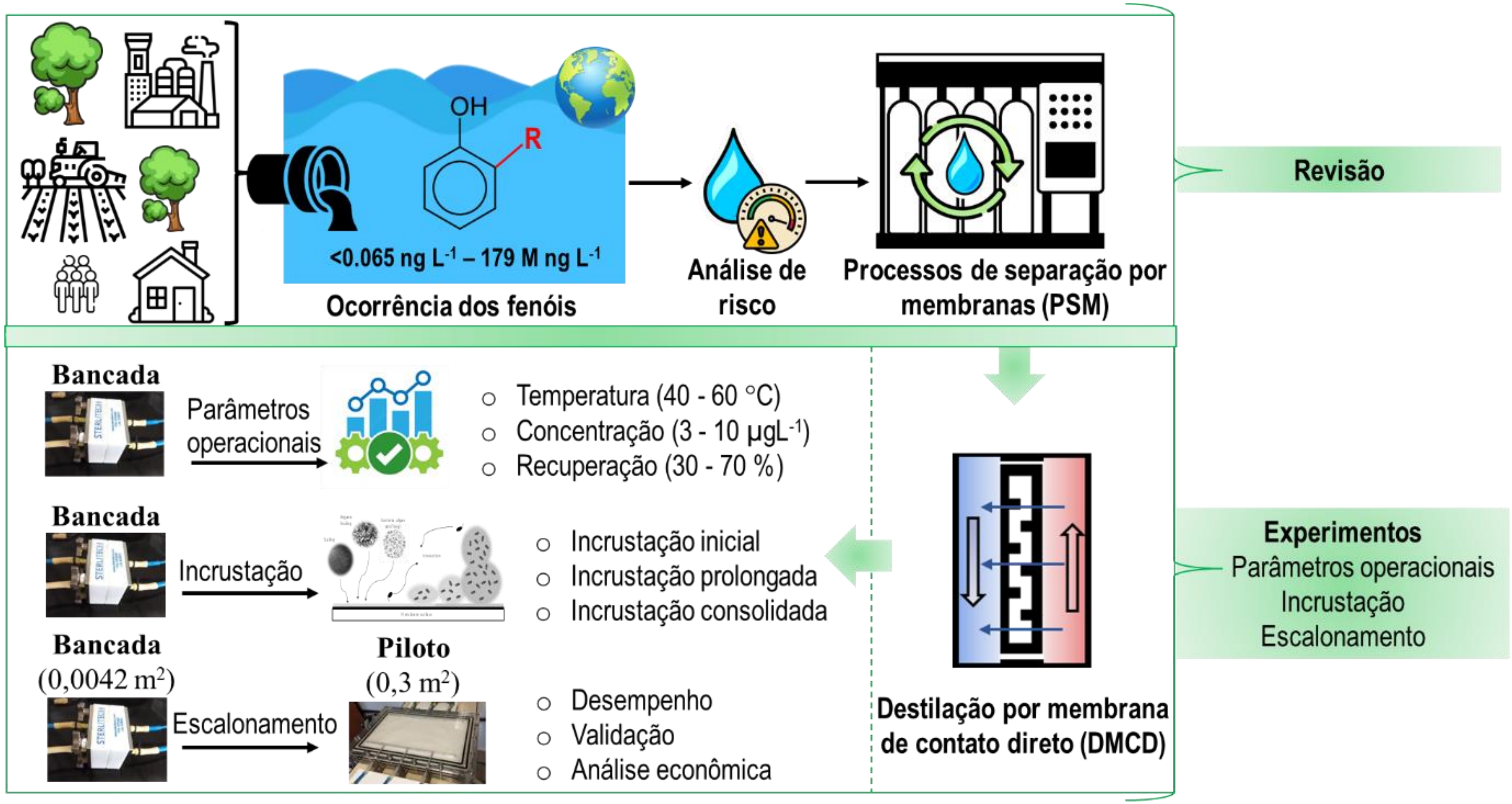
“Why science? To improve humanity's life in balance with nature... every drop of knowledge matters!”
(Por que a ciência? Para melhorar a vida da humanidade em equilíbrio com a natureza... cada gota de conhecimento importa!)
R. L. Ramos, 2023

RESUMO

A poluição das fontes de água por compostos fenólicos é um problema na sociedade contemporânea associado a uma expectativa de alto consumo deste recurso. A destilação com membranas por contato direto (DMCD) tem atraído a atenção para aplicações no tratamento de água e remoção de micropoluentes, devido a sua estabilidade, modularidade e robustez. Além disso, ela pode ser associada à fontes de energia alternativas como as renováveis e calor residual. Nesse contexto, buscando soluções para problemas estabelecidos, esse trabalho estudou a remoção de compostos fenólicos em água superficial pela DMCD. Para tanto, foi realizada uma pesquisa de revisão de literatura (2000-2023), que constatou a ocorrência de mais de 60 fenóis nas fontes de água de diversos países em concentrações variando de <0,065 a 179 M ng L^{-1}. Os riscos para a saúde humana foram estimados com as concentrações reportadas na literatura, mostrando resultados preocupantes para alguns fenóis, tais como 2-nitrofenol, 2,6-diclorofenol, 3,4,5-triclorofenol, 2,3,4,6-tetraclorofenol, 2,4-dinitrofenol, 3-metilfenol, 2,4-dimetilfenol, 2,4,6-triclorofenol e pentaclorofenol. A importância do setor de tratamento de água na remoção destes micropoluentes foi ressaltada, assim como a incorporação de mais composto fenólicos nas diretrizes de água potável para proteção das populações. As possibilidades de remoção de fenóis pelas tecnologias de membranas foram elencadas, sendo destacadas as altas remoções da osmose inversa, como uma tecnologia madura e com a menor pegada ecológica estimada, e da destilação por membrana, como uma tecnologia emergente. Experimentos foram feitos utilizando a DMCD em escala de bancada para avaliar as condições operacionais de temperatura (40, 50 e 60 °C), concentração da alimentação (3, 5, 7 e 10 µg L^{-1}), recuperação de permeado (30, 50 e 70 %) e os efeitos da incrustação na retenção dos compostos fenólicos. A tecnologia foi eficiente com >90 % de remoção dos poluentes, mesmo para operações do processo com maiores temperaturas (60 °C) e recuperação do permeado (70 %). As variações da concentração da alimentação estudadas, não afetaram a qualidade do permeado gerado e a camada de incrustação formada favoreceu a concentração dos compostos fenólicos na solução de alimentação, praticamente, sem perda de massa no processo. Porém, com a incrustação houve um alto decaimento do fluxo de permeado em um curto período de tempo, sendo indicado a necessidade de estudar estratégias de pré-tratamento da água bruta e limpeza periódica do sistema. Experimentos, também foram realizados com o objetivo de avaliar o escalonamento da unidade de DMCD de bancada (0,0042 m^2) para piloto (0,3 m^2). Além disso, foi elaborado uma análise econômica considerando um sistema de DMCD para o tratamento de água móvel (5,5 m^3 d^{-1}), distribuído (11 m^3 d^{-1}) e centralizado (535.680 m^3 d^{-1}). Dentre os resultados alcançados, destaca-se que, o escalonamento do sistema não afetou a remoção dos fenóis. Ainda, foi evidenciado que a DMCD pode ser economicamente atraente para aplicações no tratamento de águas superficiais em larga escala, devido a redução da amortização dos altos custos de investimentos iniciais com a maior produção de água. Os custos operacionais dos sistemas DMCD foram comparados quanto ao uso de energia solar e de fontes elétricas convencionais. Os maiores valores foram relacionados ao emprego da energia solar devido à aquisição dos painéis fotovoltaicos, que aumentaram o valor da amortização. Algumas estratégias foram levantadas para diminuir os custos do investimento inicial, como o tratamento parcial da água (sistema menor), da amortização, trabalhando com a capacidade de processo >10.600 m^3 d^{-1}, e da energia gasta no trocador de calor, diminuindo a variação da temperatura entre as correntes da DMCD (ΔT) de 35 °C para 30 °C (OPEX: 0,50 US$ m^{-3} - 0,19 US$ m^{-3}). Assim, a DMCD foi profundamente estudada para aplicação no tratamento de água e remoção de compostos fenólicos, pensando em um cenário moderno, robusto e mais seguro para o setor. Os desafios, também foram listados, deixando espaço para estudos futuros sobre como melhorar a eficiência energética do processo, aumentar o fluxo de permeado, reduzir custos e gerir o concentrado gerado.

Palavras-chave: Compostos fenólicos; fontes de água; risco para saúde humana; tratamento de água; destilação por membrana de contato direto; análise econômica.

RESUMO GRÁFICO

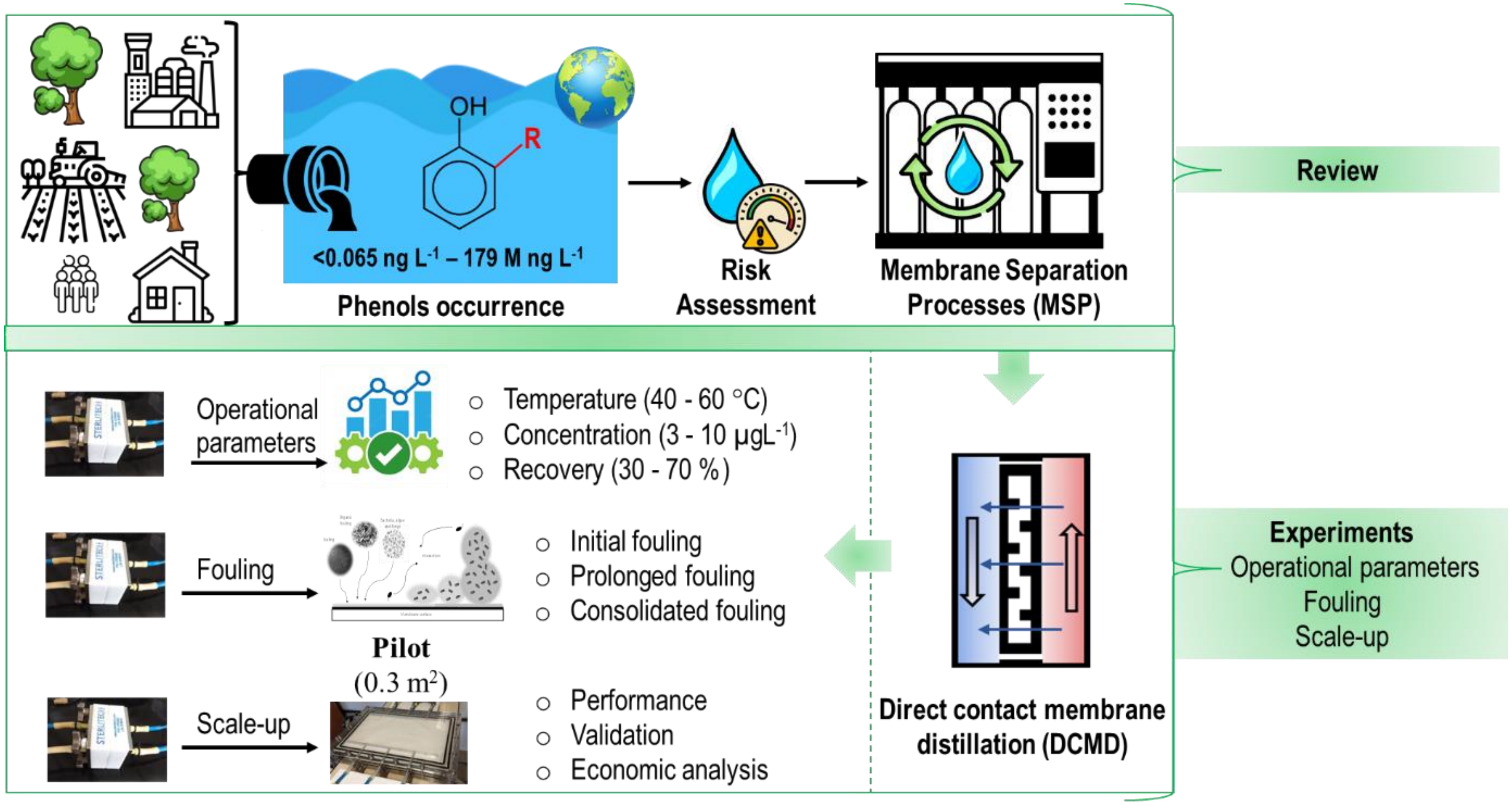


ABSTRACT

The pollution of water sources by phenolic compounds is a problem in contemporary society associated with an expectation of high consumption of this resource. Direct contact membrane distillation (DCMD) has attracted attention to applications in water treatment and removal of micropollutants, due to its stability, modularity, and robustness. In addition, it can be associated with alternative energy sources such as renewable and waste heat. In this context, seeking solutions to established problems, this work studied the removal of phenolic compounds in surface water by DCMD. Therefore, a literature review (2000-2023) was conducted, which found the occurrence of more than 60 phenols in water sources in several countries at concentrations ranging from <0.065 to 179 M ng L^{-1}. The risks to human health were estimated with the concentrations reported in the literature, showing concerning results for some phenols, such as 2-nitrophenol, 2,6-dichlorophenol, 3,4,5-Triclorophenol, 2,3,4,6-tetrachlorophenol, 2,4-dinitrophenol, 3-methylphenol, 2,4-dimethylphenol, 2,4,6-Triclorophenol, and pentachlorophenol. The importance of the water treatment sector in the removal of these micropollutants was emphasized, as well as the incorporation of more phenolic compounds in the drinking water guidelines for the protection of populations. The possibilities of phenol removal by membrane technologies were listed, highlighting the high removals of reverse osmosis as a mature technology with the lowest estimated ecological footprint, and membrane distillation as an emerging technology. Experiments were performed using bench scale DCMD to evaluate the operating conditions of temperature (40, 50, and 60 °C), feed concentration (3, 5, 7, and 10 µg L^{-1}), permeate recovery (30, 50, and 70 %), and the fouling effects on the retention of phenolic compounds. The technology was efficient with >90 % removal of pollutants, even for process operations with higher temperatures (60 °C) and permeate recovery (70 %). The variations of the feed concentration studied, did not affect the quality of the permeate generated and the fouling layer formed favored the concentration of phenolic compounds in the feed solution, practically, without loss of mass in the process. However, with the fouling there was a high decay of the permeate flux in a short period, being indicated the need to study strategies of pre-treatment of raw water and periodic cleaning of the system. Experiments were also performed to evaluate the scale-up of the DCMD unit from bench (0.0042 m^2) to pilot (0.3 m^2). Furthermore, an economic analysis was developed considering mobile (5.5 m^3 d^{-1}), distributed (11 m^3 d^{-1}), and centralized (535,680 m^3 d^{-1}) DCMD water treatment systems. Among the results achieved, it is noteworthy that the system scale-up did not affect the removal of phenols. Also, it was evidenced that DCMD can be economically attractive for applications in surface water treatment on a large scale, due to the reduction of the amortization of the high initial investment costs with the higher water production. The operating costs of DCMD systems were compared for the use of solar energy and conventional electrical sources. The highest values were related to the use of solar energy due to the acquisition of photovoltaic panels, which increased the value of the amortization. Some strategies were raised to reduce the costs of the initial investment, such as the partial treatment of water (smaller system), amortization, working with a processing capacity >10,600 m^3 d^{-1}, and the energy spent on the heat exchanger, decreasing the temperature variation between the DCMD currents (ΔT) from 35 °C to 30 °C (OPEX: 0.50 US$ m^{-3} - 0.19 US$ m^{-3}). Thus, DCMD was deeply studied for application in water treatment and removal of phenolic compounds, considering a modern, robust, and safer scenario for the sector. The challenges were also listed, leaving room for future studies on how to improve process energy efficiency, increase permeate flux, reduce costs, and manage the generated concentrate.

Keywords: Phenolic compounds; water sources; risk to human health; water treatment; direct contact membrane distillation; economic analysis.

GRAPHIC ABSTRACT



LIST OF PUBLICATIONS

Thesis related publications

RAMOS, R. L.; LEBRON, Y. A. R.; MOREIRA, V. R.; MARTINS, MATEUS F.; SANTOS, L. V. S.; AMARAL, M. C.S. Direct Contact Membrane Distillation as an approach for water treatment with phenolic compounds. Journal of Environmental Management, v. 303, 114117, 2022.

RAMOS, R. L.; MOREIRA, V. R.; LEBRON, Y. A. R.; SANTOS, L. V. S.; AMARAL, M. C.S. Fouling in the membrane distillation treating superficial water with phenolic compounds. Chemical Engineering Journal, v. 437, 135325, 2022.

RAMOS, R. L.; MOREIRA, V. R.; LEBRON, Y. A. R.; MATEUS F., SANTOS, L. V. S.; AMARAL, M. C.S. Direct contact membrane distillation for surface water treatment and phenolic compounds removal: From bench to pilot scale. Desalination, v. 574, 117225, 2024.

RAMOS, R. L.; **.**; MOREIRA, V. R.; AMARAL, M. C.S. Phenolic compounds in surface water: A review of occurrence, risks and removal by membrane separation processes. Journal of Environmental Management, v. 351, 119772, 2024.

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RAMOS, R. L.; MOREIRA, V. R.; LEBRON, Y. A. R.; SANTOS, L. V. S.; AMARAL, M. C. S. Remoção de BPA de água superficial usando destilação por membrana em escala de bancada e semi piloto. In: 32° Congresso Brasileiro de Engenharia Sanitária e Ambiental (ABES), 2023, Belo Horizonte (Brazil).

RAMOS, R. L.; LEBRON, Y. A. R.; MOREIRA, V. R.; MARTINS, M.; SANTOS, L. V. S.; AMARAL, M. Membrane distillation for phenolic compounds removal from surface water. In: Euromembrane, 2022, Sorrento (Italy).

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RAMOS, R. L.; MOREIRA, V. R.; LEBRON, Y. A. R.; MARTINS, M.; SANTOS, L. V. S.; AMARAL, M. C. S. Membrane distillation for decentralized drinking water treatment: Assessment of BPA removal. In: 23° Congresso de Engenharia Química (COBEQ), 2021, Gramado (Brazil).

RAMOS, R. L.; LEBRON, Y. A. R. ; MOREIRA, V. R. ; SANTOS, L. V. S. ; AMARAL, M. C. S. Identificação e quantificação de compostos fenólicos no rio Doce após desastre ambiental e análise de risco. In: III Simpósio da Bacia Hidrográfica do Rio São Francisco, 2020, Belo Horizonte (Brazil).

Other works

Awarded business idea (third place) in the *"E-Hackathon en Agua, Saneamiento e Higiene en Asentamientos Informales de América Latina y el Caribe (2020)"*, Banco Interamericano de Development and BID Lab, CEWAS and Young Water Solutions. Subject: Recycled membranes for gray water treatment.

DAAD fellowship for 1 year (2021/22) at the Karlsruhe Institute of Technology (KIT) in the Institute for Advanced Membrane Technology (IAMT) (Germany) under the supervision of Prof. Dr. Andrea Schäfer (sandwich PhD). Subject: Water desalination with batch and single-pass electrodialysis systems.

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

AF – Assessment factor

AGMD – Air gap membrane distillation

A_m – Membrane area

APHA – Standard methods for the examination of water and wastewater

AT – Averaging times in days

b_m – Body mass

BPA – Bisphenol A

c – Daily water consumption

C – Highest phenolic compound concentration in the water source

C_a – Bare module cost

CAPEX – Capital expenditures

C_b – Equipment costs

C_d – Solute concentrations in the distillate

C_f – Feed specific heat

CSF – Cancer slope factor

CP – Concentration polarization

C_p – Feed water specific heat

CR – Cancer risk

C_r – Solute concentrations in the retentate

DCMD – Direct contact membrane distillation

DI – Daily input

DLLME – Dispersive liquid-Liquid microextraction

DOC – Dissolved organic carbon

DWEL – Safe exposure level

E_E – Electric energy

ED – Exposure duration

ED – Electrodialysis

EDX/EDS – Energy dispersion x-ray

EFSA – European food safety authority

EPA – Environmental protection agency (United States)

EPS – Extracellular polymeric substances

E_T – Thermal energy

f – Contribution of water to exposure

FID – Flame ionization detector

GC – Gas chromatography

GOR – Gained output ratio

h_f – Feed convective heat transfer coefficient

h_m – Membrane convective heat transfer coefficient

h_p – Permeate convective heat transfer coefficient

HPLC – High-performance liquid chromatography

HRA – Human health risk assessment

ICH – International council for harmonization of technical requirements for pharmaceutical products for human use

i_r – Investment rate

J_p – Permeate flux

LEP – Liquid entry pressure

LLE – Liquid-Liquid Extraction

LOAEL – Lowest observed adverse effect level

LOD – Limit of detection

Log D – Aqueous partition coefficient

LOQ – Limit of quantification

l_s – Project lifespan

m_d – Compound mass in the distillate

MD – Membrane distillation

m_{df} – Distillate final mass

m_{di} – Distillate initial mass

MF – Microfiltration

m_f – Compound mass in the feed

m_{fi} – Feed initial mass

m_{fr} – Feed mass flow rate

M_i – Contaminant total initial mass

MOE – Margin of exposure

MPS – Membrane separation processes

MPS – Maximum permitted concentration

M_S – Mass lost

MWCO – Molecular weight cut-off

m_1 and m_2 – Permeate mass

n – Number of research

n – Factor exponent

NF – Nanofiltration

NOAEL – Non-observed adverse effect level

NOM – Natural organic matter

OPEX – Operational expenditure

P_f – Bulk vapor pressure at feed side

PKa – Negative logarithm of the acidity constant

pK_H – Henry constant

PM – Photocatalytic membrane

P_p – Bulk vapor pressure at permeate

PR – Permeate recovery

PTFE – Polytetrafluoroethylene

P_1 – Membrane surface vapor pressure at feed side

P_2 – Membrane surface vapor pressure at permeate side

Q_m – Total heat flux through the membrane

R_m – Membrane resistance

RO – Reverse osmosis

RR – Recovery rate

RF – Removal factor

R_{fb} – Feed boundary layer resistance

$R_{fouling}$ – Fouling resistance

R_{pb} – Permeate boundary layer resistance

R_t – Total resistance

RW – Raw water

S_a – Base variable

S_b – Real equipment variables

SBSE – Stir-Bars Sorptive Extraction

SEC – Specific energy consumption

SEM – Scanning electron microscopy

SGMD – Sweeping gas membrane distillation

SPE – Solid phase extraction

STP – Sewage treatment plant

T – Temperature

TDI – Tolerable daily intake

TE – Thermal efficiency

T_f – Temperature at bulk for feed

T_{fin} – Temperature at the feed in

T_{fou} – Temperature at the feed out

TN – Total nitrogen

TOC – Total organic carbon

T_p – Temperature at bulk for permeate

TPC – Temperature polarization coefficient

TrOCs – Trace organic compounds

TS – Total solids

TSS – Total suspended solids

$T_{w,f}$ – Temperature at interface of feed

$T_{w,p}$ – Temperature at interface of permeate

t_1 and t_2 – Time

UF – Ultrafiltration

UPLC/UHPLC – Ultra-performance liquid chromatography

V_d – Distillate volume

VMD – Vacuum membrane distillation

VOC – Volatile and semi-volatile organic compounds

V_r – Retentate volume

WHO – World health organization

WTP – Water treatment plant

WWTP – Wastewater treatment plant

ΔH_v – Vaporization heat

ΔP – Pressure experienced by the membrane

ρ – Water density

η – Pump efficiency

2CP – 2-chlorophenol

2MP – 2-methylphenol

2NP – 2-nitrophenol

24DMP – 2,2-dimethylphenol

24DCP – 2,4-dichlorophenol

26DCP – 2,6-dichlorophenol

234TCP – 2,3,4-trichlorophenol

235TCP – 2,3,5-trichlorophenol

2356TCP – 2,3,5,6-trichlorophenol

246TCP – 2,4,6-trichlorophenol

245TCP – 2,4,5-trichlorophenol

345TCP – 3,4,5-trichlorophenol

3MP – 3-methylphenol

4C3MP – 4-chloro-3-methylphenol

TABLE OF CONTENTS

CHAPTER I – THEME PRESENTATION

1.1 BACKGROUND

The water resources quality is deteriorating over time due to the continuous addition of undesirable chemicals, population and economic growth, longer periods of river flow reduction, and environmental disasters (UN, 2023). In recent years, with the development of analytical techniques, several articles have reported the presence of phenolic compounds in aquatic environments and drinking water with concentrations ranging from <0.065 to 179 M ng L^{-1} (PETRIE et al., 2016; WANG and WANG, 2018; CHAKRABORTY et al., 2021). In Brazil, Ramos et al. (2021) monitored the occurrence of phenols in raw and drinking water from a conventional water treatment plant (WTP) in the state of Minas Gerais, revealing the presence of seventeen phenolic compounds. The average concentration range of these pollutants in the raw water was 260 – 14,370 ng L^{-1} and in the treated water was 230 – 12,990 ng L^{-1} during one year of monitoring. Other concerning results of Ramos et al. (2021) were that five phenols increased their concentration and two were generated as by-products after the WTP.

The presence of phenolic compounds in drinking water, even at low concentrations, can cause adverse effects on human health (ZHONG et al., 2018). Potential risks reported include cancer, genetic malformations, and damage to the immune system (MOHAMMADI and KAZEMI, 2014). Phenols and their derivatives are introduced into rivers through natural degradation, agricultural practices, domestic sewage, and industrial effluent discharges (WANG and WANG, 2018). The World Health Organization (WHO) establish a maximum permitted concentration (MPC) of phenolic content in drinking water of 1 µg L^{-1} (WHO, 2017). Phenolic compounds are on the priority pollutant list of the United States Environmental Protection Agency (EPA, 2014), which determined, depending on the compound, the MPC for human consumption in water from 0.03 µg L^{-1} to 4,000 µg L^{-1} (EPA, 2019). However, in general, the guidelines do not present MPC for most of the phenols detected in water sources, being a necessary objective to be reached to prevent contamination.

The conventional WTP, which comprises coagulation, flocculation, sedimentation, and filtration, is still widely used and is ineffective in removing many phenolic compounds (KARABELAS and PLAKAS, 2011). There are different physical, chemical, and biological methods, such as activated carbon adsorption, chemical oxidation, and aerobic and anaerobic biological degradation, which have been used to remove these compounds from water. However, these methods have many limitations, such as incomplete treatment, high cost, generation of toxic by-products, and instability (JIN et al., 2007; MOHAMMADI and

KAZEMI, 2014). For example, the biodegradation of chlorophenol is not viable because it has slow and incomplete kinetics and the products formed are more toxic to the environment and to humans than the precursors (AGHAV et al., 2011). For a conventional WTP to remove these pollutants it would be necessary to resort to alternative techniques, such as membrane separation processes (MSP).

A variety of membranes have been developed to remove contaminants from water, ranging from particles and pathogens to dissolved organic compounds and salts. Treatment plants typically use polymeric membranes for microfiltration (MF) or ultrafiltration (UF) in conjunction with reverse osmosis (RO) and, in some cases, nanofiltration (NF). Advances in membrane technology, including new materials, coatings, and manufacturing methods, as well as membrane bioreactors, electrodialysis (ED), direct osmosis, photocatalytic membrane, pervaporation, and membrane distillation (MD), have been developed to improve selectivity, energy consumption, fouling resistance, and capital costs. MD is a thermally conducted separation process in which a hydrophobic microporous membrane separates a hot feed stream and a cold receiving phase (LISBOA et al., 2021). The driving force of mass transport is the temperature gradient, which results in a water vapor pressure differential, causing vapor transport through the membrane pores. The main competitive advantage of MD is that the distillation occurs below the normal boiling point of the feed solution (BANAT et al., 2007) and one of the attractive features of the technology is the theoretical rejection of 100 % of non-volatile components, such as salts, inorganic compounds, and macromolecules (THOMAS et al., 2017).

MD can be applied in a variety of feed solutions for different water treatment scenarios, as it is robust, compact/modular, stable, easy to transport, and can remove at the same time some micropollutants, salts, metals, and other toxic substances (THOMAS et al., 2017). Comparing MD with NF, RO, and ED, it has some advantages, such as versatility in energy sources, which allows its association with geothermal, solar, and industrial waste heat. In addition, MD works at ambient pressure, which increases system safety and reduces equipment costs (MANNA and PAL, 2016). Besides that, it is more resistant to concentration polarization (CP) than other membrane separation processes, allowing the treatment of concentrated solutions in the feed (COSTA et al., 2021). Despite advantages, membrane fouling can affect the long-term performance and stability of the process (TIJING et al., 2015).

Fouling in MD is impacted by the operating conditions (*e.g.:* temperature and flow velocity), the membrane properties, and especially the feed solution characteristics, such as pH, organic and inorganic compounds concentration, typical microbiota, solubility, and hydrophobicity (ALKHATIB et al., 2021). Fouling can occur due to the accumulation of unwanted materials on the membrane surface or inside the pores (pore blockage). According to the material, fouling is divided into inorganic, organic, and biological (MENG et al., 2009). Inorganic scale is mainly caused by crystallization and precipitation of salts such as carbonates, phosphates, sulfates, sodium chloride, and metallic deposits. Organic fouling occurs due to the adsorption or deposition of colloidal organic compounds such as proteins, polysaccharides, humic acids, and polymers or extracellular polymeric substances (EPS) (COSTA et al., 2021). Biological fouling, or biofouling, consists of microorganisms' deposition, growth, and execution of metabolic activity on the membrane surface, forming a complex layer that covers the membrane due to a polymeric matrix secreted (MANSOURI et al., 2010).

In previous studies, MD biofouling did not receive much attention, as it usually operates at higher temperatures, which most of the microorganisms cannot survive. Therefore, the consequences were underestimated in assuming that biofouling could be inhibited by high temperatures in the feed concentration (GRYTA, 2002). However, it has been noticed that biofouling can compromise MD performance, resulting in flux decay and compound removal can decrease. In addition, it can reduce membrane lifespan and potentially lead to membrane pore wetting (LIU et al., 2020). MD fouling is often considered less severe and less compact than in other membrane processes since the MD membrane has larger pores and no pressure is applied (COSTA et al., 2021). It is noteworthy that more studies is needed to expand the knowledge of the biofilm formation consequences on MD performance.

Among the MD configurations, there are variations according to how the steam is recovered in the permeate side, as it migrates through the membrane. It can be classified as direct contact MD (DCMD), air gap MD (AGMD), vacuum MD (VMD), and sweeping gas MD (SGMD) (QTAISHAT and BANAT, 2013). DCMD is the oldest and most used process (ASHOOR et al., 2016), having liquid phases in direct contact with both sides of the membrane, where there is a simultaneous transfer of heat and mass determined by the heat flux and transfer coefficients in the feed and permeate sides (QTAISHAT et al., 2008). In DCMD, the vapor diffusion path is limited to the thickness of the membrane, thus reducing the heat and mass transmission resistances. Condensation inside the pores is avoided by selecting the appropriate temperature difference (ASHOOR et al., 2016). The operating temperature is one of the main factors affecting the system. Higher temperatures are preferable for an increase in mass transfer, as the vapor pressure difference between the sides increases, consequently, the permeate flux will increase (YU et al., 2012). However, there is always a threshold for the feed temperature due to the temperature polarization, which results in the reduction of the temperature difference between the two sides of the membrane, due to the increase in heat transfer, and it can decrease the permeate flux (LISBOA et al., 2021).

DCMD is widely used in research on bench-scale systems. It is essential to extrapolate these studies to larger scales as a pilot since the combination of results can be better interpreted for real applications of the technology. DCMD can be used in centralized, decentralized, and mobile water treatment systems (*e.g.:* trucks, trailers, among others). Decentralized drinking water systems, also known as distributed water treatment, are an important element in the process of achieving the 2030 Agenda for Sustainable Development (UN, 2019), as centralized processes are often deficient or nonexistent in developing countries (PETER-VARBANETS, 2009). The decentralized system places small plants close to the use point for more flexibility and efficiency, as this eliminates the need for expensive pipelines to connect to central WTP. It can be an ideal solution for a variety of residential, commercial, and industrial applications including small communities, university towns, commercial developments, hotels and resorts, industrial plants, mining, oil and gas fields, construction sites, and many others. There are good prospects for decentralized membrane systems. Chafidz et al. (2016) worked on the development of a mobile and energy-independent solar MD unit. This treatment plant can be operated in remote areas where electricity and clean water are not readily available. Due to its portability, it can be used in emergencies where clean water is essential for survival, such as natural disasters. Thus, with water scarcity, stricter environmental regulations, and the cost of capital equipment on the rise, many companies are choosing mobile water treatment for emergency, seasonal, and short-term needs (SUEZ, 2021). The focus to continue researching and developing systems with low cost, low maintenance, operational ease, sustainability, and independence of public services (energy sources) is fundamental to increasing applications.

Costs incurred for DCMD, as for any other membrane technology, are a function of installation capacity, type and power quality, need for pre-treatment, energy cost, system life, and amortization of investments (SAFFARINI et al., 2012). MD life cycle costs (including both capital goods investment recovery (CAPEX) and operating expenses (OPEX)) vary greatly depending on the type of system dimensioned and the energy source, even for installations powered by the same energy type (THOMAS et al., 2017). In recent years, there has been a continuous reduction in the price of installation and operation of photovoltaic cells (SAMPAIO and GONZÁLEZ, 2017). The trend is for solar energy to be one of the main energy sources in the close future, as unlike fossil fuels, solar panels and collectors are technologies whose efficiency increases and the value decreases over time, and can be a viable alternative to reduce effectively the MD process expenses. These aspects have led to further field testing of small distributed solar-powered MD systems for commercial-scale water treatment applications (MA et al., 2021).

The water treatment with phenolic compounds challenges MD, which has applications focused on the separation of non-volatile components. However, an understanding of the transport of volatile and semi-volatile substances present in water treatment is needed (SALLS et al., 2018). It is generally assumed that these compounds will be poorly rejected by MD, and may even be concentrated in the distillate stream relative to the feed solution if the contaminants have higher vapor pressures than water (WIJEKOON et al., 2014). Some studies have examined DCMD in the retention of phenolic compounds in water, finding that it is linked to the volatility and hydrophobicity of the contaminant (WIJEKOON et al., 2014; KUJAWA et al., 2015; SALLS et al., 2018). Retention varied widely from 54 % to 95 %, showing that the behavior of each phenolic compound can also vary with the technology (WIJEKOON et al., 2014). The trace organic contaminants removal by MD is influenced by the vapor pressure (indicated by the Henry constant, H or, pKH = -Log H) and the aqueous partition coefficient (Log D) of the compound. Wijekoon et al. (2014) reported that pKH/Log D<2.5 lead to poor removal of these compounds by the technology. This result interpretation is complicated due to the incomplete mass balance, as a consequence of biotransformation, losses due to evaporation, and sorption during the tests.

For polymeric membranes, three basic mechanisms govern the compound rejection, such as size exclusion, electrostatic effects, and membrane adsorption due to physicochemical interactions between solute, solvent, and membrane. Size exclusion is generally predominant for high-pressure membranes (BELLONA et al., 2004). Rejection efficiencies are also largely affected by solute properties (molecular size, charge, volatility, and hydrophobicity) and membrane characteristics (pore size, surface charge, hydrophobicity, roughness, structure, and functional groups) (ZHAO et al., 2018). Furthermore, the degree of each factor's influence will vary with the membrane properties and the system operating parameters and conditions, as the type of fouling layer formed can reduce or increase the retention of pollutants present in water by membranes, especially for NF, RO, and ED processes (BELLONA et al., 2004). Although for MD more research is required to comprehend the mechanisms involved in the pollutants retention, specially volatile and semi-volatile compounds in the condition of organic fouling and biofilm formation, considering the differentiated driving force and transport mechanism.

In this context, a literature review was carried out to verify the occurrence of phenolic compounds in water sources, the possible risks to human health were estimated, and the application of MSP as an alternative treatment was studied. DCMD was highlighted in the water treatment and the removal of phenols, therefore, the main aim of this work was to investigate experimentally the mechanisms that involve the retention of volatile and semi-volatile phenolic compounds by the technology and how the operational variables (temperature, concentration, and recovery) and fouling can influence the phenols retention. In addition, the DCMD scale-up from bench to pilot scale was studied and an economic analysis was estimated considering mobile, distributed, and centralized water treatment systems.

1.2 HYPOTHESIS

To evaluate the DCMD technology and observe the potential applications, some hypotheses raised were:

- The permeate recovery rate, temperature, and feed concentration affect the phenolic compounds removal with emphasis on temperature. The increase in temperature decreases the removal of phenolic compounds with pK_H/Log D<2.5.
- Membrane biofouling can occur during long-term DCMD operation for water treatment, which reduce the permeate flux and can compromise the efficiency of phenolic compounds removal.
- The scale-up of the DCMD system does not affect the removal of phenolic compounds.
- DCMD can be an economically viable system for water treatment in the different scenarios evaluated.

1.3 JUSTIFICATION AND ORIGINALITY

The study of the occurrence and human health risk of phenolic compounds in water sources is directly linked to public health problems. It is expected with the results achieved in the literature review to draw attention to the growing contamination of water resources around the world, the requirement to modernize the water treatment sector with technologies capable of removing micropollutants, and the urgent need to update drinking water guidelines for the protection of populations.

In this scenario of water resources contamination by different types of complex pollutants and situations of environmental disasters, it is essential to think about the development of new robust and compact water treatment systems, since conventional water treatment routes are inefficient. DCMD combined with solar energy can be an alternative to produce high-quality drinking water. There are few scientific works published for the potabilization of surface water using this technology, which brings an innovative character to the study. DCMD is widely used in bench scale and is easy to operate, as it has a simple configuration and allows a high good quality flux when operated under the correct conditions. In this sense, the work had a stage carried out on a pilot scale, which aimed to produce data closer to reality, enriching the research and scientific contribution.

The studies in the literature involving the evaluation of this technology in the removal of semi-volatile and volatile compounds, such as phenols, are scarce. Thus, some gaps still need to be filled, such as understanding the mechanisms that involve the retention of compounds in MD and the influence of the operational parameters. The solar energy considered in the economic analysis can be justified by the fact that Brazil, a country located mostly in the intertropical region, has great potential for taking advantage of this renewable energy source throughout the year. In addition, it brings benefits to the water treatment system, as it enables its use in remote regions where there is no electrification by the conventional network, and can be applied in decentralized and mobile treatment systems, thus considerably reducing dependence on the oil market and reducing emissions of polluting gases into the atmosphere.

Therefore, the aim is that the DCMD dimensioned treatment system is able to produce water free of these toxic compounds and, thus, reduce the risks for the population, being a realistic and beneficial treatment alternative for the water sector. The research is a continuation of the investigation already started in the Graduate Program in Sanitation, Environment and Water Resources master's in the scope of identification and quantification of phenolic compounds in two rivers in Minas Gerais and treated water from a conventional water system and the presentation of MD as a preliminary treatment. Other works were also carried out by the research group validating the efficiency of MD in removing pharmaceuticals and metals from water. In this way, it is expected with this research to contribute to knowledge consolidation and enable more MD applications close to full-scale use in the Brazilian context, favoring the development of technology based on sustainable principles for pollution control.

1.4 OBJECTIVE

1.4.1 General objective

The objective of this research was to evaluate the potential of direct contact membrane distillation in surface water treatment focusing on phenolic compounds retention in bench and pilot scales for drinking water production.

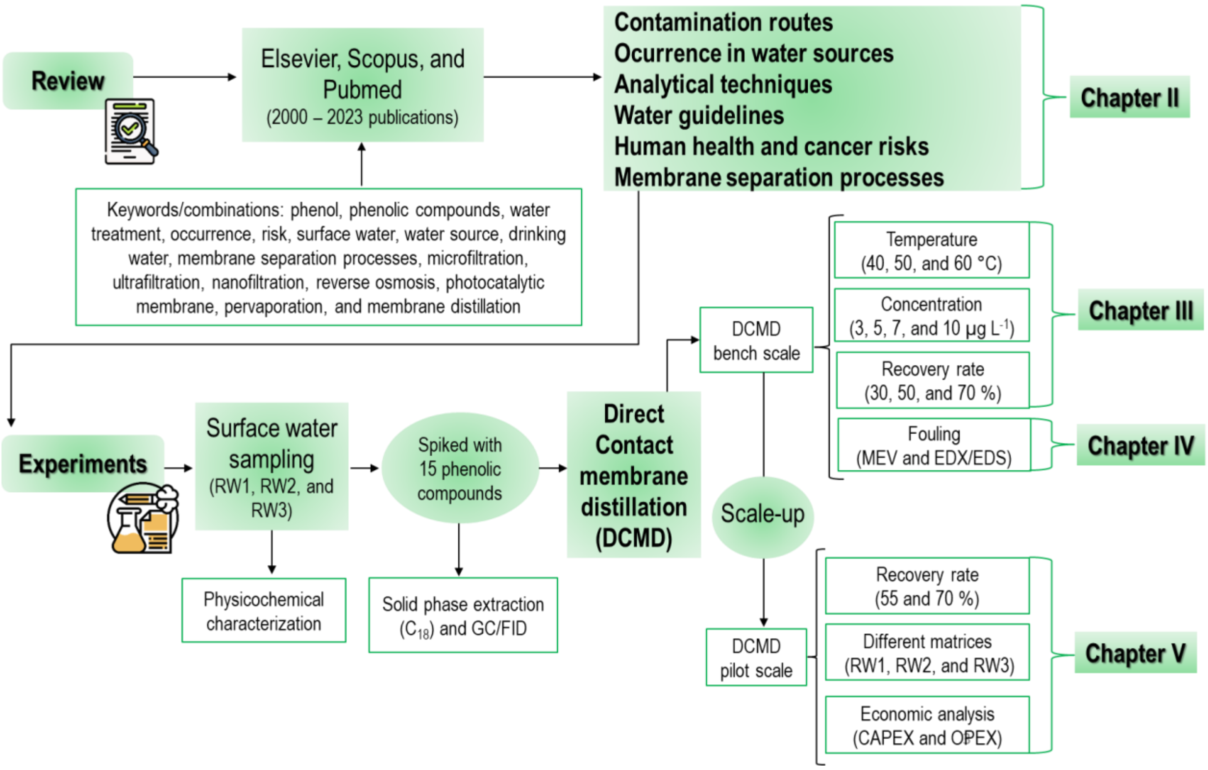
1.4.2 Specific objectives

- Compile information about the occurrence and human health risks of phenolic compounds in water sources around the world, then evaluate the MSP as an alternative for water treatment.
- Assess the effect of temperature, feed phenolic concentration, and permeate recovery on the phenolic compounds retention in DCMD at bench scale.
- Investigate the DCMD fouling mechanisms and the effect on the micropollutants retention at bench scale.
- Study the effects of the scale-up of the DCMD system (from bench to pilot) in the retention of phenols.
- Economically evaluate a mobile, distributed, and centralized water treatment system using DCMD associated with solar energy and conventional electricity.

1.5 GENERAL METHODOLOGY AND MATERIALS

The methodology for this research is illustrated in Figure 1-1 and described in subsequent sections. Note that each chapter of the thesis has the methodology used described in more detail.

Figure 1-1: Flowchart of the research methodology



*RW = raw water; GC = gas chromatography; FID = flame ionization detector.

1.5.1 Surface water sampling

Three samplings were carried out in two Brazilian watersheds, one in the Velhas River (RW1) and two samplings in the Doce River at different locations (RW2 and RW3). These points were selected due to the importance of the water bodies for public supply and their vulnerability in situations of environmental disasters. The site characteristics are described in Table 1-1.

Table 1-1: Characteristics of the sampling sites

Sample	Watershed	Collect point	Characteristics	Water use	Feed solution
RW1 	Velhas River	Velhas River in the city of Nova Lima. Coordinates: 19°59'30,1"S 43°49'39,7"W	Temperature range: 18 - 27 ° C; annual precipitation: 1390 mm; flux rate: 300 $m^3 s^{-1}$	Drinking water supply	DCMD bench and pilot scale systems (chapter III, IV, and V)
RW2 	Doce River	Doce River upstream of the Casca river outfall. Coordinates: 20°.1'11,18''S 42°.44'40,69''W	Temperature range: 21.6 - 26.9 °C; annual precipitation: 1109 mm; flux rate: 900 $m^3 s^{-1}$	Agricultural and mining	DCMD pilot scale system (chapter V)
RW3 	Doce River	Doce River upstream of the community of Cachoeira dos Óculos. Coordinates: 19°.33'15,05''S 42°.31'17,70''W	Temperature range: 21.6 - 26.9 °C; annual precipitation: 1109 mm; flux rate: 900 $m^3 s^{-1}$	Agricultural	DCMD pilot scale system (chapter V)

RW1 was used as a feed solution in Chapters III and IV, while in Chapter V all raw waters were evaluated (RW1, RW2, and RW3). The samplings were carried out considering the method of sampling, preservation, and storage of NBR 9898 for the analysis of phenols (ABNT, 1987) and the recommendations of EPA 528 (EPA, 2000).

1.5.2 Characterization of raw water and streams obtained during system operation

The raw water and the streams obtained during the operation of the DCMD systems were characterized in terms of their physicochemical properties in accordance with the recommendations of the *Standard Methods for the Examination of Water and Wastewater* (APHA, 2012). The parameters and their respective methods are shown in Table 1-2.

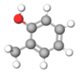
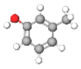
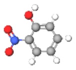
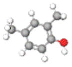
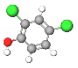
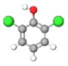
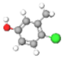
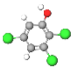
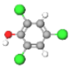
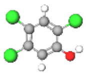
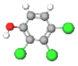
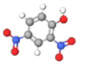
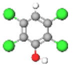
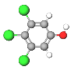
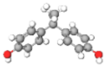
Table 1-2: Methodology for the characterization of the samples

Parameter	Method	Parameter	Method
Turbidity (Hach 2100AN Turbidimeter)	2130B	**Cations determination**	
pH (Qualxtron QX 1500 pHmeter)	4500B	Calcium (Ca)	3500-CaA
Absorption UV (254 nm) (Hach DR 2800 Spectrometer)	2120C	Magnesium (Mg)	3500-Mg
Apparent color (Hach DR 2800 spectrometer)	2120C	Sodium (Na)	3500-Na
Real color (Hach - DR 2800)	2120C	Potassium (K)	3500-K
Total suspended solids (TSS)	2540D	Iron (Fe)	3500-Fe
Total solids (TS)	2540B	Aluminum (Al)	3500-Al
Total organic carbon (TOC) (Shimadzu TOC-V CNP TOC)	5310	Arsenic (Ar)	3500-As
Electric conductivity (Hanna HI 9835 Conductivity Meter)	2510B	Lead (Pb)	3500-Pb
Alkalinity	2320B	Sulfur (S)	3500-S
Total nitrogen (TN)	4500-NC	Silica (Si)	4500-Si

1.5.3 Phenolic compounds

Fifteen phenolic compounds (Table 1-3) were studied, six from the EPA's list of priority compounds, such as 4-chloro-3-methylphenol, 2-nitrophenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 4-nitrophenol (EPA, 2014). In addition, bisphenol A, some EPA-listed isomers, and other phenols (2-methylphenol, 3-methylphenol, 2,6-dichlorophenol, 2,3,5-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4-trichlorophenol, 2,3,5,6-tetrachlorophenol, and 3,4,5-trichlorophenol) were considered, due to the use in industrial segments and recurrence in water sources. Analytical standards from Sigma-Aldrich® (EPA 8040A Phenol Calibration Mix and Bisphenol A (99%)) were used to spike the raw water with the compounds.

Table 1-3: Phenolic compounds selected for the study

Compound	Acronyms	CAS	Molar mass (g mol^{-1})	Vapor pressure at 25 °C (mmHg)[ab]	pKa[c]	pKH at pH 7[a]	Log D[b]	pKH/Log D	Molecular formula	Molecular structure
2-methylphenol	2MP	95-48-7	108.05	0.29	10.29	5.92	2.09	2.83	C_7H_8O	
3-methylphenol	3MP	108-39-4	108.05	0.20	10.10	6.07	2.09	2.90	C_7H_8O	
2-nitrophenol	2NP	88-75-5	139.02	0.113	7.23	4.89	1.36	3.59	$C_6H_5NO_3$	
2,4-dimethylphenol	24DMP	105-67-9	122.07	0.102	10.60	6.02	2.36	2.55	$C_8H_{10}O$	
2,4-dichlorophenol	24DCP	120-83-2	161.96	0.09	7.89	5.66	3.05	1.86	$C_6H_4Cl_2O$	
2,6-dichlorophenol	26DCP	87-65-0	161.96	0.0889	6.79	5.57	2.33	2.39	$C_6H_4Cl_2O$	
4-chloro-3-methylphenol	4C3MP	59-50-7	142.01	0.05	9.55	-	2.83	-	C_7H_7ClO	
2,3,5-trichlorophenol	235TCP	933-78-8	195.92	0.022	6.45	5.14	2.84	1.81	$C_6H_3Cl_3O$	
2,4,6-trichlorophenol	246TCP	88-06-2	195.92	0.008	6.23	-	2.78	-	$C_6H_3Cl_3O$	
2,4,5-trichlorophenol	245TCP	95-95-4	195.92	0.0075	7.43	4.94	3.24	1.52	$C_6H_3Cl_3O$	
2,3,4-trichlorophenol	234TCP	15950-99-0	195.92	0.00156	7.10	5.38	3.26	1.65	$C_6H_3Cl_3O$	
4-nitrophenol	4NP	100-02-7	139.02	0.0000979	7.15	9.38	1.31	7.16	$C_6H_5NO_3$	
2,3,5,6-tetrachlorophenol	2356TCP	935-95-5	229.88	0.000168	5.14	6.03	2.01	3.00	$C_6H_5NO_3$	
3,4,5-trichlorophenol	345TCP	609-19-8	195.92	0.000496	7.84	5.70	3.68	1.55	$C_6H_3Cl_3O$	
bisphenol A	BPA	80-05-7	228.11	0.000000227	9.60	9.40	3.63	2.59	$C_{15}H_{16}O_2$	

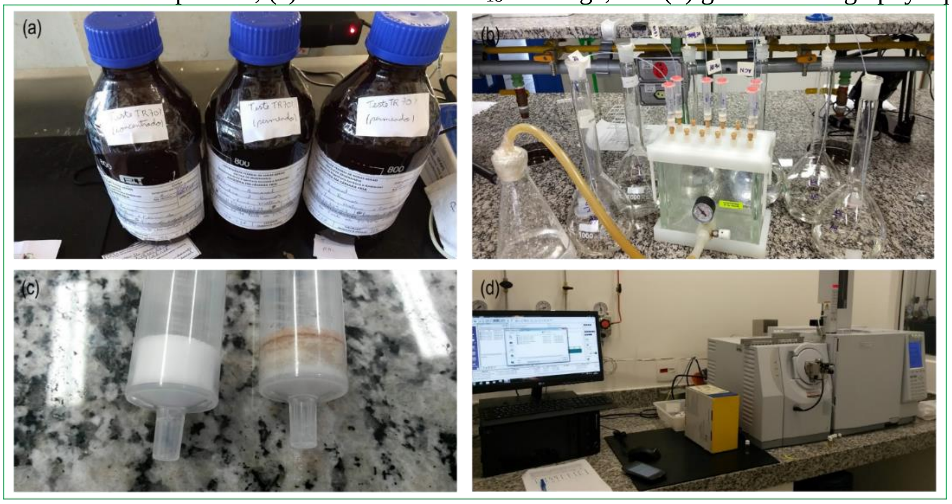
[a]Chemspider (2018); [b]EPA (2018); [c]PubChem (2018).

