

UNIVERSIDADE FEDERAL DE MINAS GERAIS
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**RETHINKING GOLD MINING WASTEWATER TREATMENT USING MEMBRANE
DISTILLATION AND SOLVENT EXTRACTION FOR MINIMAL WASTE DISCARD AND
RESOURCES RECOVERY**

Belo Horizonte
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"Rethinking gold mining wastewater treatment using membrane distillation and solvent extraction for minimal waste discard and resources recovery"

VICTOR REZENDE MOREIRA

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RESUMO

As instalações destinadas ao tratamento de efluentes industriais apenas para descarte não são mais interessantes do ponto de vista ambiental e econômico. Em vez disso, elas começaram a ser projetados também para a recuperação de subprodutos. Unidades de tratamento isoladas muitas vezes são ineficazes para esse fim, o que motiva pesquisas que investigam tratamentos integrados e híbridos. Efluentes derivados da mineração configuram-se como uma fonte alternativa para recuperação de subprodutos. Neste estudo, propõe-se a integração das técnicas de destilação por membranas (MD) e extração por solvente (SX) para o beneficiamento do efluente gerado na indústria de processamento de ouro. Em um primeiro momento, a SX foi investigada para a reciclagem de ácido mineral (H_2SO_4) e cobre do concentrado de MD. Cinco extratantes (Alamine 336, Aliquat 336, Cyanex 923, TEHA e Versatic Acid) foram preferencialmente diluídos em querosene ou 1-decanol (30 vol%) em experimentos de extração conduzidos a 60 °C. A natureza endotérmica da extração (ΔH : 38.8 kJ/mol) seria vantajosa para a recuperação do ácido e a integração com o processo de MD, uma vez que seu concentrado é produzido em temperaturas elevadas. Portanto, MD e SX foram integrados para o beneficiamento de águas residuais da mineração de ouro e melhor uso dos recursos naturais. O sistema permitiu a recuperação de água (taxa de recuperação: 34%) para fins de reúso, através do sistema de MD, H_2SO_4 (taxa de recuperação: 95%), por SX utilizando tris-2-etilhexilamina, e cobre (taxa de recuperação: 99%), por SX utilizando LIX 84-I. Foram obtidos resultados econômicos favoráveis a recuperação de água (0,23 US\$/m³) e cobre (4,25 US\$/kg_{Cu}), com preços inferiores aos praticados atualmente para ambas as *commodities*. Para o H_2SO_4 , os gastos operacionais corresponderam a 0,423 US\$/kg_{H₂SO₄}, ligeiramente superior ao seu preço comercial. Estudos complementares investigaram os processos de SX não dispersivos (NDSX), definindo primeiramente as condições operacionais favoráveis a recuperação de subprodutos para posterior integração com o processo de MD. Para tanto, foram empregados os contadores de membrana (MCs), que valendo-se da fase orgânica apropriada, têm mostrado seletividade para o composto de interesse e recuperações de até 99% em estudos teóricos. Os resultados positivos se devem aos avanços no desenvolvimento de membranas hidrofóbicas, configurações e set-up dos módulos, que ainda contribuíram para processos de menor consumo específico de energia, menor geração de resíduos, maior confiabilidade e unidades de menor exigência de área. Por fim, avaliou-se o sistema integrado para recuperação simultânea de água, H_2SO_4 , e cobre. De forma geral, o sistema integrado se insere em uma perspectiva que aparta do foco linear de aproveitamento de matéria-prima, priorizando processos de reciclagem e reaproveitamento.

Palavras-chave: contadores de membrana de fibra oca; sistemas baseados em membranas; beneficiamento de metais; intensificação de processos; recuperação de recursos.