1.5.4 Instrumental analysis

The identification and quantification of phenolic compounds in the raw water and the DCMD streams were based on the methodologies proposed by the EPA (528, 3535A, and 8041) and the tests for validation of the analytical method were based on *the International Council for Harmonization of Requirements Technicians for Pharmaceutical Products for Human Use* (ICH, 2005). The pre-concentration method adopted was solid phase extraction with a C_{18} / 18% cartridge (500 mg / 6 mL - Applied Separations) and methanol (Exodus Scientif®) as eluent. For the identification and quantification of phenolic compounds, gas chromatography (Shimadzu CGMS-QP2010 SE) with a flame ionization detector (FID), a Zebron ZB-

MultiResidue column (30 mx 0.32 mm x 0.50 µm), and the helium (White Martins with 99.999% purity) carrier gas was used. The methodology developed and the validation is described in details by Ramos et al. (2021). Figure 1-2 shows photos of the phenolic compounds analysis performed.

Figure 1-2: Mix of photos of the phenolic compounds analysis performed: (a) samples collected, (b) used manifold and extraction process, (c) clean and used C_{18} cartridge, and (d) gas chromatography equipment



1.5.5 Description of DCMD systems

The DCMD experiments of Chapters III and IV were conducted in the bench scale system, while the experiments of Chapter V were run using both bench and pilot systems. Figure 1-3 shows a schematic diagram and photo of the bench scale system, in which a natural acetal copolymer cell manufactured by Sterlitech Corp., with a filtration area of 0.0042 m^2 was used. The pilot system, on the other hand, had an acrylic module produced and developed by Alvares et al. (2019) with three sheets of membrane and a filtration area of 0.3 m^2 (Figure 1-4). The membrane used in both units was polytetrafluoroethylene (PTFE 023005) from Sterlitech Corp. with 0.2 µm pores. The two systems had a chiller for cooling the permeate, electric heaters for feeding, pumps for recirculating water, and a scale to measure the increase in permeate mass. The filtration protocol is described in each chapter.

Figure 1-3: DCMD bench scale schematic diagram and photo

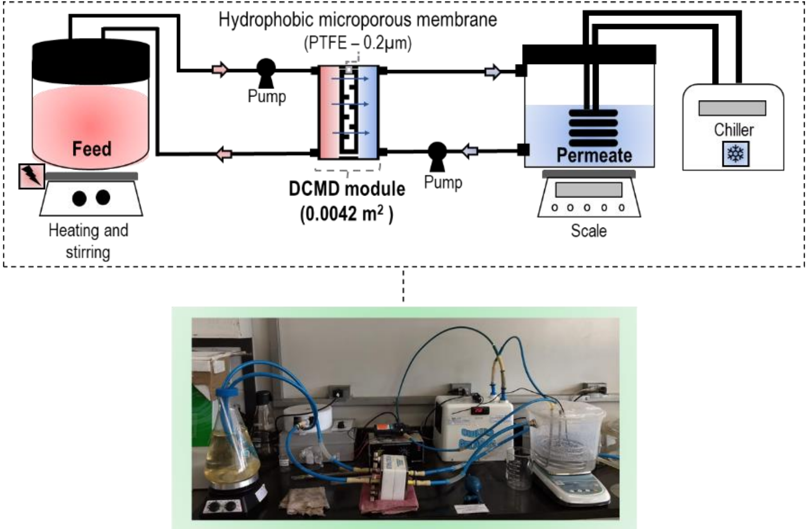
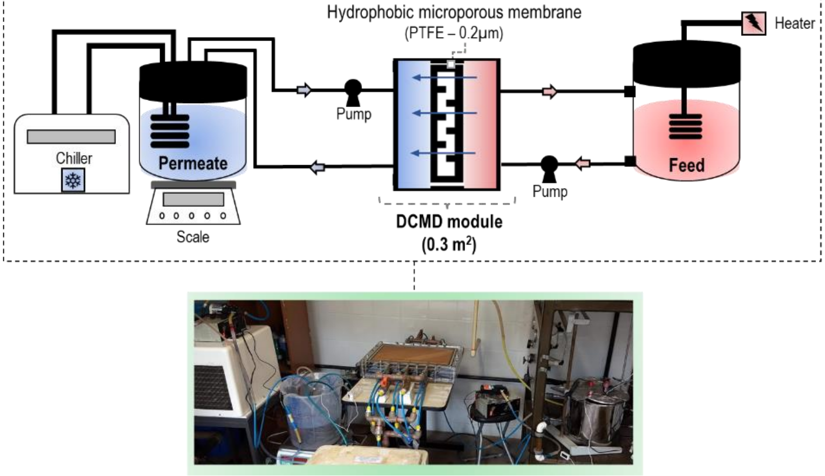


Figure 1-4: DCMD pilot scale schematic diagram and photo



1.5.6 DCMD systems performance and calculations

To evaluate the performance of DCMD systems the permeate flux was continuously measured, the permeate recovery was evaluated, the retention of the compounds was verified, mass balances were carried out to determine losses of specific contaminants during experiments when it happens, resistances were calculated (feed boundary layer, membrane, and permeate boundary layer), and temperature polarization coefficient (TPC) was estimated. The equations used for the calculations are described in detail in each chapter where they were needed.

1.5.7 Effect of operating conditions on the retention of phenolic compounds

Experiments at the DCMD bench scale system in Chapter III were carried out to verify the best operational conditions in the retention of phenolic compounds, varying in the feed temperatures of 40 °C, 50 °C, and 60 °C, and the phenols concentrations of 3 µg L^{-1}, 5 µg L^{-1}, 7 µg L^{-1}, and 10 µg L^{-1}. The effects of different permeate recovery (30 %, 50 %, and 70 %) were also evaluated.

1.5.8 Assessment of membrane fouling in retention of phenolic compounds

Still at the DCMD bench scale system, in Chapter IV the effects of membrane fouling on the retention of phenols were studied. The system was operated continuously until the flux decreased in order to identify the effects of organic fouling and biofilm formation. After the tests, the membrane was subjected to scanning electron microscopy (SEM) analysis to produce high-resolution and magnification images with a three-dimensional appearance to assess the membrane surface structure. The EDX (energy dispersive X-ray detector, or EDS) was used to determine which chemical elements were on the membrane surface.

1.5.9 DCMD from bench to pilot scale

In Chapter V, the technology stability was analyzed by all aspects of the DCMD scale-up (flux, energy, and different feed temperatures). In addition, to validate the efficiency and robustness of the DCMD system in the treatment of the phenols, experiments were conducted at the pilot scale analyzing the recovery (55 % and 70 %) and varying the water matrices. The water from the Velhas River (RW1) and Doce River of different locations (RW2 and RW3), which have different physical-chemical characteristics, such as color and turbidity, were used in the MD feed. The permeates obtained were analyzed and compared regarding the removal of phenolic compounds.

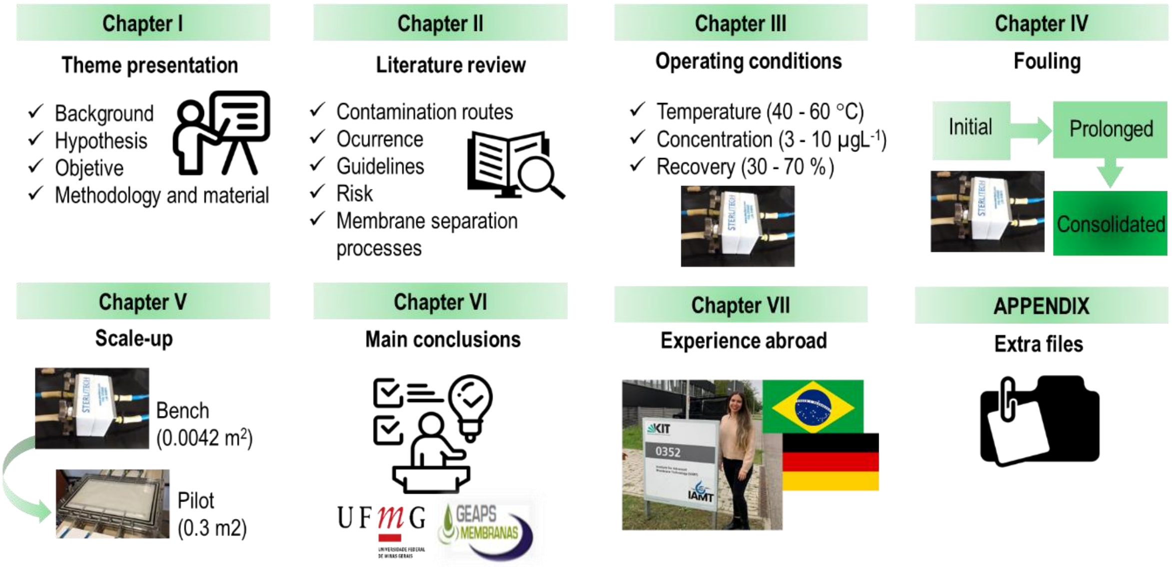
1.5.10 Economic analysis

The economic evaluation of the proposed MD technology was done in Chapter V considering a mobile (5.5 m^3/day), a distributed (11 m^3/day), and a centralized (535,680 m^3/day) water treatment system. It was taken into account the investment of capital goods (CAPEX) and the operating expenses (OPEX) of the process associated with solar energy and conventional electricity source.

1.6 DOCUMENT STRUCTURE

The thesis is divided into seven chapters (Figure 1-5) and APPENDIX. Each Chapter was named: Chapter I) Theme presentation; Chapter II) Review of phenolic compounds in water sources: occurrence, risk, and removal by membrane separation processes; Chapter III) Direct contact membrane distillation for water treatment with phenolic compounds; Chapter IV) Fouling evaluation in the membrane distillation: superficial water treatment with phenolic compounds; Chapter V) Direct contact membrane distillation from bench to pilot scale for water treatment and phenolic compounds removal; Chapter VI) Final considerations; Chapter VII) Experiences abroad. The thesis format is in articles, which indicates that each chapter is independent.

Figure 1-5: Thesis structure



Chapter I aims to introduce and contextualize the whole theme discussed in the study. It also shows the goals to be accomplished and demonstrates the relevance of the work developed. Chapter II presented a literature review on phenolic compounds occurrence in water sources, estimate the human health risks for the concentrations reported, and the membrane separation processes as an alternative for water treatment and phenols removal as reported in the first specific objective. Chapter III answers the second specific objective and the first hypothesis, showing the performance of DCMD in the retention of phenolic compounds in trace concentration under different operating conditions. Chapter IV deals with the membrane fouling influence on micropollutants retention and responds to the third objective and second hypothesis. Chapter V shows the effect of the DCMD system scale-up on the removal of phenols and the economic analysis for real applications in water treatment systems, answering the remaining objectives and hypotheses. Chapter VI highlights the main conclusions of the work. In addition, Chapter VII shares some of the experiences lived during the sandwich period in Germany. APPENDIX presents the supplementary materials to the main text.

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CHAPTER II – REVIEW OF PHENOLIC COMPOUNDS IN WATER SOURCES: OCCURRENCE, RISK, AND REMOVAL BY MEMBRANE SEPARATION PROCESSES

2.1 INTRODUCTION

Phenolic compounds are regarded as a major contaminant to the environment and water pollution, which can exist in water from natural occurrences or anthropogenic activities. The phenolic compounds are classified as organic compounds and in their chemical structure have hydroxyl group(s) attached to one or more aromatic rings (SAID et al., 2021). The occurrence of these compounds in aquatic environments has been widely reported in many articles from different parts of the world (LUO et al., 2014; RAMOS et al., 2021a) and the increase of phenols in drinking water, even at lower concentrations (ng or $\mu g\ L^{-1}$), is an international public health concern (ACOSTA et al., 2018; ZHONG et al., 2018).

The list of priority pollutants of the United States Environmental Protection Agency (EPA, 2014), which includes pollutants that should receive high priority for the development of water quality criteria and effluent limitation guidelines because they are often found in water sources and wastewater, has eleven phenols. While the World Health Organization (WHO) establishes a permitted concentration value in drinking water for five specific phenols (WHO, 2017) and other Brazilian (CONAMA 357 and Consolidation N° 5) and international agencies, such as Directive 2020/2184 (Europe), and GB 5749-2006 (China), have also guidelines values for few phenols. Much still needs to be done to regulate and monitor the presence of these polluting compounds in water sources and drinking water to avoid environmental and human health risks, since phenols tend to persist in the environment and accumulate in humans and animals (YADAV, et al., 2011).

The potential human health risks identified in toxicological and epidemiological studies for different phenolic compounds include cancer, endocrine dysregulation, genetic malformations, protein degeneration, and damage to the immune system, tissue, central nervous system, kidney, liver, and pancreas (MCKINLAY et al., 2008; MOHAMMADI and KAZEMI, 2014). The International Agency for Research on Cancer (IARC, 2023) classified pentachlorophenol as carcinogenic to humans (group 1), tetrabromobisphenol as probably carcinogenic (group 2A), and phenolphthalein, 2,4,6-trichlorophenol, polychlorophenols and their sodium salts, and 2-amino-4-chlorophenol as possibly carcinogenic (group 2B). The phenolic compounds most associated with endocrine disruptor and commonly found in water sources are bisphenol A (BPA), octylphenols, and nonylphenols (WEE and ARIS, 2017; SURANA et. al, 2022).

Conventional water treatment plants (WTP), which normally consists of coagulation, flocculation, sedimentation, filtration, and disinfection steps, have to deal with these pollutants and are considered inefficient in removing many organic micropollutants (KAMSONLIAN et al., 2021) and responsible for the production of byproducts, such as chlorophenols (GILCA et al., 2020) and may increase reactive and non-specific toxicity of transformation products (LEUSCH et al., 2019). Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membrane separation processes (MSP) have been studied as more robust techniques to remove phenolic compounds and other contaminants from water, ranging from particles and pathogens to dissolved organic compounds which can impart color, odor, and taste to the water (ANKU et al., 2017; SURANA et. al, 2022). The membrane properties (pore size, wettability, surface charge, roughness, thermal resistance, chemical stability, permeability, thickness, and mechanical strength) can affect the micropollutants removal (WARSINGER et al., 2018). Advances in membrane technology, including new materials, coatings, and engineering methods, such as photocatalytic membrane, pervaporation, and membrane distillation (MD), have been developed to improve selectivity, energy consumption, fouling resistance, and capital costs encouraging more MSP applications in the water treatment (KAMSONLIAN et al., 2021) and, consequently, the reduction of human health risk in the consumption of drinking water (RAMOS et al., 2021b).

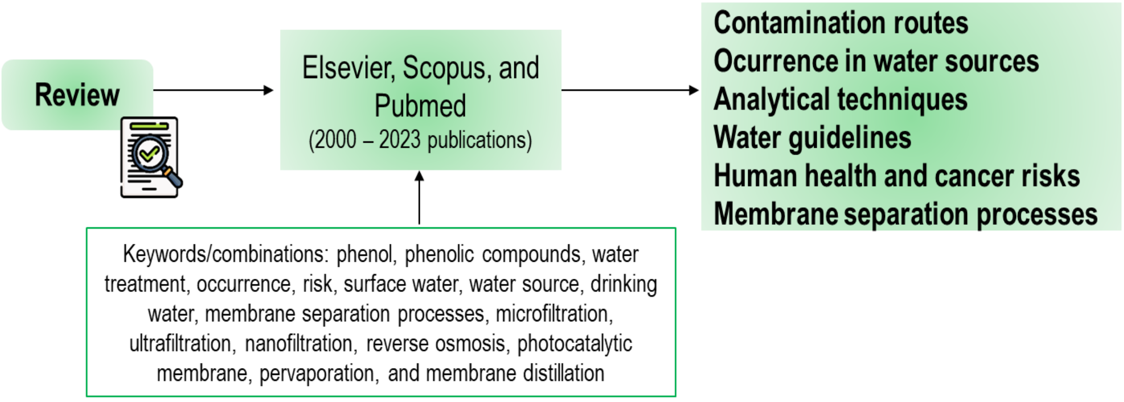
With that, this review aims to provide comprehensive information on phenolic compounds occurrence in water sources in different countries and show the human health risk possibilities based on the concentrations reported in the literature, that can be used to support legislative decisions, policy frameworks, and risk mitigation. In addition, some guidelines information for phenols were listed. The term “water sources” used in this study refers to water bodies, including surface water (rivers, lakes, and canals), groundwater, and drinking water that are potentially available for public consumption. The MSP application in water treatment for the reduction of phenols exposure in drinking water was discussed and the knowledge gaps and potential research in this area were identified.

Different from other publications, this review brings an analysis in a global context of the occurrence of phenolic compounds and focuses on the water treatment to produce drinking water and not on wastewater treatment, which is normally discussed about phenols. Therefore, it is expected to answer the following research questions: 1) What are the main routes of water contamination by phenols and the main legislations available? 2) What is the concentration range of phenolic compounds in water sources reported in the literature? Which are the most studied compounds and analytical methodologies used? 3) How is the risk range for human health and cancer potential of these compounds quantified in water? 4) What are the mechanisms, advantages, challenges, and ecological footprint of membrane technology in water treatment and phenols removal?

2.2 METHOD

This study employs a scoping review following four steps: 1) identifying relevant studies, 2) selecting studies, 3) charting the data, and 4) collating, summarizing, and reporting the results. For that, an investigation on Elsevier, Scopus, and Pubmed considering papers published between the years 2000 – 2023 was done to collect the data (Figure 2-1). A broad search of keywords and combinations between them were used to ensure that potential publications were not missed, such as phenol, phenolic compounds, water treatment, occurrence, risk, surface water, water source, drinking water, membrane separation processes, membrane technology, microfiltration, ultrafiltration, nanofiltration, reverse osmosis, photocatalytic membrane, pervaporation, and membrane distillation.

Figure 2-1: Flowchart of the proposed research



2.3 PHENOLIC COMPOUNDS OCURRENCE

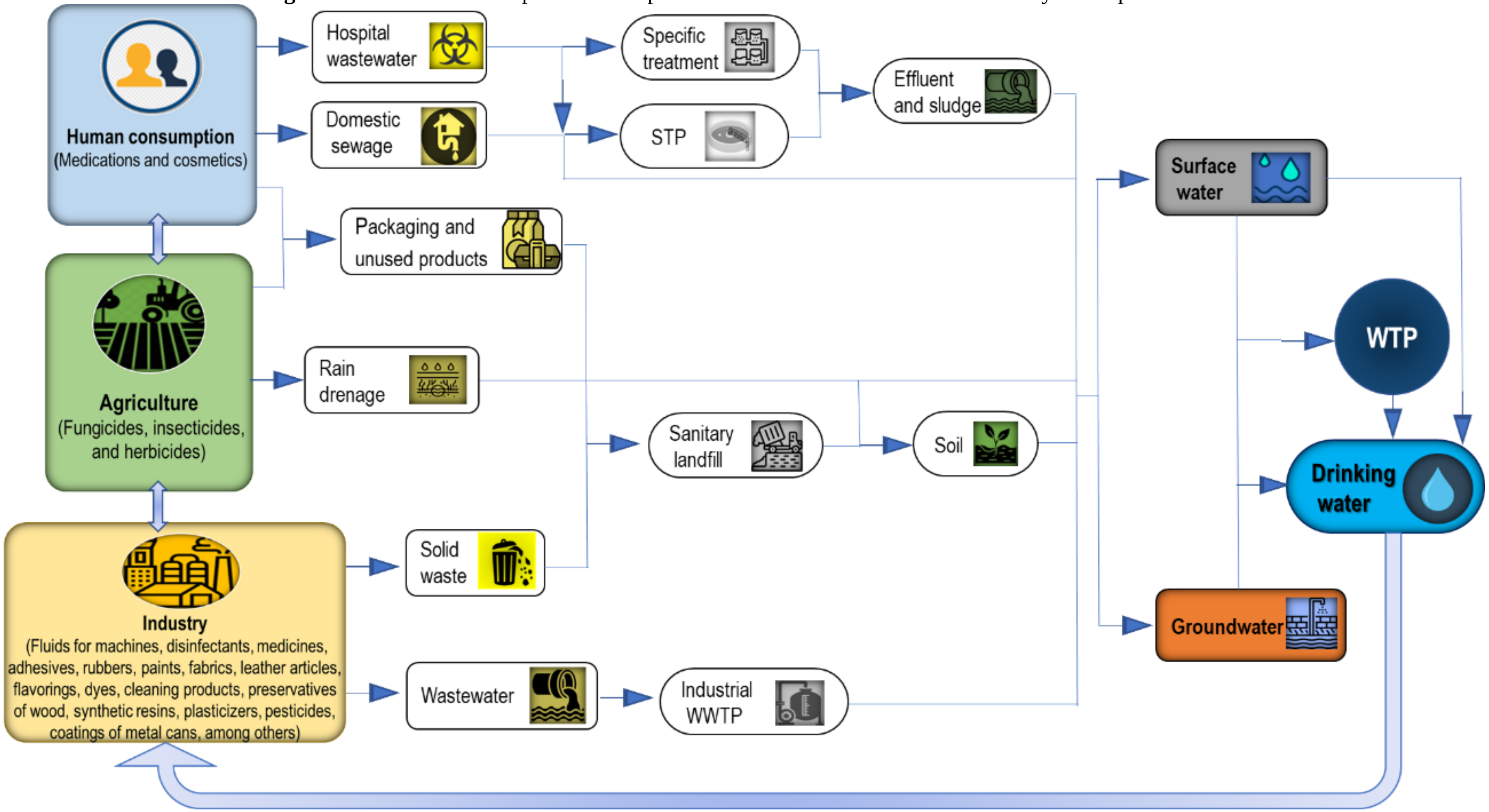
2.3.1 Main routes of water sources contamination

Phenols and their derivatives are introduced into the aquatic environment through natural degradation, human consumption, agricultural practices, and discharges of industrial effluents (WANG and WANG, 2018). The natural occurrence of phenols in water is due to the decomposition of organic matter present in the water body or in a nearby region, which, due to the runoff of rainwater, contaminates the aquatic environment (ROBINSON, 1965). Furthermore, plants can produce this compound when exposed to external stimuli or other factors such as ultraviolet radiation from sunlight, chemical stressors (such as pesticides), and microbial infections (MANDAL et al., 2010). Humans and animals produce phenol as a metabolic waste (TSURUTA et al., 1996) and the potential of simple organisms, such as microorganisms, to degrade naturally occurring substrates into phenolic compounds, is well established (TOMS and WOOD, 1970).

Chemical and petrochemical industries are the main ones responsible for phenols discharges in the water sources. Human beings constantly use phenolic compounds in their day-to-day activities from products of rubber processing, glues and adhesives, resins, electrical components, plastics, steel, paper and cellulose, dyes, gas, textile, tannery, pharmaceutical, and petroleum (JIN et al., 2007; WANG and WANG, 2018). In the agricultural sector, the source of these pollutants present in water is the use of pesticides, herbicides, and insecticides (LI et al., 2021).

In addition, domestic and municipal waste and wastewater also contribute to the discharge of phenols into water sources. As these compounds have been used in many products, from disinfectants, soaps, perfumes, and even medical products, which are usually drained directly into the municipal sewer, they can contaminate surface water if a proper treatment was not adopted (FROMME et. al., 2002). Municipal solid waste also adds to the discharge of phenol mainly from leachate in landfills (EL-SAADONY et al., 2023; PISHARODY et al., 2022). Therefore, the direct or indirect release of phenolic compounds into water bodies by the main reported routes occurs daily, intensifying water pollution. Figure 2-2 shows the schematic diagram of the main routes that these compounds can be introduced in nature by human origin around the globe.

Figure 2-2: Main routes of phenolic compounds introduction in the water sources by anthropic actions

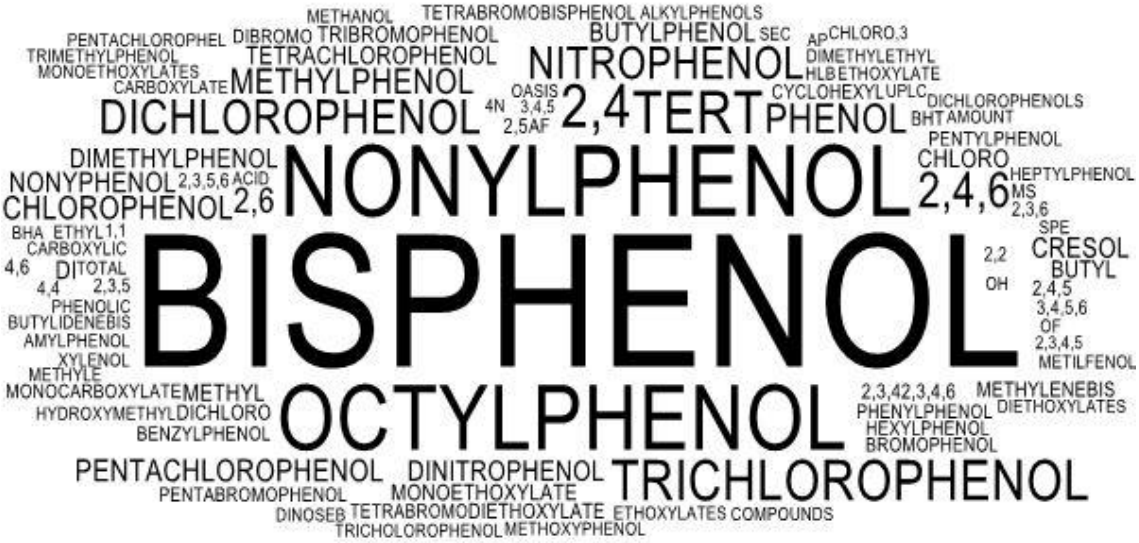


*STP = Sewage Treatment Plant; WWTP = Wastewater Treatment Plant; WTP = Water Treatment Plant.

2.3.2 Phenols in the water sources

Several articles (n=120) report the presence of phenolic compounds in aquatic environments and drinking water (APPENDIX I), drawing attention to the importance of treating effluents containing these compounds and the final safety step of water treatment to protect humans from exposure to phenols. Figure 2-3 shows the phenolic compounds names investigated in these studies. The most identified compound was bisphenol A (n=93), followed by 4-tert-octylphenol (n=35), 2,4,6-trichlorophenol (n=18), 4-n-nonylphenol (n=16), 2,4-dichlorophenol (n=16), phenol (n=13), 2-nitrophenol (n=11), and pentachlorophenol (n=10).

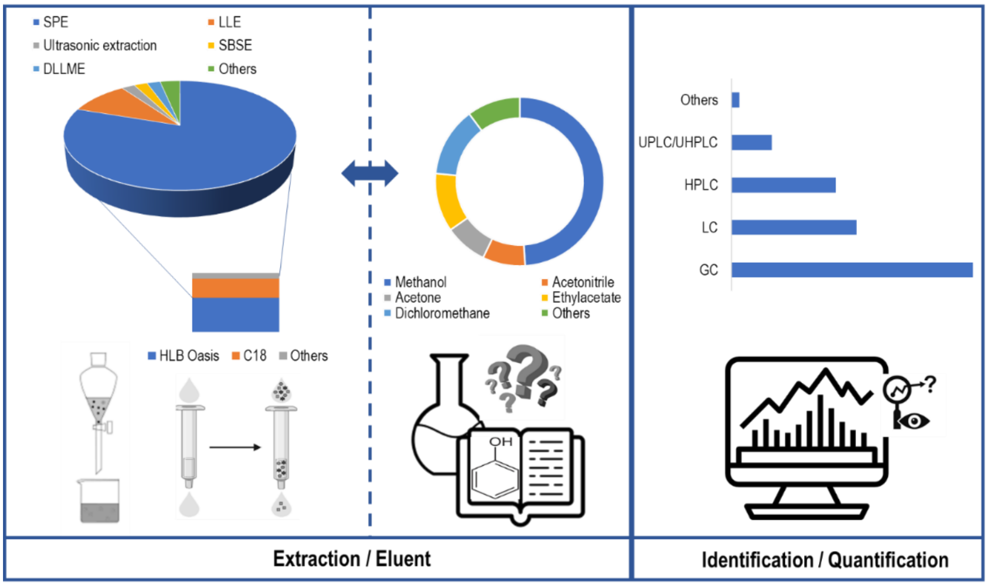
Figure 2-3: Word cloud of the most cited phenolic compounds in the literature. The greater the word font, the greater the number of studies found about the phenol in water sources



It is notable from the number of publications that greater attention has been paid to the compounds considered endocrine disruptors (bisphenol, octylphenol, and nonylphenol). This growing interest for years has been attributed to the causes of serious and widespread diseases associated with them, particularly abnormal endocrine systems in exposed individuals and populations (WEE et al., 2017). In addition, chlorophenols have also been much investigated, especially the occurrence as disinfection by-products related to drinking water treatment processes and to the characteristics of raw water. As the emerging pollutants, normally in low concentrations, are not removed by conventional processes in WTP, they end up appearing in treated water or in the distribution system, due to the combination of disinfecting agents, especially chlorine, with precursors such as pesticides, pharmaceuticals, detergents, brominated and iodinated compounds (GILCA et al., 2020). The main characteristics of the most studied phenolic compounds and those that are in the EPA priority pollutants list that have been cited in the literature are presented in APPENDIX II.

The identification/quantification of these compounds in aquatic environments is not simple. In addition to the very low concentrations, the levels of the chemical element in these environments are affected by several factors, such as pH, dilution by flow with other sources, seasonal changes (rainy and dry weather), sediment resuspension, and physical-chemical variations in general (RAMOS et al., 2021c). The methodologies adopted to identify and quantify phenols are very sensitive and, with the advancement of analytical techniques, detection limits are becoming smaller and more precise. Choosing the most suitable method of pre-concentration and analytical techniques is crucial for obtaining satisfactory results. The main analytical methods used in the studies (APPENDIX I) for phenolic compounds in water sources are shown in Figure 2-4.

Figure 2-4: Reported analytical methods for identification/quantification of phenolic compounds in water sources



*SPE = Solid Phase Extraction; LLE = Liquid-Liquid Extraction; DLLME = Dispersive Liquid-Liquid Microextraction; SBSE = Stir-Bars Sorptive Extraction; GC = Gas Chromatography; HPLC = High-Performance Liquid Chromatography; UPLC/UHPLC = Ultra-Performance Liquid Chromatography.

Among the researched articles, 80 % used solid phase extraction (SPE) to extract phenolic compounds from water, with the HBL Oasis cartridge being the most used. Liquid-liquid extraction (LLE) represented only 10 %, the minority used were ultrasonic extraction (2 %), dispersive liquid-liquid microextraction (DLLME) (2 %), stir-bars sorptive extraction

(SBSE) (2 %), and others. The high application of SPE for the phenols pre-concentration and extraction was already expected since it is a technique that emerged to address the disadvantages presented by LLE, increasing the analyte concentration (from 100 to 5000 times) and reducing the matrix interference in the processes (JARDIM, 2010). Other methods are still being researched to improve pre-concentration approaches, such as DLLME (CUNHA et al., 2022), SBSE (QUITANA et al., 2007), and ultrasonic extraction (LIU et al., 2017).

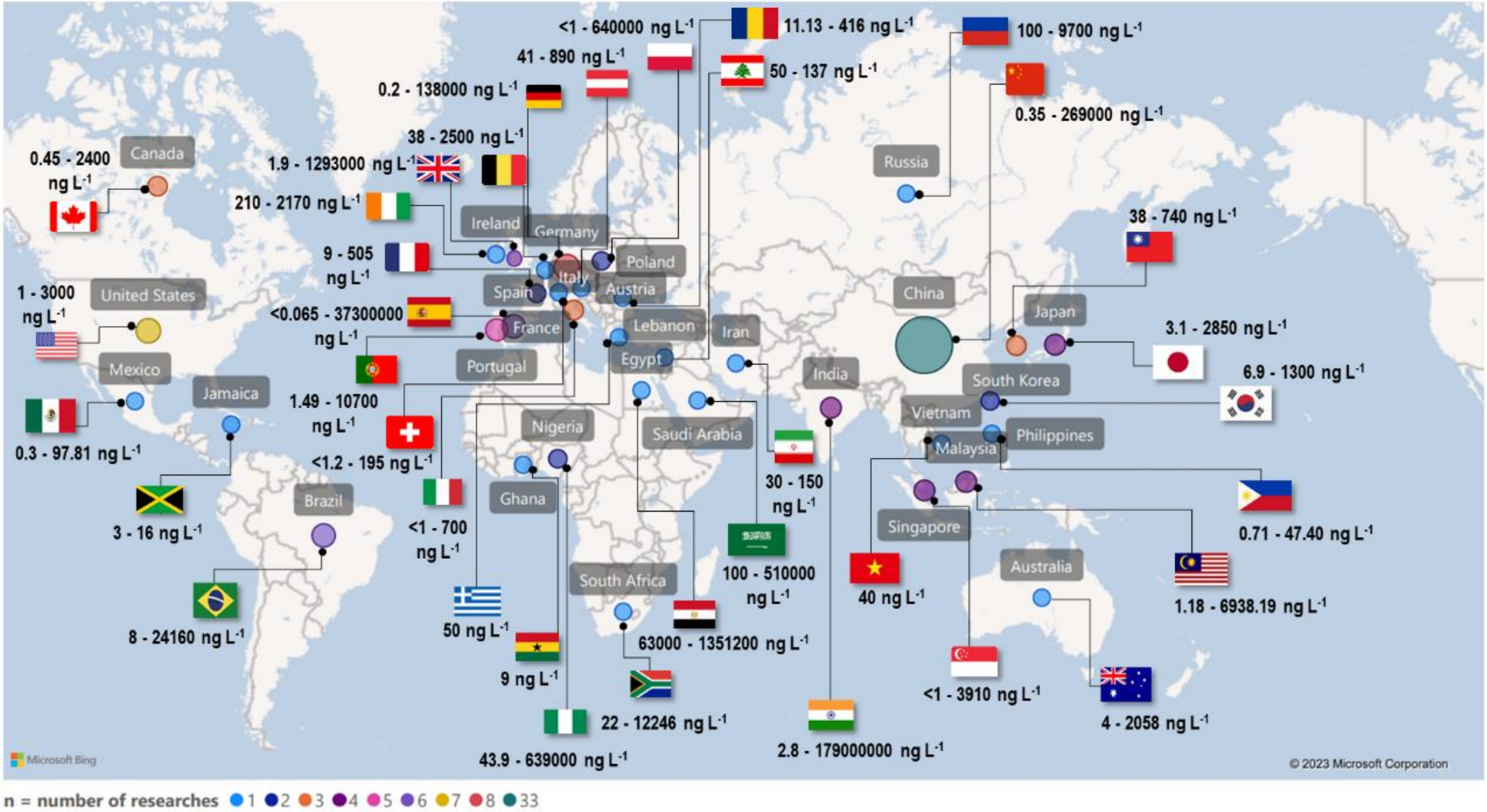
The solvent choice for phenols elution is directly related to the good recovery of the compounds. The extraction solvent must be immiscible with the solution to be extracted and the phenols soluble in the solvent. For the aqueous medium, the solvent used must be organic. Methanol, a polar solvent, was the most used in the studies (48 %), followed by dichloromethane (14 %), a solvent with low polarity. The combination of these solvents with others, such as acetonitrile (XU et al., 2011), acetone (ZHANG et al., 2007), ethylacetate (LOOS et al., 2007), methylene chloride (MICHAŁOWICZ et al., 2011), ammonium hydroxide (KASPRZYK-HORDERN et al., 2008), hexane (DUPUIS et al., 2012), diethylether (MICHAŁOWICZ et al., 2011), and sodium sulphate solution (SELVARAJ et al., 2014), was executed in several studies and can improve the process.

For a successful approach, the determination of phenolic compounds in different sample matrices must be performed by a technique that has high efficiency in the separation of analytes, high resolution, and high sensitivity. Gas chromatography (GC) was adopted in most studies (60 %), and it is already consolidated as the most used technique for phenols (SHAMSIPUR et al., 2016). The other techniques employed were liquid chromatography (LC) (31 %), high-performance liquid chromatography (HPLC) (26 %), and ultra-performance liquid chromatography (UPLC/UHPLC) (10 %) to identify/quantify these compounds in concentrations of ng and μg L^{-1}.

The pollutants concentrations quantified in different countries varied widely depending on the compound properties, the contaminated environment under study, and the analytical technique adopted, ranging from <0.065 ng L^{-1} in Central Spain (n=6) (ESTEBAN et al., 2014), for octylphenol monocarboxylate in a river, to 179,000,000 ng L^{-1} in India (n=4), for phenol in the River Ganga and Sunderban wetland along the Bay of Bengal (CHAKRABORTY et al., 2021) (Figure 2-5). Other countries with the highest reported concentrations were also Spain, which quantified 37,300,000 ng L^{-1} of nonylphenol in the Llobregat River basin (Catalonia, NE Spain) (CÉSPEDES et al., 2005), and Egypt (n=1) with 1,351,200 ng L^{-1} of 2,6-di-tert-butyl-4-methylphenol in the Nile River (ZAMZAM at al., 2019). The United Kingdom (n=4) that evaluated the impact of wastewater treatment of pharmaceuticals, personal care products, endocrine disruptors, and illicit drugs on the quality of receiving surface water, demonstrating that even with treatment high concentrations of phenolic compounds, especially of 4-tert-octylphenol (1,293,000 ng L^{-1}), still end up in the rivers (KASPRZYK-HORDERN et al., 2009). Elevated concentrations were also reported in drinking water from Poland (n=2) after chlorination treatment which quantified 640,000 ng L^{-1} of pentachlorophenol (MICHAŁOWICZ et al., 2011), and in Nigeria (n=2) a concentration of 639,000 ng L^{-1} for 2,4-dinitrophenol (OTITOJU et al., 2023). In groundwater, the highest reported concentration was in Saudi Arabia (n=1), which quantified 510,000 ng L^{-1} of 2-methyl-4,6-nitrophenol (ALQUWAIZANY et al., 2019).

China (n=33), was the country with the highest number of studies found on the occurrence of phenolic compounds in water. The maximum reported concentration was 260,000 ng L^{-1} for 3-methylphenol (3-cresol) in a research on the occurrence of 50 phenolic compounds in three rivers in Tianjin (ZHONG et al., 2018). In Brazil (n=6), the maximum quantified concentration was 241,600 ng L^{-1} for 4-chloro-3-methylphenol in raw river water used for water supply (RAMOS et al., 2021c). In another study, Ramos et al. (2021a) reported a concerning result in monitoring the occurrence of phenols in superficial raw water and drinking water for one year. Five phenols (2-methylphenol, 2-nitrophenol, 2,6-dichlorophenol, 2,4,5-trichlorophenol, and bisphenol A) increased their concentration in relation to the value found in the raw water and two were generated as by-products (4-chloro-3-methylphenol and 2,3,5,6-tetrachlorophenol) after the raw water passes through a conventional WTP. It was attributed to external factors and the use of an aerated grit chamber in the treatment since compounds originally attached to the grits could be peeled off due to air agitation, especially BPA and nonylphenol. In addition, it was evident that the chlorination step played an important role in the increasing production of chlorophenols in drinking water. These high concentrations reported worldwide demonstrate that treatments are still not efficiently designed to specifically attenuate all phenols in the water, putting human health at risk and highlighting the need for more comprehensive guidelines.

Figure 2-5: Phenolic compounds range concentrations quantified (min–max) in water sources worldwide



2.4 GUIDELINES AND RISK ASSESMENT

2.4.1 Guidelines for phenolic compounds in water

The water potability guideline is defined as the set of values allowed as parameters of water quality for human consumption. The water that is distributed to the population must be subject to the guidelines, which are still very limited regarding standards for emerging pollutants such as phenolic compounds (SEIBERT et al., 2020), especially considering the wide occurrence, variety, and specificity of these compounds detected in the water sources as reported in section 2.3.2. In 1996, the European Union Water Framework Directive (EU WFD) established the concept of priority substances. A few years later, in 2004, the United States Environmental Protection Agency proposed a Contaminant Candidate List following a similar idea, to identify and prioritize contaminants that may require regulation. It included trace organic contaminants such as some phenolics (*e.g.*: 2,4,6-thrichlorophenol, 2,4-dichlorophenol, 2,4-dinitrophenol, and 2-methyl-phenol (o-cresol) (EPA, 2023). The list was updated in the following years (2006, 2016, and 2022) and its current version included three additional compounds, among them the bisphenol A (EPA, 2022). It is noted that efforts are made to incorporate these contaminants into existing frameworks and expand the monitoring programs.

These lists are important tools to include new contaminants that are known or anticipated to occur in public water systems in the drinking water regulations. Table 2-1 shows the phenolic compounds that already have the maximum permitted concentration (MPC) for surface and drinking water in the Brazilian and international legislation. Note that more than 60 different phenolic compounds were detected in water sources in the literature reported (APPENDIX I), but only 13 phenols are regulated by reference values in guidelines. Among the countries identified with the highest concentrations of phenolic compounds in water sources, the European countries (United Kingdom, Spain, and Poland) have their own specific legislation and follow the WHO guidelines and the European Union recommendations. In countries such as India, Egypt, and Nigeria, it was not possible to identify the current legislation. Some details of the specific legislation of China are also in Table 2-1.

The WHO in the fourth edition of Guidelines for Drinking-water Quality brings a comprehensive preventive risk management approach for ensuring drinking water quality by establishing a MPC for phenolic content (1 µg L^{-1}), 2,4,6- trichlorophenol (200 µg L^{-1}), and pentachlorophenol (9 µg L^{-1}) (WHO, 2017). In addition, the WHO recommended that two phenols may be considered as representative of endocrine-disrupting compounds, for assessing the occurrence of endocrine-disrupting compounds where necessary, with values of 0.1 µg L^{-1} for BPA and 0.3 µg L^{-1} for nonylphenol (EUROPEAN COMMISSION, 2020). The recast Drinking Water Directive (2020/2184) is Europe's main law on drinking water (EUROPEAN COMMISSION, 2023). These guidelines follow a similar path to what is recommended by the WHO. However, the pentachlorophenol and 2,4,6-trichlorophenol do not appear in the guidelines. Furthermore, based on the opinion of the European Food Safety Authority (EFSA), it was decided that the BPA should be added to the Directive with a health-based parametric value of 2.5 µg L^{-1}, less restrictive compared to the WHO value (EUROPEAN COMMISSION, 2020).

In the USA, nationwide drinking water quality standards are regulated by the EPA, but legislation concerning surface water quality is updated by each State (STARLING et al., 2019). EPA recommended for water quality criteria / human health criteria (EPA, 2019) a greater number of phenolic compounds, a total of eleven, to be monitored compared to the other guidelines studied with the MPC ranging from 0.03 µg L^{-1} to 4,000 µg L^{-1} according to each phenol. The national standard of the people of the Republic of China / GB 5749-2006 (CHINE, 2006) provides recommendations similar to the WHO, but with less restrictive values for BPA (10 µg L^{-1}) and phenol (2 µg L^{-1}). The Brazilian National Environment Council (CONAMA) stated by Resolutions 357/2005, regarding the superficial water quality standards, include five phenolic compounds (BRASIL, 2005), while the Ministry of Health in the Consolidation N° 5, concerning the drinking water quality (BRASIL, 2017), includes only two phenols, being them 2,4,6-trichlorophenol and pentachlorophenol, following the WHO values recommendation.

The existing legislation in general does not establish the MPC of all phenols detected in surface and drinking water, but if the water meets the requirements presented in the guideline, it will be considered potable and will be distributed to the population even though it is not free of phenolic compounds considered harmful to health, which may cause future damage arising from its consumption.

Table 2-1: National and international guidelines for phenolic compounds

Compounds	**National Legislation (Brazil)**				**International Legislation**			
	CONAMA 357[a]			**Consolidation N° 5**[b]	**WHO**[c]	**EPA**[d]	**Directive 2020/2184 (Europe)** [e, f]	**GB 5749-2006 (China)**[g]
	Class I e II - Sweet water	Class I - Sweet water for fishing and cultivation of organisms	Class III - Sweet water	Water for human consumption	Water for human consumption	Humam health for the consumption of water + organims	Water for human consumption	Drinking water quality
2-chlorophenol	0.1 µg L^{-1}	0.1 µg L^{-1}				30 µg L^{-1}		
2-methyl-4,6-dinitrophenol						2 µg L^{-1}		
dinitrophenols						10 µg L^{-1}		
2,4-dinitrophenol						10 µg L^{-1}		
2,4-dimethylphenol						100 µg L^{-1}		
2,4-dichlorophenol	0.3 µg L^{-1}	0.3 µg L^{-1}				10 µg L^{-1}		
4-chloro-3-methylphenol						500 µg L^{-1}		
2,4,6- trichlorophenol	10 µg L^{-1}	2.4 µg L^{-1}	10 µg L^{-1}	200 µg L^{-1}	200 µg L^{-1}	1.5 µg L^{-1}		200 µg L^{-1}
2,4,5- trichlorophenol						300 µg L^{-1}		
pentachlorophenol	9 µg L^{-1}	3.0 µg L^{-1}	9 µg L^{-1}	9 µg L^{-1}	9 µg L^{-1}	0.03 µg L^{-1}		9 µg L^{-1}
nonylphenol					0.3 µg L^{-1}		0.3 µg L^{-1}	
bisphenol A					0.1 µg L^{-1}		2.5 µg L^{-1}	10 µg L^{-1}
phenol	3 µg L^{-1*}	10 µg L^{-1*}	10 µg L^{-1*}		1 µg L^{-1}	4000 µg L^{-1}	1 µg L^{-1}	2 µg L^{-1}

(a)BRASIL, 2005;(b)BRASIL, 2017;(c)WHO, 2017;(d)EPA, 2019;(e)EUROPEAN COMMISSION, 2006; (f)EUROPEAN COMMISSION, 2020; (G)CHINE, 2006. * total phenols - substances that react with 4-aminoantipyrine.

2.4.2 Human health and cancer risks

The toxicological risk assessment studies of phenolic compounds are a significant basis for environmental and human health risk management and safe decision-making. Since these compounds persist in the treated water, the risk assessments for human health (HRA) can be performed by the margin of exposure (MOE) determination (WHO, 2017). MOE is obtained through the ratio between the safe exposure level (DWEL) and the highest concentration detected in the evaluated environment. DWEL can be estimated by tolerable daily intake (TDI) (Equation 2.1) obtained directly from the literature or calculated from the ratio between the non-observed adverse effect level (NOAEL) or the lowest observed adverse effect level (LOAEL), and an assessment factor of 100 and 10000, respectively.

$$DWEL = {(TDI \cdot b_m \cdot f)}/{c} \qquad \text{Equation 2.1}$$

Where b_m is the body mass regarded 60 kg, f is the contribution of water to exposure (10 %), and c is the daily water consumption considered 3 L.

HRA decrease when the MOE value is higher than 100 (EPA, 2012). The cancer risk (CR) also can be calculated (Equation 2.2), as reported previously that some phenolic compounds are considered carcinogenic (IARC, 2023).

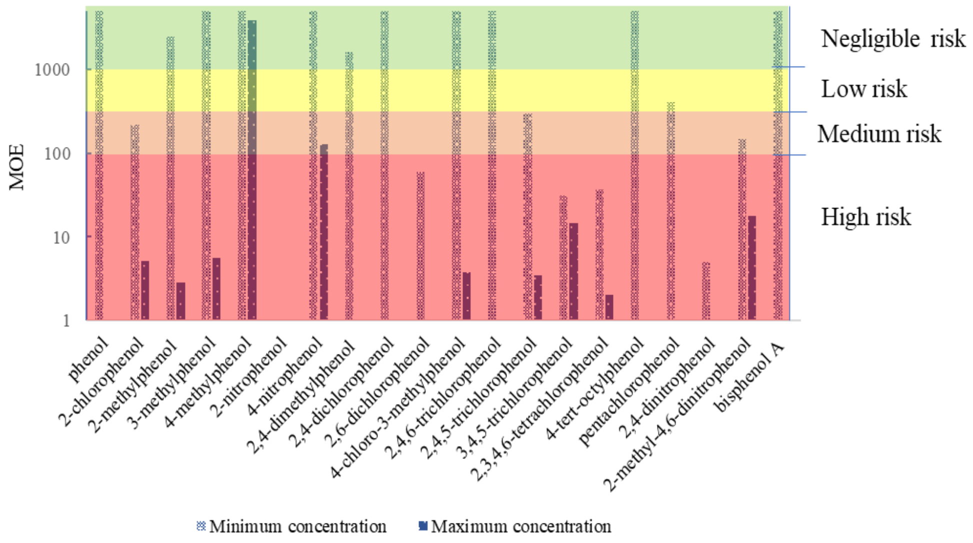
$$CR = {(C \cdot DI \cdot ED \cdot CSF)}/{(b_m \cdot AT)} \qquad \text{Equation 2.2}$$

where C is the highest phenolic compound concentration found in the water source, DI is daily input (3 L day^{-1}), ED is the exposure duration (183 days), CSF is the cancer slope factor (mg kg^{-1} day^{-1}), b_m is body weight (60 kg), and AT is the averaging times in days (AT$_{\text{Adult}}$ = 10950 days). CR can be classified as negligible risk (CR <10^{-6}), possible for cancer (CR >10^{-6}), and unacceptable risk (CR >10^{-4}) (YAHAYA et al., 2019).

As the consumption of phenolic compounds present in the water sources reported in the literature (APPENDIX I) happens continuously and tends to increase over time if precautionary measures are not taken, a risk assessment for human health and cancer was performed to assess the overall risk scenario with the available data (Figure 2-6 and Table 2-2). It was considered the minimum and maximum concentration values reported for the most recurrent compounds and those present on the EPA priority list (APPENDIX II). The NOAEL, LOAEL, and CSF data used in the calculations are in the supplementary material (APPENDIX III).

Most of the compounds evaluated in the concentration range (min-max) studied presented HRA ranging from negligible to high. 2-chlorophenol, pentachlorophenol, and 2-methyl-4,6-dinitrophenol had HRA between medium and high. Emphasis must be given to those compounds whose HRA was considered high in both ranges, even at the lowest concentration, being them 2-nitrophenol, 2,6-dichlorophenol, 3,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol, and 2,4-dinitrophenol. With regard to CR, the risk was considered between negligible and negligible except for 3-methylphenol, 2,4-dimethylphenol, 2,4,6-trichlorophenol, pentachlorophenol, and 2,4-dinitrophenol which was negligible to possible. Among the compounds that showed the highest HRA and CR, only 2,4,6-trichlorophenol and pentachlorophenol are contemplated in most of the presented legislation. 2,4-dinitrophenol and 2,4-dimethylphenol only have reference values in the EPA and other phenols do not have any reference. With that, the application of the proper technologies for water treatment is fundamental to reduce these risks.

Figure 2-6: Human health risk assessment of the range of phenolic compounds concentration (min-max) quantified in water sources reported in the literature



* The risk columns that did not appear on the graph are due to the very small value on the scale and the high associated risk. Note that it was not possible to calculate the HRA for 4-n-octylphenol and 4-n-nonylphenol, as data about NOAEL and LOAEL were not found in the literature. In addition, the CR was also not calculated for these compounds as well as for 2-nitrophenol, as no information was found about CSF.

Table 2-2: Results of the risk calculation for human health (HRA) and cancer

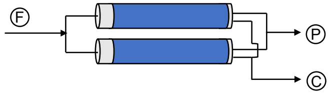
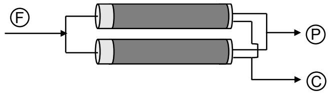
Phenolic compounds	Concentration (min - max ng L^{-1})	HRA		Cancer risk	
		MOE	Risk	CR	Risk
phenol	22 - 179000000	204545.45 - 0.03	Negligible - High		
2-chlorophenol	41 - 1740	219.51 - 5.17	Medium - High	1.71E-10 - 7.27E-9	Negligible - Negligible
2-methylphenol (o-Cresol, 2-cresol)	60 - 52600	2500 - 2.85	Negligible - High	2.51E-10 - 2.2E-7	Negligible - Negligible
3-methylphenol (m-Cresol, 3-cresol)	65.4 - 269000	22935.78 - 5.58	Negligible - High	2.73E-10 - 1.12E-6	Negligible - Possible
4-methylphenol (p-Cresol, 4-cresol)	30 - 380	50000 - 3947.37	Negligible - Negligible	1.25E-11 - 1.59E-10	Negligible - Negligible
2-nitrophenol	12.74 - 17600	0.01 - 8.52E-06	High - High		
4-nitrophenol	200 - 25400	16500 - 129.92	Negligible - Medium		
2,4-dimethylphenol (2,4-xylenol)	37 - 90600	1621.62 - 0.66	Negligible - High	6.18E-10 - 1.51E-06	Negligible - Possible
2,4-dichlorophenol	1.1 - 19960	8181.82 - 0.45	Negligible - High	2.76E-12 - 5.00E-08	Negligible - Negligible
2,6-dichlorophenol	150 - 34100	60 - 0.26	High - High		
4-chloro-3-methylphenol	35.99 - 241600	25006.95 - 3.73	Negligible - High		
2,4,6-trichlorophenol	1.4 - 261000	6428.57 - 0.03	Negligible - High	1.29E-11 - 2.40E-06	Negligible - Possible
2,4,5-trichlorophenol	30 - 2600	300 - 3.46	Medium - High	2.51E-09 - 2.17E-07	Negligible - Negligible
3,4,5-trichlorophenol	290 - 610	31.03 - 14.75	High - High		
2,3,4,6-tetrachlorophenol	240 - 4430	37.5 - 2.03	High - High	6.02E-09 - 1.11E-07	
4-tert-octylphenol	0.2 - 1293000	2250000 - 0.35	Negligible - High		
pentachlorophenol	1.1 - 640000	409.09 - 7.03E-04	Medium - High	4.60E-12 - 2.67E-06	Negligible - Possible
2,4-dinitrophenol	120 - 639000	5 - 9.38E-04	High - High	2.01E-10 - 1.07E-06	Negligible - Possible
2-methyl-4,6-dinitrophenol	80 - 680	150 - 17.65	Medium - High	2.61E-11 - 2.22E-10	Negligible - Negligible
bisphenol A	0.45 - 2970000	333333.33 - 0.05	Negligible - High		

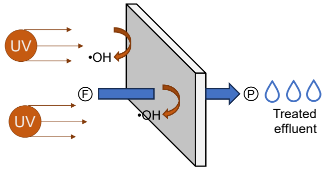
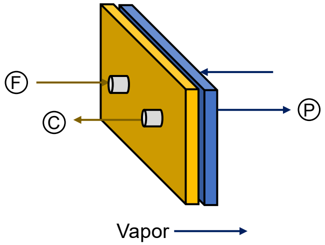
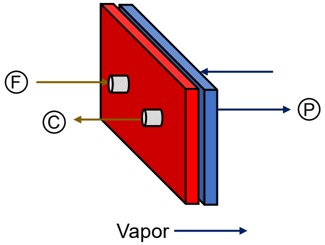
2.5 MEMBRANE TECNOLOGY FOR PHENOLIC COMPOUND REMOVAL FROM WATER SOURCES

The removal of phenolic compounds from water might be required to safeguard the health of humans and aquatic organisms through possible contamination of these toxic chemicals. Membrane technologies are reliable methods for separating phenols from water (ANKU et al., 2017). Its application in the water treatment sector has several advantages, such as being modular, adapting better to any treated flow and occupying a smaller area, production of stable water quality, the potential to accomplish the selective and efficient transport of specific components, high efficiency in removing compounds even in residual concentration, the system works without the addition of chemicals, and the possibility of using alternative energy sources, such as renewable energy and residual heat reducing dependency on fossil fuels and emission of greenhouse gases (DRIOLI and CURCIO, 2007).

Different types of membrane technology already focused on removing phenols from water sources, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), photocatalytic membrane (PM), pervaporation, and membrane distillation (MD) (SAID et al., 2021). They were compared in Table 2-3 for their removal mechanisms, advantages, limitations, average specific energy consumption (SEC), and ecological / carbon footprint. In complement, Figure 2-7 bring a summary of different phenolic compounds removal by the membrane processes. APPENDIX IV shows in detail the literature data used in this analysis.

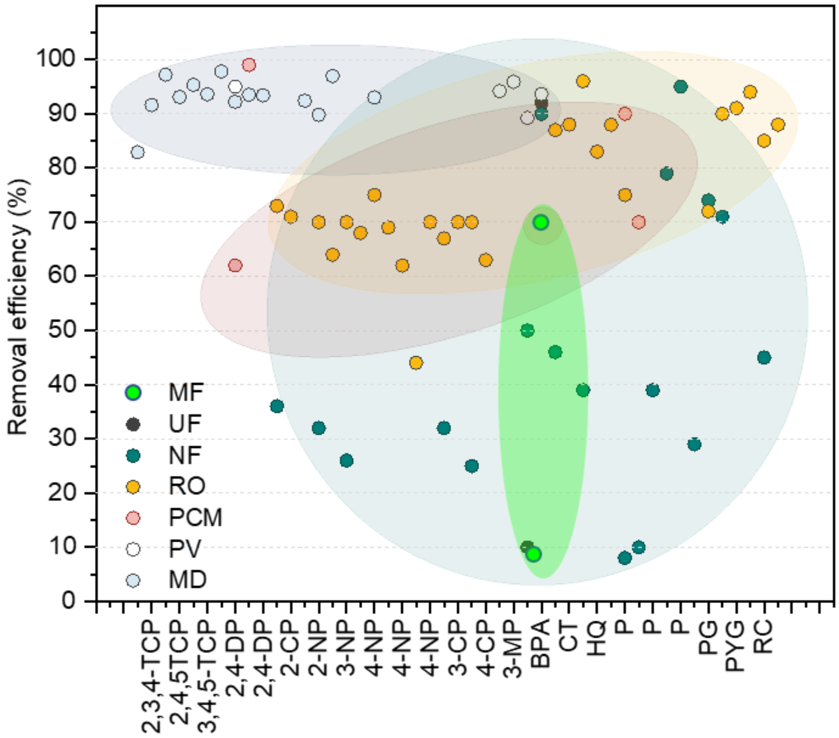
Table 2-3: Membrane technology applied in the removal of phenolic compounds

Membrane technology	**Schematic diagram of the process**	**Technology maturity level**	**Driving force**	**Removal mechanisms**	**SEC (kWh/m^3)**	**Ecological / carbon footprint (kg/m^3)**	**Advantages**	**Disadvantages**
Microfiltration		M	Hydraulic pressure	Sieving and adsorption	n.a.	n.a.	Effective removal of large particles and suspended solids. Highest permeability, lowest pressure requirement. Better used as pre-treatment to other technologies	Limited efficiency for removing phenols from surface water
Ultrafiltration		M	Hydraulic pressure	Sieving and adsorption	n.a.	n.a.	Effective removal of large particles and suspended solids. Highest permeability, lowest pressure requirement. Better used as pre-treatment to other technologies	Limited efficiency for removing phenols from surface water
Nanofiltration		M	Hydraulic pressure	Sieving, electrostatic repulsion, adsorption, and Donnan exclusion	0.009	0.0006	Combines higher permeate flux and rejection efficiency of phenolic compounds.	The high-pressure requirement can limit its use. Fouling is more pronounced and may require pre-treatments
Reverse osmosis		M	Hydraulic pressure	Sieving, electrostatic repulsion, and solvent drag	0.065	0.0475	Highest rejection rate of phenolic compounds and other dissolved contaminants	Lowest permeability among the membrane pressure-driven MSPs. The energy requirement can limit its use. Require pre-treatments to prevent fouling, which is more pronounced compared to the other MSPs

Membrane technology	**Schematic diagram of the process**	**Technology maturity level**	**Driving force**	**Removal mechanisms**	**SEC (kWh/m³)**	**Ecological / carbon footprint (kg/m³)**	**Advantages**	**Disadvantages**
Photocatalytic membrane		E	Light energy and hydraulic pressure	Oxidation and size exclusion	n.a.	n.a.	Can achieve higher removal rates of phenolic compounds as a result of its oxidation mechanisms. The fouling rate can be lower than in classical MSPs.	It is a technology that requires additional studies prior to being considered in full-scale applications.
Pervaporation		E	Vapor pressure gradient	Differences in volatility, solubility, and diffusion compared with the mixture being treated	n.a.	n.a.	Lower fouling rate and can be favored when waste heat is considered. Theoretical rejection of 100% of non-volatile compounds.	It is a technology that requires additional studies prior to being considered in full-scale applications. Limited efficiency in the removal of semi-volatile phenolic compounds.
Membrane distillation		E	Vapor pressure gradient	Differences in volatility, solubility, and diffusion compared with the mixture being treated	7770	5633	Lower fouling rate and can be favored when waste heat is considered. Theoretical rejection of 100% of non-volatile compounds.	Limited efficiency in the removal of semi-volatile phenolic compounds.

*For the schematic diagrams: F: feed stream, P: permeate stream, and C: concentrate stream. In terms of technology maturity level: E: emerging. M: mature. SEC: specific energy consumption (average values from different studies; references provided in the supplementary material APPENDIX IV). n.a.: not available.

Figure 2-7: Diverse phenolic compounds removal by membrane technologies



*Where: MF: microfiltration, UF: ultrafiltration, NF: nanofiltration, RO: reverse osmosis, PCM: photocatalytic membranes, PV: pervaporation, and MD: membrane distillation. 2,3,4-TCP: 2,3,4-trichlorophenol, 2,4,5-TCP: 2,4,5-trichlorophenol, 3,4,5-TCP: 3,4,5-trichlorophenol, 2,4-DP: 2,4-dichlorophenol, 2-CP: 2-chlorophenol, 2-NP: 2-nitrophenol, 3-NP: 3-nitrophenol, 4-NP: 4-nitrophenol, 3-CP: 3-chlorophenol, 4-CP: 4-chlorophenol, 3-MP: 3-methylphenol, BPA: bisphenol-A, CT: catechol, HQ: hydroquinone, P: phenol, PG: phloroglucinol, PYG: pyrogallol, RC: resorcinol.

2.5.1 Microfiltration and ultrafiltration

Microfiltration is membranes with relatively large pore sizes (0.1 – 10 µm), differing from ultrafiltration which has smaller pore sizes (0.01 – 0.1 µm). Due to its characteristics, microfiltration can separate suspended solids, colloidal matter, and large molecular weight compounds, whereas ultrafiltration advances in terms of separation and generally retains low molecular weight compounds as well.

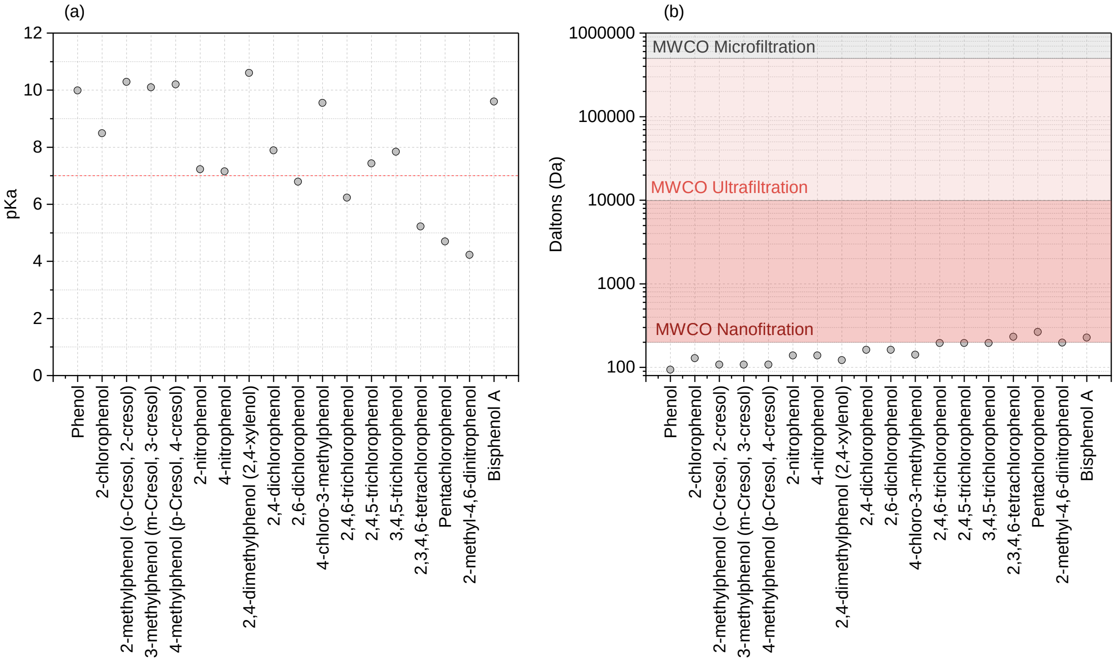
In both cases, the membrane represents a physical barrier to the contaminants, preventing their passage if larger than their pores. Based on that, sieving represents the main mechanism in phenolic retention in both cases. Phenolic compounds larger in size are therefore retained by the membrane, while water and smaller molecules pass through it. A different mechanism involved in both MSPs is adsorption since the membranes can also exhibit surface adsorption properties. In that case, phenolics can potentially interact with the membrane surface through hydrophobic interactions, leading to their adsorption and subsequent removal. When adsorption is considered, then the characteristics of the phenolics besides their molecular weight should be considered. Although it occurs, the adsorption onto the membrane surface is an undesired mechanism since it may lead to fouling. The expectation when it comes to surface water treatment, though, is that phenolic compounds would have a lower contribution to fouling compared with other contaminants, *e.g.*: suspended solids and colloids, that are present in higher concentrations.

Bing-Zhi et al. (2008) considered the use of ultrafiltration (2,000 – 10,000 MWCOs) membranes to remove bisphenol A from drinking water, obtaining removal rates greater than 92 % from an aqueous solution of concentration ranging from 100 to 600 µg/L. The efficiency observed, however, could not be attributed to the contaminant retention through size exclusion given that bisphenol A is a compound smaller than the membrane pores. As mentioned by the authors, the efficiency observed would be mainly attributed to the adsorption phenomenon of the phenolic compound onto the membrane surface. To confirm, an increase in medium pH to values close to the pKa of bisphenol A resulted in a decrease in removal efficiency to 9.3 %. Under such circumstances, the contaminant becomes negatively charged and repulsion forces between the phenolic compound and the membrane, also negatively charged, reduce the interaction that would lead to bisphenol A adsorption.

The same authors used microfiltration membranes in a similar approach intended to remove bisphenol A from drinking water (BING-ZHI et al., 2010). The outcomes were similar and reinforced the fact that adsorption would be the prevailing mechanism for phenolic compound removal. The concern is the extent to which phenolic compounds would contribute to membrane fouling after being adsorbed onto its surface over its lifecycle. Susanto et al. (2009) demonstrated for an aqueous solution composed of polyphenolic compounds that significant water flux and changes in membrane surface occurred after static adsorption tests for all membranes assessed. Fouling was classified as reversible and also irreversible, which raises attention to the phenomena observed and their impact on the membrane. It is important to mention that the concentration used in the experiments was higher, in the order of g/L, which might not be representative of surface water. Even so, the impacts over a long period of time should be better examined.

Figure 2-8 (a) was prepared to extrapolate the outcomes observed for bisphenol A to other phenolic compounds. Notably, most compounds would present a negative charge in natural waters of pH values close to 7. For membranes negatively charged, it would result in a lower interaction and removal efficiency. The results are complemented by the data presented in Figure 2-8 (b), which confirms the low expectation for these contaminants to be removed by micro- or ultrafiltration membranes by mechanisms of size exclusion. Effective removal of phenolics by nanofiltration membranes would only be possible for larger compounds, and, among the hydraulic-driven membrane separation processes, reverse osmosis seems to be the most effective.

Figure 2-8: Summary of (a) pKa and (b) Dalton values for different phenolic compounds



2.5.2 Nanofiltration and reverse osmosis

Following ultrafiltration, nanofiltration membranes have a lower pore size of approximately 0.001 – 0.010 µm, being an intermediate process between ultrafiltration and reverse osmosis. Selectivity starts to be observed in nanofiltration membranes, allowing water and small solutes to be passed while retaining divalent ions, organic molecules, and larger particles. From all pressure-driven processes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis), nanofiltration has gained special attention as an effective technology for the removal of phenolics from surface water. That is because it combines a high permeate flux, characteristic of porous membranes, with a high selectivity, characteristic of dense membranes.

The nanofiltration membrane also acts as a physical barrier to the contaminants and operates based on size exclusion. In complement, charge effects start to contribute as well since nanofiltration membranes possess a charged surface that enables the rejection of charged species through electrostatic repulsion. This property is advantageous for the removal of phenolic compounds, which often carry charges. Therefore, the mechanisms of rejection in nanofiltration are three: sieving, complemented by electrostatic repulsion, and Donnan exclusion. The latter represents the contribution of ions in the feed solution to create an osmotic pressure difference across the membrane. This pressure difference favors the retainment of ions and charged organic compounds, including phenolics, on the feed stream.

Zhang et al. (2006) concluded that even for nanofiltration membranes the prevailing mechanism remains the adsorption onto its surface. The authors suggested that the retention of a contaminant by the other mechanisms described (sieving, electrostatic repulsion, and Donnan exclusion) only occurs after the membrane was saturated with the compound. In complement, the authors demonstrated that the water matrix, especially the ions concentration, can affect the degree of hydration of the component, reducing its equivalent size and later retention. The presence of natural organic matter, though, did not modify the retention of phenolics by the membrane used (Desal 5 DK), which values varied from 50 – 90 % in the experiments.

In an attempt to provide an in-depth comprehension of how different types and functional groups of phenolic compounds would impact the performance of nanofiltration membranes, Arsuaga et al. (2011) studied the correlation between flux decline and organic retention for phenol and eleven phenolic derivatives in an aqueous solution (membrane used: NF 90; compounds: phenol, catechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol). To induce fouling, the authors considered a solution with an initial concentration of 100 mg/L, for a total filtration volume of 10 L, 0.014 m^2 of membrane area, and a transmembrane pressure of 10 bar. The authors claimed that a significant flux decline occurs as the molecule substituent changes in the order of hydroxyphenols > chlorophenols > nitrophenols.

The decline in relative flux from hydroxyphenols to chlorophenols and nitrophenols is likely due to the interaction of solute molecules with the membrane surface through adsorption, driven by hydrophobic forces (VAN DER BRUGGEN et al., 1999). However, it is important to consider an additional factor, namely the interaction based on dipole moments, to explain the significantly lower relative fluxes observed for aqueous nitrophenols. It is expected that solutes with higher dipole moments would have an easier entry into the membrane structure and lead to an increased partition coefficient between the membrane and solution (VAN DER BRUGGEN et al., 1999). Consequently, nitrophenols are expected to cause a more efficient decline in flux compared to chlorophenols. APPENDIX IV complements the discussion of nanofiltration membranes applied to phenolics removal from water. It presents different parameters, including the removal efficiency according to each compound and membrane used.

Of all MSPs, reverse osmosis is the most restrictive. Pore size is no longer a discussion in this technology, which membranes are dense and can effectively remove a wide range of contaminants, including monovalent ions. For that, it requires a high hydraulic pressure typically exceeding the osmotic pressure of the feed solution, driving the water molecules through the membrane by diffusion. The diffusion rate of phenolics is significantly lower compared to water molecules due to their size and structure. In complement, phenolic compounds can also be rejected by the membrane through electrostatic repulsion between the charged solute and the charged membrane surface.

To validate the performance of reverse osmosis membranes, Hidalgo et al. (2015) considered their use for 4-nitrophenol and 4-nitroaniline, the first being a phenolic compound. At the pH from which the experiments were made (pH = 6), charges on 4-nitrophenol (pKa 4-nitrophenol: 7.14 (KIM et al., 2019)) do not exist and the Donnan effect would not explain the rejection observed.

Although adsorption was also pointed out as a contributor to phenolics removal, electrostatic repulsion may have occurred as well. Under this pH, the membrane used (RO90) has a negative charge, and hydrogen bonding interactions between 4-nitrophenol and the membrane are fully reduced. As a result, a lower transport of 4-nitrophenols across the membrane was observed, leading to a rejection of approximately 70 %. Under such a circumstance of transport across the membrane, it is always valuable to mention that the Stikes-Einsten law predicts an inverse proportionality between the size of a component and its diffusion rate so that the transport will be smaller for larger components. This is an aspect to be considered while interpreting the results of phenolics removal through reverse osmosis.

For being more susceptible to fouling, cleaning strategies and their impact on reverse osmosis membrane lifetime should always be assessed, which does not diminish the importance of establishing proper cleaning protocols for other membranes.

2.5.3 Photocatalytic membrane

In photocatalytic membranes, composite materials are incorporated onto the membrane surface. That represents an advancement to conventional photocatalysis, reducing the loss of photocatalysts in the reaction bulk. The materials have photocatalistic properties activated by luminous energy (typically ultraviolet light). When a photocatalyst is illuminated, electron-hole pairs are generated, leading to the formation of reactive oxygen species, such as hydroxyl radicals. These can degrade organic pollutants, including phenolic compounds, through oxidative reactions. The membrane supporting the photocatalysts acts as a physical barrier to suspended solids and remaining particles from the composite materials, allowing the passage of water molecules.

Without ultraviolet radiation, the filtration processes may lead to fouling, and flux decline occurs due to the adsorption of pollutants (LEE et al., 2001), as in previous membrane technologies. However, under luminous energy, most pollutants degrade, and fouling is alleviated, improving the process performance and stability (PIDOU et al., 2009). It should be mentioned that inorganic contaminants may persist and could compromise the efficiency of the photocatalysts once they accumulate on the membrane surface.

Several studies focused on phenolics degradation and removal by this technology, including 2,4-dichlorophenol (LIU et al., 2009), phenol itself (ROTA et al., 1996; BARNI et al., 1995), 2,6-dimethyl phenol (ROTA et al., 1996; HOU et al., 2023; CHEN et al., 2020), 1,2,3-benzenetriol, and 4-chloro phenol (ROTA et al., 1996). Under light radiation and using UiO-66, added by hydrogen peroxide, Chen et al. achieved a 70 % removal efficiency of phenol from an aqueous solution. At different experimental conditions and using a metal halogen lamp, Hou et al. (2023) achieved 90 % phenol removal efficiency and stable performance in terms of permeate flux.

Even so, photocatalytic membranes are still considered an emerging technology, requiring advancements to extend their use on large scales. Zhang et al. (2014) suggested that more efforts are required to improve the activity of photocatalytic membranes. In addition to the challenges related to membrane morphology and its effective area (contact area between the photocatalyst, target pollutant, and light), advancements are required to consider alternative luminous and energy sources (*e.g.*: light-induced photocatalytic membranes (SHI et al., 2019). Another concern presented by Zhang et al. (2014) was membrane aging, especially the polymeric ones, which can be accelerated by the photogenerated reactive oxygen species shortening their lifespan. The challenges do not diminish the fact that, in technical terms, photocatalytic membranes are a promising alternative for phenolics removal from water matrices.

2.5.4 Pervaporation

Pervaporation operates based on the selective permeation of volatile compounds through a nonporous membrane. For that, the feed solution is conventionally heated to promote the vaporization of volatile compounds. The generated vapor then comes into contact with the membrane, where selective permeation occurs. In this process, the driving force is the vapor pressure gradient across the membrane, generally aided by a vacuum or a carrier gas on the permeate side to maintain the vapor pressure gradient.

Phenolic compounds, however, are semi-volatile in nature and can vaporize when the feed solution is heated, leading to their permeation through the membrane depending on their solubility and diffusion properties. Volatility then becomes an important physicochemical property of phenolic compounds when their removal is considered by pervaporation (CAO et al., 2022). As an emerging technology, advancements are also required to improve their removal efficiency, e.g.: the synthesis of membranes of low affinity for phenolics, allowing the preferential vaporization and permeation of water through the membrane (CAO et al., 2021).

As in other membrane technology, the concentration in the feed solution may affect the performance of pervaporation, especially at higher temperatures (HAO et al., 2009). Hao et al. (2009) observed phenol fluxes increasing from 0.017 to 0.26 kg/m².h in experiments ran at 80 °C and for feed concentrations increasing from 300 to 8,000 mg/L. As a result, the permeate obtained achieved a phenol content of approximately ~19.7 %, which may limit its usage. The transport of volatile compounds across the membrane was reported by other authors as well (DAS et al., 2008; CAO et al., 2021). For Cao et al. (2021), it was suggested an additional process following pervaporation to separate phenol from the permeate obtained. In addition to phenol, the authors considered the phenolics p-cresol, p-chlorophenol, and p-nitrophenol (concentration tested: <6,000 ppm), which were recovered from the permeate as crystals after a process of de-sublimation in a cold trap.

It must be clarified that the studies currently available in the scientific database consider high phenolics concentrations, which might not represent real scenarios of water treatment. There is a research gap related to this aspect, which impedes a proper assessment of this technology in water treatment targeting the removal of phenolic compounds.

2.5.5 Membrane distillation

Membrane distillation is a thermal-driven process that uses a hydrophobic porous membrane to separate volatile compounds from a liquid mixture. Similar to pervaporation, volatility becomes an important physicochemical characteristic if the removal of phenolics is made by membrane distillation. The process operates based on a temperature difference across the membrane, allowing volatile compounds to pass through while retaining non-volatile contaminants. The membranes used are generally hydrophobic, preventing water from passing through it but only vapor. The vapor passes through the pores and is condensed on the cold side as a purifies liquid.

The performance of membrane distillation for the removal of phenolics (15 compounds) was investigated by Ramos et al. (2022). An interesting observation to be made is that the authors considered concentration values similar to those observed in natural environments (3 – 10 µg/L), which provides a better understanding of membrane distillation in real applications. As expected, an increase in feed temperature (40 – 60 °C) led to a decrease in phenolics retention. At this point, it is important to remember that the technology relies on the vapor pressure of the constituents to promote their separation. According to Antoine’s Equation, the vapor pressure and temperature are exponentially related, which means that small increments in the feed temperature result in a significant increase in the vapor pressure. In that case, the distillate flux increases so rises the transport of phenolic compounds.

Different from what was observed in previous processes, the volatility seems to have a greater impact on membrane distillation performance than hydrophobicity (RAMOS et al., 2022a), presenting a significant correlation with the removal efficiency ($r_{Spearman}$: 0.8; p-value: 0.002). Even so, high removal rates were reported by Ramos et al. (2022) for phenolics, achieving values greater than 93.3 %.

When it comes to fouling, there is a lower expectation that it would occur in membrane distillation compared to pressure-driven processes. A different study assessed the development of a fouling layer in the membrane distillation process while treating phenolic compounds in natural waters (RAMOS et al., 2022b). Although it reduced the permeate flux, it did not affect the distillate quality, but the opposite. The dynamic layer formed on the membrane surface acted as an additional barrier to phenolics, preventing them to reach the membrane surface or adsorbing them.

Despite the interesting outcomes reported, and as the technology of pervaporation, membrane distillation is still considered an emerging process that requires advancements in order to compete with other well-established pressure-driven technologies. The high membrane costs and the lack of modules for large applications are still limitations when it comes to this technology (MOREIRA et al., 2023a). Another observation to be made is the heat required to maintain the temperature difference between the feed and distillate streams. In cases where residual heat or renewable energy sources are available, that should not be a concern. However, the requirement of a heat-exchange system may derail the use of membrane distillation for water treatment (MOREIRA et al., 2023a; GHAFFOUR et al., 2019).

As for other membrane technology, APPENDIX IV also include studies that investigated the retention of phenolic compounds by membrane distillation.

2.5.6 Treatment for membrane concentrate enriched with phenols

One of the main disadvantages of membrane technology is the generation of the concentrate, as the filtration processes are designed to separate pollutants and not to degrade them requiring waste stream disposal (COUTO et al., 2018). Thus, the concentrate generated in membrane applications for the removal of phenolic compounds might require additional treatment to eliminate the risk of contamination or proper disposal in the environment. The current scientific database lacks specific strategies to degrade phenolic compounds from membrane separation processes concentrate.

For other trace organic contaminants, such as pharmaceuticals and personal care products, Couto et al. (2018) suggested the use of advanced oxidation processes due to their capacity to break down the organic matter and, therefore, eliminate these compounds. Different from membrane technology, which transfer the pollutant from one phase (feed stream) to another (concentrated stream), advanced oxidation techniques are capable to mineralize the contaminants. Alvim et al. (2020) compared the efficiency of ultraviolet light (UV), UV/H_2O_2, and ozonation for the removal of different trace organic contaminants from membrane distillation concentrate. UV/H_2O_2 and ozonation achieved complete mineralization for all contaminants, also reducing the color, total nitrogen and total organic carbon from membrane distillation concentrate. From an operational perspective, advanced oxidation technologies seem to be better employed for concentrate management rather than feed stream due to the lower volume to be treated, requiring more compact systems.

Another strategy used for concentrate management is recycling it back to the beginning of the treatment process (GUIMARÃES et al., 2022; MOREIRA et al., 2023b). Depending on the preliminary and primary treatment used, they can alleviate the concentration of phenolic compounds without their build-up in the treatment train. The alternative should be properly assessed given that some conventional treatment processes have generally low efficiency for removing contaminants at low concentrations (WANG et al., 2022). Wang et al. (2022) investigated the performance of coagulation-flocculation processes in trace organics removal (pharmaceuticals) reporting efficiencies of ~38 - <70 % for compounds whose initial concentrations were 0.1 $\mu g\ L^{-1}$. It is always important to bear in mind that their concentration in surface water is generally low, and the implications derived from that should be properly assessed.

Their disposal seems to be an alternative, as long as it complies with the standards for safe practice (BACKER et al., 2022). However, regulations are yet to advance on trace organics discharge, especially in terms of phenolic compounds as previously reported. Until then, their monitoring of concentrate while it is being disposed (discharged) of would not be a concern to most facilities. Other strategies for concentrate and brine solutions management were presented by Backer et al. (2022) and included its treatment by adsorption, crystallization, and other hybrid systems intended to reduce its volume or recovery by-products from it, in an approach of zero liquid discharge. The most appropriate alternative would certainly rely on the concentrate characteristics and the solutions may be specific to each case. It is worth highlighting the importance of new studies that explore the treatment of the concentrate generated by the different membrane processes.

2.5.7 Membrane technology selection and the ecological footprint

After a discussion of different processes, it is reasonable to inquire which one would be the most adequate for phenolics removal from water matrices. From a technical perspective, considering the removal efficiency, membrane distillation, photocatalytic membranes, and reverse osmosis had the highest removal rates (Figure 2-7). The first two, however, require additional studies and advancements in their manufacturing processes in order to expand their use in full-scale facilities. Porous membranes such as microfiltration, ultrafiltration, and some high permeable nanofiltration would have a low efficiency for phenolics removal. Considering that the main removal mechanism for these membranes is adsorption (Table 2-3), which in turn is driven by a chemical potential difference (or concentration gradient), the expectation is a lower removal rate than reported by most authors (APPENDIX IV), which studies were made at high concentration of phenolics in the feed stream. When fouling is brought into the discussion, membrane distillation would withstand the reverse osmosis process. Despite being an emerging technology, it would have great potential for trace organics removal, especially phenolic compounds.

To better guide the decision process, the ecological footprint was considered as a new variable to represent the environmental impacts associated with these technologies. Santos et al. (2022) suggested that the approach would contribute to a decision of a technology more environmentally safe. The ecological footprint measures the natural resources required and waste generated along the manufacturing of a given product, focused on CO_2 emissions. These results were shown in Figure 2-7 and APPENDIX IV for different technologies. The estimations were based on the protocol presented by the International Energy Agency (IEA, 2015), which considers 0.725 kg-CO_2 per kWh generated by fossil fuels. That would represent a worst-case scenario, in which all the energy required would be supplied by fossil fuels.

When reverse osmosis and membrane distillation are compared, it is notably seen that the first process would present the lowest CO_2 emission given its lower energy requirement per cubic meter of permeate produced. While the average values obtained for reverse osmosis were in the order of ~0.06 kg-CO_2/m^3, the process of membrane distillation would be responsible for emissions greater than 2,900 kg-CO_2/m^3. The difference observed is explained by the energy required to maintain the temperature difference across the membrane. The necessity for heating systems represents a challenge for membrane distillation due to its costs, and as demonstrated, their potential environmental impact. Once again is reinforced the necessity for alternative heating processes and different module set-ups (MOREIRA et al., 2023a), is now justified by the lower CO_2 emissions. After all, from a technical and environmental point of view, reverse osmosis seems to be a better alternative to overcome the occurrence of phenolic compounds in drinking water.

2.6 FUTURE PERSPECTIVES

Several phenolic compounds on the market can go to water sources and be quantified in trace concentrations with the advances in analytical techniques, although there are still few studies on the occurrence thinking about the diversity of phenols. The risk results presented in this research indicate that emphasis should be given to those compounds that showed high HRA and the risk of cancer and are still not in the guidelines. In addition, more efforts are needed to work with unstudied phenolic compounds, to fill the gaps on the occurrence, detection/quantification, toxicities, persistence, and risk assessment.

The reduced number of phenolic compounds in water treatment guidelines is a critical point that was highlighted and addressing more phenols is still a challenging step to be achieved. An ever-increasing interface is needed between the environmental and sanitary law (which deals with the right to health) and science (with its advanced research on compounds identification and risk assessment) in the construction of updated water potability guidelines since interventions in the environment are constant and it reflects on the sanitary conditions of water resources and, consequently, on people's health.

The conventional WTP requires adaptations to remove phenols present in water sources to avoid the high risks reported in the literature and to produce more reliable and safer water. The PSM, mainly RO as a mature technique and MD as an emerging technique, has shown to be robust technologies for removing these pollutants with high efficiency from water sources. However, energy costs for its operation, as in the case of MD, need to be reduced and more studies carried out to expand large-scale applications. The concentrate generated from PSM requires special attention for its disposal or post-treatment, but there are few studies focused on this issue. For prospects, a revolution in the water treatment sector is expected to deal with all these micropollutants that are reported every day and associated with diseases growing in society.

2.7 CONCLUSION

The occurrence of phenolic compounds in water sources was studied based on articles published in the literature between 2000-2023. These compounds may have natural or anthropogenic origins, mainly related to human consumption, the chemical and petrochemical industry, and agriculture (pesticides). More than 60 different phenols were identified and quantified in water sources in different parts of the world during this period. The most identified compound was bisphenol A (n=93) and the most used analytical techniques were SPE (80 %) with the HBL Oasis cartridge, methanol as eluent (48 %), and Gas chromatography (60 %). The highest concentration reported was 179,000,000 ng L^{-1} for surface water (channels) in India.

Among this large number of quantified compounds, the drinking water guidelines address only 13 phenols, leaving many pollutants unreported. This is still a major challenge in water management to avoid risks to human health, especially for those phenols that were calculated the HRA, such as 2-nitrophenol, 2,6-dichlorophenol, 3,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol, and 2,4-dinitrophenol, and showed high values even at the lowest concentrations reported in the evaluated literature.

In this scenario, water treatment processes play a key role in preventing phenols from being consumed by the population and reducing the associated risks. Membrane technology has been applied in water treatment and phenol removal. The mechanisms, advantages, and disadvantages of the main technologies were detailed, highlighting the high phenols removal from water by membrane distillation, as an emergent technology, and reverse osmosis, as a mature technology with the smallest measured ecological footprint.

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CHAPTER III – DIRECT CONTACT MEMBRANE DISTILLATION AS AN APPROACH FOR WATER TREATMENT WITH PHENOLIC COMPOUNDS

3.1 INTRODUCTION

Membrane distillation (MD) has attracted attention to applications in different areas, such as desalination (FAHMEY et al. 2017; KADI et al., 2019), water and wastewater treatment (LAQBAQBI et al., 2019, GROSSI, 2020), chemical substance concentration (FENG et al., 2016, COUTO et al., 2019), among others (CRISCUOLI et al., 2002, JULIAN et al., 2020). In MD the temperature gradient across the membrane surface results in a difference in water vapor pressure between both sides (feed and permeate) and leads to a vapor transport through the membrane pores (ALWATBAN et al., 2019). It is considered a stable process and can be integrated with residual heat or renewable energy source (*e.g.*: solar power) to decrease its operational expenditures (ASHOOR et al., 2016, SOOMRO and KIM, 2018). The direct contact membrane distillation (DCMD) is the simplest configuration among all MD designs available (AHMEDA et al., 2020), capable of producing water with a high quality.

The hydrophobic microporous membrane in the DCMD process separate a hot feed stream and a cold permeate solution, both in direct contact with the membrane. Due to its arrangement, the heat losses through conduction in the membrane matrix are higher than other MD configurations (PERFILOV et al., 2018), which leads to higher temperature polarization effects. To overcome these losses, researchers have focused their effort on localized heating processes near to the membrane surface (AHMEDA et al., 2020), *e.g.*: membranes embedded and coated with photothermal particles (SAID et al., 2019). Despite of the heat loss associated with DCMD, it must be emphasized that its main competitive advantage is that the distillation process occurs below the normal boiling point of the feed solution (BANAT et al., 2007).

The feed temperature typically ranges from 60 to 90 °C (ASHOOR et al., 2016), although a temperature gradient around 15 °C is enough to ensure a proper driving force for vapor transport. In addition to heat loss, the membrane wetting is also a shortcut in DCMD application in large scale operations. The phenomenon is caused when the transmembrane pressure exceeds the membrane liquid entry pressure (LEP), which is affected by three main factors: feed solution surface tension, membrane material, and membrane structure (AHMED and LALIA, 2017). If wetting occurs, the rejection efficiency declines and the permeate quality becomes compromised. In this sense, many studies are focused on the synthesis of novel membranes to overcome this disadvantage (TIJING et al., 2014; HAN et al., 2019; JIAO et al., 2020). Complementary to novel membranes, the decision for the most appropriate operating temperature, feed concentration, and permeate recovery rate can improve the technology performance, thus reducing its disadvantages (MOHAMMADI and KAZEMI, 2014; KUANG et al., 2019).

The feed temperature is one of the main factors that affect the system. Higher temperature is preferable for an increase in the mass transfer by increasing the difference in vapor pressure between the feed and permeate phases (YU et al., 2012). Consequently, the vapor flux will be higher. However, there is always a threshold for the feed temperature, since the operating temperature and feed composition can indirectly influence the LEP by changing the contact angle and surface tension (YU et al., 2012). Other phenomenon observed is the temperature polarization. Not only mass transfer increases at higher feed bulk temperatures, but also heat transfer, leading to a lower temperature gradient across the membrane interface and, therefore, more pronounced temperature polarization effects (KUANG et al., 2019).

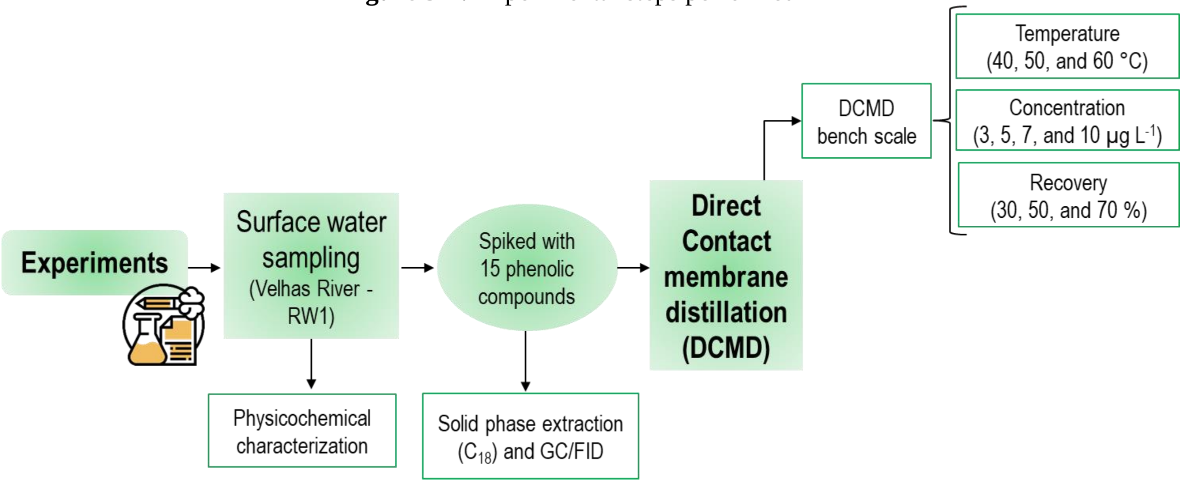
The operating temperatures is also a challenge in the treatment of volatile and semi-volatile organic compounds (VOC), such as phenols derivates that are often found in surface water and are not efficient removed by conventional water treatments (MOHAMMADI and KAZEMI, 2014). Most study in DCMD applications were focused on non-volatile substances rejection, and there is still a research gap in the literature regarding the behavior of VOC retention by DCMD in a real surface water treatment. From the studies available, all conducted in a synthetic aqueous media (WIJEKOON et al., 2014; ASIF et al., 2018), the discussions on VOC retention efficiency were limited to their volatility, assumed to be easily transferred through the membrane pores as vapor molecules (WU et al., 2018; RAZA et al., 2018). However, the hydrophobic species present in the water have high affinity with the membrane surface, which can result in blocked pores, membrane wetting or the transport through adsorption-desorption mechanism (VELIOGLU et al.; 2018; HOU et al., 2020). Therefore, Wijekoon et al. (2014) indicated that the relation between these two characteristics, volatility, and hydrophobicity, should be more important than these characteristics analyzed separately.

In this sense, this work aims to evaluate the DCMD performance for the retention of fifteen phenolic compounds by varying the feed temperature (40 °C, 50 °C, and 60 °C), feed concentration (3 µg L^{-1}, 5 µg L^{-1}, 7 µg L^{-1}, and 10 µg L^{-1}), and the permeate recovery rate (30 %, 50 %, and 70 %). The phenolic compounds were selected based on the list of priority compounds from the Environmental Protection Agency (EPA - United States) and the risk to human health related to contaminated water consumption. It is expected that this research contributes to a better comprehension of VOCs removal by MD, reassuring that the technology may have a clear potential in removing volatile and semi-volatile organic compounds from water at trace concentrations. Moreover, it is intended to demonstrate a potential applicability of DCMD units for higher drinking water quality production.

3.2 MATERIALS AND METHODS

Figure 3-1 presents a flowchart of the experimental steps performed and it is described in detail in the following sections.

Figure 3-1: Experimental steps performed



3.2.1 Water sampling

All samples were collected in the Velhas river located in Minas Gerais, Brazil (19°59'30,1"S 43°49'39,7"W). The river belongs to the third largest Brazilian watershed in terms of territorial extension (São Francisco) and is one of the areas most affected by pollution from domestic and industrial wastewater, agriculture, livestock, among other activities (PINTO et al., 2019). Amber glass bottles were used for water sampling, immersed countercurrent and below the water surface, approximately 15 to 30 cm, avoiding stagnation areas as recommended by the EPA method 528 (EPA, 2000). The main physicochemical characteristics of the raw water are in Table 3-1.

Table 3-1: Raw water physicochemical characteristics

Parameter	Value	Parameter	Value
Turbidity (NTU)	14.2	Ca (mg L^{-1})	21.1
pH	7.3	Mg (mg L^{-1})	6.4
UV-Vis 254 nm	0.02	Na (mg L^{-1})	5.68
Perceived color (mg Pt-Co L^{-1})	74	K (mg L^{-1})	1.07
Real Color (mg Pt-Co L^{-1})	< 5	Fe (mg L^{-1})	< 0.1
TSS (mg L^{-1})	16	Al (mg L^{-1})	< 0.1
TS (mg L^{-1})	108	As (mg L^{-1})	< 0.1
DOC (mg L^{-1})	1.22	Pb (mg L^{-1})	< 0.1
Electric conductivity (µS cm^{-1})	116.8	S (mg L^{-1})	2.69
Alkalinity (mg $CaCO_3$ L^{-1})	29.3	Si (mg L^{-1})	6.41
TN (mg L^{-1})	1.37		

The raw water was spiked with fifteen phenolic compounds using the following analytical standards, EPA 8040A Phenol Calibration Mix and Bisphenol A (99 %), both purchased from Sigma-Aldrich®. The compounds were selected according to the EPA's list of priority compounds and were monitored in the raw water and DCMD generated streams. The compounds were: 4-chloro-3-metylphenol (4C3MP), 2-nitrophenol (2NP), 2,4-dimethylphenol (24DMP), 2,4-dichlorophenol (24DCP), 4-nitrophenol (4NP), bisphenol A (BPA), 2-metylphenol (2MP), 3-metylphenol (3MP), 2,6-dichlorophenol (26DCP), 2,3,5-trichlorophenol (235TCP), 2,4,5-trichlorophenol (235TCP), 2,4,6-trichlorophenol (246TCP), 2,3,4-trichlorophenol (234TCP), 2,3,5,6-tetrachlorophenol (2356TTCP), and 3,4,5-trichlorophenol (345TCP).

3.2.2 Analytical method

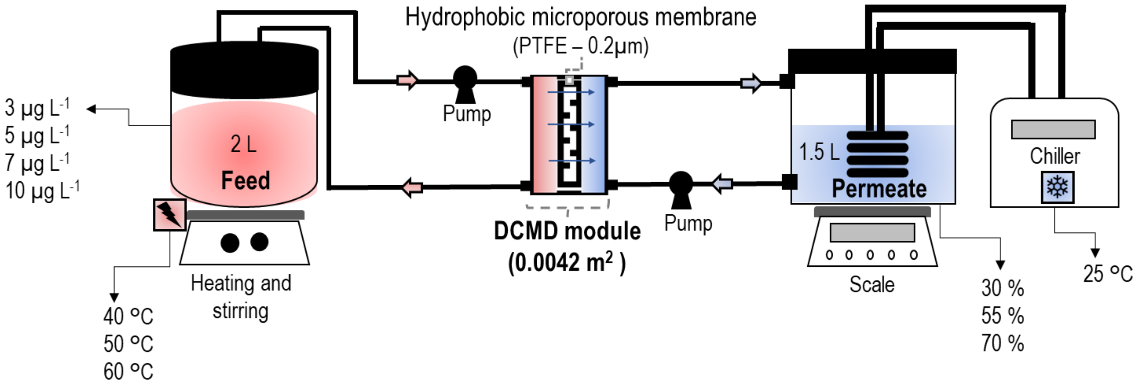
The raw surface water and the DCMD permeate were analyzed according to the *Standard Methods for the Examination of Water and Wastewater* (APHA, 2012) in the following parameters: pH (pHmeter Qualxtron QX 1500), electric conductivity (Hanna conductivity meter HI 9835), alkalinity, total suspended solids (TSS), perceived color (Hach DR 2800 spectrophotometer), NH_4^+, Na, K, Mg, Li, and Fe ions concentrations (Ion Chromatograph ICS-1000 - Dionex). In addition, the raw water was also characterized by UV absorption (254 nm - Hach DR 2800 Spectrometer), color (Hach DR 2800 spectrophotometer), dissolved organic carbon (DOC) and total nitrogen (TN) (Shimadzu TOCV CNP), turbidity (Hach 2100AN turbidimeter), Al, As, Pb, and Si ions concentrations (Ion Chromatograph ICS-1000 - Dionex), real color (Hach DR 2800 spectrophotometer), and total solids (TS).