ABSTRACT

Facilities intended for wastewater treatment only for disposal are no longer interesting from an environmental and economic point of view. Instead, they began to be designed for by-product recovery as well. Isolated treatment units are often ineffective for this purpose, which motivates research that investigates integrated and hybrid treatments. Mining-derived effluents are seen as an alternative source for by-product recovery. This study proposes the integration techniques of membrane distillation (MD) and conventional solvent extraction (SX; also referred to as liquid-liquid extraction) for gold mining wastewater treatment. At first, SX was investigated for mineral acid (H_2SO_4) and copper recycling from the MD concentrate. Five extractants (Alamine 336, Aliquat 336, Cyanex 923, TEHA, and Versatic Acid) were preferentially diluted in kerosene or 1-decanol (30 vol%) in extraction experiments conducted at 60 °C. The endothermic nature of acid extraction (ΔH : 38.8 kJ/mol) would be advantageous for its recovery and integration with the MD process since its concentrate is produced at elevated temperatures. Therefore, MD and SX were integrated for the beneficiation of gold mining wastewater and better use of natural resources. The system allowed the recovery of water (recovery rate: 34%) for reuse purposes, through the MD system, H_2SO_4 (recovery rate: 95%), by SX using tris-2-ethylhexylamine, and copper (recovery rate: 99%), by SX using LIX 84-I. Favorable economic results were obtained for the recovery of water (0.23 US\$/m³) and copper (4.25 US\$/kg_{Cu}), with prices lower than those currently practiced for both commodities. For H_2SO_4 , operating expenses corresponded to 0.423 US\$/kg_{H₂SO₄}, slightly higher than its commercial price. Additional studies investigate the non-dispersive SX (NDSX) processes, first defining the operational conditions favorable to by-product recovery for later integration with the MD. Membrane contactors (MCs) should be used at this stage, which has shown selectivity for the compound of interest and recoveries of up to 99% in theoretical studies. The positive results are due to advances in the development of hydrophobic membranes, configurations, and module set-up, which also contributed to processes with lower specific energy consumption, less waste generation, greater reliability, and units with a smaller area requirement. Finally, membrane distillation and non-dispersive solvent extraction were integrated to simultaneously recover water, H_2SO_4 , and copper. In summary, the integrated and hybrid system departs from a linear perspective of raw materials usage, prioritizing recycling and reuse processes.

Keywords: hollow fiber membrane contactors; membrane-based systems; metals beneficiation; process intensification; resources recovery.

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LIST OF ABBREVIATIONS AND ACRONYMS

δ_t	Thermal efficiency of membrane distillation
ω_m	Total heat flux in membrane distillation
$[A]_{aq}$	Component of interest in the aqueous phase
$[A]_{org}$	Component of interest in the organic phase
μ	Dynamic viscosity
AC_f	Amortization costs
AMD	Acid mine drainage
C_a	Bare module cost
CAPEX	Capital expenditure
C_b	Equipment cost
CEPCI	Chemical Engineering plant cost index
c_p	Isobaric specific heat
D_A	Distribution coefficient
D_A'	Distribution coefficient for the stripping process
D_{aq}	Diffusivity of the species of interest in the aqueous phase
d_h	Hydraulic diameter
D_i	Diffusivity of solutes in both non-associated solvents and water
d_i	Internal diameter of the fiber
d-LLE	Dispersive liquid-liquid extraction, also referred to as solvent extraction
d_{lm}	Logarithmic mean diameter
DMP	Dimethyl phthalate
d_o	External diameter of the fiber
D_{org}	Diffusivity of the species of interest in the organic phase
EU	European Union
FTIR	Fourier-transform infrared spectroscopy
Gz	Gratz number
HDTMS	Hexadecyltrimethoxysilane
h_f	Convective heat transfer associated with the feed stream
h_m	Convective heat transfer associated with the membrane
h_p	Convective heat transfer associated with the distillate/permeate stream
ICIS	Independent commodity intelligence service
IQR	Interquartile range represented in boxplot graphs
i_r	Investment rate
J	Distillate/permeate flux in the membrane distillation process
k_{aq}	Mass transfer coefficient associated with the aqueous phase