The phenolic compounds identification and quantification were done using solid phase extraction and gas chromatograph (GC - 2010-Plus, Shimadzu) equipped with the flame ionization detector (FID), based on EPA methods (528, 3535A, and 8041). In order to guarantee a reliable result, the protocol was validated as recommended by the International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use (ICH, 2017). In the pre-concentration process, C_{18}/18% cartridges (500 mg/6 mL - Applied Separations) were used, conditioned with 5 mL of methanol and 5 mL of MilliQ (ThermoScientific Smart2Pure 3 UV) water. Then the sample pH was adjusted to 2 (with a 0.1 mol L^{-1} sulfuric acid solution) and 1 L of sample was percolated in the cartridge (20 mL min^{-1}). After the concentration process, the cartridge remained under vacuum for complete moisture removal (20 min). Elution was carried out using 2 times 1 mL of methanol (Exodus Scientific®). The GC chromatographic condition was 40 °C for 4 minutes, 4 °C min^{-1} to 240 °C and finally 240 °C for 5 minutes. The injection volume of the samples was 2 µL in splitless mode, with the injector temperature at 275 °C. In addition, the FID detector temperature was maintained at 300 °C and an Air/H_2 mixture (400/40 mL min^{-1}) was used for the combustion while a N_2/Air mixture (30 mL min^{-1}) was used as make-up gas. Besides that, the methodology and the validation details can be seen in Ramos et al. (2021).

3.2.3 DCMD experimental setup and procedure

The Figure 3-2 shows the schematic diagram of the DCMD system in the assembled bench scale. The flat-sheet membrane module was constituted from a natural acetal copolymer manufactured by Sterlitech Corp., with an effective filtration area of 0.0042 m^2 and a commercial polytetrafloroethylene membrane (PTFE 023005 - Sterlitech Corp.) with an average pore size of 0.2 µm, porosity between 60 – 80 %, and contact angle with water of 125°. The experimental unit was equipped with two supply tanks, a precision scale (Mícron Scientific – S 0.01g), two thermometers, two peristaltic pumps (Provitec GA5200 MB), a feed electric heating system, and a permeate chiller system (AquaCooler, Australia). The feed tank was sealed and covered with aluminum foil to minimize loss by evaporation and photodegradation during the experiments.

Figure 3-2: Schematic diagram of the DCMD system



Initially, the volumes of feed (raw surface water spiked with phenolic compounds) and permeate (distilled water) were, respectively, 2 L and 1.5 L and both streams were recirculated in counter-current mode at 1.0 L min^{-1}. In all experiments, the permeate mass, the permeate and feed temperature, and the permeate electric conductivity were monitored every 10 minutes. The tests to verify the DCMD best operational conditions for the phenolic compounds retention were performed varying: i) the feed temperature (40 °C, 50 °C, and 60 °C); ii) the feed concentration (3 µg L^{-1}, 5 µg L^{-1}, 7 µg L^{-1}, and 10 µg L^{-1}); and iii) the permeate recovery rate (RR) (30 %, 50 %, and 70 %). The effect of feed temperature and RR was assessed at 5 µg L^{-1} of phenols as a recurrent concentration in the natural environment. Whereas the effect of feed concentration and recovery rate were assessed at 60 °C to achieve higher permeate fluxes. In all tests the permeate temperature was set as 25 °C.

3.2.4 Calculations

The permeate membrane flux was calculated according to Equation 3.1.

$$J_p = \frac{m_2 - m_1}{(t_2 - t_1) \cdot A_m} \qquad \text{Equation 3.1}$$

Where J_p = permeate flux (kg m^{-2} h^{-1}); t_1 and t_2 = time (h); $m_2 - m_1$ = permeate mass increase (kg) between times t_1 and t_2; and A_m = membrane area (m^2).

The permeate recovery rate (RR, %) was estimated by Equation 3.2.

$$RR = \frac{m_{df} - m_{di}}{m_{fi}} \qquad \text{Equation 3.2}$$

Where m_{di} = distillate initial mass (kg), m_{df} = distillate final mass (kg), and m_{fi} = initial feed mass (kg).

The phenolic compounds removal factor was calculated using Equation 3.3.

$$RF = \frac{m_f - m_d}{m_f} \qquad \text{Equation 3.3}$$

Where m_f = compound mass in the feed (µg), m_d = compound mass in the distillate (µg). The mass balance (Equation 3.4) was performed to determine the losses during the experiments.

$$M_s = M_i - (C_r \cdot V_r) - (C_d \cdot V_d) \qquad \text{Equation 3.4}$$

Where M_s = mass lost (µg), M_i = contaminant total initial mass (µg), C_r= solute concentrations in the retentate (µg L^{-1}), C_d = solute concentrations in the distillate (µg L^{-1}), V_r = retentate volume (L), and V_d = distillate volume (L).

The layers and membrane resistances were estimated by Equations 3.5 – 3.9 (SRISURICHAN et al., 2006).

$$R_{fb} = \frac{P_f - P_1}{J} \qquad \text{Equation 3.5}$$

$$R_m = \frac{P_1 - P_2}{J} \qquad \text{Equation 3.6}$$

$$R_{pb} = \frac{P_2 - P_p}{J} \qquad \text{Equation 3.7}$$

$$R_t = \frac{P_f - P_p}{J} \qquad \text{Equation 3.8}$$

$$R_{fouling} = R_t - R_m - R_{pb} - R_{fb} \qquad \text{Equation 3.9}$$

Where R_{fb}= feed boundary layer resistance (Pa m^2 h kg^{-1}), R_m= membrane resistance (Pa m^2 h kg^{-1}), R_{pb} = permeate boundary layer resistance (Pa m^2 h kg^{-1}), R_t = total resistance (Pa m^2 h kg^{-1}), $R_{fouling}$ = fouling resistance (Pa m^2 h kg^{-1}), P_1 = membrane surface vapor pressure at feed side (Pa), P_2 = membrane surface vapor pressure at permeate side (Pa), P_f = bulk vapor pressure at feed side (Pa), P_p = bulk vapor pressure at permeate (Pa).

The vapor pressures were calculated according to Equation 3.10 and the membrane surface temperatures were estimated by Equations 3.11 and 3.12 (considering a steady-state energy balance in the system) (SRISURICHAN et al., 2006).

$$P = EXP\left(23.238 - \frac{3841}{T - 45}\right) \qquad \text{Equation 3.10}$$

$$T_{w,f} = \frac{h_m\left(T_p + \left({}^{h_f}/_{h_p}\right)T_f\right) + h_f T_f - J\Delta H_v}{h_m + h_f(1 + \frac{h_m}{h_p})} \qquad \text{Equation 3.11}$$

$$T_{w,p} = \frac{h_m\left(T_f + \left({}^{h_p}/_{h_f}\right)T_p\right) + h_p T_p + J\Delta H_v}{h_m + h_p(1 + \frac{h_m}{h_f})} \qquad \text{Equation 3.12}$$

Where in Equation 3.10 T = temperature (K). In addition, in Equations 3.11 and 3.12, $T_{w,f}$,= temperature at interface of feed (K), $T_{w,p}$ = temperature at interface of permeate (K), T_f = temperature at bulk for feed (K), T_p = temperature bulk for permeate (K), h_m= membrane convective heat transfer coefficient (W m^{-2} h^{-1}), h_p = permeate convective heat transfer coefficient (W m^{-2} h^{-1}), h_f = feed convective heat transfer coefficient (W m^{-2} h^{-1}), and ΔH_v = vaporization heat (J kg^{-1}).

The temperature polarization coefficient (TPC) was appraised using the Equation 3.13.

$$TPC = \frac{T_{w,f} - T_{w,p}}{T_f - T_p} \qquad \text{Equation 3.13}$$

The specific energy consumption (SEC, kwh m^{-3}) was calculated (Equation 3.14 – 3.15) to the temperatures assessed (ELMARGHANY et al., 2019).

$$SEC = \frac{Q_m \cdot \rho}{J_p \cdot A_m}/3600 \qquad \text{Equation 3.14}$$

$$Q_m = m_{fr} \cdot c_p(T_f - T_p) \qquad \text{Equation 3.15}$$

Where Q_m is the total heat flux through the membrane (kW); ρ is the water density (kg m^{-3}); m_{fr} feed mass flow rate (kg s^{-1}); and c_p the feed water specific heat (kJ kg^{-1} K^{-1}).

The thermal efficiency (TE) was expressed based on Equation 3.16 (ELMARGHANY et al., 2019).

$$TE(\%) = \frac{J_p \cdot A_m \cdot \Delta H_v}{Q_m} \cdot 100 \qquad \text{Equation 3.16}$$

3.2.5 Statistical analyzes

Statistical analyzes were carried out with Action Stat® version 3.6 developed by Estatcamp. It utilizes the R language, the main statistical programming language in use worldwide, connected to Excel for statistical applications using Excel's friendly interface. The results below the quantification limit (LOQ) were utilized while the values below detection limit (LOD) were established equal zero. Descriptive statistics were calculated to show the minimum and maximum values, average, standard deviation, median, geometric average, mode, coefficient of variation, coefficient of asymmetry, coefficient of kurtosis, 25 % percentile and 75 % percentile of the phenolic compounds removal percentage and the permeate flux and electric conductivity in all tests analyzed. The Kruskal Wallis non-parametric test was used to compare the flux medians at different temperatures evaluated, and the global medians of phenols removal for the different temperatures, concentrations and RR tested. It stands out, that Kruskal Wallis test was selected to obtain greater reliability, since the number of available data is relatively small (n = 15 - 46). In addition, the time trend analysis the flux with the recovery rate was also evaluated using the non-parametric Mann-Kendall test. Statistical significance was set at 5 %.

3.3 RESULTS AND DISCUSSION

3.3.1 Feed temperature effect over DCMD performance

Figure 3-3 summarizes the descriptive statistics in box-whisker diagrams of the permeate flux and its electric conductivity for the different temperatures and APPENDIX V presented these detailed results. The flux medians were compared by using the Kruskal-Wallis and multiple comparisons test (APPENDIX VI) and the results confirmed a significant difference ($p<0.05$) of the fluxes at the temperatures studied, since flux increased with higher temperatures considering the exponential relationship between temperature and vapor pressure (PERFILOV et al., 2018). Moreover, the difference between the initial and final permeate flux (minimum and maximum values presented in Figure 3-3 (a), respectively) increases when the temperature varied from 40 to 60 ºC, indicating a greater potential for membrane fouling at higher temperatures. The fouling increase observed for higher temperature could be the result of the greater flux effect on the recovery rate, and consequently on the higher concentration of water constituents in this condition. The results are in accordance with the resistance the feed boundary layer resistance (R_{fb}) reported in Table 3-2, which were greater at higher temperature conditions. It is known that in DCMD systems, temperature polarization (TPC) usually increases with the feed temperature, increasing R_{fb} and permeate resistance (R_{pb}) and, consequently, decreasing the permeate flux (KUANG et al., 2019). However, comparing the results, the TPC did not influence the system, it was between 0.78 and 0.80 for all temperatures (Table 3-2). In addition, as the permeate electric conductivity remained practically constant over time (Figure 3-3 (b)), it can be said that there was no membrane wetting.

Figure 3-3: Box-whisker graph for permeate flux (a) and electric conductivity (b) along the tests under different temperature conditions

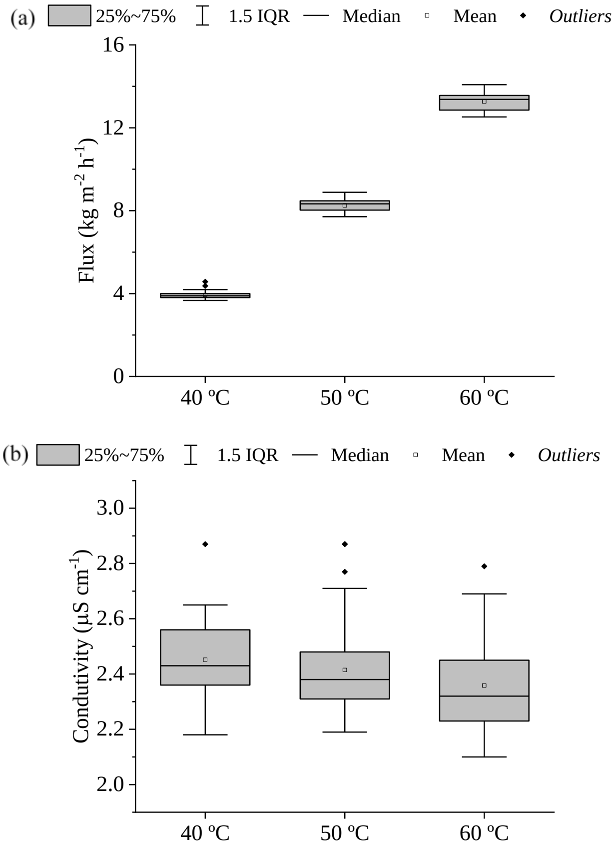


Table 3-2: Layer resistances and temperature polarization (TPC)

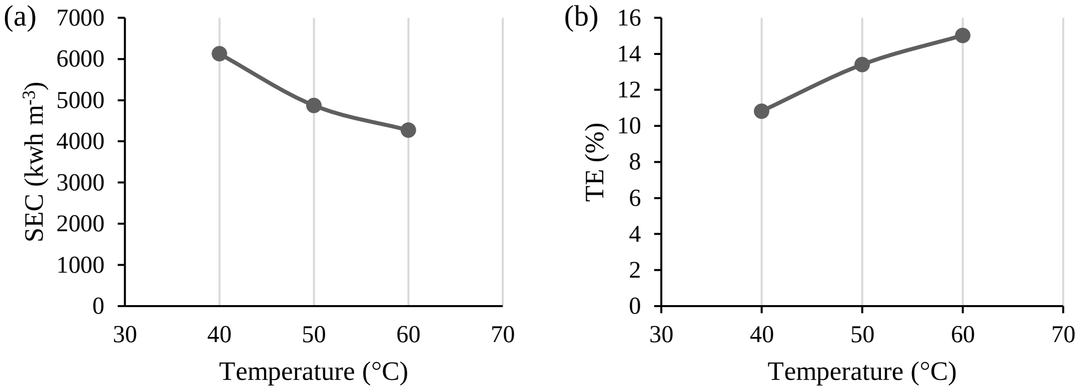
Temperature (°C)	**Resistances (Pa m^2 h kg^{-1})**					**TPC**
	R_{fb}[1]	R_{pb}[2]	$R_{fouling}$[3]	R_m[4]	R_{total}[5]	
40	163.84	104.93	46.87	1036.71	1352.35	0.80
50	203.22	90.55	70.34	1004.29	1368.40	0.79
60	260.80	83.33	64.80	1096.28	1505.21	0.78

[1]Resistance to filtration, [2]resistance to permeate, [3]resistance to fouling, [4]membrane resistance, and [5]total resistance.

According to the Kruskal-Wallis and multiple comparisons results there was no significant difference of the permeate electric conductivity at 40 - 50 °C and neither at 50 - 60 °C (APPENDIX VI). However, a significant difference ($p=0.035$) was obtained when the permeate electric conductivity from 40 and 60 °C were compared, with lower median value at 60 °C. A reasonable explanation to that fact is the higher permeate flux obtained at this temperature, which were enough to dilute the ions concentration that may have transferred to the permeate.

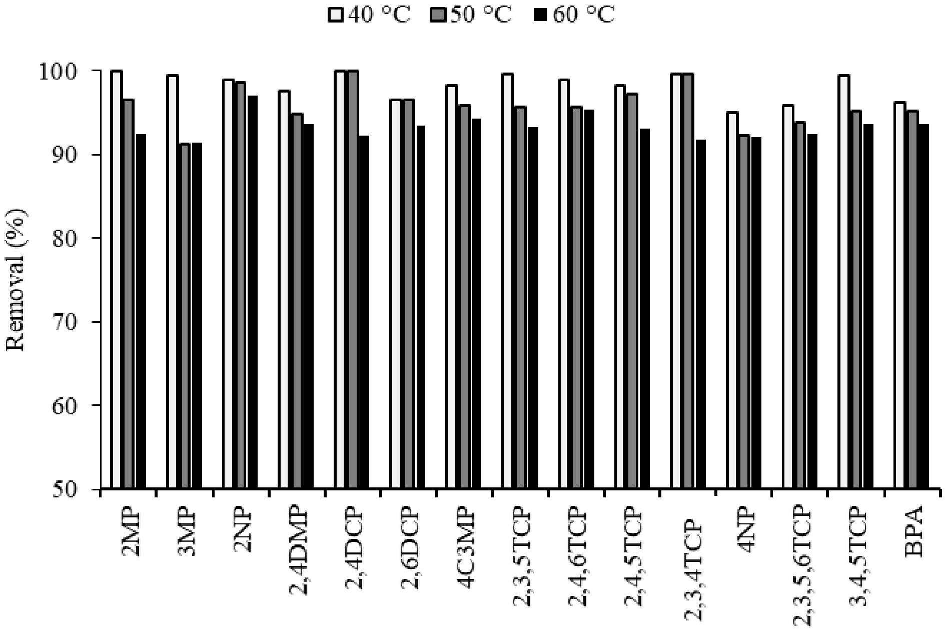
The SEC and TE energy indicators were used to assess the energy efficiency and thermal performance of the DCMD (Figure 3-4), respectively. The SEC values decreased at higher temperatures, due the fact that the permeate flux increased sufficiently to overcome the augmentation of heat loss expected to occur at higher temperatures. The system performed its best SEC at 60 °C. Grossi et al. (2020) measured the SEC for a DCMD to treat a contaminated superficial water and found also lower values for the temperature of 60 °C when compared to 40 and 50 °C. Furthermore, the calculated TE values increased with the feed temperature growth, as reported in the literature (ZHANG et al., 2015). In addition, Criscuoli et al. (2008) reports a TE value of 17 %, which is close to that found in this research at 60 °C. Therefore, considering the greater flux and the absence of membrane wetting, the temperature of 60 °C may be the best alternative for the system operation.

Figure 3-4: SEC (a) and TE (b) for the temperatures evaluated



Although there is an increase in the process flux by varying the temperature between 40 - 60 ºC, the removal of phenolic compounds has an inverse relationship as shown in Figure 3-5 and the descriptive statistics for these tests are in APPENDIX VII.

Figure 3-5: Summary of phenols removal efficiency with temperature variation

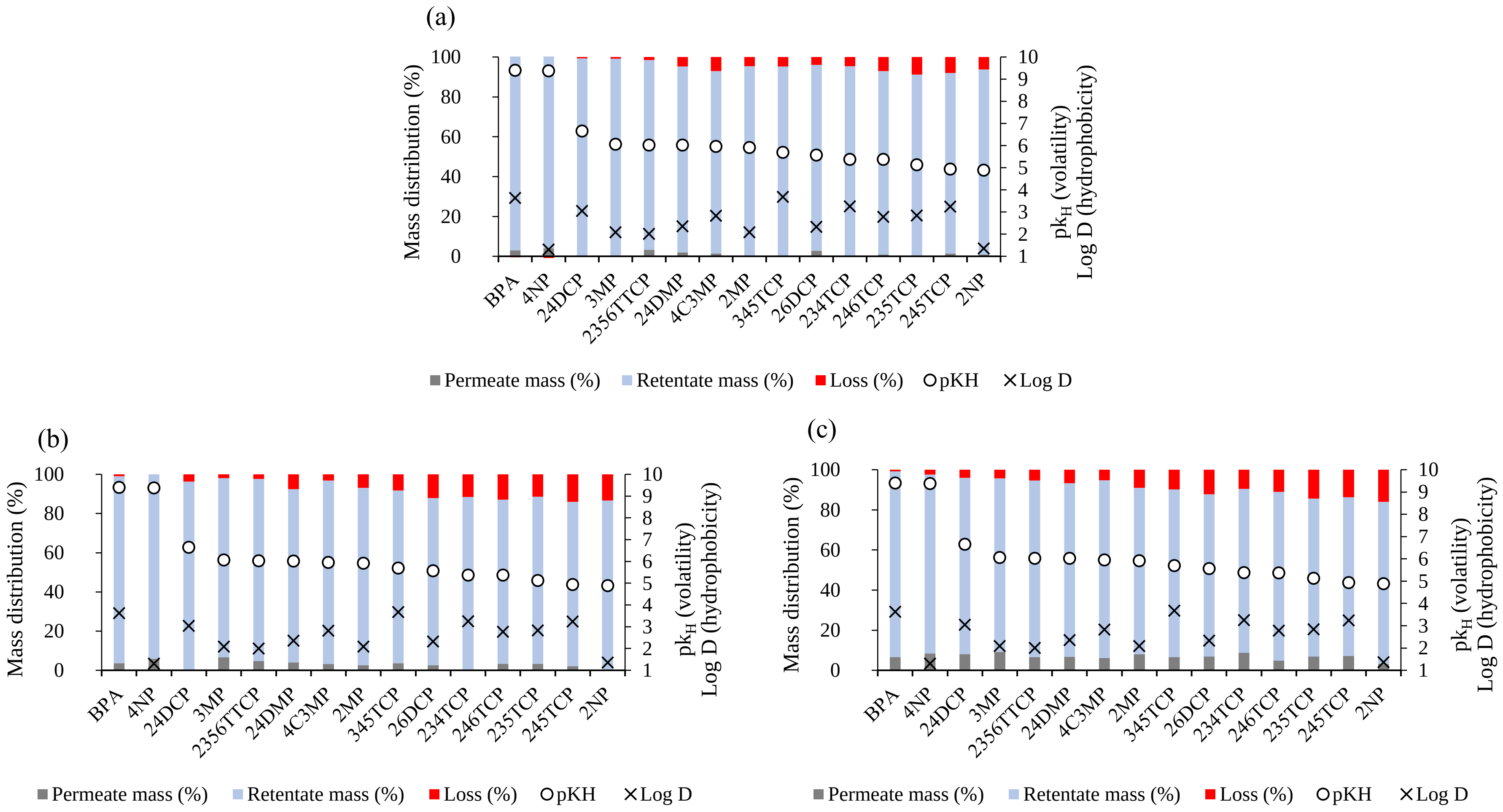


As can be seen, the phenolic compounds retention decreases as the process temperature increases, with average removals between 98.2 ± 1.6 % to 93.3 ± 1.4 % for the temperatures of 40 and 60 ºC, respectively. Theoretically, the membrane distillation is permeable only to vapors, however, the increase in temperature increases the vapor pressure of phenolic compounds, favoring their volatilization and their transport through the membrane pores [38]. In the literature, there is still no consensus on the retention efficiency of these compounds. Some researchers reported that this efficiency for different phenols ranged from 54 – 70 % (WIJEKOON et al., 2014) to 99 % (HAMZAH and LEO, 2016).

The comparison between the global removal efficiency at the different feed temperatures showed a significant difference ($p<0.05$), demonstrating the contribution of the compound's volatility in their rejection (APPENDIX VIII). Among all tests, the one performed at 50 ºC presented a greater amplitude (APPENDIX VII) in the compound's removal values (91.1 - 99.9 %). For this test, 25 % of the compounds were removed less than or equal to 94.9 % ($P_{25\%}$), whereas 75 % were removed at values less than or equal to 96.8 % ($P_{75\%}$). On the other hand, the tests carried out at 40 and 60 ºC presented smaller amplitudes, 4.9 % and 5.7 %, respectively.

To better understand how compounds removal occurred by the DCMD, the in Figure 3-6 presents the phenols mass distribution in 40, 50, and 60 °C, in addition to the compound's hydrophobicity (Log D) and volatility (pK_H).

Figure 3-6: Phenols mass distribution in T = 40 °C (a), T = 50 °C (b), and T = 60 °C (c), and the compounds Log D and pKH



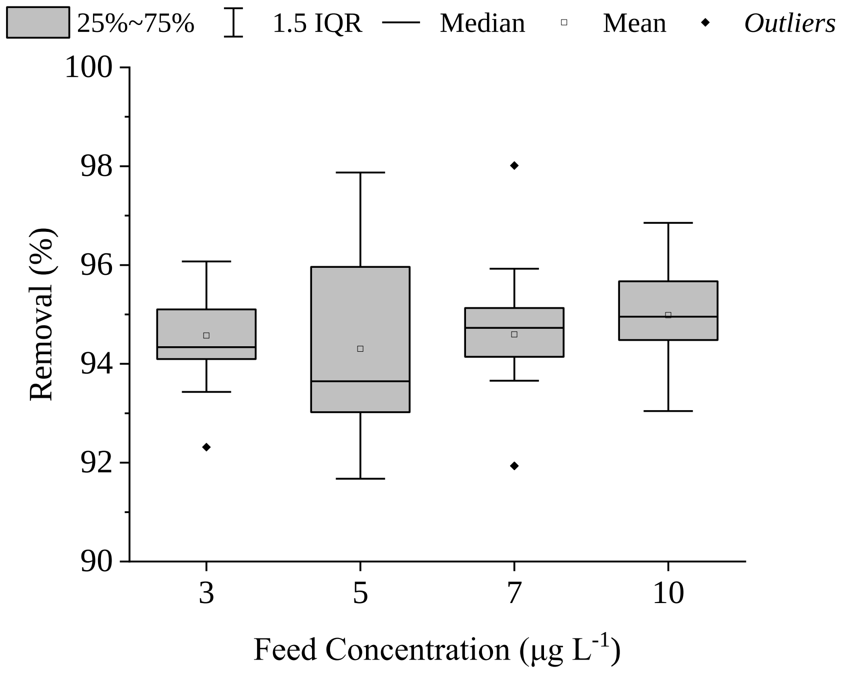
It is noted a compounds mass increase in the permeate stream with the temperature increase, which corroborates to the fundamental role of compounds volatility in the technology efficiency. Besides that, the loss (%) reported in Figure 3-6, which could be associated to volatilization or adsorption on the membrane surface, had a significant correlation with each phenolic compound volatility ($r_{Spearman}>0.8$; p-value<0.002 - APPENDIX IX) whereas hydrophobicity and the ratio between these two properties (pk_H/Log D) had no correlation or the correlation was non-significant (APPENDIX X - XI, respectively). In other words, a higher loss was noticed for more volatile compounds and the compound hydrophobicity did not play a role in the system phenols loss, indicating that the loss of the compounds is not significant associated with adsorption on the membrane surface. These aspects are important because some authors have indicated that more hydrophobic substances (Log D>3) can lead to low pollutant removal or adsorption on the membrane surface (WIJEKOON et al., 2014; YAO et al., 2018). However, for the compounds in question in trace concentrations, volatility has shown to be the parameter that most influences the process.

3.3.2 Feed concentration effect over DCMD performance

The compounds concentration in the range evaluated did not affect the membrane performance confirmed by the results presented in APPENDIX XII - XIII. It is noted that the permeate flux does not decrease significantly and the resistances found for all tests presented remarkably close values as well as the TPC, not influencing the system. In addition, it can be said that there wasn’t membrane wetting checking the low initial and final permeate conductivities.

The concentration effect on the phenolic compound’s removal is shown in Figure 3-7 (APPENDIX IV). Similarly, to the temperature tests, the removal values obtained for different phenolic compounds concentrations were compared by the Kruskal-Wallis statistics for greater results confidence. In this case, the p-value = 0.4108 (Kruskal-Wallis χ^2 = 2.877) showed no statistical difference between the compared medians. The result corroborates to the DCMD robustness in removing these compounds in the concentrations which they are found in nature. It is worth mentioning that these concentrations values were defined based on monitoring data presented in the literature for superficial water (RAMOS et al., 2021; FILIPOV et al., 2002; MICHAŁOWICZ et al., 2011). Thus, the technology robustness could be extrapolated in eventual water treatment for real scales operation.

Figure 3-7: Box-whisker graph for the phenolic compound's removal in the different concentrations (operating temperature: 60 °C; n = 15)



Although there was no significant difference between the global removal medians, greater amplitudes were observed for the experiments with 5 and 7 µg L^{-1} (6.2 and 6.1 %, respectively). In the test performed with a concentration of 5 µg L^{-1}, 25 % of the compounds showed removal values lower than or equal to 93 % ($P_{25\%}$), whereas 75 % of the compounds presented removal values less than or equal to 95.6 % ($P_{75\%}$). For the test performed with a concentration of phenolic compounds equal to 7 µg L^{-1}, the values of $P_{25\%}$ and $P_{75\%}$ were, respectively, 94.1 and 95.1 %. It is noteworthy that this variation was not attributed to any specific phenolic compound.

3.3.3 Recovery rate effect over DCMD performance

The permeate flux and electric conductivity data (APPENDIX XV) at the studied recovery rates (30, 50, and 70 %) are presented in the Figure 3-8, which reveals a slightly flux decay at 50 % RR (J/J_0=0.92) in relation to 30 % RR (J/J_0=0.93), but it remained compared to 70 % RR (J/J_0=0.89). It is confirmed by the Mann-Kendall test result (p-value = 4.23E-13), showing a tendency to reduce the flux with the recovery rate increase (APPENDIX VI). Therefore, the negative angular coefficient found reaffirmed this tendency. Besides that, a significant linear correlation was found ($p<0.0001$) for flux and RR (APPENDIX XVII) and the residual analysis for this regression was carried out (APPENDIX VIII).

The reduction observed in flux can be justified by the increase in the resistance to fouling ($R_{fouling}$) with the RR growth presented in Table 3-3, which indicates a possible membrane fouling. However, it is noteworthy that the reduction was relatively low analyzing the relationship between the final and initial flux (0.89). Remembering that, a high recovery rate means a high process yield (SILVA et al., 2021).

Regarding to the electric conductivity, it increased slightly from the 30 % RR, indicating the presence of ionic impurities in the permeate, but later it was stabilized (from 50 % to 70 % RR). This increase in electric conductivity can be attributed to the intermittent operation of the membrane distillation unit since it was necessary to interrupt the test and start it at the other day in the 30 % RR. Guillen-Burrieza et al. (2011) demonstrated that when a membrane cools down during the shutdown period, some substances can condense on the membrane pore resulting in some locally wetted pores which could worsening the distillate quality at the next day in the beginning of operation. Then, with the continuous evaporation and diffusion of vapor during the process, the wet pores can recharge their hydrophobicity (HEJAZI et al., 2019).

Figure 3-8: Permeate flux and permeate electric conductivity according permeate recovery rate (RR)

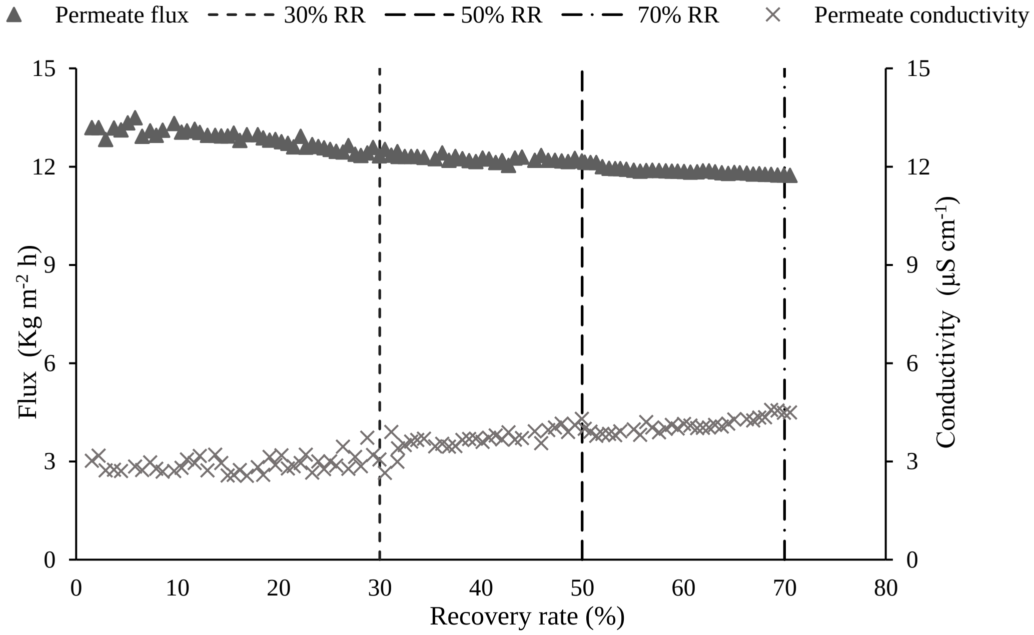
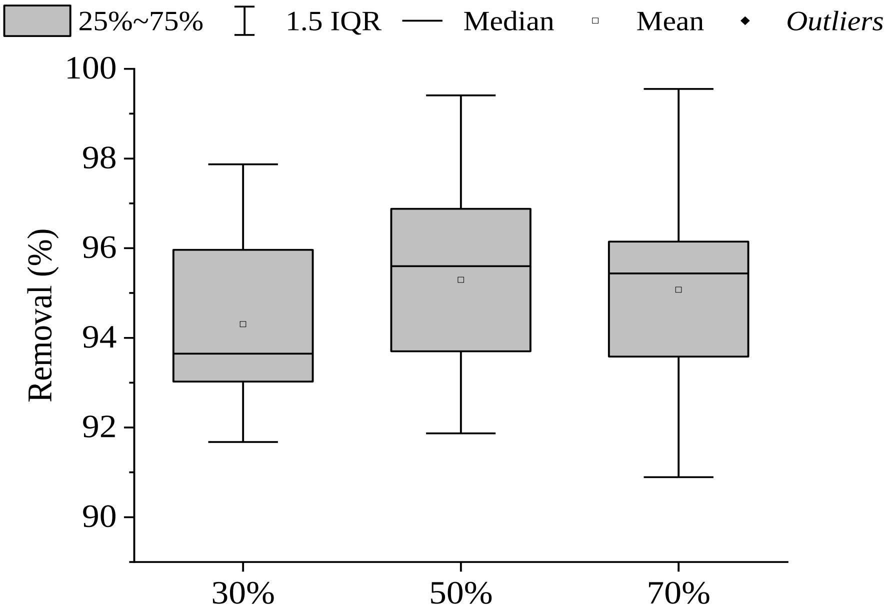


Table 3-3: Parameters and correlation coefficient of the calibration curves used in the sample's quantification

Recovery rate (%)	**Resistances (Pa m^2 h kg^{-1})**				
	R_{fb}	R_{pb}	$R_{fouling}$	R_m	R_{total}
30	264.14	84.70	114.15	1041.01	1504.00
50	272.85	87.49	152.25	1041.01	1553.60
70	274.84	120.34	189.41	1021.99	1606.58

The phenolic compounds removal efficiency in the studied recovery rates are presented in Figure 3-9 and APPENDIX XIX. The average values varied between 94.3 ± 1.9 % and 95. 0 ± 2.2 %, for the 30 % RR and 70 % RR, respectively. However, the phenols removal values at the different RR did not show any significant difference after being compared by the Kruskal-Wallis test (χ^2 = 2.322; p = 0.3132). Moreover, it is important to highlight that the phenols removal efficiency amplitudes were close in the three recovery rates studied. Thus, with that result is possible to achieve higher recovery rates without compromising the permeate quality in terms of phenolic compounds, what made the operation becomes more advantageous in operational and economic terms.

Figure 3-9: Box-whisker chart for removing phenolic compounds at different recovery rates (operating temperature: 60 ºC; n = 15)



The permeate physicochemical parameters for 30 %, 50 %, and 70 % RR are shown in Table

4-3, which have also been efficiently removed by technology, reassuring the potential of DCMD to generate a high-quality permeate for applications in the production of pollutant-free drinking water. With the current scenario of water resources contamination by different types of complex pollutants, such as the phenols studied, and situations of environmental disasters, it is essential to think about the development of new robust and compact water treatment systems such as DCMD. This technology can be applied for end-of-pipe process after pre-treatments when necessary for particles removal and decontamination and associated with solar energy for decentralized/centralized treatment systems in communities that do not have access to conventional water and energy network. It is worth mentioning that the low fouling propensity of DCMD systems can dispenses a feed solution pre-pretreatment (DAVEY et al., 2021), as in other conventional membrane separation process that also produce a high-quality water, such as reverse osmosis and nanofiltration.

Table 3-4: Permeate sample fiscal chemical characteristics of 30 %, 50 %, and 70 % RR

Sample	**pH**	**Perceived color (mg Pt-Co L^{-1})**	**TSS (mg L^{-1})**	**Electric conductivity (µS cm^{-1})**	**Alkalinity (mg $CaCO_3$ L^{-1})**	**NH_4^+ (mg L^{-1})**	**Ca (mg L^{-1})**	**Mg (mg L^{-1})**	**Na (mg L^{-1})**	**Li (mg L^{-1})**	**Fe (mg L^{-1})**
Raw water	7.3	74	16	116.80	29.3	< 1.25	21.10	6.40	5.68	< 0.20	< 0.1
Permeate 30 % RR	7.09	< 5	< 0.01	2.65	2.1	< 1.25	< 2.50	< 1.25	< 1.0	< 0.20	< 0.1
% removal	-	> 93.24	> 99.94	98	93	-	-	-	-	-	-
Permeate 50 % RR	7.37	< 5	< 0.01	3.99	3.1	< 1.25	< 2.50	< 1.25	< 1.0	< 0.20	< 0.1
% removal	-	> 93.24	100	97	89	-	-	-	-	-	-
Permeate 70 % RR	7.22	< 5	< 0.01	4.49	4.6	< 1.25	< 2.50	< 1.25	< 1.0	< 0.20	< 0.1
% removal	-	> 93.24	> 99.94	96	84	-	-	-	-	-	-

3.4 CONCLUSION

Based on the experimental results, the temperature increase in DCMD contributed to a greater permeate flux but lower phenolic compounds removal. The influence of volatility in rejection of this compounds in trace concentration was highlighted in comparison to the hydrophobicity. Therefore, 40 °C was the greatest temperature for the compound's removal. However, at 60 °C more than 90 % of the pollutants were removed, the permeate flux was relatively higher and it was the best system SEC, so depending on the feed initial quality and the treatment purpose this temperature can be used. The results indicate the DCMD robustness for removal phenolic compounds in the concentrations under study (3 – 10 µg L^{-1}) representing real contamination scenarios as reported in the literature.

The DCMD operated in a stable manner up to a 30 % RR, without significant resistance to filtration. However, at 50 % RR, the resistance to filtration due to fouling leads to a decrease in the permeate flux. Although the relation between the final and initial flux was relatively low (J/J_0=0.89). Regarding to permeate quality, the pollutants removal reached average values of 94.3 ± 1.9 % and 95.0 ± 2.2 % for 30 % and 70 % RR, respectively, not presenting significant statistical difference. The physicochemical parameters evaluated were also efficiently removed. Therefore, the technology proved to be efficient in reducing phenols in the different RR studied. Nevertheless, it is recommended to work at a RR equivalent to the point prior to flux decay (RR<30 %) to avoid fouling and performance loss, but even at superior RR the permeate quality was not compromised. The fouling control strategies can be used to make the operation with a higher RR more sustainable and studies in this line need to be developed. For conventional membrane processes, these strategies are already well outlined.

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CHAPTER IV – FOULING EVALUATION IN THE MEMBRANE DISTILLATION: SUPERFICIAL WATER TREATMENT WITH PHENOLIC COMPOUNDS

4.1 INTRODUCTION

Membrane distillation (MD) has shown strong promise for treating superficial water with complex pollutants, such as pharmaceuticals (COUTO et al., 2020), pesticides (ASIF et al., 2018), metals (GROSSI et al., 2020), and phenolic compounds (RAZA et al., 2018; RAMOS et al., 2021). The phenols are present in natural water worldwide (RAMOS et al., 2021; WANG and WANG, 2018; PETRIE et al., 2016). It is still a challenge to remove them by conventional water treatments (KARABELAS and PLAKAS, 2011), therefore the implementation of more robust treatments, such as MD, is increasingly needed in the water sector. The MD combines a thermal process and membrane technology, in which the mass transfer is driven by the vapor pressure difference across the microporous hydrophobic membrane (ZHANG et al., 2021). This technology has the potential to become a sustainable alternative when integrated with solar energy, thermal collectors, or industrial waste heat sources, since it does not require high intensity heat to produce a higher quality water (KARAM et al., 2019).

The direct contact membrane distillation (DCMD) is one of the MD processes most used for general applications because of its simplest configuration, since the evaporation and condensation are taking place inside the membrane module (LAQBAQBI et al., 2018). The membrane fouling can affect the performance and stability of the process in the long-term applications, and it is necessary to understand the formation and mechanism of fouling that occurs specifically for DCMD (KARAM et al., 2019; TIJING et al., 2015) and how this can affect the removal of volatile and semi-volatile compounds such as phenols. The fouling can reduce the water quality and its recovery, which increase the system's operational cost. It can occur due to the accumulation of unwanted materials on the membrane surface or inside the pores (pore blockage). According to the fouling material, it is divided into inorganic (scaling), organic, colloidal, and biological fouling (FORTUNATO et al., 2018; KARIMA et al., 2021). The Alkhatib (2021) cited the identification of two more types of fouling that are less known and linked to specific feed solutions being them membrane degradation (GRYTA, 2012) and chemical oxidation by residual chlorine (GOH et al., 2018).

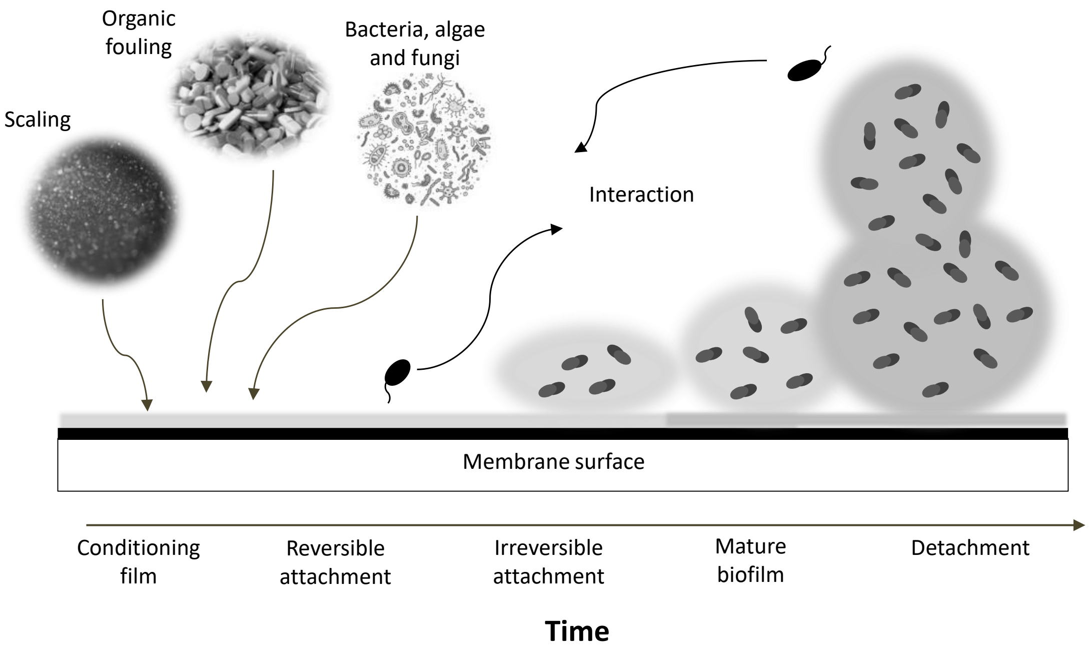
Fouling in MD involves several mechanisms such as adsorption, accumulation, or precipitation that can occur separately or simultaneously. In this sense, a variety of parameters influence membrane fouling especially the composition of the feed solution that can determine the membrane fouling type. The magnitude of MD permeate flux can be strongly affected by the fouling type, since the deposits formed on the membrane surfaces mainly cause a reduction in the driving force, however, in some cases changes in the membrane morphology can also be observed (COSTA et al., 2021). It is noteworthy that the hydrophobic characteristic of MD membranes increase the absorption of organic materials on the membrane surface and proteins exhibit a very high tendency to deposit on hydrophobic membranes (HABIMANA et al., 2014). The $CaCO_3$ precipitation was also considered a major challenge during the production of demineralized water through the MD process from natural water, as the $CaCO_3$ deposit forms local "mountains" on the membrane surface which additionally causes an increase in the hydraulic resistance to the feed flux (HOANG, 2015). The scale layers formed on the membrane surface can be divided into two basic categories: porous and homogeneous (non-porous). In the first case, a decline in permeate flux mainly results from an increase in thermal resistance (temperature polarization), while non-porous scale formation causes a significant increase in mass transfer resistance and the permeate flux value approaches exponentially to zero (PIYADASA et al., 2017).

The identification of diverse foulants and analyzing fouling mechanisms would contribute to the advancements in fouling mitigation strategies (ALKHATIB et al., 2021). Some efforts have been made to develop methods to prevent or mitigate this process, ranging from traditional methods, such as chemical cleaning (PENG et al., 2015), to membrane surface modifications (GRYTA, 2021; ANARI et al., 2019), but the integration of various techniques with operational methods has proven to be effective (GOH et al., 2019). In addition, water pretreatment can also be applied to remove compounds that can promote fouling (RAY et al., 2021). However, more studies are still needed focusing on the MD systems application to reduce problems with fouling.

Another point of attention in the MD is the membrane wettability, which can occur associated with fouling and is usually due to three main factors, namely the surface tension of the process solution, the material, and the membrane structure (CHAMANI et al., 2021). With the membrane wettability, the liquid penetrates the pores, reducing its selectivity and harming its separation objectives (GRYTA, 2021), which can decrease the rejection of phenolic compounds, since the compounds are able to pass through the membrane together with other contaminants. The use of polytetrafluoroethylene (PTFE) membranes, which are more hydrophobic than other materials, in addition to have thermal and chemical stability, can help to avoid problems in the MD operation because it is less susceptible to wetting (ASHOOR et al., 2016). Most commercial MD installations uses PTFE membranes (THOMAS et al., 2017; REN et al., 2020).

In surface waters, natural organic matter (NOM) is abundant, this rich organic content can decrease membrane hydrophobicity and induce membrane wetting (CHANG and LEOW, 2020), as hydrophobic membranes do not have a hydration layer that prevents organic foulant adhere directly to the membrane surface (ALKHATIB et al., 2021). The adsorption of organic matter on the membrane surface can occur due to hydrophobic interactions, chemical, and electrostatic affinity (SCHÄFERA et al., 2000). The NOM can attach to each other and form different structures, in addition, to help the formation of biofouling, as they often provide nutrition for the bacteria present in the water (GOH et al., 2018). The Figure 4-1 shows the mechanism of biofilm development, that in recent studies suggest a three-phase model (JIANG et al., 2019), similar to other membrane processes, where occurs the establishment of the conditioning film and first settlement of pioneer microorganisms, followed by the biological succession, and the growth and dispersion of the biofilm.

Figure 4-1: Biofouling development



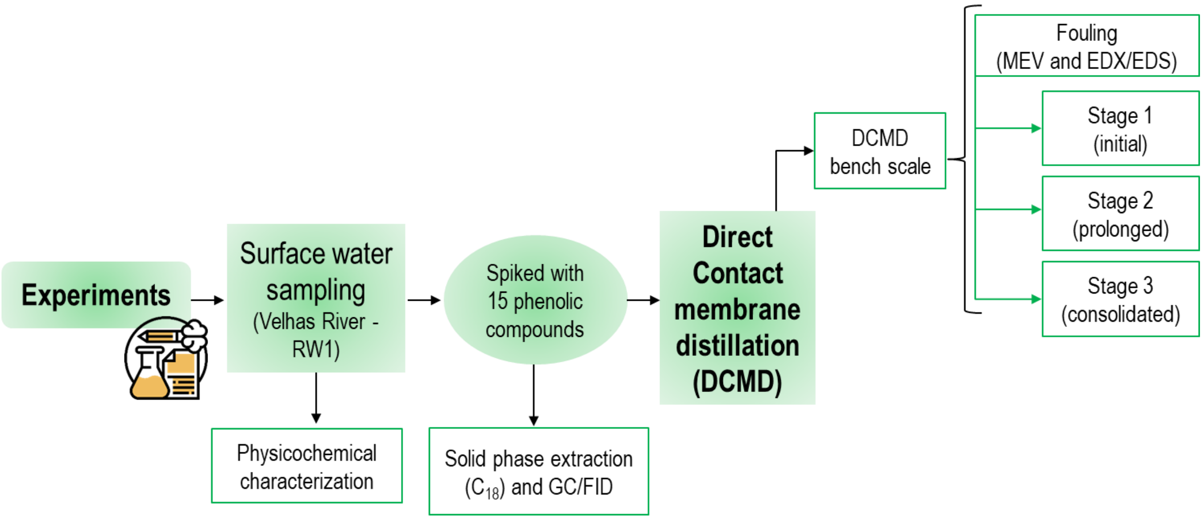
Source: Adapted from Costa et al. (2021)

Although DCMD has proved applicable for micropollutants treatment in many studies, fouling condition is a complex phenomenon and still not well understood in MD compared to the membrane pressure-driven process, especially for volatile and semi volatile compounds, considering the differentiated driving force and mechanism of transport in MD. Therefore, the DCMD performance and fouling mechanism were assessed while treating superficial water with fifteen phenolic compounds in trace concentration. The effect of fouling on the micropollutants retention was systematically investigated through permeate flux, permeate electric conductivity, pollutant removal factor, and membrane surface characteristics. The study aims to improve the comprehension of the MD to remove phenolic compounds in trace concentration and, consequently, the production of higher quality water.

4.2 MATERIALS AND METHODS

Figure 4-2 presents a flowchart of the experimental steps performed and it is described in detail in the following sections.

Figure 4-2: Experimental steps performed



4.2.1 Characteristics of the superficial water

The superficial water samples were obtained from the Velhas river located in Minas Gerais (Brazil) following recommendations for water sampling and preservation presented on the EPA method 528 (EPA, 2000). This water body has been impacted by sewage discharge, industrial and agriculture wastewater. The turbidity and total solids (TS) were characterized with 14,2

NTU and 108 mg L^{-1}, respectively. The water pH was 7.3 and the dissolved organic carbon 1.22 mg L^{-1}. Before DCMD treatment, the superficial water was spiked with fifteen phenolic compounds, defined based on the EPA's list of priority compounds, using the EPA 8040A Phenol Calibration Mix and Bisphenol A (99 %) standards purchased from Sigma-Aldrich®. The compounds monitored in the raw water and DCMD permeate were: 4-chloro-3-metylphenol (4C3MP), 2-nitrophenol (2NP), 2,4-dimethylphenol (24DMP), 2,4-dichlorophenol (24DCP), 4-nitrophenol (4NP), bisphenol A (BPA), 2-metylphenol (2MP), 3-metylphenol (3MP), 2,6-dichlorophenol (26DCP), 2,3,5-trichlorophenol (235TCP), 2,4,5-trichlorophenol (235TCP), 2,4,6-trichlorophenol (246TCP), 2,3,4-trichlorophenol (234TCP), 2,3,5,6-tetrachlorophenol (2356TTCP), and 3,4,5-trichlorophenol (345TCP).

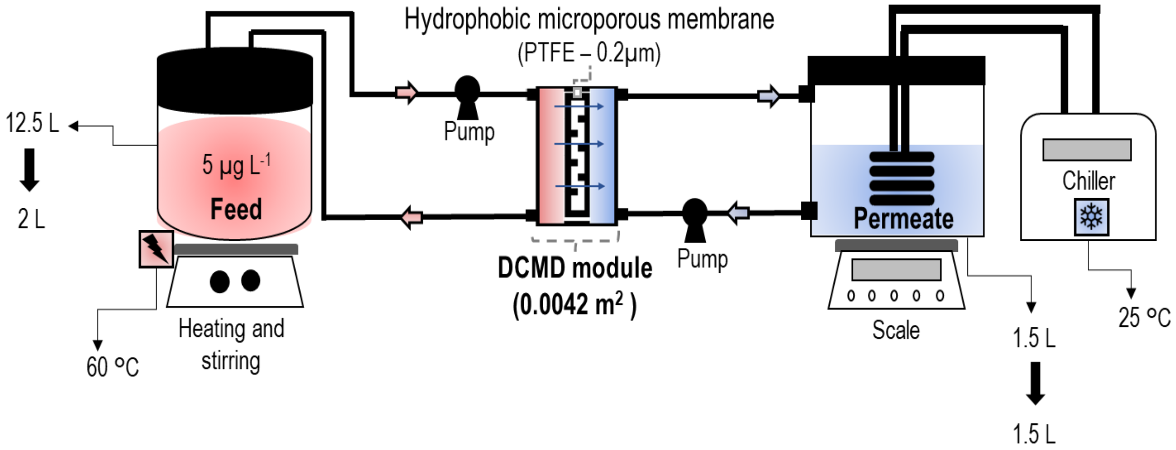
4.2.2 Analytical method

The phenolic compounds identification and quantification were performed using solid-phase extraction, with C_{18}/18% cartridges (500 mg/6 mL - Applied Separations) in the pre-concentration process and methanol (Exodus Scientific®) as solvent, and gas chromatography (GC - 2010-Plus, Shimadzu) equipped with the flame ionization detector (FID), based on EPA methods (528, 3535A, and 8041). To guarantee a reliable result, the protocol was validated as recommended by the International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use (ICH, 2005). The methodology and the validation details can be seen in Ramos et al. (2021).

4.2.3 Experimental set-up and running conditions

The schematic diagram of the DCMD set-up used in this study for superficial water treatment is shown in Figure 4-3.

Figure 4-3: The schematic diagram of the DCMD set-up



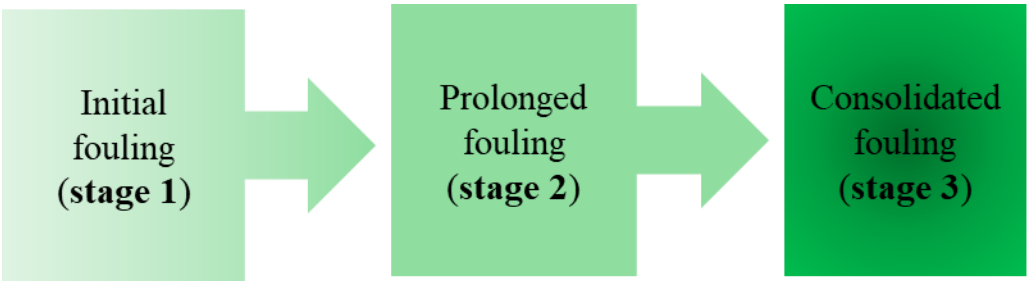
The commercial polytetrafloroethylene membrane (PTFE 023005) manufactured by Sterlitech Corp. with an average pore size of 0.2 µm, porosity between 60 – 80 %, and contact angle with water of 125° was used in one membrane module (natural acetal copolymer - Sterlitech Corp.) with an effective filtration area of 0.0042 m^2. The experimental set-up was equipped with a permeate tank, a precision scale (Mícron Scientific – S 0.01g), a permeate chiller system (AquaCooler, Australia), a feed tank, two peristaltic pumps (Provitec GA5200 MB), and a feed electric heating system. It is important to note that the feed tank was sealed and covered with aluminum foil to minimize loss by evaporation and photodegradation.

The raw surface water (12.5 L) was spiked with phenolic compounds in the concentration of 5 µg L^{-1} and was used in the feed tank. Distilled water was used in the permeate tank with a volume of 1.5 L. In addition, the test was continuously monitored to observe the membrane fouling process. After fouling formation (observed by the drastic reduction in permeate flux), the feed solution was replaced by 2 L of the water with the same concentration and the permeate was also replaced by 1.5 L of distilled water to observe the effect of the fouling layer on compound retention. The streams were recirculated in counter-current mode at 1.0 L min^{-1} and the permeate and feed temperatures were set as 25 °C and 60 °C, respectively. In the experiment, the permeate mass, the permeate and feed temperature, and the permeate electric conductivity were monitored every 10 minutes.

4.2.4 Membrane fouling analysis

Considering the MD application for producing high quality drinking water by removing micropollutant, it is important to evaluate the technology robustness, checking the pollutants behavior with the fouling process. Therefore, the flux decay, resistances, and wetting time were calculated according to Section 4.2.5 for the three stages of fouling (Figure 4-4) according to the permeate flux decay, which were defined considering the first 10 hours of the test as initial fouling (stage 1), the period of greater flux decay (145 hours) as prolonged fouling process (stage 2), and the test after the fouling layer formation with the feed solution exchange (10 hours) as consolidated membrane fouling (stage 3). Besides the flux decline analysis, the membrane surface was also evaluated for the surface water spiked with phenolic compounds. In this regard, a fouled membrane sample was properly cut, dried at room temperature (25 °C) and subjected to scanning electron microscopy (SEM) by X-ray in energy dispersion (EDX/EDS). In addition, extracellular polymeric substances (EPS) was also evaluated on the surface of the membrane (APPENDIX XX).

Figure 4-4: Flowchart of evaluated fouling stages



4.2.5 Calculation

The permeate membrane flux was calculated according to Equation 4.1.

$$J_p = \frac{m_2 - m_1}{(t_2 - t_1) \cdot A_m}$$ Equation 4.1

Where J_p = permeate flux (kg m^{-2} h^{-1}); t_1 and t_2 = time (h); $m_2 - m_1$ = permeate mass increase (kg) between times t_1 and t_2; and A_m = membrane area (m^2).

For the estimated resistances, the Equations 4.2 – 4.6 (SRISURICHAN et al., 2006) were used.

$$R_{fb} = \frac{P_f - P_1}{J}$$ Equation 4.2

$$R_m = \frac{P_1 - P_2}{J}$$ Equation 4.3

$$R_{pb} = \frac{P_2 - P_p}{J}$$ Equation 4.4

$$R_t = \frac{P_f - P_p}{J}$$ Equation 4.5

$$R_{fouling} = R_t - R_m - R_{pb} - R_{fb}$$ Equation 4.6

Where R_{fb}= feed boundary layer resistance (Pa m² h kg^{-1}), R_m= membrane resistance (Pa m² h kg^{-1}), R_{pb} = permeate boundary layer resistance (Pa m² h kg^{-1}), R_t = total resistance (Pa m² h kg^{-1}), $R_{fouling}$ = fouling resistance (Pa m² h kg^{-1}), P_1 = membrane surface vapor pressure at feed side (Pa), P_2 = membrane surface vapor pressure at permeate side (Pa), P_f = bulk vapor pressure at feed side (Pa), P_p = bulk vapor pressure at permeate (Pa).

The vapor pressures were calculated by Equation 4.7 (KHAYET, 2011) and the membrane surface temperatures, considering a steady-state energy balance in the system, were estimated by Equations 4.8 and 4.9 (SRISURICHAN et al., 2006).

$$P = EXP\left(23.238 - \frac{3841}{T-45}\right)$$ Equation 4.7

$$T_{w,f} = \frac{h_m\left(T_p + \left({}^{h_f}\!/_{h_p}\right)T_f\right) + h_f T_f - J\Delta H_v}{h_m + h_f(1 + \frac{h_m}{h_p})}$$ Equation 4.8

$$T_{w,p} = \frac{h_m\left(T_f + \left({}^{h_p}\!/_{h_f}\right)T_p\right) + h_p T_p + J\Delta H_v}{h_m + h_p(1 + \frac{h_m}{h_f})}$$ Equation 4.9

Where T = temperature (K), $T_{w,f}$,= temperature at interface of feed (K), $T_{w,p}$ = temperature at interface of permeate (K), T_f = temperature at bulk for feed (K), T_p = temperatu re bulk for permeate (K), h_m= membrane convective heat transfer coefficient (W m^{-2} h^{-1}), h_p = permeate convective heat transfer coefficient (W m^{-2} h^{-1}), h_f = feed convective heat transfer coefficient (W m^{-2} h^{-1}), and ΔH_v = vaporization heat (J kg^{-1}).

The temperature polarization coefficient (TPC) was assessed by Equation 4.10 (SRISURICHAN et al., 2006).

$$TPC = \frac{T_{w,f} - T_{w.p}}{T_f - T_p} \qquad \text{Equation 4.10}$$

To evaluate the phenolic compounds removal factor the Equation 4.11 was used.

$$RF = \frac{m_f - m_d}{m_f} \qquad \text{Equation 4.11}$$

Where m_f = compound mass in the feed (µg), m_d = compound mass in the distillate (µg). The losses during the experiments were determine with mass balance (Equation 4.12).

$$M_s = M_i - (C_r \cdot V_r) - (C_d \cdot V_d) \qquad \text{Equation 4.12}$$

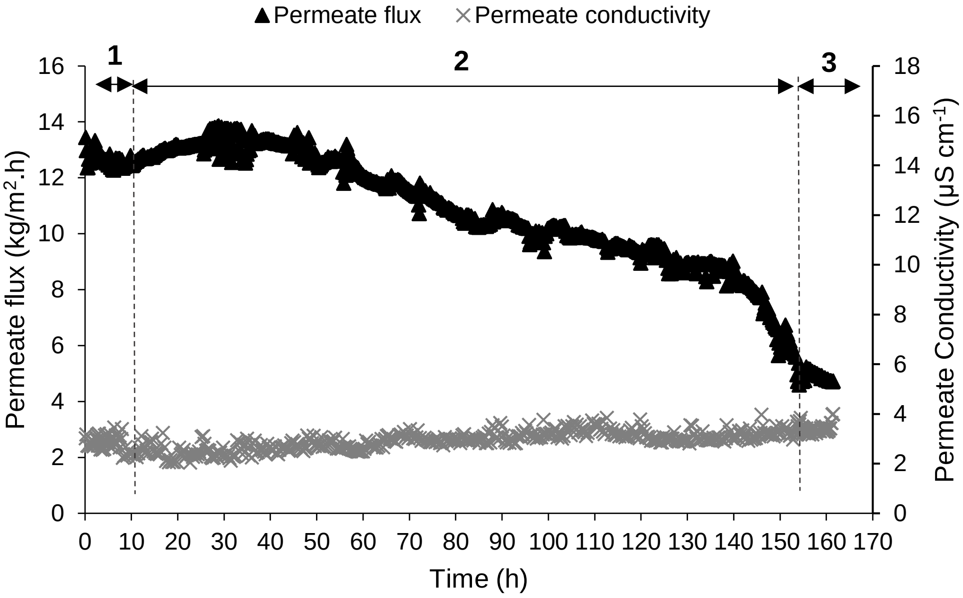
Where M_s = mass lost (µg), M_i = contaminant total initial mass (µg), C_r= solute concentrations in the retentate (µg L^{-1}), C_d = solute concentrations in the distillate (µg L^{-1}), V_r = retentate volume (L), and V_d = distillate volume (L).

4.3 RESULTS AND DISCUSSION

4.3.1 Membrane fouling

Figure 4-5 shows the decay of the permeate flux and the electric conductivity considering the three phases of the fouling process analysis. It is noteworthy that the three stages were defined considering the initial fouling (stage 1), the prolonged fouling process (stage 2), and the consolidated membrane fouling (stage 3).

Figure 4-5: Permeate flux and permeate electric conductivity



(1) initial fouling; (**2**) prolonged fouling process; (**3**) consolidated membrane fouling

The time trend analysis for the flux using the non-parametric Mann-Kendall test with 5 % statistical significance was evaluated (p-value < 0.0001) confirming this tendency to reduce the flux with time (APPENDIX XXI). To avoid the drastic decay of permeate flux in long operations with surface water, pretreatment and periodic cleaning strategies should be implemented. With the increase of fouling, due to the higher concentration of feedwater constituents, there are two peaks of flux decay, in the first moment it falls more gradually and in the second the fall is more abrupt, which may indicate the formation of a mature biofilm. This result agrees with the feed boundary layer resistance (R_{fb}) values, reported in Table 4-1, which practically doubles from stage 1 to stage 2 and in stage 3 it is even higher. In addition, the fouling resistances ($R_{fouling}$) in stages 2 and 3 are superior to stage 1. The temperature polarization (TPC) in DCMD can also be affected by the fouling process, it is believed that the fouling layer decreases temperature difference across the membrane and results in temperature polarization (FORTUNATO et al., 2021), since increasing R_{fb} and permeate resistance (R_{pb}) decreases permeate flux. However, comparing the results in Table 4-1, the TPC was not influenced by membrane fouling, it was between 0.78 and 0.79 for all stages evaluated. In addition, even with the high permeate recovery (93.26 %) achieved in stage 2, the permeate electric conductivity was not compromised, with an increase of approximately 2 µS cm^{-1} from the beginning to the end of the test, remaining constant over time. This result suggests that there was no episode of total membrane wetting and that, if some pore might have been moistened during the fouling process, it recovered its hydrophobicity (CHAMANI et al., 2021).

Table 4-1: Layer resistances and TPC

Process condition	**Resistance (Pa m^2 h kg^{-1})**					**TPC**
	R_{fb}[1]	**R_{pb}[2]**	**$R_{fouling}$[3]**	**R_m[4]**	**R_{total}[5]**	
Stage 1	255.04	81.22	2.73	1151.92	1490.92	0.78
Stage 2	627.15	198.04	1637.61	1344.31	3807.11	0.79
Stage 3	653.06	205.89	1747.46	1386.22	3992.62	0.79

[1]Resistance to filtration, [2]resistance to permeate, [3]resistance to fouling, [4]membrane resistance, and [5]total resistance.

Some studies have shown that the type of fouling layer formed can reduce membrane wettability, as when occurs the $CaCO_3$ precipitation together with $CaSO_4$ (GRYTA, 2008a), or can induce wettability, as in the case of organic fouling and biofouling formation (KARIMA et al., 2021). Although there are contradicting observations regarding the effect of organic fouling on permeate quality, as reported by GRYTA (2008b) that organic fouling did not affect the water quality in a DCMD system treating tap water even when episodes of membrane wetting were observed. The same seems to occur in this study checking the small increase in electric conductivity (Figure 4-5), as it was reported.

The SEM images of the membrane surface morphology before and after DCMD operation are combined in Figure 4-6. A severe fouling on the membrane surface was confirmed in SEM image, showing that the entire middle of the membrane surface and almost of the edge were covered by an amorphous deposited fouling layer compared to the pristine membrane, probably due to the organic elements present in the feed solution. In addition, observing the images of the membrane edge, particles were identified with lengths ranging from 1.214 to 1.1431 µm (APPENDIX XXII), which may indicate among other microorganisms associated with biofilm formation, the presence of bacteria, which are larger, as they have sizes between 0.5 - 2 µm (HORI and MATSUMOTO, 2010). The biofilm formation can also be confirmed by higher concentrations of extracellular polymeric substance (EPS) on the surface of the fouled membrane (349 mg in the 42 cm^2 membrane area), since alive and dead microorganisms are involved in a hydrated extracellular matrix made of EPS produced by organisms that compose the biofilm (COSTA et al., 2021).

As the biofilm in the MD process usually develop gradually (COSTA et al., 2021), it can be related to the also gradually decrease in permeate flux in the stage 2 (Figure 4-5) of the test. The microbial population density in the biofilm formation is related to the quorum sensing (QS) mechanism, which is the communication between cells allowed by the production, release, and detection of molecules by some biofilm components, such as bacteria (GONZALEZ and KESHAVAN, 2006). When the bacterial population density increases, the concentration of autoinducer molecules proportionally increases and when a critical mass is reached, all bacteria react through regulator proteins being activated (WEI et al., 2020). It results in the expression of genes that may generate community behaviors and the mature biofilm is formed (MADDELA et al., 2019), which can lead to the higher EPS production.

The SEM-EDX results of the pristine and fouled PTFE membrane in Table 4-2 exhibited a semi quantitative elemental analysis, showing that the pristine membrane had fluorine and carbon peaks most prominent elements on the scan, typical of PTFE composition. For the fouled membrane other elements such as O, Si, Al, Ca, Mn, Mg, K, and Fe were registered. This may be due to the combined effect of salt deposition and organic adsorption on the membrane surface during DCMD, indicating that there might be both inorganic and organic fouling.

Figure 4-6: SEM images of the virgin membrane ((A) x50; (B) x1000; (C) x4000) and the fouling layer at three different parts, being the middle ((D) x50; (E) x2000; (F) x5000), edge ((G) x50; (H) x2000; (I) x3500) and transversal section ((J) x50; (L) x1000; (M) x10000)

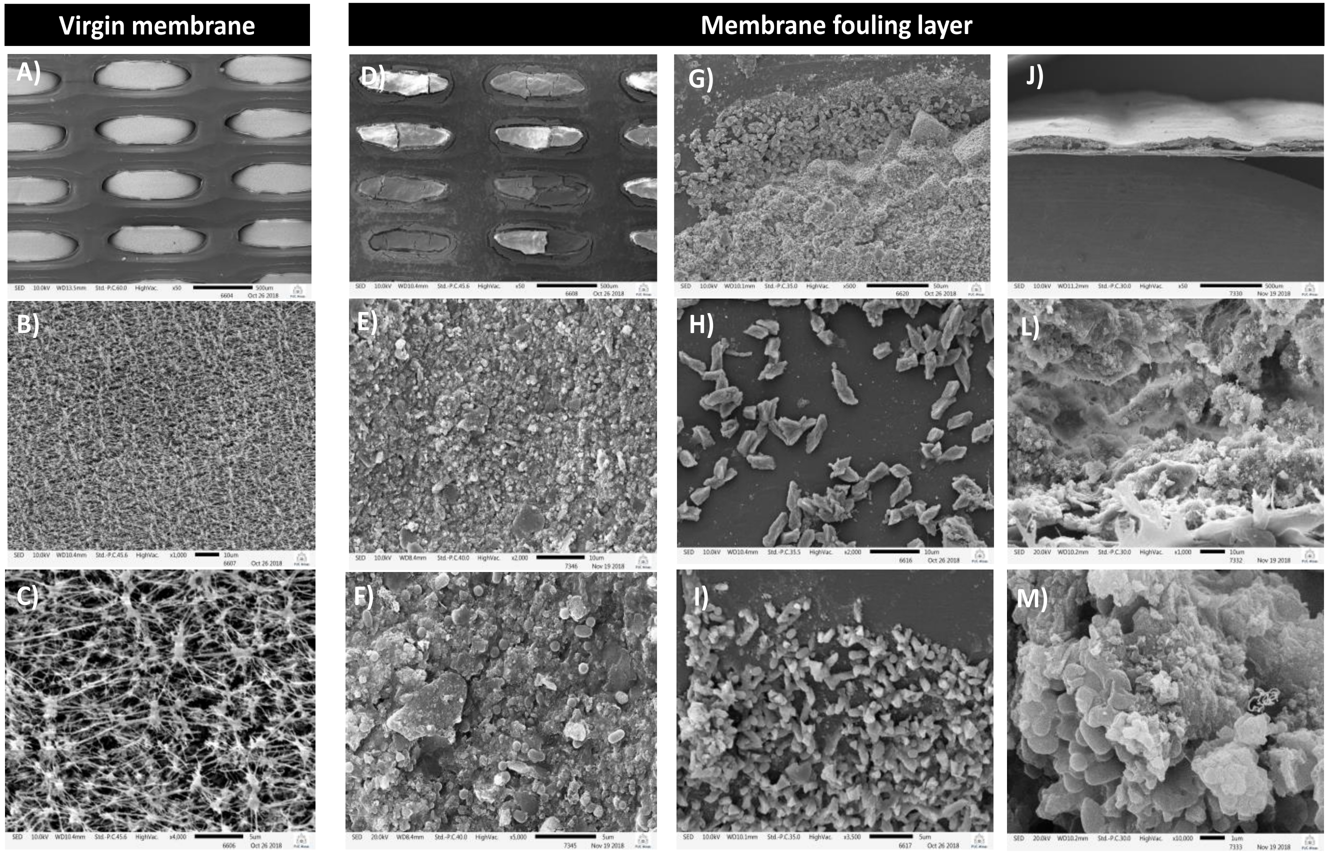
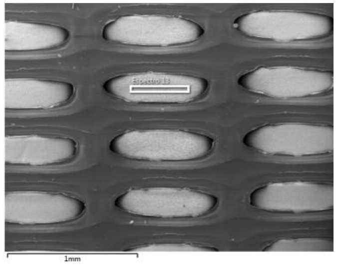
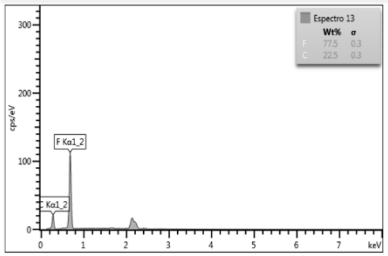
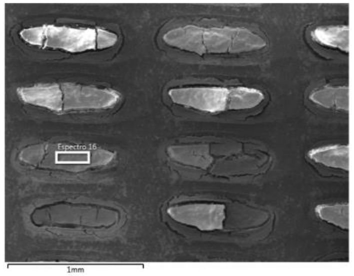
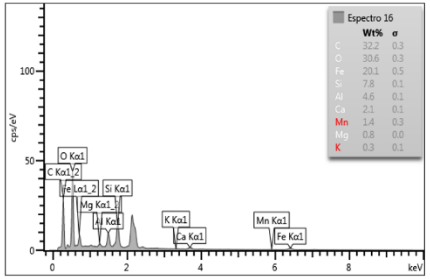
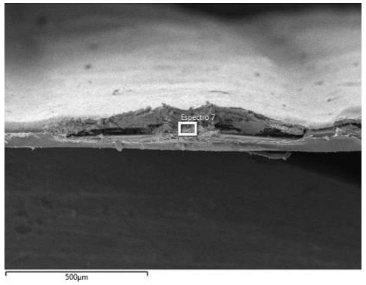
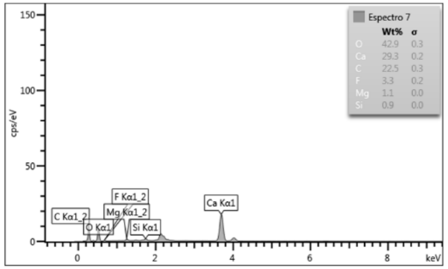
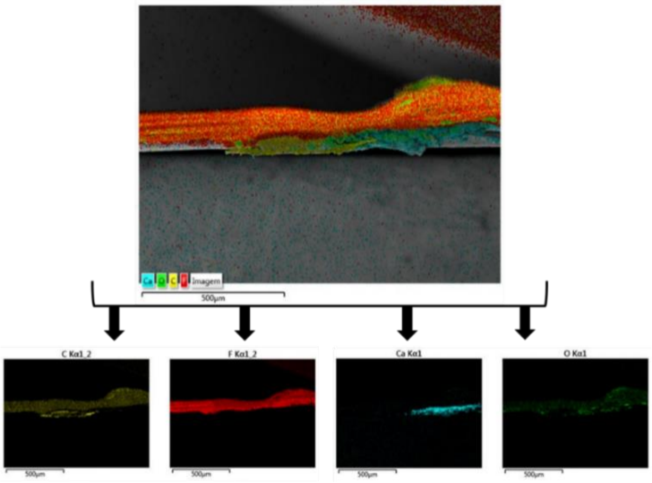


Table 4-2: SEM images (1 mm and 500 µm) and EDX elemental analysis of the PTFE membrane surface before and after de fouling process

Membrane	**Analysis**		**EDX Elemental Analysis (wt.%)**									
	SEM Images (1 mm)	EDX spectrum	C	F	O	Si	Al	Ca	Mn	Mg	K	Fe
Virgin membrane			22.5	77.5	-	-	-	-	-	-	-	-
Membrane after fouling (middle)			32.2	-	30.6	7.8	4.6	2.1	1.4	0.8	0.3	20.1
Membrane after fouling (transversal section)			22.5	3.3	42.9	0.9	-	29.3	-	1.1	-	-

The fouling layer's composition of the membrane transversal section can be observed in Figure 4-7. It is noted that the deposition of calcium on the membrane surface agrees with the information in Table 4-2 for membrane after fouling (transversal section). As mentioned in section 4.3.1, the presence of Ca may be related to the precipitation of $CaCO_3$ and $CaSO_4$ and the reduction of membrane wetting (GRYTA, 2008) in process even with organic fouling occurrence. Although the main constituent that covers the entire membrane surface is carbon, the presence of many organic materials can drastically reduce the permeate flux, as occurred in stage 3. This just confirmed the comparison between $R_{fouling}$ and R_{fb} previously reported (Table 4-1), that $R_{fouling}$ is the major resistance to filtration in stages 2 and 3 when the fouling layer is already formed. This finding demonstrates the mature biofilm formation. It is noteworthy that the bacteria in a biofilm are more resistant than isolated organisms, and fouling can have negative consequences for MD. In this regard, methods to prevent or mitigate this fouling process need to be associated with the system operation to reduce problems with overall fouling. Despite fouling observations, the membrane seems to remain stable and most probably reusable after a cleaning procedure. If its integrity was compromised, either the distillate conductivity or distillate flux would sharply increase, aspects not observed throughout the three stages monitored.

Figure 4-7: EDS mapping of the membrane transversal section after the fouling process

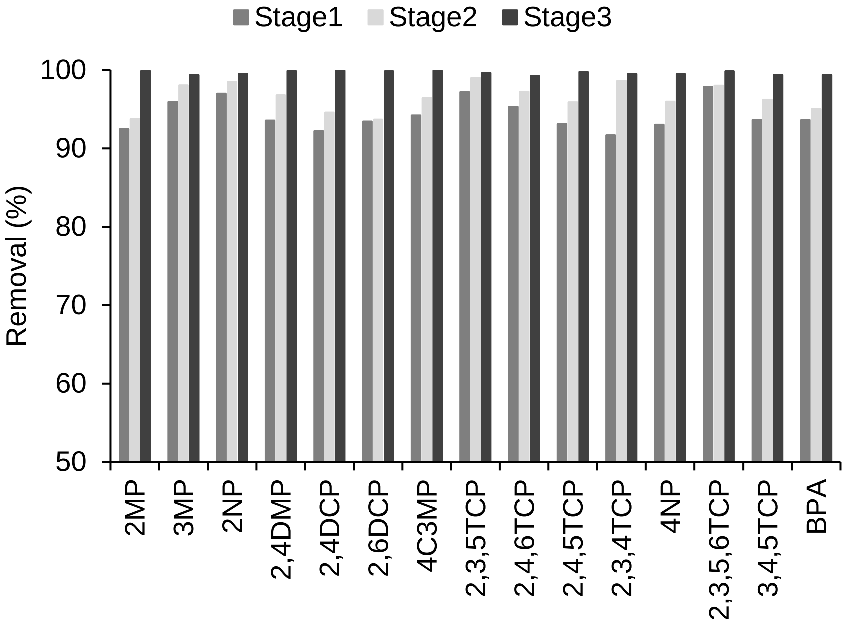


*C: Yellow, O: Green, F: Red, and Ca: Blue.

4.3.2 Fouling process and phenols retention

The performed studies have demonstrated that the magnitude of DCMD permeate flux was strongly affected by the fouling process. Although the retention of phenolic compounds increases after the fouling layer formation, as shown in Figure 4-8.

Figure 4-8: Summary of phenols removal efficiency at each stage evaluated of the fouling process



The phenolic compounds average removals for the stage 1, 2, and 3 was 94.30 ± 1.93 %, 96.53 ± 1.74 %, and 99.66 ± 0.24 %, respectively. The results are consistent with those found in the preliminary studies of Ramos et al. (2021) for removing phenols present in a real surface water under the same operating condition of these experiments (feed temperature = 60 °C). Wijekoon et al. (2014) also verified the feasibility of applying the MD process to remove trace organic compounds (TrOCs), including some phenols, during the treatment of water and wastewater. Results of both studies were suggested that the rejection of compounds with pKH<9 can be governed by the interaction between their hydrophobicity and volatility.

The Figure 4-9 presents the phenols mass distribution in stage 1, 2, and 3 to comprehend how the compounds removal occurred by the DCMD with the fouling layer formation. In general, the compound losses and the passage of compounds to the permeate side increased from stage 1 to stage 2 and in stage 3 the compounds were concentrated in the feed. Only for 2MP and 3MP a small loss was observed in stage 3. The losses of compounds in stage 2 were more significant, since the test time was longer compared to the other stages evaluated. In that case, thermal degradation, adsorption, and with a lower contribution volatilization and photodegradation, of some compounds may have occurred. The losses in step 1 could be related specially to the adsorption process, since in this process the driving force is the concentration difference (WANG et al., 2018), so at the beginning of the test, the entire system (module, membrane, hoses) was "clean", causing a greater loss due to greater driving force. Besides that, the adsorption-desorption mechanism justifies the higher passage of compounds to the permeate side in step 1. This also could explain the difference between stage 1 and 3, since in stage 3 the system would already be used and the fouling layer formed, therefore the driving force for adsorption would be minimal, favoring the concentration of the compounds in the feed solution. In addition, the fouling layer formed with the mature biofilm may also have favored the non-porous scale formation causing a significant increase in mass transfer resistance.

In this sense, evaluating the volatility and hydrophobicity of each phenolic compound studied (APPENDIX XXIII) the transport during the MD process can be better enlightened. The 4NP and BPA compounds, which have lower volatility, showed small differences in removal efficiency between the studied stages. In stage 1, the 4NP, more hydrophilic, had its removal associated with the electrostatic interactions with the membrane or with the system in general. In stage 2, after the sites are occupied, these interactions no longer have effect and the losses of the compound have decreased. BPA, which is more hydrophobic, had its removal associated with its passage to the permeate side in stages 1 and 2, probably due to the process of affinity with the membrane surface (adsorption - desorption) or passage through wet pores. This passage was reduced with the formation of the fouling layer. Among the compounds with higher volatility, 2NP, more hydrophilic, obtained greater removals along the evaluated scale stages, and in stage 2 its removal was more associated with greater losses, as well as 4 NP, which is also has more hydrophilic characteristics, probably due to evaporation and the longer test time in stage 2. The 245TCP, more hydrophobic, on the other hand, had its removal associated with passage to the permeate side in stage 1 and in stage 2 to losses in the system.

The compounds with moderate volatility and hydrophilic characteristics, such as 2MP, 3MP, 24DMP, 26DCP, 4C3MP, 235 TCP, 246TCP, and 2356TTC, showed different behavior in the mass distribution, making it difficult to establish associations with their removal efficiency. For example, the losses of 3MP, 24DM, 4C3MP, 246TCP, and 2356TTCP losses increased from stage 1 to 2, while the losses of 235 TCP and 26DCP decreased throughout the evaluated stages. Compounds with moderate volatility and hydrophobic characteristics, such as 24DCP, 234TCP and 245TCP showed less passage to the permeate side during the scaling process and lower losses in the system, except for 245TCP that increased significantly from stage 1 to stage 2.

Therefore, it was observed that although the fouling reduces the permeate flux, it did not affect the water quality and the fouling layer favored the compounds concentration in the feed solution, demonstrating the great potential of the DCMD to remove these compounds in trace concentration from surface water. The permeate physicochemical parameters can be checked in Table 4-3, showing that the parameters constituents have been efficiently removed by the technology, it confirms the robustness of DCMD in removing phenolic compounds even after severe fouling.

Figure 4-9: Phenols mass distribution in the stage 1 (a), stage 2 (b), and stage 3 (c)

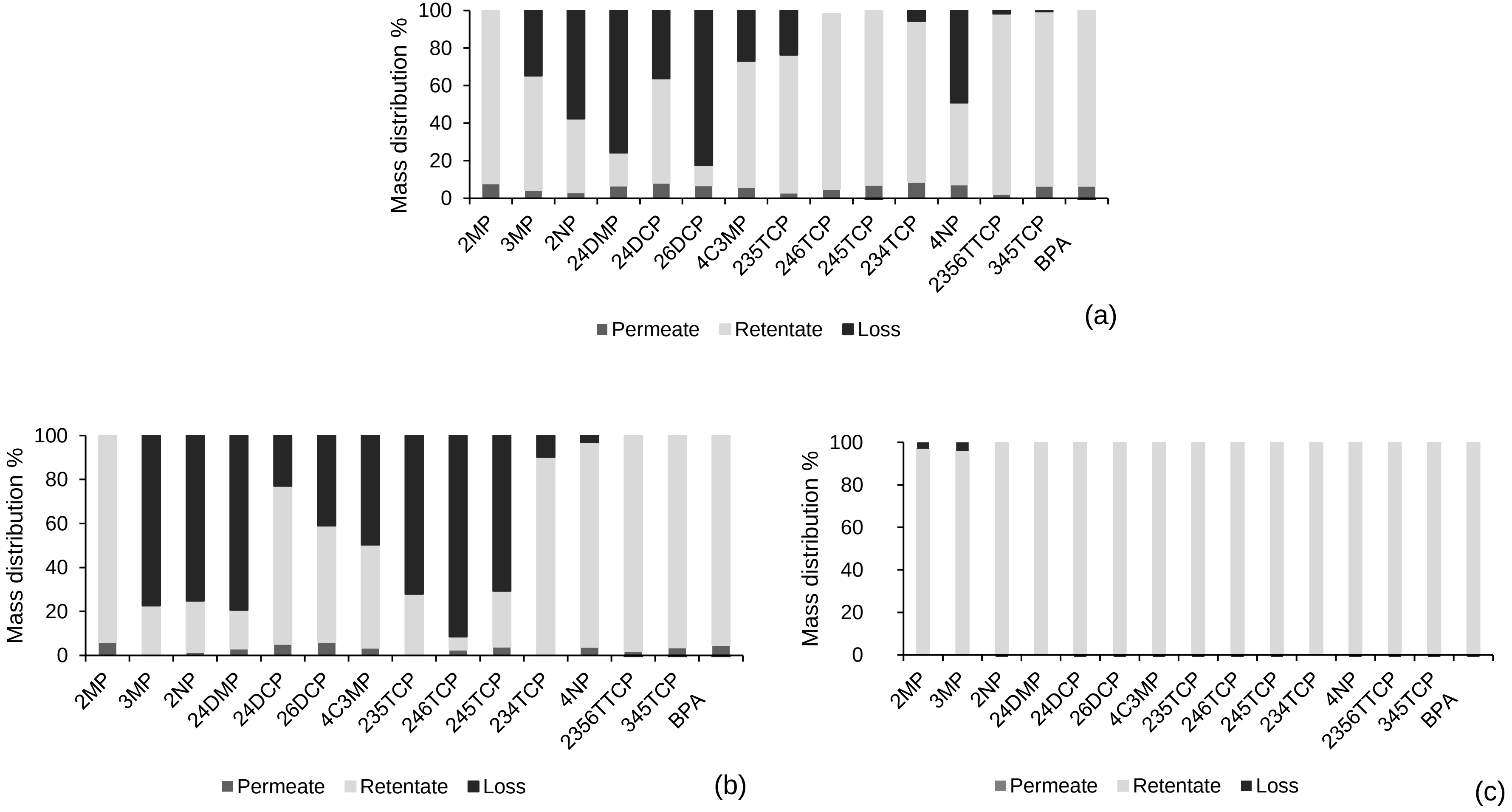


Table 4-3: Samples physicochemical characteristics

Sample	Parameter				
	Turbidity (NTU)	pH	Perceived color (mg Pt-Co L^{-1})	Electric conductivity (µS cm^{-2})	Alkalinity (mg $CaCO_3$ L^{-1})
Surface water	14.20	7.30	74	116.80	29.30
Permeate stage 1	0.89	7.18	<5	2.19	2.10
% removal	93.80	-	-	98.10	93.00
Permeate stage 2	0.92	7.02	<5	3.17	3.10
% removal	93.50	-	-	97.30	89.50
Permeate stage 3	1.40	6.89	<5	4	2.40
% removal	90.10	-	-	96.60	91.70

4.4 CONCLUSION

Membrane distillation is a promising technology for water treatment producing a drinking water free of micropollutants, such as phenolic compounds. It was observed that although the fouling reduces the permeate flux, it did not affect the water quality and the fouling layer favored the concentration of the compounds in the feed solution with practically no mass loss in the process. The volatility and hydrophobicity of each phenolic compound clarified the transport during the MD process. Fouling was mainly attributed to organic elements from surface water, noticing particles with lengths ranging from 1.143 to 1.214 µm that were associated with bacteria. Therefore, the average removals of phenolic compounds varied from 94.30 ± 1.93 % (after initial membrane fouling) to 99.24 ± 0.24 % (after consolidated membrane fouling), thus demonstrating the great potential of the technology to remove these compounds in trace concentration, which have volatile and semi-volatile characteristics. In addition, it was highlighted that long operations with surface water, pretreatment, and periodic cleaning strategies should be implemented to avoid a drastic reduction of permeate flux.

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CHAPTER V – DIRECT CONTACT MEMBRANE DISTILLATION FOR SURFACE WATER TREATMENT AND PHENOLIC COMPOUNDS REMOVAL: FROM BENCH TO PILOT SCALE

5.1 INTRODUCTION

Membrane distillation (MD) is an advancing technology in the field of water treatment, that uses a hydrophobic microporous membrane to separate solutes from the water (LIU et al., 2022). The configuration of direct contact membrane distillation (DCMD) is the most studied at bench scale among all designs available due to the simplest configuration, the high fluxes, and water quality (AHMEDA et al., 2020). In this configuration, the hot and cold stream sides are in direct contact with the membrane, consequently, more heat loss can occur due to conduction through the membrane (PERFILOV et al., 2018). With that, to avoid operating expenses, the DCMD system can be integrated with residual heat (Tan et al., 2018) or renewable energy sources (SOOMRO and KIM, 2018). The DCMD driving force is the interfacial difference of vapor pressure between the membrane sides and the water vapor transport distance is equal to the membrane thickness (PILLAI et al., 2020).

DCMD is well recognized for its high rejection factor of non-volatile solutes with a theoretical value near 100 % (ESSALHI and KHAYET, 2015), although more recent works have demonstrated the high potential of the technology in the removal of semi-volatile and volatile compounds in trace concentration (WIJEKOON et al., 2014; COSTA et al., 2023), such as phenolic compounds (RAMOS et al., 2022a), which are extremely difficult to be removed by conventional water treatment technologies (MOHAMMADI and KAZEMI, 2014) and can even be generated as by-products of these treatments (RAMOS et al., 2021a). A previous study, using a DCMD bench system and real surface water fortified with phenolic compounds (5 µg L^{-1}), demonstrated that the removal efficiency of these compounds by the technology can vary between approximately 89 % to 99 %, according to the operational conditions applied and the volatility and hydrophobicity of each compound (RAMOS et al., 2022a). Other researchers reported that phenols removal ranged from 54 to 70 % (WIJEKOON et al., 2014) to 99 % (HAMZAH and LEO, 2016). The results emphasize the potential of the technology to remove these contaminants.

Among the available studies about MD for micropollutants removal and potable water production (COUTO et al., 2020; ARCANJO et al., 2021; RAMOS et al., 2022a; RAMOS et al., 2022b), all are conducted using bench-scale systems. Understanding aspects related to the technology scale up can facilitate technical performance in real applications, thus reducing process disadvantages (ASHOOR et al., 2019). Few researchers bring a direction on how to interpret these results achieved in larger production scales, since the applications of MD are growing from the laboratory environment to pilot and real applications (EYKENS et al., 2017). Thus, it is still necessary to comprehend the differences between operations at various scales for water production and energy efficiency based on the feedwater quality to be treated, as these insights can facilitate the transition from laboratory testing to the design of industrial systems. This type of study has been indicated as a main area of focus in the MD sector to expand its full-scale applications (ASHOOR et al., 2019).

Bench-scale MD systems are convenient for testing new membranes and obtaining results on water permeability and solute rejection (HARDIKAR et al., 2022). These systems are already recognized as an alternative for the production of high water quality, but their insufficient performance, related to high energy consumption and low flux, is still considered an obstacle in larger and commercial applications (ZUO et al., 2016). However, it is noteworthy that the estimated costs of water produced from commercial MD systems integrated with residual thermal energy or renewable energy are lower than the costs of production by reverse osmosis or conventional thermal processes (JANSEN et al., 2013; DESALDATA, 2016).

The results of bench-scale MD usually cannot be directly translated to full scale due to differences in operation between scales (SWAMINATHAN et al., 2018). In general, as large-scale MD systems are designed to be energy efficient, they have a lower flux and smaller temperature difference across the membrane compared to bench-scale systems to maximize the water production per energy input. The typically lower water flux of full-scale MD is associated with the higher membrane area that leads to an increase in water production that causes heat loss associated with the latent heat of evaporation into the condensate flux, leading to a smaller temperature difference across the membrane (SWAMINATHAN et al., 2018; HARDIKAR et al., 2022).

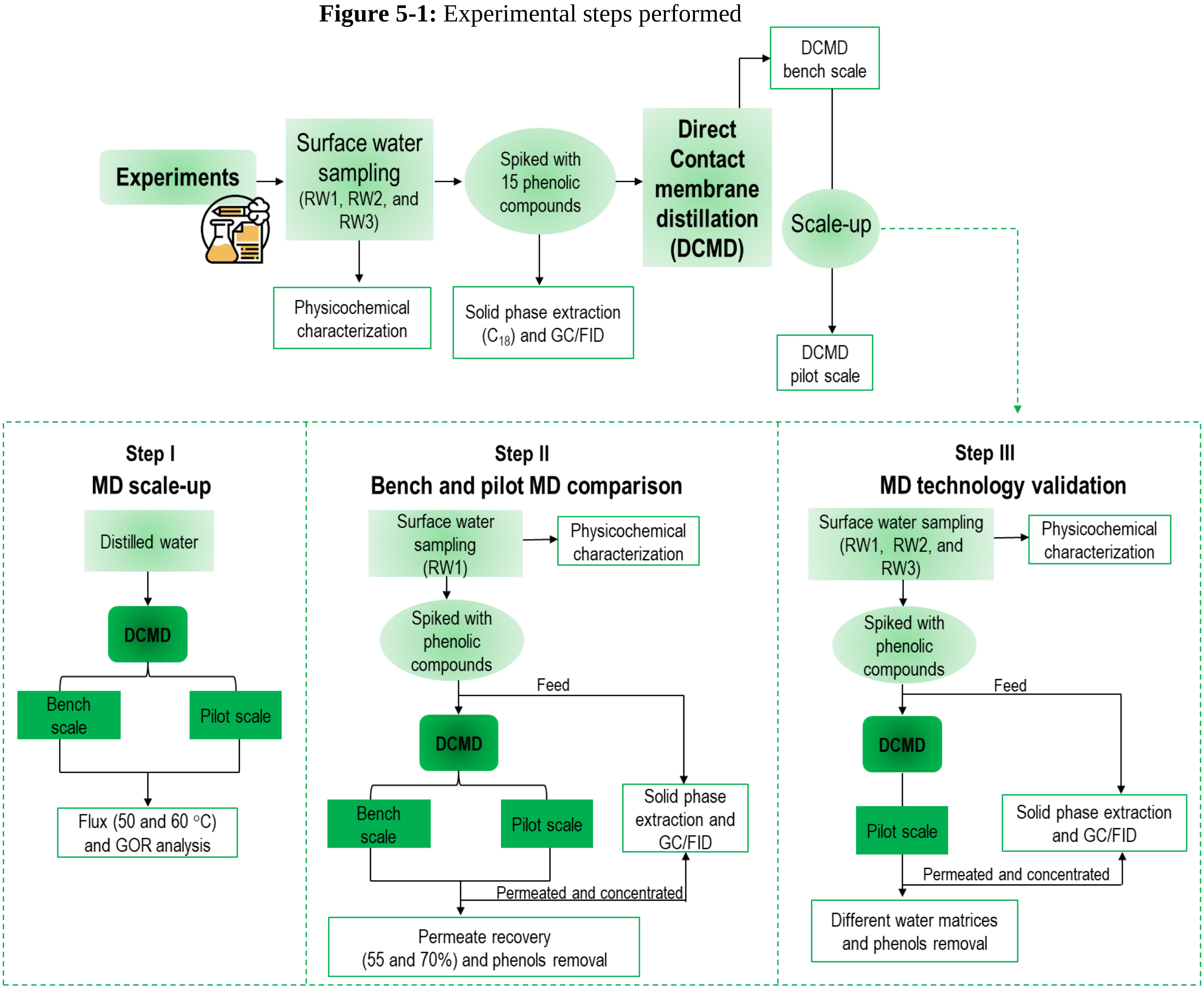
To comprehend the DCMD scaling up a quantitative and direct comparison between systems of different scales under similar conditions is required, observing permeated flux, pollutant removal, and energy efficiency (EYKENS et al., 2017), which can be estimated through the concept of gained output ratio (GOR) defined as the ratio of heat associated with mass transfer to the energy input. The GOR reflects how well the energy input in the MD system is utilized for water production (KHAYET, 2013). The GOR values of some tested MD systems can be dispersively varying from 0.3 to 8, as shown in Khayet (2013). The higher the GOR value better is the system performance in terms of energy (ALAWAD and KHALIFA, 2021). The GOR does not depend on the MD configuration and most experimental MD systems have GOR values <1 suggesting low MD performance due to poor heat recovery (KHAYET, 2013). Besides that, to bring technical-economic evaluation aiming to contribute to the practical adoption of MD considering different scenarios and more sustainable and affordable contexts can favor the application of technology in the water sector.

Therefore, a bench and pilot scale DCMD, using the same membrane and similar system design, were studied to compare the effect of system scale up on the removal of phenols, selected based on the Environmental Protection Agency (EPA - United States) list of priority compounds, from surface water to produce drinking water and the technology was validated with the application of different surface water matrices to answer the following research questions: (i) What is the effect of the DCMD system scale-up on the permeate flux and GOR? (ii) Does system scale up affect the removal of phenolic compounds at different permeate recovery? What are the main removal mechanisms involved? (iii) Is the removal of phenolic compounds and the quality of the generated permeate impacted by the surface water matrix in the DCMD pilot system? (iv) What are the main economic aspects related to capital (CAPEX) and operational (OPEX) expenditure of using the DCMD to produce drinking water? It is expected with this research, to validate the capacity of the DCMD to remove volatile and semi-volatile organic compounds from surface water, such as phenols in trace concentration, ensuring the production of potable water. In addition, it is also expected to clarify points that facilitate DCMD scale up for system designs for real applications.

5.2 MATERIALS AND METHODS

Figure 5-1 presents a flowchart of the experimental steps performed.

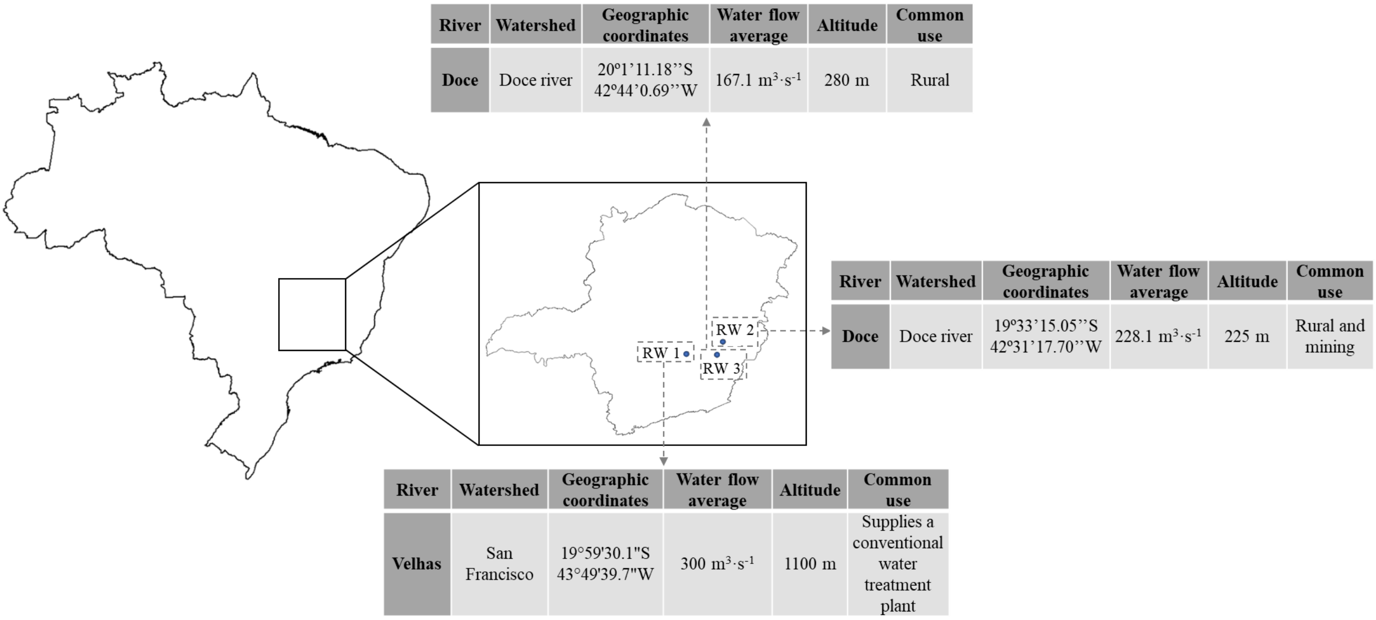
Figure 5-1: Experimental steps performed



5.2.1 Water sampling

The surface waters were collected in the Velhas river (RW1) and in two different sites of the Doce river (RW2 and RW3), both located in Minas Gerais, Brazil. The samples were obtained following the recommendations presented at EPA 528 (EPA, 2000) for sampling, preserving, and storing aqueous samples containing phenolic compounds. Briefely, the bottles were immersed countercurrent and below the water surface (15 - 30 cm) to avoid stagnation areas. Figure 5-2 presents the main characteristics and location of the sampling sites.