k_i	Local mass transfer coefficient
k_m	Membrane resistance
k_{org}	Mass transfer coefficient associated with the organic phase
$k_{p,f}$	Distillate/permeate thermal conductivity
L	Fiber effective length
LEP_w	liquid entry pressure of water
I_s	Project lifespan
MC	Membrane contactor
MD	Membrane distillation
MfW	Mining from wastewater
MSP	Membrane separation process(es)
$M_{w,i}$	Molecular weight of the “ith” specie
n	Exponent factor in costs estimation
NDSX	Non-dispersive solvent extraction
NMP	N-methyl-2-pyrrolidone
Nu	Nusselt number
O:A	Organic-to-aqueous ratio
OPEX	Operational expenditure
p_1	Vapor pressure at the membrane surface facing the feed side
p_2	Vapor pressure at the membrane surface facing the distillate/permeate side
PDMS	Polydimethylsiloxane
PEO	Polyethylene oxide
PES	Polyether sulfone
p_f	Vapor pressure at the feed bulk
PI	Process intensification
PMMA	Polymethyl methacrylate
POX	Pressure oxidation process
PP	Polypropylene
p_p	Vapor pressure at the distillate/permeate bulk
Pr	Prandtl number
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
q	Volumetric flow rate
R	Universal gas constant
Re	Reynolds number

RTD	Residence time distribution
s	Pipe cross-sectional area
S_a	Base variable for equipment costs
SBS	Styrene-butadiene-styrene
Sc	Schmidt number
S_m	Membrane surface area
S_o	Superficial area
SX	Solvent extraction
T	Temperature
t	Time
TEHA	Tris-2-ethyl hexyl amine
T_f	Feed temperature
T_p	Distillate/permeate temperature
$T_{w,f}$	Temperature at the membrane's surface facing the feed side
$T_{w,p}$	Temperature at the membrane's surface facing the distillate/permeate side
V	Total volume of the feed solution
ν	Water kinematic viscosity
v_{aq}	Average feed velocity
V_i	Molar volume of the "ith" specie at normal boiling point
α_f	Activity coefficient
β	Selectivity of the extraction process
$\Delta G^\circ_{ex} (\Delta G)$	Gibbs free-energy change related to the extraction process
$\Delta H^\circ_{ex} (\Delta H)$	Enthalpy energy change related to the extraction process
ΔH_v	Water vaporization heat
ΔS°_{ex}	Entropy energy change related to the extraction process
ε	Porosity
ρ_f	Mass transfer resistance imposed by the fouling layer
ρ_{fb}	Mass transfer resistance imposed by the feed boundary layer
ρ_{H_2O}	Water density
ρ_m	Mass transfer resistance imposed by the membrane
ρ_{pb}	Mass transfer resistance imposed by the distillate/permeate boundary layer
ρ_t	Total mass transfer resistance
τ	Temperature polarization coefficient
τ	Tortuosity

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PH.D. THESIS RESEARCH OUTCOMES

Full-length Papers published in peer reviewer journals

1. Moreira, V. R., ..., & Amaral, M. C. (2023). Recent progress in membrane distillation configurations powered by renewable energy sources and waste heat. *Journal of Water Process Engineering*, 53, 103816.
2. Moreira, V. R., ..., & Amaral, M. C. (2023). Non-dispersive solvent extraction as an alternative for sulfuric acid and copper recycling from membrane distillation concentrate of gold mining wastewater. *Chemical Engineering Journal*, 144622.
3. Moreira, V. R., ..., & Amaral, M. C. S. (2022). Enhancing industries exploitation: Integrated and hybrid membrane separation processes applied to industrial effluents beyond the treatment for disposal. *Chemical Engineering Journal*, 430, 133006.
4. Moreira, V. R., ..., & Amaral, M. C. S. (2022). Membrane distillation and dispersive solvent extraction in a closed-loop process for water, sulfuric acid, and copper recycling from gold mining wastewater. *Chemical Engineering Journal*, 435, 133874.
5. Moreira, V. R., ..., & Amaral, M. C. S. (2022). One-step recycling of mineral acid from concentrated gold mining wastewater by high-temperature liquid–liquid extraction. *Separation and Purification Technology*, 286, 120447.
6. Moreira, V. R., ..., & Amaral, M. C. S. (2021). Acid and metal reclamation from mining effluents: Current practices and future perspectives towards sustainability. *Journal of Environmental Chemical Engineering*, 9(3), 105169.
7. Moreira, V. R., ..., & Amaral, M. C. S. (2021). Mining from wastewater: Perspectives and current practices of non-dispersive solvent extraction for metallic compounds valorization. *Chemical Engineering Journal*, 425, 130711.