Figure 5-2: Sampling site main characteristics and location in Brazil (ArcGIS Desktop 10.8.2)



River	Watershed	Geographic coordinates	Water flow average	Altitude	Common use
Doce	Doce river	20°1'11.18"S 42°44'0.69"W	167.1 $m^3 \cdot s^{-1}$	280 m	Rural

River	Watershed	Geographic coordinates	Water flow average	Altitude	Common use
Doce	Doce river	19°33'15.05"S 42°31'17.70"W	228.1 $m^3 \cdot s^{-1}$	225 m	Rural and mining

River	Watershed	Geographic coordinates	Water flow average	Altitude	Common use
Velhas	San Francisco	19°59'30.1"S 43°49'39.7"W	300 $m^3 \cdot s^{-1}$	1100 m	Supplies a conventional water treatment plant

These rivers are an important source of water to supply the population, agriculture, and industries and its watersheds suffer from contamination of domestic and industrial wastewater, pesticides from agriculture, and the impact of livestock and mining activities. Observing the physical-chemical characteristics of the studied surface waters (Table 5-1), the main difference between them is the water turbidity varying between 14.2 NTU for RW1, 92.5 NTU for RW2, and 162 NTU for RW3.

Table 5-1: Physical-chemical characteristics of the studied surface waters

Parameter	**Sample average ± standard deviation**		
	RW1	RW2	RW3
Turbidity (NTU)	14.2 ± 0.4	92.5 ± 0.9	162 ± 1.6
UV-Vis 254 nm	0.02 ± 0.01	0.08 ± 0.01	0.02 ± 0.01
Perceived color (mg Pt-Co L^{-1})	74 ± 21.2	239 ± 2.4	391 ± 3.4
TSS (mg L^{-1})	16 ± 4.2	94 ± 5.7	68 ± 17
TN (mg L^{-1})	1.4 ± 0.1	1 ± 0.1	0.8 ± 0.1
Electric conductivity (µS cm^{-2})	116.8 ± 3.2	47.1 ± 0.5	63.8 ± 0.6
Alkalinity (mg $CaCO_3$ L^{-1})	29.3 ± 0.1	21.3 ± 0.2	24.3 ± 0.2
pH	7.3 ± 0.3	7.6 ± 0.1	7.6 ± 0.1
NH_4^+ (mg L^{-1})	<1.0	<1.0	<1.0
Ca (mg L^{-1})	21.1 ± 0.1	3.9 ± 0.4	4.0 ± 0.4

Parameter	Sample average ± standard deviation		
	RW1	RW2	RW3
Mg (mg L^{-1})	6.4 ± 0.1	1.8 ± 0.1	2.0 ± 0.1
Na (mg L^{-1})	5.7 ± 0.1	1.1 ± 0.1	<1.0
K (mg L^{-1})	1.1 ± 0.1	2.2 ± 0.1	1.4 ± 0.1
Fe (mg L^{-1})	1.3 ± 0.1	1.3 ± 0.1	0.9 ± 0.1

5.2.2 Chemicals

The raw surface waters were spiked with fifteen phenolic compounds using EPA 8040A Phenol Calibration Mix and Bisphenol A (99 %) analytical standards (Sigma-Aldrich®). 4-chloro-3-metylphenol (4C3MP), 2-nitrophenol (2NP), 2,4-dimethylphenol (24DMP), 2,4-dichlorophenol (24DCP), 4-nitrophenol (4NP), bisphenol A (BPA), 2-metylphenol (2MP), 3-metylphenol (3MP), 2,6-dichlorophenol (26DCP), 2,3,5-trichlorophenol (235TCP), 2,4,5-trichlorophenol (245TCP), 2,4,6-trichlorophenol (246TCP), 2,3,4-trichlorophenol (234TCP), 2,3,5,6-tetrachlorophenol (2356TTCP), and 3,4,5-trichlorophenol (345TCP) were selected to be studied based on the EPA's list of priority compounds. APPENDIX XXIV presents some characteristics of the compounds (molecular formula, molar mass, pkH, and Log D).

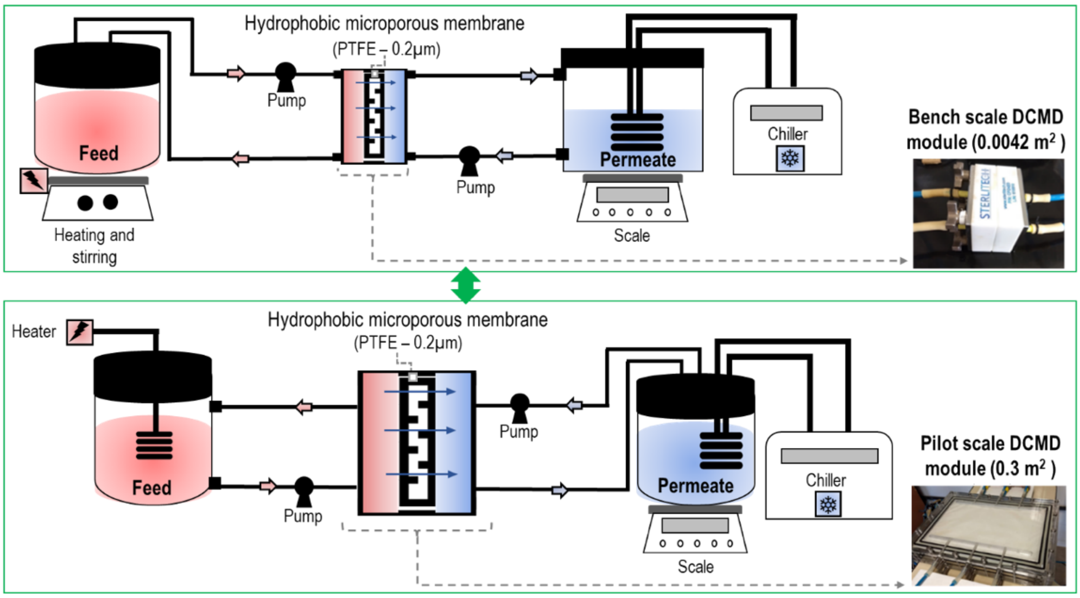
5.2.3 Membrane distillation experimental setup

Two DCMD systems were used in this research with bench and pilot modules (

Figure 5-3). The DCMD system in bench scale was constituted with a membrane module of natural acetal copolymer (Sterlitech Corp.), with a flow channel of 9.2 10^{-2} m short, 4.5 10^{-2} m high, and 2.0 10^{-3} m wide, a hydraulic diameter of 3.8 10^{-3} m and a total effective filtration area of 0.0042 m^2. The pilot system was developed based on the modelling of the thermal boundary layer and mass flux as proposed by Alvares et al. (2019). It consisted of an acrylic flat sheet membrane module (width = 0.25 m; height =0.4 m; base = 0.002 m) with three membranes in parallel resulting in a total filtration area of 0.3 m^2. The commercial polytetrafluoroethylene membrane (PTFE 023005) manufactured by Sterlitech Corp. was used in both scales, with an average pore size of 0.2 µm, porosity between 60 to 80 %, and 125° of contact angle with water. Both experimental units were equipped with two supply tanks, a precision scale (Mícron

Scientific – S 0.01g) in the bench and a digital scale in the pilot system, two thermometers, two peristaltic pumps (Provitec GA5200 MB), electric heating in the feed tank, and a chiller (AquaCooler, Australia) in the permeate tank.

Figure 5-3: Schematic of the DCMD systems and the bench and pilot modules photos



5.2.4 Experimental protocol

Before the tests with surface water, the permeate flux with distilled water using new membranes was evaluated in the bench and pilot systems to verify and compare the permeate flux and GOR of both systems at different feed temperatures (50 and 60 °C). Experiments to verify the performance of DCMD in the retention of phenolic compounds and the production of potable water at the different systems scales were performed by varying the permeate recovery (PR) (55 % and 70 %) using the surface water RW1 as a feed solution. To validate the technology, the pilot scale system with different surface water matrices was used as a feed solution (RW1, RW2, and RW3).

In the bench scale tests, initially, the volumes of surface water spiked with phenolic compounds in the feed tank was 2 L, and distilled water in the permeate tank was 1.5 L, while in the pilot scale were 4 L and 8 L, respectively. Based on a previous study, that monitored the occurrence of phenolic compounds in surface water (RAMOS et al., 2021a), the concentration of the contaminants used was 5 µg L^{-1}, a common value detected over a year of monitoring. The streams were recirculated in counter-current mode at a cross-flow velocity of approximately 0.1 m/s in both scales. In all experiments, the permeate mass and the permeate and feed temperature were monitored every 5 min, while the permeate electric conductivity was checked every 10 minutes. During the test, temperatures were maintained at 25 °C in the permeate and 60 °C in the feed, since it has been demonstrated (RAMOS et al., 2022a) that at this operational temperature more than 90 % of the phenolic compounds were removed, permeate flux was relatively higher than other evaluated temperatures and the specific energy consumption (SEC) was lower.

5.2.5 Membrane distillation performance parameters

The permeate flux in the DCMD system was calculated considering the increment of mass in the permeate during the experiment time, according to Equation 5.1.

$$J_p = \frac{m_2 - m_1}{(t_2 - t_1) \cdot A_m} \qquad \text{Equation 5.1}$$

Where J_p is the membrane permeate flux (kg m^{-2} h^{-1}); t_1 and t_2 are time (h); $m_2 - m_1$ is the permeate mass difference between times t_2 and t_1 (kg); and A_m is the membrane area used (m^2).

The efficiency of the DCMD system was measured based on the gain output ratio (GOR), which was calculated considering the thermal (E_T) and electric energy (E_E) according to Equation 5.2 (KHAYET, 2013).

$$GOR = \frac{J_p \cdot A_m \cdot \Delta H_v}{E_T + E_E} \qquad \text{Equation 5.2}$$

Where ΔH_v is the water evaporation enthalpy (J kg^{-1}) calculated as Equation 5.3.

$$\Delta H_v = 2.3842 \cdot T_{fout} + 3152.4 \qquad \text{Equation 5.3}$$

E_T was calculated by Equation 5.4 (QTAISHAT and BANAT, 2013).

$$E_T = m_f \cdot c_f \cdot (T_{fin} - T_{fout}) \qquad \text{Equation 5.4}$$

Where m_f is the feed flow rate (kg s^{-1}), c_f is the feed specific heat (J kg^{-1} K), T_{fin} is the temperature of the feed in (K), and T_{fout} out is the temperature of the feed out (K) of the module.

E_E was estimated according to Equation 5.5 (REIS et al., 2018).

$$E_E = \frac{m_f - \Delta P}{\eta} \qquad \text{Equation 5.5}$$

Where ΔP is the pressure experienced by the membrane determined experimentaly (bar) and η is the efficiency of the pump, which was considered 95 %.

For estimated the permeate recovery (PR, %) Equation 5.6 was used.

$$PR = \frac{m_{df} - m_{di}}{m_{fi}} \qquad \text{Equation 5.6}$$

Where m_{di} is the initial mass of the distillate (kg), m_{df} is the final mass of the distillate (kg), and m_{fi} is the initial mass of the feed solution (kg).

Equation 4.7 was used to calculate the removal (R, %) of each phenolic compound by the DCMD systems.

$$R = \frac{m_f - m_d}{m_f} \qquad \text{Equation 5.7}$$

Where m_f is the mass of the specific compound in the feed solution (µg) and m_d is the mass of the specific compound in the distillate (µg).

5.2.6 Water analytical chemistry

The phenols were monitored in the feed, permeate, and concentrated of the DCMD experiments according to EPA methods 528, 3535A, and 8041. The protocol for identification and quantification of the phenolic compounds was validated as recommended by the International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use (ICH, 2005). In the pre-concentration stage, solid phase extraction with C_{18}/18 % cartridges (500 mg/6 mL - Applied Separations) were used, conditioned with 5 mL of methanol and 5 mL of MilliQ water (ThermoScientific Smart2Pure 3 UV). The sample pH was adjusted to 2 with a sulfuric acid solution (0.1 mol L^{-1}) and it was percolated (1 L) in the cartridge at 20 mL min^{-1}. Methanol (Exodus Scientific®) was used for the elution (2 times 1 mL). The gas chromatography (GC - 2010-Plus, Shimadzu) condition used was 40 °C for 4 minutes, 4 °C min^{-1} to 240 °C, and ultimately 240 °C for 5 minutes. The equipment operated in splitless mode with the injector at 275 °C, the injection volume of the samples was 2 μL. The flame ionization detector (FID) was maintained at 300 °C and an Air/H_2 mixture (400/40 mL min^{-1}) was used for the combustion while an N_2/Air mixture at 30 mL min^{-1} was used as make-up gas. The analyses of each sample were carried out in triplicate. Note that, the development of the methodology and the validation of the whole process in detail has been published in previous works (RAMOS et al. 2021a, 2021b).

The DCMD feed (surface waters) and permeates of the experiments were analyzed also according to subsequent physical-chemical parameters: pH (pHmeter Qualxtron QX 1500), electric conductivity (Hanna conductivity meter HI 9835), alkalinity, total suspended solids (TSS), perceived color (Hach DR 2800 spectrophotometer), NH_4^+, Ca, Mg, Na, K, and Fe ions concentrations (Ion Chromatograph ICS-1000 - Dionex), UV absorption (254 nm - Hach DR 2800 Spectrometer), total nitrogen (TN) (Shimadzu TOCV CNP), and turbidity (Hach 2100AN turbidimeter). The analyzes followed the methods described in the *Standard Methods for the Examination of Water and Wastewater* (APHA, 2012).

5.2.7 Economic analysis

The capital (CAPEX) and operational (OPEX) expenditure of the proposed technology were estimated considering a distributed system for small communities, a polishing system for already built conventional water treatment plants (WTP), and a mobile water treatment system. For a mobile water treatment system, it was considered a water flow rate of approximately 5.5 m^3 d^{-1}, intended to attain the water demand of approximately 50 inhabitants (110 L inhabitants/day for consumption and hygiene (WHO, 2022)). For small communities, a water flow rate of approximately 11 m^3 d^{-1} was considered, intended to attain the water demand of approximately 100 inhabitants. In the case of a polishing system, it was considered the water treatment capacity of a WTP located nearby the points in which the water samples were collected (535,680 m^3 d^{-1}). Conventional electricity and photovoltaic solar energy were compared as the source of energy for the DCMD system.

The equipment costs (C_b) estimations were done by Equation 5.8 (MOREIRA et al., 2022).

$$C_b = C_a \cdot ({}^{S_b}/{}_{S_a})^n \qquad \text{Equation 5.8}$$

Where S_a is the respective base variable, S_b related to the real equipment variables, C_a is bare module cost and n is a factor exponent. The most recent chemical engineering plant cost index (CEPCI) of 2020 (569.2) and the base year were used to update the costs.

The amortization costs (AC_f) were calculated by annualizing the capital cost (C_{CapEX}) (Equation 5.9).

$$AC_f = C_{CapEX} \cdot \{{}^{i_r}/{}_{[1-(1+\ i_r)^{-ls}]}\} \qquad \text{Equation 5.9}$$

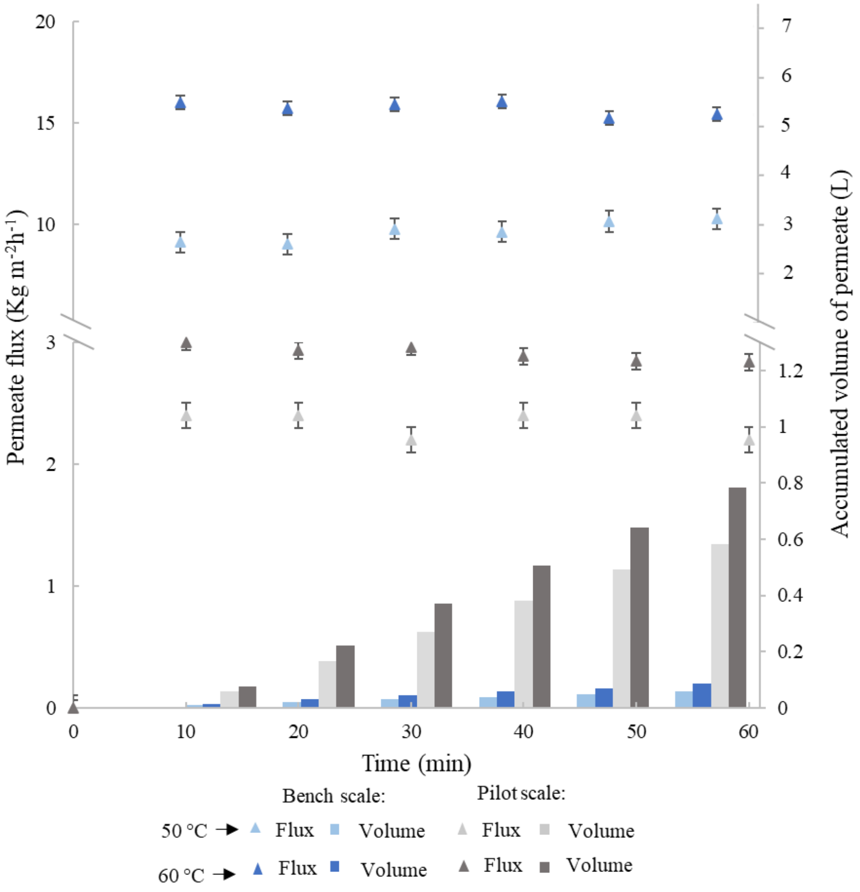
Where i_r is the investment rate (6.5 %) and l_s is the project lifespan (17 years). The maintenance rates of the DCMD and solar systems were defined as 5 % of the initial capital costs and the costs related to DCMD cleaning were based on empirical protocols (ZICO et al., 2021). Complementary information on capital and operational costs estimations are presented in APPENDIX XXIV.

5.3 RESULTS AND DISCUSSION

5.3.1 Direct contact membrane distillation module scale-up

To analyze the effect of scale up the DCMD system, the permeate flux was evaluated using distilled water in the feed at two different temperatures (50 and 60 °C) in the DCMD systems at bench and pilot scales (Figure 5-4).

Figure 5-4: Permeate flux and accumulated volume of permeate in 60 minutes experiment at bench and pilot DCMD systems with distilled water as feed solution under different temperature conditions (50 and 60 °C). The vertical bars denote 0.95 confidence intervals



As expected, the permeate flux of the DCMD system at the bench scale is higher than in the pilot scale. Between the laboratory and pilot experiments, there is a significant difference in the energy that can potentially be exchanged in modules per m^2 of the membrane surface. In the DCMD configuration, countercurrent flow generates a difference in hydrostatic pressure applied to the membrane, causing membrane compaction. It is reported in the literature that in larger-scale systems this compression can be substantial and reach 30 % in the module operating regime (HITSOV et al., 2017). Membrane compaction mainly increases the thermal conductivity of the membrane (ZHANG et al., 2013), which is quite significant at larger scales since, unlike bench-scale experiments, almost all of the energy flowing into the module is exchanged through the membrane (EYKENS et al., 2017). Therefore, if more energy is exchanged due to the sensible heat losses, less energy can be used for evaporation and hence the observed flux reduction.

In addition, the temperature had a greater contribution to permeate flux enhancement in the bench system compared to the pilot system. This can be explained due to the effect of temperature polarization that increases significantly with increasing feed temperature in the pilot module (EYKENS et al., 2017), consequently, the permeate flux suffers more impacts of this effect on a larger scale. The average permeate flux of the bench system varied between 9.9 ± 0.4 kg m^{-2} h^{-1} at feed temperatures of 50 °C and 15.8 ± 0.8 kg m^{-2} h^{-1} at 60 °C. The average permeate flux of the pilot system varied between 2.3 ± 0.2 and 2.9 ± 0.1 kg m^{-2} h^{-1} at feed temperatures of 50 °C and 60 °C, respectively. Note that for a feed temperature equal to 50 °C, the average of the pilot permeate flux is approximately 4 times smaller than the average of the bench permeate flux, while at 60 °C the ratio increases to approximately 5.5 times.

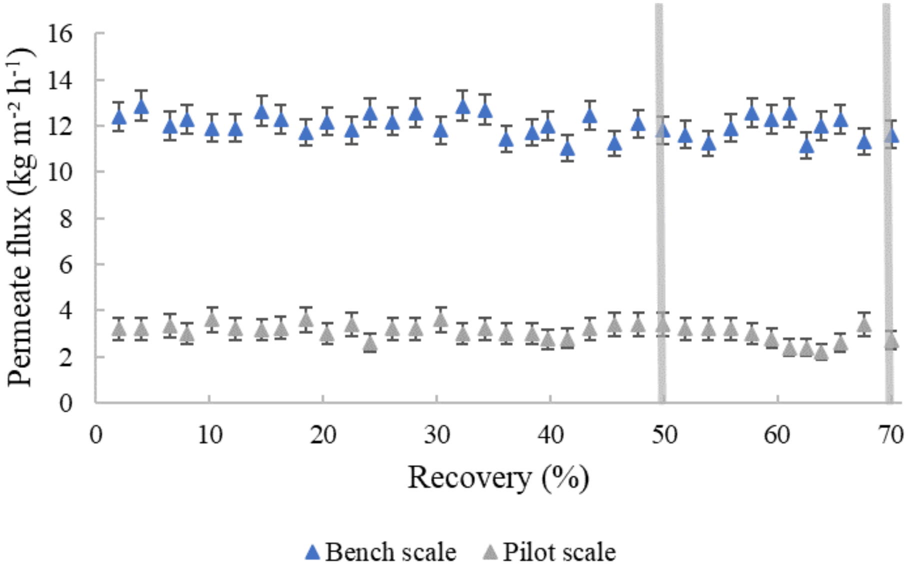
The achieved permeate flux of the pilot system was a lower value than expected in the rationalized modelling for DCMD performed by Alvares et al. (2019), which was used to predict the behavior and evaluate the design of the pilot module developed. A permeate production of 4 kg m^{-2} h^{-1} was expected at 60 °C. This emphasizes the importance of experimental tests to validate modelling studies, which are important guides, but do not always faithfully describe the practice. The permeate flux of the pilot system was considered relatively higher when compared with the experimental results of Eykens et al. (2017), which measured an average permeate flux of approximately 2 kg m^{-2} h^{-1} for a pilot DCMD system with a feed temperature of 60 °C, but the membrane filtration area was not clear in the methodology. Furthermore, the pilot module used in this study presented a high accumulated permeate volume in both evaluated temperatures.

A direct comparison between the bench and pilot systems in terms of energy efficiency, based on the GOR values, is challenging given that the energy efficiency at the bench scale is highly uncertain for some process conditions due to the large measurement error (ALKLAIBI and LIOR, 2007). Therefore, the GOR was calculated only for the pilot scale system varying between 0.77 - 0.8 with increasing temperature from 50 to 60 °C. Although increasing the temperature difference along the module increases the thermal efficiency (EYKENS et al., 2017), the increase in feed temperature was not sufficient to significantly increase the GOR. Although the GOR was close to 1, improvements in energy efficiency continue to be necessary for the DCMD system to achieve a GOR>1, which indicates an energy potential for real applications, such as in water treatment and pollutant retention like phenolic compounds.

5.3.2 Removal of phenolic compounds from bench to pilot DCMD system at different permeate recoveries

The experimental permeate flux along the recovery at bench and pilot scale DCMD systems was evaluated in Figure 5-5. The gray vertical lines highlight the recovery of 50 and 70 % when samples were collected to analyze the removal of the phenolic compounds.

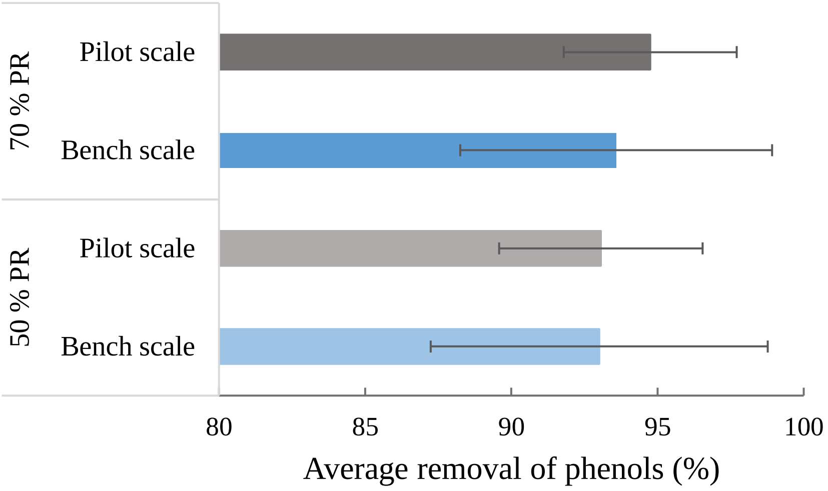
Figure 5-5: Permeate flux as a function of recovery for bench and pilot scale tests (Feed: RW1 spiked with phenolic compounds (5 μg L^{-1}) at 60 °C). Gray vertical lines highlight the 50 and 70 % recovery. The vertical bars denote 0.95 confidence intervals



As expected and explained in section 5.3.1, using real surface water as a feed solution the permeate flux at the bench scale was sharply higher than the flux at the pilot scale. The permeate flux remained practically constant throughout both tests with a slight tendency to decay close to 70 % recovery. Although the permeate flux reduction was relatively low, analyzing the relation between final (J) and initial permeate flux (J_0) at 70 % recovery, the pilot module (J/J_0 = 0.85) showed a greater tendency to fouling/scaling compared to the bench module (J/J_0 = 0.94). This result confirms that even at larger scales the DCMD system for treating surface water and removing phenolic compounds without compromising the permeate flux can work in high water recovery, which means a high capacity of process applicability, as it reduces the number of stops to clean the system using chemical agents and increases permeate production as a function of operating time.

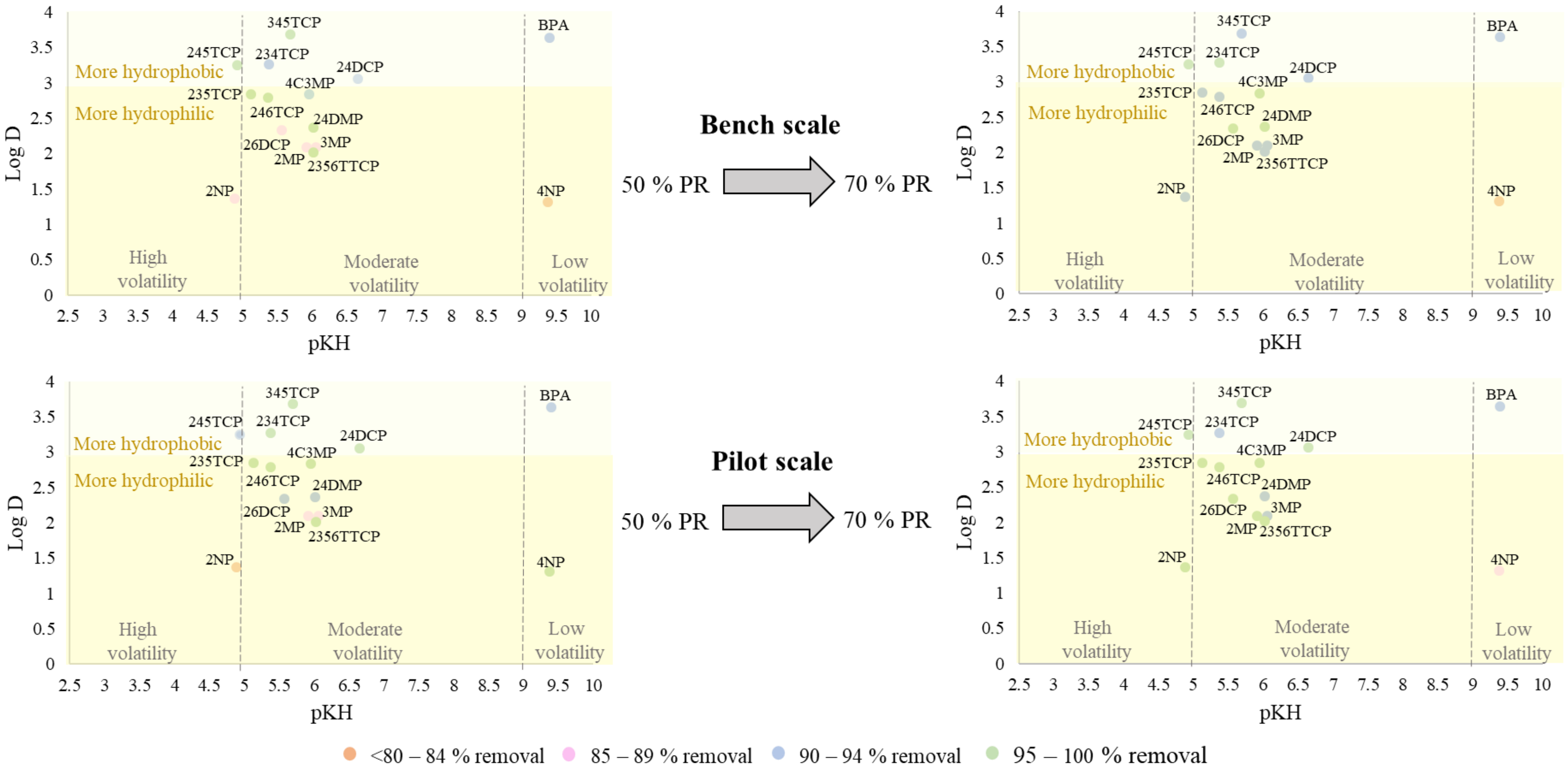
The average removal of the pollutants by the DCMD systems can be seen in Figure 5-6 (APPENDIX XXV presents the removal of each phenolic compound). Observe similar average removal of the compounds on both scales and permeate recoveries. The average contaminant removal at 50 % PR was 93 ± 5.8 % and 93.1 ± 3.5 % for bench and pilot scales, respectively. At 70 % PR, the average removal for the bench scale was 93.6 ± 5.3 %, while for the pilot was 94.7 ± 3 %. The removal results are similar to those presented in previous studies (RAMOS et al., 2022a), which reached average values ranging from 94.3 ± 1.9 % and 95.0 ± 2.2 %, for recovery of 30 % and 70 %, respectively, for the DCMD bench system. Thus, it is clear that the scale-up of the MD system did not impact the contaminants removal (<90 %) and even at large scales it can work on higher permeate recoveries producing a greater amount of water without compromising water quality in terms of phenols removal, giving operational and economic advantages to the technology application.

Figure 5-6: Removal of phenolic compounds according to the permeate recovery (PR) of 50 and 70 % at bench and pilot scale, respectively (feed: RW1 spiked with phenolic compounds (5 µg L^{-1}) at 60 °C). The horizontal bars denote the standard deviation



The main mechanisms involved in the rejection of phenolic compounds by MD at bench scale were associated with the compound hydrophobicity (Log D) and, especially, volatility (pKH) in previous studies (RAMOS et al., 2022a; RAMOS et al., 2022b). Figure 5-7 and APPENDIX XXVI show the Log D and pKH of each compound related to a removal range in the experiments of 50 % and 70 % PR at both scales.

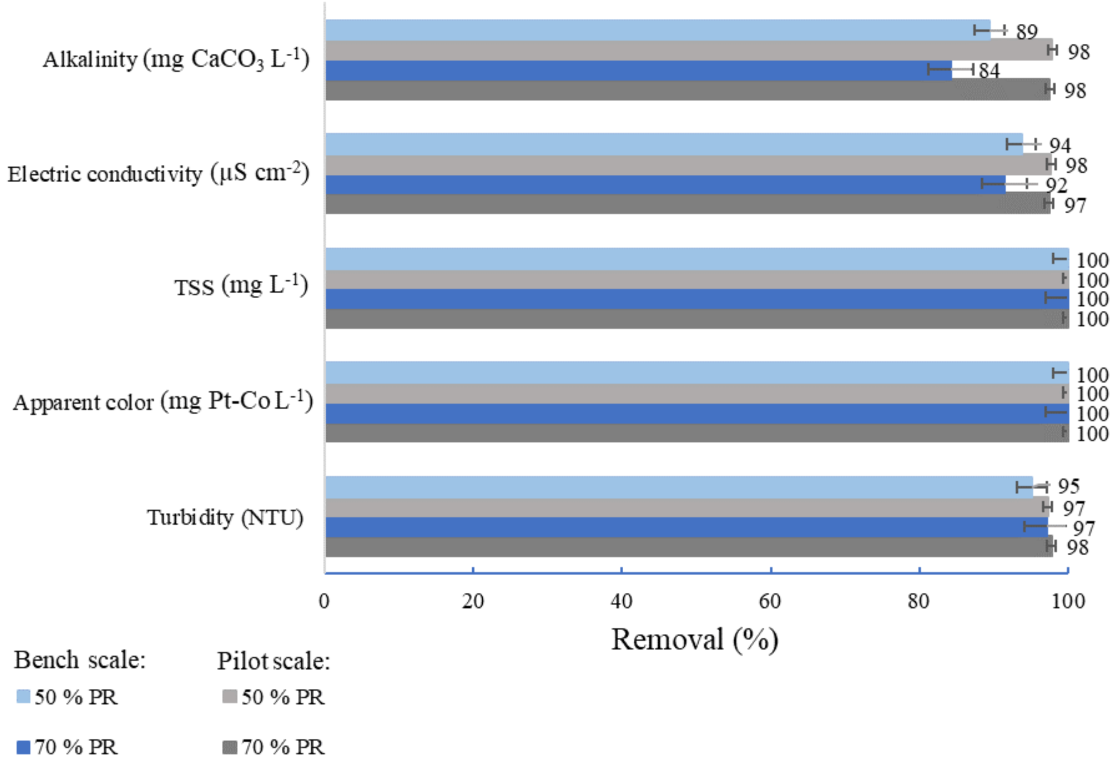
Figure 5-7: Each phenolic compound removal in different ranges at bench and pilot scale systems at 50 % and 70 % recovery and the compounds Log D and pKH (feed: RW1 spiked with phenolic compounds (5 µg L^{-1}) at 60 °C)



The BPA which is more hydrophobic and with low volatility had a stable behavior in all experiments showing a removal in the range of 90 – 94 %. 4 NP, which also has low volatility but is more hydrophilic, had the same behavior only in the bench scale experiment (<80 – 84 %). While in the pilot scale, the compound presented higher removal (95 – 100 %) at 50 % PR, due to electrostatic interactions with the membrane or with the system in general (YAHYA et al., 2021), since the pilot system has a larger area, making more active sites available at the beginning of the experiment, consequently, greater removal. The more hydrophilic and highly volatile 2NP had a distinct removal in all analyzed conditions, but always with an increase in removal as the recovery increased. Confirming that independent of the scale of DCMD systems the membrane fouling process due to longer operations with real surface water as feed solution, can favor the concentration of phenolic compounds. Especially those with high volatility, that are expected to be found in the permeate side, due to deposition of solutes and reduction of membrane pores, and reduction of active contact sites on the surface area of the membrane as proven in previous studies (RAMOS et al., 2022b). 245TCP which has high volatility and is more hydrophobic had high removals of 95 - 100 % in all conditions, except in the pilot experiment at 50 % PR which was 90 - 94 % . The more hydrophobic 345TCP, 234TCP, and 24DCP with moderate volatility had similar behavior with removals varying in the experiments, but always <90 %. 4C3MP, 246TCP, 24DMP, 26DCP, 3MP, 2MP, and 2356TTCP also with moderate volatility but more hydrophilic had distinct behaviors among them in the experiments, but with removals greater than the range of 85 – 89 %. The volatility and hydrophobicity of the phenols serve as guides to indicate the behavior of the compounds in the DCMD systems, but it is extremely difficult to determine the exact percentage of removal only considering these factors. Note that the more hydrophobic compounds had more stable and constant behavior in the experiments demonstrating that the interaction between the compound and the water is a key factor in the MD process.

In general, after analyzing the removal of each compound it can be confirmed that the scale up of the system did not affect it and in most cases the increase in permeate recovery did not impact the compound's removal and can even favor it. In addition, it must be highlighted the high permeate quality in relation to physical-chemical parameters (Figure 5-8 and APPENDIX XXVII), with great removals (>84 %) in all evaluated conditions for the purpose of using the DCMD technology in the treatment of surface water.

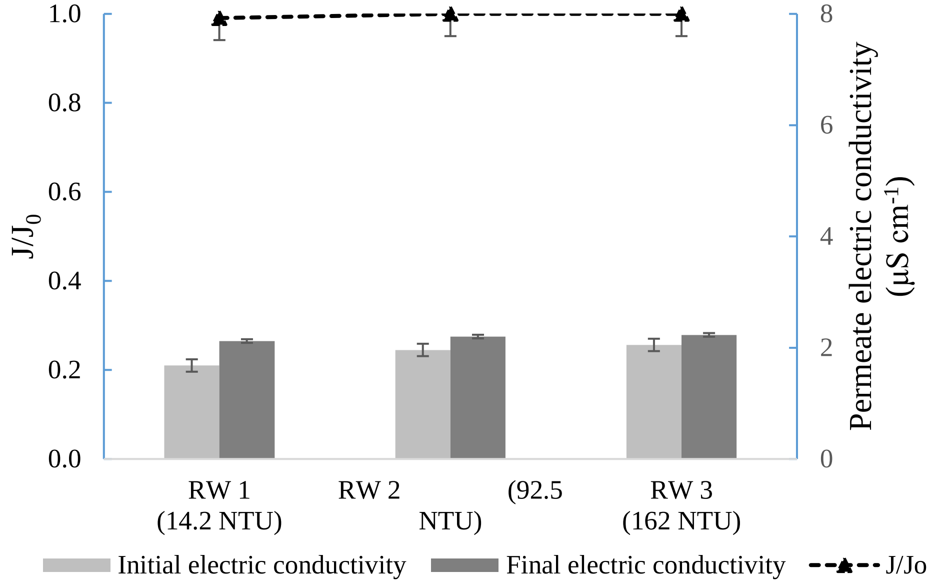
Figure 5-8: Removal of physical-chemical parameters by the DCMD systems according to the different permeate recovery (feed: RW1 spiked with phenolic compounds (5 µg L^{-1}) at 60 °C). The horizontal bars denote 0.95 confidence intervals



5.3.3 Pilot DCMD system in the treatment of different surface water

To validate the use of the pilot module, three water matrices with different characteristics, especially related to turbidity (Table 5-1), and spiked with phenolic compounds were used as feed solution. Figure 5-9 presents the system performance in relation to the flux and electric conductivity of the permeates generated in the experiments.

Figure 5-9: Relation between the final (J) and initial (J_0) permeate flux and the initial and final permeate electric conductivity in the experiments with different water matrices (feed: RW1, RW2, and RW3 spiked with phenolic compounds (5 µg L^{-1}) at 60 °C; 50 % recovery). The vertical bars denote 0.95 confidence intervals



No permeate flux reduction was observed throughout the experiments analyzing the relation between the final and initial permeate flux ($J/J_0 = 0.99 – 1$). This indicates that water turbidity did not affect the system in terms of permeate flux for water treatment. The final and initial permeate electric conductivity in all experiments were not significantly different proving that there was no membrane wetting during the tests. A similar result was found by Gryta (2018), who during a one-year operation of a DCMD system did not find a considerable flux decline using a feed solution with high turbidity. Grossi et al. (2020), who also used DCMD for purifying contaminated surface water, demonstrated that the system produced high quality water even in the worst scenario with 10,000 NTU feed solution.

Regarding the removal of phenolic compounds (Figure 5-10), a small variation was observed especially for 4NP, 234TCP, 24DMP, 2NP and 3MP. This difference in removal may be related to a greater affinity of the compounds with the solutes present in the water, since in general the compounds obtained greater removal in the higher turbidity (RW3), or this improved rejection of micropollutants can be attributed to the increased sieving effect as a result of the cake layer (formed by the deposition of particles on the membrane surface) that may have trapped the compounds (CHEN et al., 2019). However, the phenols average removal was 94.8 ± 3.0 % for RW1, 97.25 ± 2.2 % for RW2, and 98.2 ± 2.9 % for RW3 showing that it was not so affected by the change in the quality of the feed surface water. The evaluated physical-chemical parameters were also high removed (>90 %) as shown in Figure 5-11. All evaluated parameters reached the water quality of WHO guidelines (APPENDIX XXIX) for human consumption, especially for the turbidity (<5 NTU). The results achieved confirms that DCMD has its performance less susceptible to the feed composition variations, as reported in the literature (SILVA et al., 2018; GROSSI et al., 2020). This fact makes MD technology even more attractive and advantageous for applications in different scenarios, since this resistance to feed variation is not a reality in other membrane separation processes such as nanofiltration and reverse osmosis (ELAZHAR et al., 2021).

Figure 5-10: Removal of phenolic compounds by the pilot DCMD system according to the different feed surface waters (feed: RW1, RW2, and RW3 spiked with phenolic compounds (5 µg L^{-1}) at 60 °C). The horizontal bars denote 0.95 confidence intervals

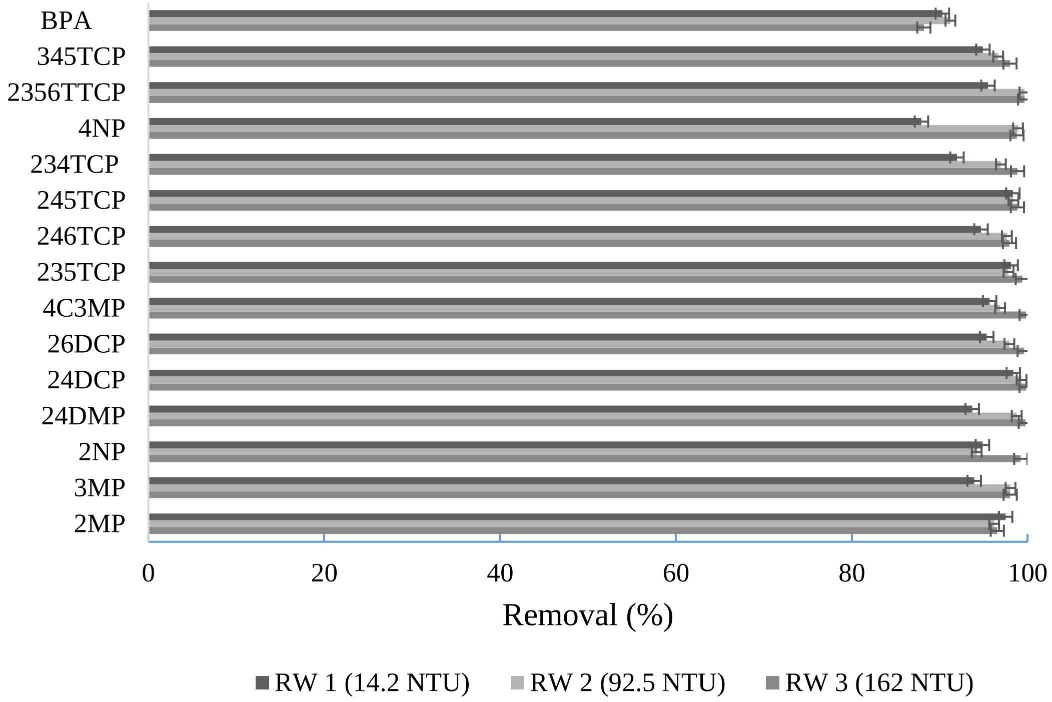
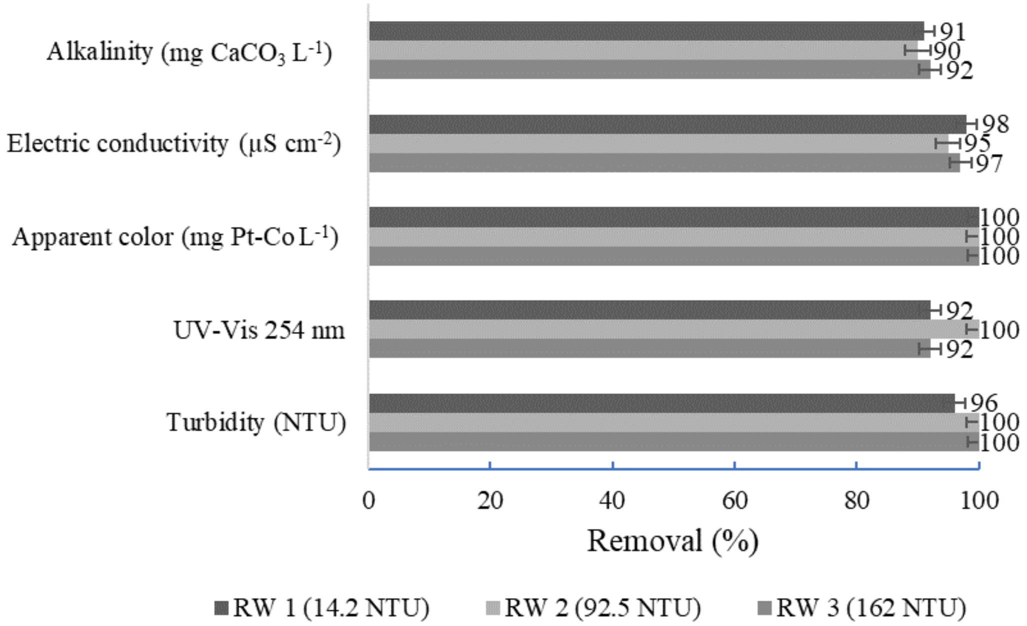


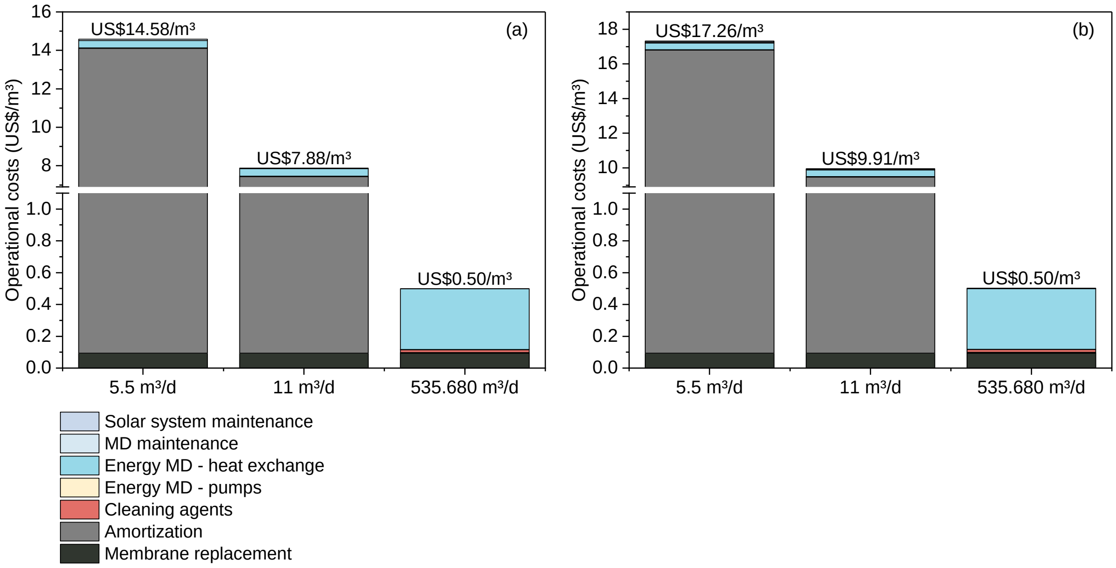
Figure 5-11: Removal of physical-chemical parameters by the pilot DCMD system according to the different feed surface waters (feed: RW1, RW2, and RW3 spiked with phenolic compounds (5 µg L^{-1}) at 60 °C). The horizontal bars denote 0.95 confidence intervals



5.3.4 Economic analysis for drinking water production

To attain the water demand of a small community, via a mobile (5.5 m^3 d^{-1}) or a distributed system (11 m^3 d^{-1}), the equipment would be more compact than centralized systems and required a lower investment cost (values of CAPEX), which varied from US$ 199,145.21 to US$ 208,757.88. In a scenario where membrane distillation would be considered in large applications (535,680 m^3 d^{-1}), as a polishing system for drinking water treatment plants, the initial investment cost corresponded to approximately US$ 112,701,955.93, justified by the large water volumes to be treated. These were systems powered by a conventional electrical source, and the breakdown of operational costs is shown in Figure 5-12 (a). The costs were compared with a system possibly powered by photovoltaic energy sources, and the breakdown of operational costs is shown in Figure 5-12 (b).

Figure 5-12: Comparison between the operational costs for membrane distillation systems powered by (a) conventional electrical source and (b) solar energy



Given the higher investment costs and lower water production, the amortization represented the greatest contribution (>94.4 %) to the total operational costs in both mobile and distributed water systems (11 m³ d^{-1} or 5.5 m³ d^{-1}). The operational costs varied between 7.88 to 14.58 US$ m^{-3}. Given the additional acquisition costs related to the photovoltaic panels, the amortization costs were higher in Figure 12b, which resulted in higher OPEX values from 9.91 to 17.26 US$ m^{-3}. The costs, though, were comparable with other studies that considered a similar treatment capacity. Palenzuela et al. (2018), for example, reported an operational cost of 15 US$/m³ for a system intended to produce 10 m³/d of treated water via a solar multi-effect distillation plant to be installed in Chile.

Comparing with RO application for surface water treatment, Cornelissen et al. (2021) to produce 6.25 m^3 d^{-1} (150 m^3 h^{-1}) of potable water calculated a CAPEX ranging from US$ 432,326.00 (4.0 M€) to US$ 1,945,467.00 (1.8 M€) depending on the pre-treatment adopted, which is in the same range of the RO installations CAPEX for brackish water published in the literature. In addition, the total operational costs of RO ranged from 0.53 US$/m³ (0.49 €/$m^3$) to 1.31 US$/m³ (1.21 €/m^3). Note that the CAPEX values for the installation of the RO system with a flow similar to the proposed mobile MD system (5.5 m³ d^{-1}) and smaller than the distributed MD system (11 m³ d^{-1}) are relatively higher. The higher OPEX for the MD and the lower OPEX of the RO presented are difficult to compare given the difference between the parameters considered.

For large-scale MD applications, however, the higher flow rate being treated compensates for the initial investment costs. The total operational costs amount to 0.50 US\$ m^{-3}. Based on these findings, membrane distillation technology becomes more attractive in large-scale application scenarios, where the high initial investment costs are offset by the significant volumes of produced drinking water. It is evident that on large scales, the primary economic variable contributing to the total operational costs is the energy required to maintain the temperature difference between the feed and distillate streams. The values correspond to approximately US\$ 0.38/m^3, which accounts for 76 % of the total reported cost. This outcome is explained by the larger amount of heat that needs to be exchanged due to the higher flow rate.

A first alternative for reducing investment costs in large-scale applications (US\$ 112,701,955.93), particularly for drinking water polishing, involves partial treatment that focuses on only a fraction of the total treated water stream for polishing purposes. The permeate obtained from membrane distillation, known for its high quality, can be blended with the remaining treated water to dilute it, resulting in a final stream that complies with drinking water standards. This approach requires smaller systems and leads to reduced initial investment costs. This strategy has been presented by several authors, such as Brião et al. (2014), who considered a mixing process between groundwater and reverse osmosis (RO) to produce drinking water from brackish water. A similar approach was adopted by Elazhar et al. (2021), who combined nanofiltration (NF) and RO for brackish water desalination. In their case, the blending strategy involved the NF concentrate and RO permeate, resulting in a stream that meets drinking water requirements while benefiting from a lower volume of concentrate to be disposed of.

The decision to opt for partial treatment, however, entails the use of a more compact system, which was previously identified as economically unfavorable due to the high investment costs resulting in significant amortization expenses. By comparing the contributions of amortization and heat exchange to the overall operational costs, it becomes possible to determine a treatment capacity threshold at which the initial investments are offset by the energy required to maintain the temperature difference between the feed and distillate streams. This result is illustrated in Figure 5-13, indicating that the investment costs, represented by amortization costs, would be recovered for a treatment capacity exceeding 10,600 m³ d^{-1}. Beyond that point, alternative strategies aimed at reducing the costs associated with energy requirements become necessary.

Figure 5-13: Comparison between the contribution of amortization and heat exchange costs to the total OPEX for different treatment capacities

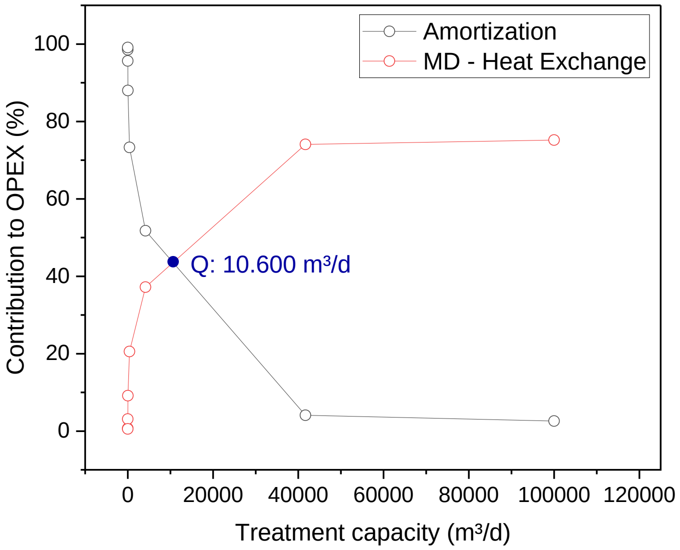
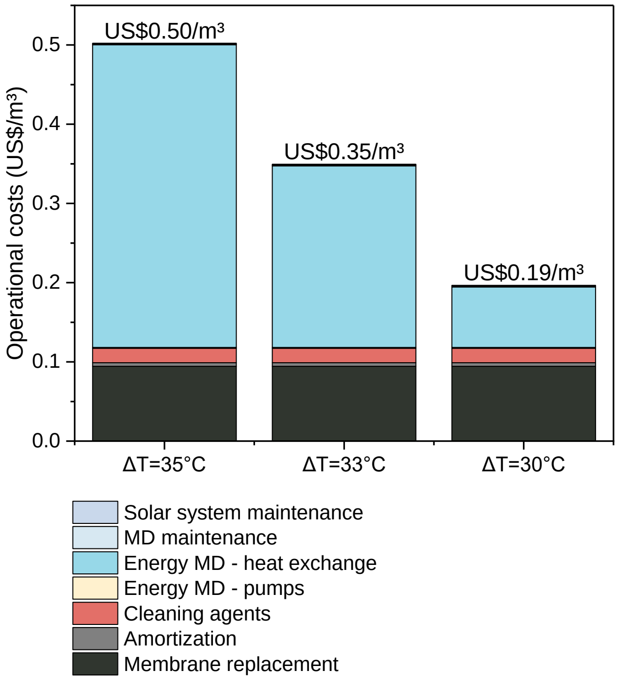


Figure 5-14 presents the results for operational costs when the temperature difference between the feed and distillate streams is reduced (treatment capacity: 535,680 m³/day), resulting in a lower heat exchange rate. It is clear that by reducing the temperature difference from 35 °C to 30 °C, the operational costs decrease from 0.50 US$/m³ to 0.19 US$/m³, despite the lower distillate flux anticipated due to the reduced temperature difference. As shown in Figure 5-14, for a temperature difference of 30 °C, additional strategies are necessary to further reduce operational costs, such as advancements in membrane manufacturing to reduce associated expenses. At this stage, membrane replacement emerges as the primary contributor to the total operational costs, accounting for 44 % of the total.

Figure 5-14: Comparison between the temperature difference between the feed and permeate in membrane distillation and how its impacts operational costs



Finally, it is important to emphasize the significance of considering the benefits of distributing water of higher quality to the population when discussing the costs associated with advanced water treatment technologies. While there may be initial investment expenses and operational costs involved, the long-term advantages of providing clean and safe drinking water cannot be understated. Improved water quality directly impacts public health, reducing the risks of waterborne diseases and enhancing overall well-being (LI and WU, 2019). These gains are indirect and challenging to quantify, yet they must be thoroughly contemplated when proposing advanced technologies for water treatment.

5.4 CONCLUSION

DCMD was evaluated as an alternative technology to be considered in the removal of phenolic compounds and water treatment. There was a drastic decrease in permeate flux with the system scaled-up, due to the inflow energy limitations in the pilot module, in addition to the probable increased effect of membrane compaction in the pilot module and temperature polarization. However, increasing the permeate recovery from 50 to 70 % did not significantly affect the flux in both operating scales of the DCMD system, as well as the experiments using different surface waters in the pilot scale. The removal of phenolic compounds did not change significantly with the module scale-up or with the different matrices of water used in the feed solution, with an average removal >90.8 % under the studied conditions. The physical-chemical quality of the permeates generated in the different experiments did not change significantly, reaching the guideline for drinking water quality. With the results achieved, DCMD proved to be a safe technology for the production of drinking water and the removal of phenolic compounds even with the system scale-up.

The technical results were complemented by a preliminary economic analysis, aiming at applications of this system in real water treatment scenarios. It was demonstrated that membrane distillation for surface water treatment is more attractive in large-scale applications due to high water production that potentially reduced the amortization cost. In addition, comparing the operating costs for MD systems powered by conventional electrical sources and solar energy, the higher costs were related to the use of solar energy due to the acquisition of photovoltaic panels that increased amortization. The importance of developing MD membranes with greater permeability and strategies to increase the heat efficiency used in the process to reduce costs, and thus enable the wider application of DCMD systems was highlighted.

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CHAPTER VI – FINAL CONSIDERATIONS

6.1 MAIN RESULTS AND CONCLUSIONS

Chapter II demonstrated through a literature review the high occurrence of phenolic compounds in water sources. More than 60 different phenols were identified and quantified in different parts of the world during 2000-2023. The most identified compound was bisphenol A (n=93) and the highest concentration reported was 179 M ng L^{-1} for phenol in surface water channels in India. It was highlighted that the drinking water guidelines need to be updated since many pollutants are not addressed. The human health and cancer risks were estimated showing concerning results for some phenols, such as 2-nitrophenol, 2,6-dichlorophenol, 3,4,5-Triclorophenol, 2,3,4,6-tetrachlorophenol, 2,4-dinitrophenol, 3-methylphenol, 2,4-dimethylphenol, 2,4,6-Triclorophenol, and pentachlorophenol. The membrane technologies were presented for water treatment and removal of phenolic compounds. Emphasizing the high removal of phenols from water by membrane distillation (MD), as an emerging technology, and reverse osmosis, as a mature technology with the lowest measured ecological footprint.

The performance of direct contact membrane distillation (DCMD) in the retention of phenolic compounds and the influence of fouling in the treatment process were evaluated in order to produce high quality water, free of these micropollutants, considering the necessity to think critically about the complexity of the water which is arriving at the water treatment plants and the importance of alternative technologies, as MD, for a future water treatment scenario.

In Chapter III, the DCMD performance was assessed for the retention of fifteen phenolic compounds in surface water by different operate conditions of temperature (40, 50, and 60 °C), feed concentration (3, 5, 7, and 10 µg L^{-1}), and permeate recovery rate (30, 50, and 70 %). Kruskal Wallis confirmed a significant difference ($p<0.05$) between the global removal of phenolic compounds at different temperatures. The increase in temperature led to a reduction in all compound’s removal. As expected, a positive correlation ($r_{Spearman}>0.8$) between the compounds’ volatility (pKH) and their losses was observed, but no correlation was found with the pKH/Log D<2.5. Regarding to the feed concentration and the recovery rate, there were no statistical difference between the removal values obtained for the phenolic compounds. These indicates the DCMD strength for that application. However, a trend for flux decay was noticed as the recovery increased, confirmed by a temporal trend analysis and Mann-Kendall tests, although the flux decay was relatively low ($J/J_0=0.89$). In addition, the technology was efficient and did not compromise the permeate quality with > 90% efficiency in pollutants removal, even for higher temperatures (60 °C) and permeate recovery (70 %).

Chapter IV provided monitoring of phenolic compounds retention with the membrane fouling. The process achieved a recovery rate of 93.26 %, without compromising the permeate quality. However, the high permeate flux decay in a short time indicated the need to implement raw water pre-treatment and periodic cleaning strategies. Fouling was mainly attributed to organic elements from surface water. It was observed particles with lengths ranging from 1.143 to 1.214 µm that were correlated with the presence of bacteria confirming the formation of biofouling during long-term DCMD operation for water treatment. However, the fouling layer formed favored the concentration of the compounds in the feed solution with practically no mass loss in the process. The average removals of phenolic compounds varied from 94.30 to 99.24 %. Thus, although fouling occurred, the technology was robust in retaining phenols and producing high-quality water.

Chapter V shows that the removal of phenolic compounds did not change significantly with the DCMD module scale-up or with the different matrices of surface water used in the feed solution, with an average removal >90.8 % under the studied conditions. It was demonstrated that membrane distillation for surface water treatment can be attractive in large-scale applications due to high water production that reduces the amortization value of the high initial investment. Comparing the operating costs for MD systems powered by conventional electrical sources and solar energy, the higher costs were related to the use of solar energy due to the acquisition of photovoltaic panels that increased amortization. Some strategies were raised to reduce the costs of the initial investment (partial treatment of water), amortization (processing capacity >10,600 $m^3\ d^{-1}$), and the energy spent on the heat exchanger (reduce ΔT from 35 °C to 30 °C).

Based on this work, DCMD was deeply studied for application in water treatment and removal of phenolic compounds, bringing relevant results for future full-scale applications, thinking of a modern, robust, and safer scenario for the water treatment sector. Although the challenges were also listed, leaving room for future studies on pretreatment, cleaning strategies, improving the energy efficiency of the process, increasing the permeate flux, reducing costs, and management of the concentrate generated that can enable real applications of the DCMD. In addition, attention was drawn to the relevant contamination of water resources worldwide by phenolic compounds, thus the modernization of the water treatment sector to remove micropollutants and updating water guidelines for the protection of populations is still a challenge to be faced.

CHAPTER VII – EXPERIENCE ABROAD

7.1 SANDWICH PHD (DAAD FELLOWSHIP)

I participated in Public Notice n° 17/2020 CAPES/DAAD - Sandwich Doctorate (DAAD-DS-20) and was approved with the German Academic Exchange Service (DAAD) scholarship for the period of October 2021 to September 2022. The scholarship was awarded to pursue part of my doctoral studies in Germany at the Karlsruhe Institute of Technology (KIT), in Karlsruhe. The doctorate title was concluded in Brazil.

During a year as visiting researcher was possible to develop several activities at the Institute for Advanced Membrane Technology (IAMT)/KIT with the supervision of Prof. Dr. Andrea Schäfer. Initially, there was training to learn how to use the batch electrodialysis (ED) systems and the pilot single-pass ED system for water desalination and pollutant removal, as well as the use of ion chromatography equipment for monitoring ions present in the water. The work with ED was an opportunity to acquire knowledge in another membrane separation process that has increased the number of water treatment applications in recent years.

The main works conducted during this period were the supervision of the master's project entitled *Electrodialysis for removal and recovery of nitrogen compounds from brackish water*, which the article is still in development. Participation in the writing of the paper *Electrodialysis for arsenic and selenium removal from brackish water to produce drinking water* (Desalination, 2023). In addition, the development of the project *Energy consumption of brackish water desalination by nanofiltration/reverse osmosis and single pass electrodialysis* and *Power distribution in the single-pass multi-stage electrodialysis for brackish water desalination*, with experiments carried out in the single-pass pilot ED system. I participated in conferences with posters and oral presentations, such as Euromembrane 2021 and 2022 and Nanofiltration 2022. At IAMT I had constant training on how to become a better scientist, group meetings, and close monitoring of Prof. Dr. Andrea Schäfer. This period abroad contributed to my personal and professional growth, I had the opportunity to work in a multicultural environment, with people from different parts of the world, use the English language daily for communication, and allowed me to meet several people who are references in working with membrane separation processes.

APPENDIX

APPENDIX I: Literature about phenolic compounds occurrence in water sources (2000 - 2023)

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
Brazil	water reservoir	GC-DCE	pentachlorophenol	<10 - 11	<10 - 22	CARMO, 2000
			2,4,6-trichlorophenol	<10		
			2,3,6-trichlorophenol	<10		
			2,3,4-trichlorophenol	<10		
			2,5-dichlorophenol	<10 - 22		
Brazil	surface water	SPE (HLB Oasis); methanol; LC–MS/MS	bisphenol A	25 - 84	ND - 84	SODRÉ et al., 2010
			4-n-octylphenol	ND		
			4-n-nonylphenol	ND		
Brazil	river water	SPE (HLB OASIS); methanol and acetonitrile; HPLC-DAD-FLD	4-octylphenol	<21	<18 - 13016	MONTAGNER and JARDIM, 2011
			4-nonylphenol	<18		
			bisphenol A	204 - 13016		
Brazil	drinking water	GC-MS	2,4,6-trichlorophenol	8 - 238	8 - 238	SARTORI et al., 2012
Brazil	drinking water and river water	SPE (C_{18}); methanol; GC-FID	2-chlorophenol	1740 - 2430	60 - 38600	RAMOS et al., 2021a
			4-chloro-3-methylphenol	ND (150) - 520		
			2-nitrophenol	190 - 430		
			2,4-dimethylphenol	ND (250) - 2190		
			2,4-dichlorophenol	420 - 1003		
			2,4,6-trichlorophenol	80 - 38600		
			4-nitrophenol	220 - 25400		
			bisphenol A	90 - 3570		
			2-methylphenol	60 - 6550		
			2,6-dichlorophenol	150 - 34100		
			2,3,5-trichlorophenol	220 - 5710		
			2,4,5-trichlorophenol	220 - 2600		
			2,3,4-trichlorophenol	680 - 3110		
			2,3,5,6-tetrachlorophenol	ND (870) - 4430		

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
Brazil	river water	SPE (C_{18}); methanol; GC-FID	2,3,4,6-tetrachlorophenol	ND - 14400	45 - 241600	RAMOS et al., 2021b
			3,4,5-trichlorophenol	290 - 610		
			4-chloro-3-methylphenol	ND - 241600		
			2-nitrophenol	290 - 1420		
			2,4-dimethylphenol	ND (650) - 730		
			2,4-dichlorophenol	ND (130) - 1490		
			4-nitrophenol	ND - 6430		
			bisphenol A	45 - 3010		
			2-methylphenol	ND - 520		
			2,6-dichlorophenol	ND - 1770		
			2,3,5-trichlorophenol	ND (310) - 1910		
			2,3,4-trichlorophenol	ND - 360		
			2,3,5,6-tetrachlorophenol	ND - 240		
			2,3,4,6-tetrachlorophenol	ND - 561		
Mexico	river water	SPE (C_{18}); GC-MS	bisphenol A	17.12 - 97.81	0.3 - 97.81	CALDERÓN-MORENO et al., 2019
			4-nonylphenol	1.23 - 44.77		
			4-tert-octylphenol	0.3 - 28.10		
United States	surface water (stormwater canals)	GC-MS	bisphenol A	1.9 - 158	1.9 - 158	BOYD et al., 2004
United States	river water	SPE (C_{18} and SDB-XC); methanol, acetone, and dichloromethane; GC-MS	bisphenol A	ND - 147.2	ND - 147.2	ZHANG et al., 2007
United States	drinking water and raw water	SPE; LC-MS/MS and GC-MS/MS	bisphenol A	ND - 14	14 - 130	BENOTTI et al., 2009
			nonylphenol	110 - 130		
			octylphenol	ND		
United States	harbor and river water	liquid–liquid extraction; methylene chloride; GC-MS-SIM	bisphenol A	4.4 - 190	4.4 - 190	SINGH et al., 2010

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
United States	drinking water and raw water	GC-MS	bisphenol A	1 - 119	1 - 119	KARALIUS et al., 2014
United States	drinking water and river water	LC-MS/MS	bisphenol A	21.9 - 44.3	12.4 - 185.6	PADHYE et al., 2014
			nonylphenol	12.4 - 185.6		
United States	lake and river water	HPLC-MS/MS and GC-MS	bisphenol A	ND - 600	250 - 3000	BARBER et al., 2015
			nonylphenol	ND - 3000		
			octylphenol	ND - 250		
Canada	drinking water and river water	liquid-liquid extraction; LC-MS and GC-MS	bisphenol A	0.45 - 18	0.45 - 841	CHEN et al., 2006
			nonylphenol	37 - 313		
			nonylphenol ethoxylates	20 - 841		
Canada	drinking water, lake, groundwater, and river water	SPE; methanol; LC-MS/MS	bisphenol A	87 - 99	87 - 99	KLEYWEGT et al., 2011
Canada	river and lake water	SPE (C_{18}); acetonitrile; HPLC-UV	2,4-dichlorophenol	1900 - 2400	1100 - 2400	KUESENG and PAWLISZYN, 2013
			2-nitrophenol	1100		
Australia	river water	SPE (Oasis HLB); GC-MS	bisphenol A	4 - 59	4 - 2058	YING et al., 2009
			4-nonylphenol	287 - 2058		
			4-t-octylphenol	13 - 94		
England	river water	SPE (Oasis MCX); methanol and ammonium hydroxide; UPLC	4-tert-octylphenol	<15 - 100	<1 - 100	KASPRZYK-HORDERN et al., 2008
			p-benzylphenol	<15 - 67		
			bisphenol A	<6 - 100		
			3,4,5,6-tetrabromo-o-cresol	<1 - 36		
England	river water	SPE (Oasis MCX); methanol and ammonium hydroxide; UPLC	4-tert-octylphenol	<15000 - 1293000	<1000 - 1293000	KASPRZYK-HORDERN et al., 2009
			p-benzylphenol	<15000 - 58000		
			bisphenol A	<6000 - 68000		
			3,4,5,6-tetrabromo-o-cresol	<1000 - 140000		

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
England	river water	microwave assisted extraction; HPL-MS	bisphenol A	62.3	62.3	PETRIE et al., 2016
England	river water	SPE (Oasis HLB); methanol; UPLC-MS/MS	bisphenol A	1.9 - 116.9	1.9 - 116.9	PETRIE et al., 2019
Ireland	river water	SPE (Oasis HLB); dichloromethane and acetonitrile; GC-MS	2-nitrophenol	210 - 2170	210 - 2170	PEñALVER et al., 2021
			2,4,6-trichlorophenol	210 - 2170		
Switzerland	river water	SPE (Oasis HLB); methanol; LC-MS/MS	bisphenol A	2 - 46	<1.2 - 195	JONKERS et al., 2009
			octylphenol	<1.2 - 6.9		
			phenylphenol	<2.1 - 16		
			nonylphenol	<29 - 195		
France	drinking water and surface water	SPE (C_{18}); hexane/dichloromethane and methanol/acetone/ethyl acetate; LCMS-MS	bisphenol A	2 - 29	2 - 124.9	DUPUIS et al., 2012
			353-nonylphenol	13.5 - 124.9		
France	surface water, groundwater, and drinking water	LC-MS/MS	bisphenol A	9 - 50	9 - 505	COLIN et al., 2013
			nonylphenol	140 - 505		
			nonylphenol 2-ethoxylate	<9 - 15		
			nonylphenol 1-carboxylic acid	10 - 35		
Spain	river water	SPE (Lichrolut RP-18); acetonitrile; HPLC-MS	bisphenol A	<90000 - 2970000	<60000 - 37300000	CÉSPEDES et al., 2005
			nonylphenol monoethoxylate	<220000 - 6870000		
			nonylphenol diethoxylate	<60000 - 3170000		
			nonylphenol	<150000 - 37300000		
			octylphenol	<9000000 - 21900000		
Spain	river water	stir-bars sorptive extraction (SBSE); GC-MS	4-tert-octylphenol	ND	ND	QUITANA et al., 2007
			4-pentylphenol	ND		
			2,4,6-trichlorophenol	ND		

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
Spain	river water	SPE (Oasis HLB); ethyl acetate; GC-MS	nonylphenol	ND	32 - 112	RODIL et al., 2010
			4-tert-butylphenol	ND		
			4-octylphenol	ND		
			2,4,6-tribromophenol	ND		
			4-n-nonylphenol	ND		
			pentachlorophenol	ND		
			bisphenol A	ND		
			pentabromophenol	ND		
			2,6-di-tert-butyl-4-(hydroxymethyl)phenol	ND		
			2,6-di-tert-butyl-4-methylphenol	32 -112		
			2-tert-butyl-4-methoxyphenol	ND		
Spain	river water	LC–MS/MS	bisphenol A	6 - 126	<0.065 - 3374	ESTEBAN et al., 2014
			octylphenol	42 - 474		
			nonylphenol	96 - 1483		
			octylphenol monocarboxylate	<0.065		
			nonylphenol monocarboxylate	369 - 3374		
			octylphenol monoethoxylate	<17		
			nonylphenol monoethoxylate	<62		
			octylphenol diethoxylate	9 - 234		
			nonylphenol diethoxylate	156 - 721		
Spain	river water	SPE (Oasis HLB); methanol; EQuan-LC-MS/MS	alkylphenols	>100	84 - 649	GORGA et al., 2015
			bisphenol A	84 - 649		

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
Spain (Iberian Peninsula)	river water	LC-MS/MS	bisphenol A	<20 - 4800	<5 - 4800	SALGUEIRO-GONZÁLEZ et al., 2015
			4-tert-octylphenol	<8 - 88		
			4-n-octylphenol	<6 - 12		
			4-n-nonylphenol	<5 - 6		
			nonylphenol	<30 - 1030		
Belgium	river water	SPE (Oasis HLB); methanol, acetone and ethylacetate; LC–MS/MS	4-tert-octylphenol	38 - 55	38 - 2500	LOOS et al., 2007
			bisphenol A	2200 - 2500		
			4-n-nonylphenol	ND		
Austria	groundwater and surface water	HPLC-MS/MS	bisphenol A	ND - 600	41 - 890	HOHENBLUM et al., 2004
			nonylphenol	ND - 890		
			octylphenol	ND - 41		
Germany	surface water of streams and rivers	SPE (ENV+); acetone; HRGC-LRMS and GC-MS	4-t-octylphenol	<20 - 189	ND - 458	BOLZ et al., 2001
			4-nonylphenol	56 - 485		
			bisphenol A	<50 - 272		
Germany	river water	SPE; GC-MS	4-t-octylphenol	155 - 189	35 - 458	KöRNER et al., 2001
			4-nonylphenol	164 - 458		
			bisphenol A	ND - 35		
Germany	drinking water and river water	SPE; methanol; HRGC-ECD	4-tert-octylphenol	0.2 - 54	0.2 - 134	KUCH and BALLSCHMITER, 2001
			4-nonylphenol	2.5 -134		
			bisphenol A	0.5 - 14		
Germany	surface water (rivers, lakes and channels)	SPE; acetone; GC-MS/MS and HPLC	bisphenol A	0.5 - 410	0.5 - 410	FROMME et al., 2002
Germany	lake water and groundwater	stir bars; GC-MS	total amount of phenolic compounds	43000 - 138000	43000 - 138000	MONTERO et al., 2005
Germany	river water	SPE; GC-NCIMS	bisphenol A	42 - 417	42 - 417	MöDER et al., 2007

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
Germany	river water	SPE; methanol; GC-MS	bisphenol A	209 - 223.6	124 - 223.6	REINSTORF et al., 2008
			t-nonylphenol	124 - 170.9		
Germany and Czech Republic (border)	river water	liquid–liquid extractions; dichloromethane; GC–MSD	bisphenol A	8.9 - 776	0.4 - 776	HEEMKEN et al., 2001
			nonylphenol	1 - 52		
			octylphenol	0.4 - 2.1		
Poland	rivers and drinking water water	SPE (C_{18}); diethyl ether and methylene chloride; GC-MS	phenol	50 - 707	20 - 640000	MICHAŁOWICZ et al., 2011
			pentachlorophenol	30 - 640000		
			2,3,4,5-tetrachlorophenol	40 - 133		
			2,4,5-trichlorophenol	30 - 272		
			2,4,6-trichlorophenol	30 - 114		
			2,4-dichlorophenol	20 - 103		
			4-methylphenol	30 - 380		
			2-chlorophenol	30		
Poland	river water	SPE (Oasis HLB); methanol, HPLC	bisphenol A	12.5 - 277.9	<1 - 834.5	STAMISZEWSKA et al., 2015
			4-tert-octylphenol	<1 - 834.5		
			4-nonylphenol	<4 - 170		
Portugal	river water	SPE; acetonitrile and dichloromethane; GC-MS and LC-APCI/MS	2,4,6-trichlorophenol	20 - 2300	20 - 2300	AZEVEDO el at., 2000
Portugal	river water	SPE (Oasis HLB); dichloromethane and methanol; HPLC-DAD and GC-MS	4-octylphenol	<2	<2.0 - 451.9	RIBEIRO et al., 2009a
			bisphenol A	<6.6 - 451.9		
			4-nonylphenol	ND		
Portugal	river water	SPE (Oasis HLB); dichloromethane and methanol; HPLC-DAD and GC-MS	4-octylphenol	ND	<80 - 10700	RIBEIRO et al., 2009b
			bisphenol A	<80 - 10700		
			4-nonylphenol	ND		
Portugal	river water	SPE (OASIS HLB); methanol; GC-MS	4-t-octylphenol	4.9 - 45.3	1.49 - 952	ROCHA et al., 2015
			4-n-octylphenol	8.1 - 61		

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
			4-n-nonylphenol	1.49 - 14		
			bisphenol A	27.5 - 190		
			nonylphenol	508 - 952		
Portugal	river water	dispersive liquid-liquid microextraction (DLLME); GC-MS	bisphenol A	54 - 4424	54 - 4424	CUNHA et al., 2022
Italy	coastal lagoon	SPE; HPLC–ESI/MS	nonylphenol	<0.5 - 211	<0.1 - 211	POJANA et al., 2007
			bisphenol A	<1 - 145		
			nonylphenol monoethoxylate carboxylate	<0.1 - 71		
Italy	river water	SPE (Oasis HLB); methanol, acetone and ethylacetate; LC-MS/MS	4-tert-octylphenol	12 - 88	12 - 700	LOOS et al., 2007
			bisphenol A	36 - 175		
			4n-nonylphenol	460 - 700		
Italy	river water and groundwater	SPE (Oasis HLB cartridges); methanol; HPLC-MS/MS	bisphenol A	ND - 171.3	ND - 171.3	PIGNOTTI et al., 2017
Greece	river water	SPE (strata-X and C$_{18}$); hexane, dichloromethane and ethyl acetate; GC-MS/MS	dinoseb	ND	ND - 50	TERZOPOULOU et al., 2015
			bisphenol A	ND		
			nitrophenol	ND		
			4-tert-octylphenol	ND		
			nonylphenol	50		
Romania	Suface water (coastal)	SPE (C$_{18}$); methanol; LC–MS/MS	bisphenol A	ND - 416	11.3 - 416	CHIRIAC et al., 2021
			bisphenol B	ND		
			bisphenol C	ND		
			bisphenol E	ND - 194		
			bisphenol F	ND - 19.7		
			bisphenol S	ND - 11.3		
Russia			phenol	50 - 9700	100 - 9700	

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
	river and drinking water	SPME; HPLC with amperometric detection	2-chlorophenol	1600		FILIPOV et al., 2002
			2,6-dichlorophenol	100		
			2,4-dichlorophenols	200		
Malaysia	river water	liquid-liquid extraction; dichloromethane and ethyl acetate; GC-MS	4-t-butylphenol	3.3 - 789.43	3.3 - 6938.19	TAN and MUSTAFA, 2004
			bisphenol A	6.33 - 1588.74		
			pentachlorophenol	ND - 62		
			4-n-octylphenol	ND - 11.06		
			nonylphenol	83.32 - 6938.19		
			4-n-heptylphenol	ND - 102.38		
			4-t-octylphenol	ND - 72.73		
			4-n-hexylphenol	ND - 5.21		
			4-n-pentylphenol	ND - 7.41		
			4-n-butylphenol	ND - 13.83		
			2,4-dichlorophenol	ND - 16.38		
Malaysia	surface water and drinking water	SPE (C_{18}); acetone and hexane; GC-MS	bisphenol A	1.4 - 214.5	1.4 - 214.5	SANTHI et al., 2012
Malaysia	river water	SPE; methanol; LC-MS/MS	bisphenol A	1.18 - 8.24	1.18 - 8.24	WEE et al., 2019
Malaysia	coastal and estuarine surface water	SPE; LC-MS/MS	bisphenol A	1.32 - 133.91	1.32 - 1890.51	ZAINUDDIN et al., 2023
			bisphenol F	160.47 - 1890.51		
			bisphenol S	2.95 - 30.52		
Philippines	lake water	SPE; LC-MS/MS	bisphenol A	0.71 - 47.40	0.71 - 47.40	ANA and ESPINO, 2020
China	surface water	MDL and RSD; dichloromethane, ethyl acetate, acetone, and methanol; GC-MS	2,4-dichlorophenol	<1.1 - 19960	<1.1 - 28650	GAO et al., 2007
			pentachlorophenol	<1.1 - 594		
			2,4,6-trichlorophenol	<1.4 - 28650		
China	river water	SPE; methanol and ethyl acetate; GC	2-phenylphenol	8 - 2506	6 - 33231	PENG et al., 2008
			bisphenol A	6 - 881		

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
China	river water	SPE (Oasis HLB); ethyl acetate; GC-MS	nonylphenol	36 - 33231	43.5 - 639.1	GONG et al., 2009
			bisphenol A	43.5 - 639.1		
China	river water	SPE (Oasis HLB);methanol and dichloromethane; GC-MS/NCI	4-tert-octylphenol	1- 2470	1 - 8890	ZHAO et al., 2009
			bisphenol A	2 - 1030		
			4-nonylphenol	28 - 8890		
China	river water	SPE (C_{18}); dichloromethane; GC-MS	4-chloro-3-methylphenol	ND - 35.9	35.9 - 1547	ZHONG et al., 2010
			phenol	ND - 205.6		
			2-nitrophenol	ND - 1547		
			2-chlorophenol	ND - 166.1		
			2,4,5-trichlorophenol	ND - 65.3		
			2,4,6-trichlorophenol	ND - 840.4		
			2,4-dichlorophenol	ND - 143.1		
			2,5-dichlorophenol	ND - 116.8		
			2-cresol	ND -199.5		
			3-cresol	ND - 65.4		
China	river water	GC	2,4-dichlorophenol	<1.1 - 19960	<1.1 - 28650	JIN et al., 2011
			pentachlorophenol	<1.1 - 594		
			2,4,6-trichlorophenol	<1.4 - 28650		
China	lake water	Liquid-liquid extraction; HPLC	phenol	35000	35000	ZHANG et al., 2011
China	drinking water and surface water	SPE (Oasis HLB); methanol; UPLC-ESI-MS/MS	bisphenol A	128 - 512	128 - 918	FAN et al., 2013
			nonylphenol	558 - 918		
China	lake water	SPE (Oasis HLB); methanol; LC-MS	bisphenol A	48.24 - 725.94	48.24 - 725.94	YUAN et al., 2014
China	river water	SPE (C_{18}); methanol; GC-MS	4-tert-octylphenol	1.54 - 45.8	0.35 - 385	ZHANG et al., 2014
			bisphenol A	8.24 - 263		
			nonylphenol monoethoxylates	8.92 - 385		

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
China	river water	SPE (Oasis HLB); methanol; UHPLC	nonylphenol diethoxylates	19.6 - 321	6.63 - 207	YAN et al., 2014
			4-n-nonylphenol	0.35 - 3.77		
			4-t-nonylphenol	106 - 344		
			bisphenol A	6.63 - 207		
China	surface water	GC-MS	2,4,6-tribromophenol	ND - 320	32 - 920	XIONG et al., 2014
			bisphenol A	ND - 860		
			pentabromophenol	ND - 37		
			tetrabromobisphenol A	ND - 920		
China	river water	SPE; HPLC-MS/MS	2,6-di-tert-butyl-4-methylphenol	84 - 90	74 - 101	LIU et al., 2015
			2,2'-methylenebis(6-cyclohexyl-4-methyl)phenol	84 - 101		
			4,4-Methylenebis(2,6-di-tert-butylphenol)	89 - 91		
			4,4-Butylidenebis(2-(1,1-dimethylethyl)-5-methyl-phenol)	74 -76		
			2,2-Methylenebis(6-cyclohexyl-4-methyl)phenol	84 -101		
			4-tert-octylphenol	95 - 98		
China	river water, reservoir, and groundwater	SPE (C_{18}); methanol; HPLC-MS	4-t-octylphenol	ND - 96.87	4.29 - 3336.7	WANG et al., 2015
			bisphenol A	ND - 3336.7		
			4-n-nonylphenol	4.29 - 12.23		
China	river water	SPE (Oasis HLB); methanol; LC-MS/MS	bisphenol A	ND - 98	98 - 1110	YAMAZAKI et al., 2015
			bisphenol S	ND - 135		

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
China	river water	SPE (Oasis HLB); GC-MS	bisphenol F	448 - 1110	325 - 13000	GONG et al., 2016
			4-t-octylphenol	0 - 325		
			bisphenol A	>0 - 1400		
			4-nonylphenol	>0 - 13000		
China	lake water	SPE (Oasis HLB); methanol; HPLC-MS/MS	nonylphenol	21.23 - 305.10	27.95 - 565.40	LIU et al., 2016
			bisphenol A	27.95 - 565.40		
			4-tert-octylphenol	108.70 - 298.50		
China	river water	SPE (Oasis HLB); methanol; LC-MS/MS	4-tert-octylphenol	1.20 - 3.99	1.20 - 3352.86	DIAO et al., 2017
			bisphenol A	12.41 - 62.75		
			4-nonylphenol	233.04 - 3352.86		
China	lake water	ultrasonic extraction; HPLC-MS/MS	4-tert-octylphenol	ND - 1758.40	4.17 - 1758.40	LIU et al., 2017a
			bisphenol A	49.38		
			nonylphenol	4.17 - 5.64		
China	river water	SPE (Oasis HLB); HPLC-MS/MS	4-tert-octylphenol	ND - 100	ND - 1121	LIU et al., 2017b
			nonyphenol	1.4 - 858		
			bisphenol A	ND - 563		
			tetrabromobisphenol A	ND - 32.3		
			4-tert-butylphenol	225 - 1121		
			4-butylphenol	ND - 6430		
			4-hexylphenol	ND - 27.5		
			2,4-di-tert-amylphenol	ND - 56.4		
China	drinking water	liquid-liquid extraction; UPLC-ESI-tqMS	2,6-dibromo-4-chlorophenol	<0.5 - 12.1	<0.5 - 215.0	PAN et al., 2017
			2,4,6-trichlorophenol	<2.7 - 215		
			2,4,6-tribromophenol	<2.6 - 56.9		
			2,6-dichloro-4-bromophenol	<1.1 - 43.5		
China	river water		4-tert-octylphenol	ND - 108	2.54 - 5050	PENG et al., 2017

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
China	river water	SPE (Oasis HLB); HPLC-MS/MS, ESI	bisphenol A	2.54 - 892	4.37 - 137.35	ZHOU et al., 2017
			4-nonylphenol	25.1 - 5050		
		GC-MS	phenol	35.72 - 137.35		
			2-nitrophenol	12.74 - 116.98		
			2,4-dichlorophenol	4.37 - 63.78		
			2,4,6-trichlorophenol	ND (2.73) - 35.66		
			pentachlorophenol	ND (3.96) - 7.34		
China	lake water	SPE (Oasis HLB); methanol; HPLC-MS/MS	bisphenol A	28 - 560	0.7 - 1600	YAN et al., 2017
			bisphenol F	ND (3.5) - 1600		
			bisphenol S	ND (4.5) - 1600		
			bisphenol Z	ND (2.7) - 45		
			bisphenol B	ND (6.4) - 28		
			bisphenol AP	1 - 56		
			bisphenol AF	0.7 - 84		
China	river water	SPE (C_{18}); dichloromethane; GC-MS	phenol	ND - 15500	99 - 269000	ZHONG et al., 2018
			2,4-dichloro-3-ethyl-6-nitrophenol	ND - 99		
			2-sec-butylphenol	ND - 11100		
			2,3,6-trimethylphenol	ND - 24700		
			2-nitrophenol	ND - 17600		
			4-nitrophenol	ND - 1950		
			2,6-dichlorophenol	ND - 3100		
			2,4-dichlorophenol	ND - 3350		
			2,5-dichlorophenol	ND - 4630		
			4-chlorophenol	ND - 1210		
			2,4-xylenol	ND - 90600		
			4-cresol	ND - 271		

Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
China	river water	SPE (C_{18}); methanol; GC-MS	3-cresol	ND - 269000	<1.2 - 1573.1	WANG et al., 2018
			2-cresol	ND - 52600		
			4-t-octylphenol	<1.2 - 126		
			nonyphenol	108.1 - 634.8		
			bisphenol A	<1.5 - 1573.1		
China	river water	SPE (Oasis HLB); methanol; LC-tandem MS	4-tert-octylphenol	156.1	<50 - 3079.4	LUO et al., 2019
			4-n-nonyphenol	<50		
			bisphenol A	3079.4		
China	drinking water and surface water	SPE; UPLC-MS/MS	bisphenol A	ND (6.5) - 34.9	0.61 - 34.9	ZHANG et al., 2019
			bisphenol S	ND		
			bisphenol F	ND (0.86) - 12.56		
			bisphenol E	ND (0.61) - 6.18		
			bisphenol B	ND (3.2) - 14.3		
			bisphenol AF	ND (4.7) - 10.8		
China	lake water	SPE (Oasis HLB); GC-MS/TQ8050	phenol	50 - 1800	50 - 1800	WANG et al., 2020
			3-metilfenol	0 - 900		
			2,4,6-trichlorophenol	50 - 250		
			2,4-dichlorophenol	0 - 250		
China	river water	SPE (Oasis HLB); acetonitrile and ethyl acetate; UPLC-TQMS	4-tert-octylphenol	0.4 - 1040	0.4 - 123300	CHEN et al., 2020
			4-nonyphenol	2.6 - 58546		
			bisphenol A	11.4 - 123319		
China	river water	SPE; UPLC	phenol	ND - 3840	30 - 5960	CHEN et al., 2021
			4-nitrophenol	ND - 1150		
			3-methylphenol	ND - 1740		
			2,4-dinitrophenol	ND - 2690		
			2-nitrophenol	ND - 380		

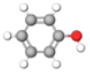
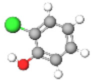
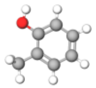
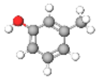
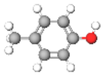
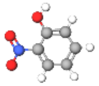
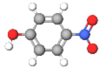
Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
China	drinking and raw water	SPE (Oasis HLB); HPLC	2,4-dimethylphenol	ND - 840	250 - 2750	LI et al., 2022
			2-chlorophenol	ND - 1740		
			2,4-dichlorophenol	ND - 3760		
			2,4,6-trichlorophenol	ND - 2480		
			pentachlorophel	30 - 5960		
			4-chloro-m-cresol	ND - 4530		
			2,6-dichloro-4-bromophenol	0 - 500		
			2,6-dibromo-4-chlorophenol	0 - 250		
			2,4,6-tribromophenol	250 - 2750		
China	river water	SPE (Oasis HLB); methanol; HPLC-MS/MS	bisphenol A	16.94 - 175.6	16.94 - 175.6	YU et al., 2023
Taiwan	drinking water and raw water	SPE (C_{18}); methanol; UPLC-MS/MS	bisphenol A	ND - 38	38 - 361	CHEN et al., 2013
			octylphenol	ND - 60		
			nonylphenol	68 - 361		
Taiwan	drinking water and surface water	liquid–liquid extraction; dichloromethane; GC-MS	bisphenol A	<740	<440 - 740	GOU et al., 2016
			nonylphenol	<440		
Singapore	surface water (river and canal)	SPE; acetonitrile and methanol; LC-MS/MS	octylphenol	<1 - 590	<1 - 3910	XU et al., 2011
			nonyphenol	110 - 3910		
			bisphenol A	30 - 625		
Singapore	surface water and groundwater	SPE; methanol; HPLC–ESI–MS/MS	bisphenol A	ND - 324	ND - 324	TRAN et al., 2013
Singapore	river water	HPLC; LDO−HSs	phenol	130 - 540	120 - 590	TANG et al., 2013
			4-nitrophenol	ND (380) - 590		
			2-nitrophenol	ND		
			2-methyl-4,6-dinitrophenol	ND (80) - 220		
			2,4-dinitrophenol	ND (120) - 450		

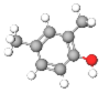
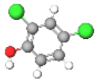
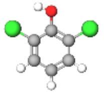
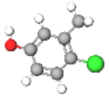
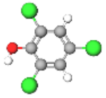
Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
			2,4-dimethylphenol	ND		
			4-chloro-3-methylphenol	ND		
			2,4-dichlorophenol	ND		
			2,4,6-trichlorophenol	ND		
			pentachlorophenol	ND		
			2-chlorophenol	ND - 230		
Singapore	coastal surface water	LC-MS/MS	bisphenol A	5 - 1918	5 - 1918	BAYEN et al., 2016
South Korea	river water	SPE; LC-MS/MS	octylphenol	25	6.9 - 59	YOON et al., 2010
			bisphenol A	6.9 - 59		
South Korea	river water	GC-MS and laser-induced fluorescence (LIF)	bisphenol A	ND - 39.4	ND - 39.4	KO et al., 2007
South Korea	river water	SPE (Oasis HLB); methanol; LC-MS/MS	bisphenol A	1 - 272	42 - 1300	YAMAZAKI et al., 2015
			bisphenol S	ND - 42		
			bisphenol F	121 - 1300		
Vietnam	groundwater	SPE; GC-MS	bisphenol A	ND - 40	ND - 40	DUONG et al., 2015
Japan	river water	SPE; methanol; LC-MS/MS and LC-MS	4-tert-octylphenol	6.9 - 47.5	4.8 - 144	FURUICHI et al., 2004
			4-nonyphenol	51.6 - 144		
			bisphenol A	4.8 - 76.3		
Japan	surface seawater	HPLC	nonyphenol	30.4 - 104	20.2 - 104	HASHIMOTO et al., 2005
			bisphenol A	20.2 - 30.1		
Japan	river water	SPE (Oasis HLB); methanol; HPLC	bisphenol A	＜500 - 900	＜500 - 900	KANG and KONDO, 2006
Japan	surface water (river and bay)	SPE (Oasis HLB); methanol; LC-MS/MS	bisphenol A	ND (3.1) - 431	3.1 - 2850	YAMAZAKI et al., 2015
			bisphenol S	ND (1.5) - 15		
			bisphenol F	ND (90) - 2850		
Iran	river water	SPE (CDS); methanol; GC-MS	phenol	ND	30 - 150	FARAJI et al., 2012
			pentachlorophenol	ND		

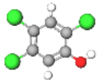
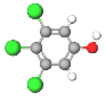
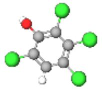
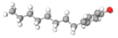
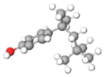
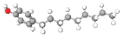
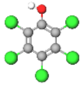
Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
			2,3,4,6-tetrachlorophenol	ND		
			2,4,6-trichlorophenol	30		
			2,4-dichlorophenol	150		
			4-chloro-3-methylphenol	ND		
			2,4-dimethylphenol	ND		
			2-chlorophenol	ND		
Saudi Arabia	groundwater	GC-MS	2,4-dinitrophenol	10000 - 230000	100 - 510000	ALQUWAIZANY et al., 2019
			4-nitrophenol	200 - 2000		
			2-nitrophenol	100 - 2200		
			2,4-dimethylphenol	10000 - 50000		
			2-methyle-4,6-dinitrophenol	10000 - 510000		
			2,4,6-tricholorophenol	10000 - 270000		
Lebanon	drinking water	SPE (C_{18}); acetonitrile; HPLC	bisphenol A	50 - 137	50 - 137	DHAINI and NASSIF, 2014
Nigeria	river water	ultrasonication and liquid-liquid extraction; GC-MS	4-t-octylphenol	57.1 - 68.6	43.9 - 79.4	OKETOLA and FAGBEMIGUN, 2013
			4-nonyphenol	43.9 - 79.4		
			bisphenol A	ND		
Nigeria	drinking water, groundwater, and surface water		2,4-dinitrophenol	154000 - 639000	78000 - 639000	OTITOJU et al., 2023
			2,4,6-trichlorophenol	78000 - 261000		
			phenol	123000 - 169000		
Ghana	drinking water and raw water	GC-MS	bisphenol A	ND - 9	ND - 9	KARALIUS et al., 2014
Jamaica	drinking water and raw water	GC-MS	bisphenol A	3 - 16	3 - 16	KARALIUS et al., 2014
South Africa	river water	GC-MS	phenol	ND (22) - 140	22 - 12246	YAHAYA et al., 2019
			2,4-dinitrophenol	ND		
			2,4,6-trichlorophenol	ND (34) - 723		

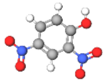
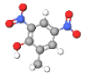
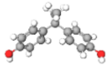
Country	Water source	Analytical method	Compound	Concentration range reported (ng L^{-1})	Min - max quantified value (ng L^{-1})	Reference
			2,4-dichlorophenol	ND (87) - 759		
			4-chloro-3-methylphenol	ND (313) - 676		
			2,4-dimethylphenol	ND (37) - 815		
			2-methyl-4,6-dinitrophenol	ND - 680		
			4-nitrophenol	ND - 1212		
			2-chlorophenol	ND (41) - 136		
			pentachlorophenol	ND (77) - 635		
			2-nitrophenol	ND (55) - 1205		
Egypt	river water	liquid–liquid microextraction; methanol; UPLC-MS/MS	2,6-di-tert-butyl-4-methylphenol	63000 - 1351200	63000 - 1351200	ZAMZAM et al., 2020
India	river water	SPE (C_{18}); ethyl acetate and then sodium sulfate; GC-MS	octylphenol	ND - 16.3	2.8 - 2200	SELVARAJ et al., 2014
			bisphenol A	2.8 - 136		
			nonylphenol	ND - 2200		
India	surface water (river, lake and canal)	SPE (Oasis HLB); methanol; LC-MS/MS	bisphenol A	ND (54) - 1950	15 - 7200	YAMAZAKI et al., 2015
			bisphenol S	ND (15) - 7200		
			bisphenol F	ND (27) - 289		
India	surface water (canals)	molecular spectrophotometry after distillation	phenol	80000000 - 179000000	80000000 - 179000000	KUMAR and PACHA, 2015
India	surface water	SPE (C18); GC-MS	bisphenol A	40 - 4460	40 - 4460	CHAKRABORTY et al., 2021

APPENDIX II: Characteristics of the most reported phenolic compounds in the literature

Compound	**Acronyms**	**CAS**	**Molar mass (g mol^{-1})**	**Vapor pressure at 25 °C (mmHg)[ab]**	**Solubility in water at 25 °C (mg L^{-1})[ab]**	**pKa[c,d]**	**pkH**	**Log D[c,d] at pH 7**	**Molecular formula**	**Molecular structure[e]**	**Main usage[b,f]**	**Oral effect[b,f]**	**EPA list**
phenol	P	108-95-2	94.11	0.35	82819.44	9.99	6.478	1.63	C_6H_5OH		Plastic industry; resins; biomolecules extraction; cosmetics industry; disinfectants	Anorexia, weight loss, diarrhea, vertigo, salivation, a dark coloration of the urine and blood, and liver damage	✓
2-chlorophenol	2CP	95-57-8	128.56	2.53	11300	8.49	4.951	2.21	C_6H_5ClO		Biocide; disinfectant; agricultural chemicals; insecticide	Possible carcinogenic for liver, lymphoma and lungs, immune system hypersensitivity, hepatic and renal toxicity	✓
2-methylphenol (o-Cresol, 2-cresol)	2MP	95-48-7	108.05	0.29	22200	10.29	5.921	2.09	C_7H_8O		Synthetic resins; plasticizers; dye; pesticide; herbicide; disinfectant; sebacic acid production	Body weights loss and neurotoxicity	✓
3-methylphenol (m-Cresol, 3-cresol)	3MP	108-39-4	108.05	0.2	21500	10.1	6.067	2.09	C_7H_8O		Flavoring; glues; dyes; ink; coatings; cleaning products; leather products	Body weights loss and neurotoxicity	✗
4-methylphenol (p-Cresol, 4-cresol)	4MP	106-44-5	108.14	0.11	21500	10.2	6	2.09	C_7H_8O		Flavoring; glues; dyes; ink; coatings; cleaning products; leather products	Maternal toxicity (clinical signs of hypoactivity, respiratory distress, ocular irritation, and death)	✗
2-nitrophenol	2NP	88-75-5	139.02	0.113	2503.98	7.23	4.893	1.36	$C_6H_5NO_3$		Dyes; rubber products; fungicides; glucose reagent; pH indicator		✓
4-nitrophenol	4NP	100-02-7	139.02	0.0000979	11601.77	7.15	9.382	1.31	$C_6H_5NO_3$		Fungicides; insecticides; dyes; leather browning; pH indicator		✓

Compound	Acronyms	CAS	Molar mass (g mol^{-1})	Vapor pressure at 25 °C (mmHg)[ab]	Solubility in water at 25 °C (mg L^{-1})[ab]	pKa[c,d]	pkH	Log D[c,d] at pH 7	Molecular formula	Molecular structure[e]	Main usage[b,f]	Oral effect[b,f]	EPA list
2,4-dimethylphenol (2,4-xylenol)	24DMP	105-67-9	122.07	0.102	7867.55	10.6	6.022	2.36	$C_8H_{10}O$		Fungicide; disinfectant; pharmaceuticals; plastics; insecticides; rubber; dyes	Affects the nervous and hematologic systems	✓
2,4-dichlorophenol	24DCP	120-83-2	161.96	0.09	4498.72	7.89	6.659	3.05	$C_6H_4Cl_2O$		Dye; wood preservative; pesticide; potassium ammonia ion indicator; antiseptic; herbicide	Possible carcinogenic for liver, lymphoma and lungs, immune system hypersensitivity, hepatic and renal toxicity	✓
2,6-dichlorophenol	26DCP	87-65-0	161.96	0.0889	1900	6.79	5.573	2.33	$C_6H_4Cl_2O$		Intermediate for 2,4,6-trichlorophenol	Possible carcinogenic for liver, lymphoma and lungs, immune system hypersensitivity, hepatic and renal toxicity	✗
4-chloro-3-methylphenol	4C3MP	59-50-7	142.01	0.05	3835.46	9.55	5.959	2.83	C_7H_7ClO		Fluids for machines; pharmaceutical preservatives; disinfectants; preservatives for cosmetics; medications; glues; rubbers; paints; leather products		✗
2,4,6-trichlorophenol	246TCP	88-06-2	195.92	0.008	799.63	6.23	5.377	2.78	$C_6H_3Cl_3O$		Antiseptic, pesticide for wood, leather and for glue preservation	Possible carcinogenic for liver, lymphoma and lungs, immune system hypersensitivity, hepatic and renal toxicity	✓

Compound	Acronyms	CAS	Molar mass (g mol^{-1})	Vapor pressure at 25 °C (mmHg)^{ab}	Solubility in water at 25 °C (mg L^{-1})^{ab}	pKa^{c,d}	pkH	Log D^{c,d} at pH 7	Molecular formula	Molecular structure^{e}	Main usage^{b,f}	Oral effect^{b,f}	EPA list
2,4,5-trichlorophenol	245TCP	95-95-4	195.92	0.0075	114.1	7.43	4.938	3.24	$C_6H_3Cl_3O$		Fungicide (paper mill); herbicide; intermediate in pesticide production	Possible carcinogenic for liver, lymphoma and lungs, immune system hypersensitivity, hepatic and renal toxicity	✗
3,4,5-trichlorophenol	345TCP	609-19-8	195.92	0.000496	64.49	7.84	5.699	3.68	$C_6H_3Cl_3O$		Pharmaceuticals; dyes; polymers	Possible carcinogenic for liver, lymphoma and lungs, immune system hypersensitivity, hepatic and renal toxicity	✗
2,3,4,6-tetrachlorophenol	2346TTCP	58-90-2	231.881	0.000666	23	5.22	5.079	2.56	$C_6H_2Cl_4O$		Pesticide; wood preservative; fungicide	Possible carcinogenic for liver, lymphoma and lungs, immune system hypersensitivity, hepatic and renal toxicity	✗
4-n-octylphenol	4NOP	1806-26-4	206.32	0.000098	3.11	10.8		5.19	$C_{14}H_{22}O$		Organic synthesis; pharmaceuticals; agrochemicals; dyestuff fields	Changes to weight, development, and the female reproductive system	✗
4-t-octylphenol	4TOP	140-66-9	206.32	0.03	5.113	10.3	5.66	5.25	$C_{14}H_{22}O$		Detergents; industrial cleaners; emulsifiers	Changes to weight, development, and the female reproductive system	✗
4-nonylphenol	4NNP	104-40-5	220.35	0.000818	7	10.14	5.76	5.76	$C_{15}H_{24}O$		Laundry detergents; personal hygiene; automotive; latex paints; lawn care products	Neuroimmune, reproductive, and estrogenic effects	✓
pentachlorophenol	PCP	87-86-5	266.3	0.00011	14.008	4.7	7.611	2.45	C_6HCl_5O		Pesticide; preservative of wood and wood products	Cause problems in the liver, thyroid, nervous system, immune system, reproduction and	✓

Compound	Acronyms	CAS	Molar mass (g mol^{-1})	Vapor pressure at 25 °C (mmHg)[ab]	Solubility in water at 25 °C (mg L^{-1})[ab]	pKa[c,d]	pkH	Log D[c,d] at pH 7	Molecular formula	Molecular structure[e]	Main usage[b,f]	Oral effect[b,f]	EPA list
												development, and it is carcinogenic	
2,4-dinitrophenol	24DNP	51-28-5	184.11	0.00039	2790	4.09		1.67	$C_6H_4N_2O_5$		Dye; wood preservative; pesticide; potassium and ammonia ion indicator; antiseptic; herbicide	Weight loss and affects the ophthalmic system	✓
2-methyl-4,6-dinitrophenol	2M46DNP	534-52-1	198.13	0.00012	197.94	4.23	5.854	-0.49	$C_7H_6N_2O_5$		Insecticide	Weight loss and affects the neurological system	✗
bisphenol A	BPA	80-05-7	228.11	0.000000227	120	9.6	9.404	3.63	$C_{15}H_{16}O_2$		Production of plastic polycarbonates and epoxy resins; component in the coating of metal cans	Histone acetylation, haematological, biochemical, and hormonal changes	✓

Source: [a]Chemspider (2023); [b]EPA (2023c); [c]PubChem (2023); [d]Quitana et al. (2007); [e]Molview (2023); [f]EPA (2023d)

APPENDIX III: Phenolic compounds TDI, CSF, NOAEL, and LOAEL for risk calculation

Compound	**Abbreviation**	**TDI[ab] (ug kg^{-1} bw day^{-1})**	**CSF for water[b] (mg/kg/d)**	**NOAEL[ab] (mg kg^{-1} bw day^{-1})**	**LOAEL[ab] (mg kg^{-1} bw day^{-1})**
phenol	P	1500	NR		
2-chlorophenol	2CP	3	0.005		
2-methylphenol (o-Cresol, 2-cresol)	2MP	50	0.005 (soil)		
3-methylphenol (m-Cresol, 3-cresol)	3MP		0.005 (soil)	50	
4-methylphenol (p-Cresol, 4-cresol)	4MP		0.0005 (soil)	50	
2-nitrophenol	2NP		NR	0.005	
4-nitrophenol	4NP		NR	110000	
2,4-dimethylphenol (2,4-xylenol)	24DMP	20	0.02	50	
2,4-dichlorophenol	24DCP	3	0.003		
2,6-dichlorophenol	26DCP	3	NR		
4-chloro-3-methylphenol	4C3MP	300	NR		
2,4,6-trichlorophenol	246TCP	3	0.011		
2,4,5-trichlorophenol	245TCP	3	0.1		
3,4,5-trichlorophenol	345TCP	3	NR		
2,3,4,6-tetrachlorophenol	2346TTCP	3	0.03		
4-n-Octylphenol	4NOP		NR	NR	NR
4-t-Octylphenol	4TOP		NR	15	
4-nonylphenol	4NNP		NR	NR	NR
pentachlorophenol	PCP		0.005		1.5

Compound	**Abbreviation**	**TDI[ab] (ug kg^{-1} bw day^{-1})**	**CSF for water[b] (mg/kg/d)**	**NOAEL[ab] (mg kg^{-1} bw day^{-1})**	**LOAEL[ab] (mg kg^{-1} bw day^{-1})**
2,4-dinitrophenol	24DNP		0.002		2
2-methyl-4,6-dinitrophenol	2M46DNP		0.00039	4	
bisphenol A	BPA	50	NR	50	

Source: [a]EPA (2023a); [b]EPA (2023b); NR = Not Reported

APPENDIX IV: Summary of different phenolic compounds and their removal by membrane technology. SEC: specific energy consumption

Phenolic compound	Feed water	Membrane technology	Membrane used	Operating pressure (bar)	Feed flow rate (m^3/s)	Permeate flow rate (m^3/s)	SEC (kWh/m^3)	CO_2 emission (kg/m^3)	Removal (%)	References
2,3,4-trichlorophenol	Real surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000011	13312.727	9651.7273	82.9	RAMOS et al., 2021b
	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>91.6	RAMOS et al., 2022a
2,3,5-trichlorophenol	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>97.2	RAMOS et al., 2022a
2,4,5-trichlorophenol	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>93.1	RAMOS et al., 2022a
2,4,6-trichlorophenol	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>95.3	RAMOS et al., 2022a
3,4,5-trichlorophenol	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>93.6	RAMOS et al., 2022a
2,3,5,6-tetrachlorophenol	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>97.8	RAMOS et al., 2022a
2,4-dichlorophenol	Synthetic water	Photocatalytic membrane	TiO_2	-	-	-	-	-	~95	ROTA et al., 1996
	Synthetic water	Pervaporation	Polyurethane urea membrane	not applied	not applied	-	-	-	-	DAS et al., 2008
	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>92.2	RAMOS et al., 2022a
	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>93.5	RAMOS et al., 2022a
	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>93.4	RAMOS et al., 2022a
	Synthetic water	Photocatalytic membrane	Fe-TiO2-activated carbon fiber	-	dead-end filtration	-	-	-	62 - >99	LIU et al., 2009

Phenolic compound	Feed water	Membrane technology	Membrane used	Operating pressure (bar)	Feed flow rate (m^3/s)	Permeate flow rate (m^3/s)	SEC (kWh/m^3)	CO_2 emission (kg/m^3)	Removal (%)	References
2-chlorophenol	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	73	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	71	ARSUAGA et al., 2011
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	36	ARSUAGA et al., 2011
2-metylphenol	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>92.4	RAMOS et al., 2022a
2-nitrophenol	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	70	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	64	ARSUAGA et al., 2011
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	32	ARSUAGA et al., 2011
	Real surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000011	13312.727	9651.7273	89.8	RAMOS et al., 2022b
	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>97.0	RAMOS et al., 2022a
3-nitrophenol	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	70	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	68	ARSUAGA et al., 2011
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	26	ARSUAGA et al., 2011
4-nitrophenol	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	75	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	69	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	62	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	RO-90	5	0.0833	0.000018	0.064	0.047	~44	HIDALGO et al., 2015
	Synthetic water	Reverse osmosis	RO-90	25	0.0833	0.000087	0.066	0.048	~70	HIDALGO et al., 2015

Phenolic compound	Feed water	Membrane technology	Membrane used	Operating pressure (bar)	Feed flow rate (m^3/s)	Permeate flow rate (m^3/s)	SEC (kWh/m^3)	CO_2 emission (kg/m^3)	Removal (%)	References
p-nitrophenol	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>93.0	RAMOS et al., 2022a
	Synthetic water	Pervaporation	Poly(ether-b-amide)	not applied	not applied	-	-	-	-	CAO et al., 2021
3-chlorophenol	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	67	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	70	ARSUAGA et al., 2011
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	32	ARSUAGA et al., 2011
4-chlorophenol	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	70	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	63	ARSUAGA et al., 2011
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	25	ARSUAGA et al., 2011
p-chlorophenol	Synthetic water	Pervaporation	Poly(ether-b-amide)	not applied	not applied	-	-	-	-	CAO et al., 2021
	Synthetic water	Pervaporation	Polyurethane urea membrane	not applied	not applied	-	-	-	-	DAS et al., 2008
4-chloro-3-methyylphenol	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>94.2	RAMOS et al., 2022a
3-metylphenol	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>95.9	RAMOS et al., 2022a
p-cresol	Synthetic water	Pervaporation	Poly(ether-b-amide)	not applied	not applied	-	-	-	-	CAO et al., 2021
bisphenol A	Synthetic water	Ultrafiltration	Poly-etheruslphone (PES)	1	dead-end filtration	-	-	-	10 - 92	BING-ZHI et al., 2008
	Synthetic water	Nanofiltration	DESAL 5DK	mai/20	dead-end filtration	-	-	-	50 - >90	ZHANG et al., 2006

Phenolic compound	Feed water	Membrane technology	Membrane used	Operating pressure (bar)	Feed flow rate (m^3/s)	Permeate flow rate (m^3/s)	SEC (kWh/m^3)	CO_2 emission (kg/m^3)	Removal (%)	References
	Synthetic water	Microfiltration	Polyvinylidenefluoride	1	dead-end filtration	-	-	-	10 - 70	BING-ZHI et al., 2010
	Real surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000011	13312.727	9651.7273	89.2	SHARIFIAN et al., 2022
	Spyked surface water	Membrane distillation	Polytetrafluoroethylene	not applied	0.00002	0.000017 - 0.000054	4000 - 6000	2900 - 4350	>93.6	RAMOS et al., 2022a
Catechol	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	87	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	88	ARSUAGA et al., 2011
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	46	ARSUAGA et al., 2011
Hydroquinone	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	96	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	83	ARSUAGA et al., 2011
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	39	ARSUAGA et al., 2011
Phenol	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	88	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	75	ARSUAGA et al., 2011
	Synthetic water	Photocatalytic membrane	Cobalt-doped MIL-88B(Fe)	0.75	dead-end filtration	-	-	-	90	HOU et al., 2023
	Synthetic water	Photocatalytic membrane	Pt@UiO-66-NH2	-	-	-	-	-	>70	CHEN et al., 2020
	Synthetic water	Pervaporation	Poly(ether-b-amide)	not applied	-	-	-	-	-	CAO et al., 2021
	Synthetic water	Pervaporation	Poly(ether block amide)	not applied	-	-	-	-	-	HAO et al., 2009
	Synthetic water	Pervaporation	Polyurethane urea membrane	not applied	-	-	-	-	-	DAS et al., 2008

Phenolic compound	Feed water	Membrane technology	Membrane used	Operating pressure (bar)	Feed flow rate (m^3/s)	Permeate flow rate (m^3/s)	SEC (kWh/m^3)	CO$_2$ emission (kg/m^3)	Removal (%)	References
	Synthetic water	Nanofiltration	NF-99	25	0.00003	0	0.0129	0.0093	~8 - 10	BÓDALO et al., 2009
	Synthetic water	Nanofiltration	NF-99	25	0.00004	0	0.0161	0.0117	~8 - 10	BÓDALO et al., 2009
	Synthetic water	Nanofiltration	NF-99	25	0.00006	0	0.0211	0.0153	~8 - 10	BÓDALO et al., 2009
	Synthetic water	Nanofiltration	NF-97	25	0.00003	0	0.0086	0.0062	~8 - 39	BÓDALO et al., 2009
	Synthetic water	Nanofiltration	NF-97	25	0.00004	0	0.0074	0.0054	~8 - 39	BÓDALO et al., 2009
	Synthetic water	Nanofiltration	NF-97	25	0.00006	0	0.0076	0.0055	~8 - 39	BÓDALO et al., 2009
	Synthetic water	Nanofiltration	DSS-HR98PP	25	0.00003	0	0.002	0.0015	~79 - 95	BÓDALO et al., 2009
	Synthetic water	Nanofiltration	DSS-HR98PP	25	0.00004	0	0.0029	0.0021	~79 - 95	BÓDALO et al., 2009
	Synthetic water	Nanofiltration	DSS-HR98PP	25	0.00006	0	0.0039	0.0028	~79 - 95	BÓDALO et al., 2009
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	29	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	72	ARSUAGA et al., 2011
Phloroglucinol	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	90	ARSUAGA et al., 2011
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	74	ARSUAGA et al., 2011
	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	91	ARSUAGA et al., 2011
Pyrogallol	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	94	ARSUAGA et al., 2011
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	71	ARSUAGA et al., 2011
Resorcinol	Synthetic water	Reverse osmosis	TFC-HR	20	-	-	-	-	85	ARSUAGA et al., 2011

Phenolic compound	Feed water	Membrane technology	Membrane used	Operating pressure (bar)	Feed flow rate (m^3/s)	Permeate flow rate (m^3/s)	SEC (kWh/m^3)	CO_2 emission (kg/m^3)	Removal (%)	References
	Synthetic water	Reverse osmosis	BW30	20	-	-	-	-	88	ARSUAGA et al., 2011
	Synthetic water	Nanofiltration	NF-90	20	-	-	-	-	45	ARSUAGA et al., 2011

APPENDIX V: Descriptive statistics for flux and electric conductivity at different test temperatures

Test / Parameter	**T = 40 °C** Flux (kg m^{-2} h^{-1})	**T = 40 °C** Electric conductivity (µS cm^{-1})	**T = 50 °C** Flux (kg m^{-2} h^{-1})	**T = 50 °C** Electric conductivity (µS cm^{-1})	**T = 60 °C** Flux (kg m^{-2} h^{-1})	**T = 60 °C** Electric conductivity (µS cm^{-1})
N° of data	45	27	46	44	46	25
Minimum	3.67	2.18	7.71	2.19	12.52	2.10
Maximum	4.57	2.87	8.89	2.87	14.08	2.79
Average	3.93	2.45	8.25	2.41	13.26	2.36
Standard deviation	0.18	0.15	0.29	0.16	0.43	0.19
Median	3.89	2.43	8.33	2.38	13.37	2.32
Geometric average	3.93	2.45	8.25	2.41	13.26	2.35
Mode	4.10	2.43	8.48	2.25	13.52	2.32
Coef. of variation	0.05	0.06	0.04	0.07	0.03	0.08
Coef. of asymmetry	1.54	0.59	-0.29	1.29	-0.17	0.85
Coef. of kurtosis	2.93	1.00	-0.74	1.76	-1.08	-0.44
$P_{25\%}$	3.81	2.36	8.03	2.31	12.85	2.23
$P_{75\%}$	4.01	2.56	8.48	2.49	13.56	2.46

APPENDIX VI: Kruskal-Wallis test and multiple comparisons of flux and electric conductivity at different temperatures

Kruskal-Wallis test statistics	**p-value**
Comparison of permeate flux	
Kruskal-Wallis	3.581E-27
40 - 50 °C	3.122E-25
40 - 60 °C	7.540E-27
50 - 60 °C	6.719E-23
Comparison of permeate electric conductivity	
Kruskal-Wallis	0.042
40 - 50 °C	0.199
40 - 60 °C	0.034
50 - 60 °C	0.199

APPENDIX VII: Descriptive statistics for the retention (%) of phenolic compounds at different test temperatures

Test / Parameter	**Temperatures (°C)**		
	40	50	60
N° of data	15	15	15
Minimum	95.03	91.18	91.31
Maximum	99.94	99.94	97.01
Average	98.24	95.85	93.30
Standard deviation	1.62	2.42	1.46
Median	98.86	95.68	93.25
Geometric average	98.22	95.82	93.29
Mode	-	-	-
Coef. of variation	60.59	39.56	63.99
Coef. of asymmetry	-0.79	-0.09	1.16
Coef. of kurtosis	-0.70	0.07	1.93
$P_{25\%}$	97.10	94.97	92.34
$P_{75\%}$	99.43	96.84	93.66

APPENDIX VIII: Comparison between independent medians of global phenols removal at different temperatures (α = 5 %)

Kruskal-Wallis test statistics	**p-value**
Kruskal-Wallis	7.11E-06
40 - 50 °C	2.21E-03
40 - 60 °C	2.39E-08
50 - 60 °C	1.10E-03

APPENDIX IX: Spearman's correlation between loss (%) and compound volatility (pK_H)

Temperature (°C)	**N**	**r**	$t_{(N-2)}$	**p-value**
40	15	-0.821	-5.193	0.0002
50	15	-0.932	-9.281	<0.0001
60	15	-0.967	-13.875	<0.0001

APPENDIX X: Spearman's correlation between loss (%) and compound hydrophobicity (Log D)

Temperature (°C)	**N**	**r**	$t_{(N-2)}$	**p-value**
40	15	0.230	0.854	0.4083
50	15	0.196	0.722	0.4825
60	15	0.029	0.103	0.9194

APPENDIX XI: Spearman's correlation between loss (%) and the ratio between the compound volatility and hydrophobicity (pk_H/Log D)

Temperature (°C)	**N**	**r**	$t_{(N-2)}$	**p-value**
40	15	0.230	0.854	0.4083
50	15	0.196	0.722	0.4825
60	15	0.029	0.103	0.9194

APPENDIX XII: Descriptive statistics of the permeate flux and electric conductivity with the variation of phenolic compounds in the feed concentration

Test / Parameter	**C = 3 μg L^{-1}**		**C = 5 μg L^{-1}**		**C = 7 μg L^{-1}**		**C = 10 μg L^{-1}**	
	Flux (kg m^{-2} h^{-1})	Electric conductivity (μS cm^{-1})	Flux (kg m^{-2} h^{-1})	Electric conductivity (μS cm^{-1})	Flux (kg m^{-2} h^{-1})	Electric conductivity (μS cm^{-1})	Flux (kg m^{-2} h^{-1})	Electric conductivity (μS cm^{-1})
N° of data	45	41	46	24	46	44	47	38
Minimum	13.16	2.14	12.52	2.10	13.05	4.26	13.71	2.04
Maximum	14.63	3.33	14.10	2.79	14.76	5.69	15.16	2.99
Average	13.70	2.72	13.25	2.36	14.02	4.90	14.72	2.37
Standard deviation	0.26	0.30	0.43	0.19	0.32	0.43	0.28	0.28
Median	13.62	2.73	13.31	2.32	14.05	4.89	14.77	2.30
Geometric average	13.70	2.70	13.24	2.35	14.02	4.89	14.71	2.36
Mode	13.62	2.48	13.52	2.32	14.38	4.35	14.50	2.17
Coef. of variation	0.02	0.11	0.03	0.08	0.02	0.09	0.02	0.12
Coef. of asymmetry	2.11	-0.11	-0.16	0.85	-1.16	0.30	-0.90	0.67
Coef. of kurtosis	5.35	-0.85	-1.03	-0.18	2.84	-1.23	1.74	-0.74
$P_{25\%}$	13.59	2.47	12.85	2.23	13.96	4.53	14.50	2.16
$P_{75\%}$	13.68	2.94	13.54	2.46	14.19	5.29	14.95	2.61

APPENDIX XIII: DCMD performance for the different feed concentrations of phenolic compounds (flux, electric conductivity, resistances, and temperature polarization (TPC))

Concentration (μg L^{-1})	**Flux (kg m^{-2} h^{-1})**				**Flux decay**	**Electric conductivity (μS cm^{-1})**		**Resistances (Pa m^{2} h kg^{-1})**					**TPC**
	J_w[a]	J_{eo}[b]	J_{ef}[c]	J_{af}[d]		C_0[e]	C_f[f]	R_{fb}	R_{pb}	$R_{fouling}$	R_m	R_{total}	
3	19.57	14.1	13.59	19.57	0.04	2.98	3.19	244.44	78.46	37.80	1025.59	1386.30	0.77
5	19.29	13.19	12.52	19.29	0.05	2.27	2.26	260.34	83.17	59.01	1102.69	1505.22	0.78
7	22.71	14.76	14.09	22.29	0.05	2.52	2.49	239.14	77.02	46.36	974.97	1337.59	0.77
10	23.82	14.71	14.07	23.42	0.04	2.29	2.33	239.23	77.03	44.51	978.62	1339.41	0.77

[a]Flux with distilled water (J_w), [b]initial (J_{eo}) and [c]final (J_{ef}) flux with superficial water, [d]flux after physical cleaning (J_{af}) and [e]initial (C_0) and [f]final (C_f) permeate electric conductivity.

APPENDIX XIV: Descriptive statistics of the phenolic compound's retention percentage at different feed concentrations

Test / Parameter	**Concentrations (μg L^{-1})**			
	3	5	7	10
N° of data	15	15	15	15
Minimum	92.32	91.68	91.93	93.04
Maximum	96.07	97.87	98.01	96.85
Average	94.57	94.30	94.59	94.99
Standard deviation	0.98	1.93	1.49	0.98
Median	94.34	93.65	94.73	94.96
Geometric average	94.57	94.28	94.58	94.98
Mode	-	-	-	-
Coef. of variation	96.15	48.95	63.43	96.70
Coef. of asymmetry	-0.47	0.67	0.15	-0.06

Test / Parameter	Concentrations (μg L^{-1}) 3	5	7	10
Coef. of kurtosis	0.74	-0.73	1.64	0.06
P$_{25\%}$	94.15	93.08	94.15	94.51
P$_{75\%}$	95.06	95.64	95.10	95.67

APPENDIX XV: Descriptive statistics of the permeate flux and electric conductivity with the permeate recovery rate variation

Test / Parameter	30% RR		50% RR		70% RR	
	Flux (kg m^{-2} h^{-1})	Electric conductivity (μS cm^{-1})	Flux (kg m^{-2} h^{-1})	Electric conductivity (μS cm^{-1})	Flux (kg m^{-2} h^{-1})	Electric conductivity (μS cm^{-1})
N° of data	44	43	32	32	32	29
Minimum	12.33	2.56	12.04	2.99	11.73	3.78
Maximum	13.49	3.73	12.45	4.3	12.12	4.57
Average	12.85	2.1	12.23	3.73	11.86	4.11
Standard deviation	0.29	0.24	0.09	0.26	0.09	0.23
Median	12.93	2.85	12.24	3.70	11.86	4.075
Geometric average	12.85	2.90	12.23	3.72	11.86	4.11
Mode	12.93	2.95	12.31	3.65	11.75	3.84
Coef. of variation	0.02	0.08	0.01	0.07	0.01	0.06
Coef. of asymmetry	-0.03	1.05	0.32	-0.28	1.27	0.50
Coef. of kurtosis	-0.72	1.63	0.23	1.24	2.19	-0.57
P$_{25\%}$	12.60	2.72	12.17	3.57	11.80	3.96
P$_{75\%}$	13.07	3.06	12.31	3.9	11.89	4.28

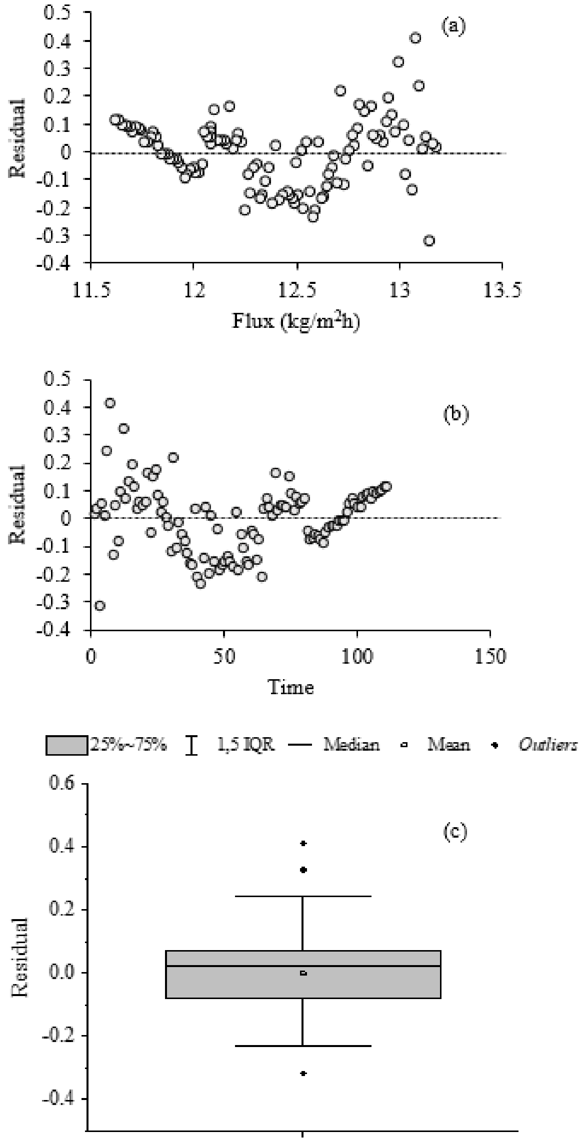
APPENDIX XVI: Mann-Kendall test applied to the time trend analysis of permeate flux with recovery rate

Mann-Kendall	
Statistic	-0.90225333
p-value	4.23E-13
Sample size	111
Null hypothesis ($p \leq 0.05$)	There is no trend
Alternative Hypothesis ($p > 0.05$)	There is a trend

APPENDIX XVII: Analysis of variance (ANOVA) for the flux linear regression

	gl	SS	MS	F	p-value
Regression	1	22.10347	22.10347	1545.727	3.28E-66
Residual	109	1.55867	0.0143		
Total	110	23.66214			

APPENDIX XVIII: Residual analyzes for the linear regression



APPENDIX XIX: Descriptive statistics of the phenolic compounds retention percentage at different recovery rates

Test / Parameter	**Recovery rate (%)**		
	30	50	70
N° of data	15	15	15
Minimum	91.68	91.87	90.89
Maximum	97.87	99.41	99.55
Average	94.30	95.29	95.07
Standard deviation	1.93	1.97	2.28
Median	93.65	95.60	95.44
Geometric average	94.28	95.28	95.05

Mode	-	-	-
Coef. of variation	48.95	48.31	41.76
Coef. of asymmetry	0.67	0.23	0.09
Coef. of kurtosis	-0.73	-0.06	-0.08
$P_{25\%}$	93.08	93.84	93.70
$P_{75\%}$	95.64	96.51	96.14

APPENDIX XX: EPS present on the membrane surface referring to the filtration area

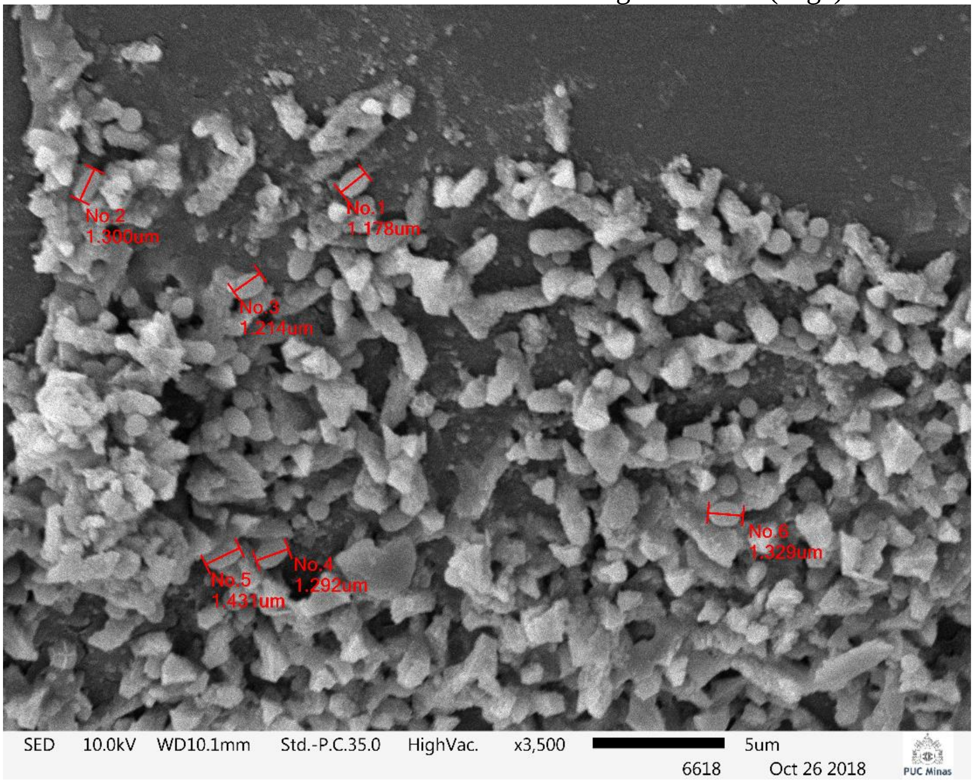
SMP (mg/42 cm^2)			**EPS (mg/42 cm^2)**		
DQO	Proteínas	Carboidratos	DQO	Proteínas	Carboidratos
0	114.85	2.39	0	349.58	17.03

APPENDIX XXI: Mann-Kendall test applied to the time trend analysis of permeate flux with test time

	Mann-Kendall
Statistic	-0.822
p-value	<0.0001
Sample size	965

As the computed p-value is lower than the significance level alpha=0.05, one should reject the null hypothesis H0 (There is no trend in the series), and accept the alternative hypothesis Ha (There is a trend in the series)

APPENDIX XXII: Surface of the fouling membrane (edge)



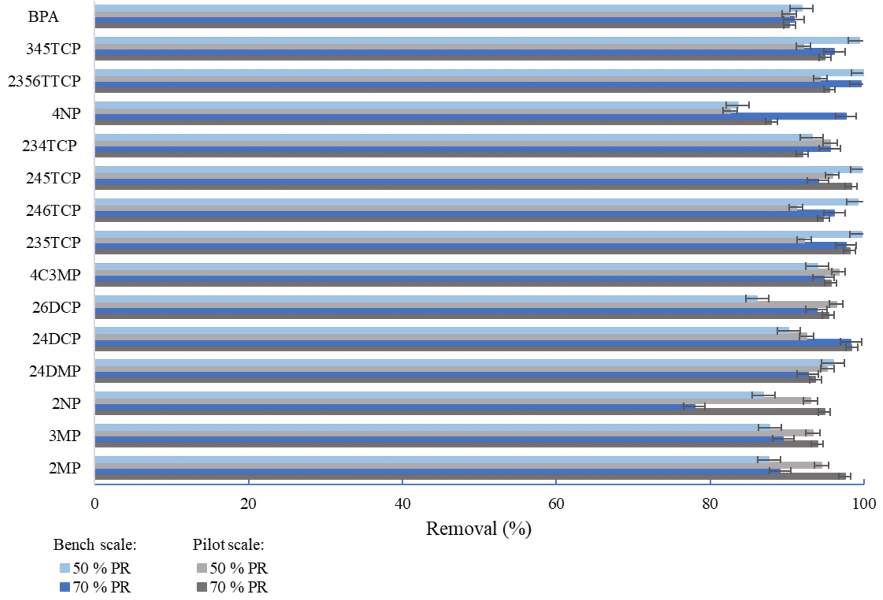
APPENDIX XXIII: Characteristics and removal of compounds in the analyzed stages

Compounds	Volatility (pkH)		Hydrophobicity (Log D)		pkH/Log D	Trend according to WIJEKOON et al. (2014)	Stage 1	Stage 2	Stage 3
2MP	5.921	moderate volatility	2.09	more hydrophilic	2.8	> 2.5 high rejection	92.48	93.76	99.90
3MP	6.067	moderate volatility	2.09	more hydrophilic	2.9	> 2.5 high rejection	95.96	98.07	99.36
2NP	4.893	high volatility	1.36	more hydrophilic	3.6	> 2.5 high rejection	97.01	98.50	99.53
24DMP	6.022	moderate volatility	2.36	more hydrophilic	2.6	> 2.5 high rejection	93.59	96.81	99.90
24DCP	6.659	moderate volatility	3.05	more hydrophobic	2.2	< 2.5 low rejection	92.24	94.60	99.93
26DCP	5.573	moderate volatility	2.33	more hydrophilic	2.4	< 2.5 low rejection	93.46	93.68	99.86
4C3MP	5.959	moderate volatility	2.83	more hydrophilic	2.1	< 2.5 low rejection	94.23	96.42	99.94
235TCP	5.132	moderate volatility	2.84	more hydrophilic	1.8	< 2.5 low rejection	97.23	99.01	99.67
246TCP	5.377	moderate volatility	2.78	more hydrophilic	1.9	< 2.5 low rejection	95.32	97.26	99.24
245TCP	4.938	high volatility	3.24	more hydrophobic	1.5	< 2.5 low rejection	93.14	95.89	99.76
234TCP	5.381	moderate volatility	3.26	more hydrophobic	1.7	< 2.5 low rejection	91.68	98.64	99.55
4NP	9.382	low volatility	1.31	more hydrophilic	7.2	> 2.5 high rejection	93.03	96.00	99.51
2356TTCP	6.029	moderate volatility	2.01	more hydrophilic	3	> 2.5 high rejection	97.87	98.04	99.88
345TCP	5.699	moderate volatility	3.68	more hydrophobic	1.5	< 2.5 low rejection	93.67	96.24	99.41
BPA	9.404	low volatility	3.63	more hydrophobic	2.6	> 2.5 high rejection	93.65	95.05	99.42
			Average removal				94.304	96.53	99.66

APPENDIX XXIV: Characteristics of phenols

Phenolic compounds	Acronyms	Molecular formula	Molar mass	pkH	Log D
2-methylphenol	2MP	C_7H_8O	108.05	5.92	2.09
3-methylphenol	3MP	C_7H_8O	108.05	6.07	2.09
2-nitrophenol	2NP	$C_6H_5NO_3$	139.02	4.89	1.36
2,4-dimethylphenol	24DMP	$C_8H_{10}O$	122.07	6.02	2.36
2,4-dichlorophenol	24DCP	$C_6H_4Cl_2O$	161.96	6.66	3.05
2,6-dichlorophenol	26DCP	$C_6H_4C_{l2}O$	161.96	5.57	2.33
4-chloro-3-metylphenol	4C3MP	C_7H_7ClO	142.01	5.96	2.83
2,3,5-trichlorophenol	235TCP	$C_6H_3Cl_3O$	195.92	5.13	2.84
2,4,6- trichlorophenol	246TCP	$C_6H_3Cl_3O$	195.92	5.38	2.78
2,4,5- trichlorophenol	245TCP	$C_6H_3Cl_3O$	195.92	4.94	3.24
2,3,4- trichlorophenol	234TCP	$C_6H_3Cl_3O$	195.92	5.38	3.26
4-nitrophenol	4NP	$C_6H_5NO_3$	139.02	9.38	1.31
2,3,5,6-tetrachlorophenol	2356TCP	$C_6H_2Cl_4O$	229.88	6.03	2.01
3,4,5- trichlorophenol	345TCP	$C_6H_3Cl_3O$	195.92	5.70	3.68
4,4'-(propane-2,2-diyl)diphenol (bisphenol A)	BPA	$C_{15}H_{16}O_2$	228.11	9.40	3.63

APPENDIX XXV: Removal of each phenolic compounds according to the permeate recovery (PR) of 50 and 70 % at bench and pilot scale, respectively (feed: RW1 spiked with phenolic compounds (5 µg L^{-1}) at 60 °C). The horizontal bars denote 0.95 confidence intervals



APPENDIX XXVI: Expenditures considered for capital costs (CAPEX) and operational costs (OPEX) estimation. The scenario powered by conventional electrical source disconsidered the costs related to solar panels.

Mobile system (5.5 m^3/d)	**Description**	**Base variable**		**Bare module cost**	**n**	**CEPCI (base year)**	**CEPCI (2020)**	**Real variable**	**Real cost**
Feed tank	Floating Head Carbon Steel	m^3	90	$ 10,211.33	0.60	567.5	569.2	2.76	$ 1,265.85
Permeate tank	Floating Head Carbon Steel	m^3	90	$ 10,211.33	0.60	567.5	569.2	2.76	$ 1,265.85
Feed pump	Centrifugal, stainless steel shaft power	kW	1	$ 15,345.00	0.70	567.5	569.2	1	$ 15,390.97
Permeate pump	Centrifugal, stainless steel shaft power	kW	1	$ 15,345.00	0.70	567.5	569.2	1	$ 15,390.97
Heat exchanger - permeate	Multiple pipe, copper/carbon steel	m^2	10	$ 19,515.00	0.62	567.5	569.2	1	$ 4,695.35
Heat exchanger - feed	Solar panels	m^3/h	20	$ 82,606.55	0.60	567.5	569.2	5.5	$ 38,186.79
MD module		m^3/h	0.102	$ 600.00	0.60	567.5	569.2	5.5	$ 6,584.27
Construction costs		m^3/h	1	$ 19,073.41	0.60	567.5	569.2	5.5	$ 53,204.09
Engineered project		m^3/h	1	$ 19,073.41	0.60	567.5	569.2	5.5	$ 53,204.09
Smal truck		und	1	$ 48,000.00	0.60	567.5	569.2	1	$ 48,143.79
Total									$ 237,332.02
Total w/o solar panels									$ 199,145.23

Distributed system (11 m^3/d)	**Description**	**Base variable**		**Bare module cost**	**n**	**CEPCI (base year)**	**CEPCI (2020)**	**Real variable**	**Real cost**
Feed tank	Floating Head Carbon Steel	m^3	90	$ 10,211.33	0.60	567.5	569.2	4.58	$ 1,715.36
Permeate tank	Floating Head Carbon Steel	m^3	90	$ 10,211.33	0.60	567.5	569.2	4.58	$ 1,715.36
Feed pump	Centrifugal, stainless steel shaft power	kW	1	$ 15,345.00	0.70	567.5	569.2	1	$ 15,390.97

Permeate pump	Centrifugal, stainless steel shaft power	kW	1	$ 15,345.00	0.70	567.5	569.2	1	$ 15,390.97
Heat exchanger - permeate	Multiple pipe, copper/carbon steel	m²	10	$ 19,515.00	0.62	567.5	569.2	1	$ 4,695.35
Heat exchanger - feed	Solar panels	m³/h	20	$ 82,606.55	0.60	567.5	569.2	11	$ 57,880.35
MD module		m³/h	0.102	$ 600.00	0.60	567.5	569.2	11	$ 9,979.89
Construction costs		m³/h	1	$ 19,073.41	0.60	567.5	569.2	11	$ 80,642.31
Engineered project		m³/h	1	$ 19,073.41	0.60	567.5	569.2	11	$ 80,642.31
Deployment area		ha	1	$ 1,744.40	0.60	567.5	569.2	0.5	$ 1,154.32
Total									$ 269,207.19
Total w/o solar panels									$ 211,326.84

WTP 535,680 m³/d	**Description**	**Base variable**		**Bare module cost**	**n**	**CEPCI (base year)**	**CEPCI (2020)**	**Real variable**	**Real cost**
Feed tank	Floating Head Carbon Steel	m³	90	$ 10,211.33	0.60	567.5	569.2	4.58	$ 279,931.87
Permeate tank	Floating Head Carbon Steel	m³	90	$ 10,211.33	0.60	567.5	569.2	4.58	$ 279,931.87
Feed pump	Centrifugal, stainless steel shaft power	kW	1	$ 15,345.00	0.70	567.5	569.2	10	$ 77,137.56
Permeate pump	Centrifugal, stainless steel shaft power	W	1	$ 15,345.00	0.70	567.5	569.2	10	$ 77,137.56
Heat exchanger - permeate	Multiple pipe, copper/carbon steel	m²	10	$ 19,515.00	0.62	567.5	569.2	3720	$ 768,076.02
Heat exchanger - feed	Solar panels	m³/h	20	$ 82,606.55	0.60	567.5	569.2	535680	$ 37,587,095.89
MD module		m³/h	0.102	$ 600.00	0.60	567.5	569.2	535680	$ 6,480,871.82
Construction costs		m³/h	1	$ 19,073.41	0.60	567.5	569.2	535680	$ 52,368,559.65

Engineered project	m³/h	1	$ 19,073.41	0.60	567.5	569.2	535680	$ 52,368,559.65
Deployment area	ha	1	$ 1,744.40	0.60	567.5	569.2	1	$ 1,749.63
Total								$ 150,289,051.51
Total w/o solar panels								$ 112,701,955.63

APPENDIX XXVII: Removal of each phenolic compounds according to the permeate recovery (PR) of 50 and 70 % at bench and pilot scale and the compounds volatility (pKH) and hydrophobicity (Log D) (feed: RW1 spiked with phenolic compounds (5 µg L^{-1}) at 60 °C). The removal ranges were divided into <80 - 84 % (orange), 85 - 89 % (pink), 90 - 94 % (blue), and 95 - 100 % (green)

			50 % PR bench scale		**70 % PR bench scale**		**50 % PR pilot scale**		**70 % PR pilot scale**	
Compound	**pKH**	**Log D**	Removal efficiency (%)	Removal range (%)	Removal efficiency (%)	Removal range (%)	Removal efficiency (%)	Removal range (%)	Removal efficiency (%)	Removal range (%)
2MP	5.92	2.09	88	85 - 89	89	85 - 89	94	90 - 94	98	95 - 100
3MP	6.07	2.09	88	85 - 89	89	85 - 89	93	90 - 94	94	90 - 94
2NP	4.89	1.36	87	85 - 89	78	<80 - 84	93	90 - 94	95	95 - 100
24DMP	6.02	2.36	96	95 - 100	93	90 - 94	95	95 - 100	94	90 - 94
24DCP	6.66	3.05	90	90 - 94	98	95 - 100	93	90 - 94	98	95 - 100
26DCP	5.57	2.33	86	85 - 89	94	90 - 94	96	95 - 100	95	95 - 100
4C3MP	5.96	2.83	94	90 - 94	95	95 - 100	97	95 - 100	96	95 - 100
235TCP	5.13	2.84	100	95 - 100	98	95 - 100	92	90 - 94	98	95 - 100
246TCP	5.38	2.78	99	95 - 100	96	95 - 100	91	90 - 94	95	95 - 100
245TCP	4.94	3.24	100	95 - 100	94	90 - 94	96	95 - 100	98	95 - 100
234TCP	5.38	3.26	93	90 - 94	96	95 - 100	96	95 - 100	92	90 - 94
4NP	9.38	1.31	84	<80 - 84	98	95 - 100	83	<80 - 84	88	85 - 89
2356TTCP	6.03	2.01	100	95 - 100	100	95 - 100	94	90 - 94	95	95 - 100
345TCP	5.70	3.68	99	95 - 100	96	95 - 100	92	90 - 94	95	95 - 100
BPA	9.40	3.63	92	90 - 94	91	90 - 94	90	90 - 94	90	90 - 94

APPENDIX XXVIII: Physical-chemical characterization of raw water and permeates according to 50 and 70 % recovery

Parameter	**RW1**	**Permeate of bench scale** 50 % recovery	70 % recovery	**Permeate of pilot scale** 50 % recovery	70 % recovery	**WHO guideline**
Turbidity (NTU)	14.2	0.7	0.4	0.4	0.3	<5
Removal (%)	-	95	97	97	98	-
Perceived color (mg Pt-Co L^{-1})	74	< l.d.*	< l.d.	< l.d.	< l.d.	-
Removal (%)	-	100	100	100	100	-
TSS (mg L^{-1})	16	< l.d.	< l.d.	< l.d.	< l.d.	-
Removal (%)	-	100	100	100	100	-
Electric conductivity (µS cm^{-2})	121.3	4	4.5	2.8	2.5	-
Removal (%)	-	96.7	96.3	98	97	-
Alkalinity (mg $CaCO_3$ L^{-1})	29.1	3.1	4.6	2.1	2.1	<200
Removal (%)	-	89	84	98	98	-

* Limit of detection.

APPENDIX XXIV: Physical-chemical characterization of raw waters and permeates of experiments with different water matrices (RW1, RW2, and RW3) in the MD pilot system

Parameter	**Samples** RW1	Permeate RW1	RW2	Permeate RW2	RW3	Permeate RW3	**WHO guideline**
Turbidity (NTU)	14.2	0.6	92.5	0.1	162	0.2	<5
Removal (%)	-	96	-	100	-	100	-
UV-Vis 254 nm	0.012	0.001	0.083	< l.d.*	0.02	0.002	-
Removal (%)	-	92	-	100	-	92	-
Perceived color (mg Pt-Co L^{-1})	74	< l.d.	239	< l.d.	391	< l.d.	-
Removal (%)	-	100	-	100	-	100	-
TSS (mg L^{-1})	16	< l.d.	94	< l.d.	68	< l.d.	-
Removal (%)	-	100	-	100	-	100	-

Parameter	Samples						WHO guideline
	RW1	Permeate RW1	RW2	Permeate RW2	RW3	Permeate RW3	
Electric conductivity ($\mu S\ cm^{-2}$)	121.3	2.1	47.1	2.2	63.8	2.2	-
Removal (%)	-	98	-	95	-	97	-
Alkalinity (mg $CaCO_3\ L^{-1}$)	29.1	2.7	21.3	2.1	24.3	1.9	<200
Removal (%)	-	91	-	90	-	92	-

* Limit of detection.

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