Extended abstracts published in international and national conferences

1. Moreira, V. R., ..., & Amaral, M. C. (2023). Uma abordagem econômica da prática de descarte zero de efluentes no setor de mineração de ouro: integração dos processos de destilação por membranas e extração para eliminação de efluentes e recuperação de commodities. Em: 32º Congresso Brasileiro de Engenharia Sanitária e Ambiental.
2. Moreira, V. R., ..., & Amaral, M. C. (2022). Integrated membrane distillation and solvent extraction for water, sulfuric acid, and copper recovery from gold mining wastewater. Em: Euromembrane.
3. Moreira, V. R., ..., & Amaral, M. C. (2021). Refining gold mining effluent by dispersive solvent extraction for further beneficiation. Em: Web Encontro Nacional de Engenharia Química.
4. Moreira, V. R., ..., & Amaral, M. C. (2021). Experimental investigation of direct contact membrane distillation for gold mine wastewater treatment. Em: Euromembrane.

5. Moreira, V. R., ..., & Amaral, M. C. (2021). Sulfuric acid and water reclamation from mining wastewater by membrane distillation: performance and cost analysis. Em: 23° Congresso Brasileiro de Engenharia Química.
6. Moreira, V. R., ..., & Amaral, M. C. (2021). Extractable but not recoverable: sulfuric acid extraction from gold mining wastewater by dispersive solvent extraction using Alamine 336. Em: IV Workshop de Tecnologias Limpas.
7. Moreira, V. R., ..., & Amaral, M. C. (2021). Acid recovery from gold mining wastewater by solvent extraction: a single step in a journey of thousand miles. Em: IV Workshop de Tecnologias Limpas.

CHAPTER 1 – INTRODUCTION, OBJECTIVES, AND RESEARCH HYPOTHESIS

1 Introduction

For centuries, the mining sector has provided the basic and raw materials that society needs to develop and grow. Not only is easy to perceive our current dependence on the resources offered by the mining industry, but also its limitation in providing them in the near term. As mineral resources become scarcer, alternatives have been sought to attain the current and future demand in an old and never-ending discussion [1]–[3]. It should be noted that mining activities are responsible for half of the global carbon emissions, in addition to a 90% loss (on average) of local biodiversity [4], going in complete disagreement with the current political and economic scenario geared towards increasingly sustainable process of lower environmental impact.

Due to the scarcity of ore sites availability, the mineral segment has been forced to lean towards secondary by-products recovery from wastewater derived throughout their ore processing. Based on the high wastewater volume generated and its composition rich in several value-added compounds, the alternative represents a reasonable option to attain a future demand for mineral goods. To overcome this problem, different strategies involving process miniaturization, which has lower capital cost but higher energy and safety efficiency, have been proposed. When it comes to gold mining wastewater, a few options are available for recovery, which has already proven to be an effective and promising alternative from an economic point of view.

Foureaux *et al.* [5] and Reis *et al.* [6] investigated processes for water reclamation from gold mining wastewater. The liquid waste is recognized by the high concentration of sulfuric acid ($\text{pH} < 2$), which promotes the solubilization of different metallic species (e.g.: copper). At the first moment, the authors proposed a membrane distillation (MD) process for water recovery and its further reuse, which represented major savings to the annual operating cost of the gold mining plant. Instead of acquiring freshwater from a local supplier, which costs ranged from 1.8 to 3.0 US\$/m³, MD could produce a high-quality permeate for an operational cost of 0.13–0.27 US\$/m³, which represents annually savings of US\$ 88.300,00 for the local mining plant.

In both studies, an additional operating unit besides the MD modules would be required to recover other by-products. Therefore, besides the promising results reported by the authors, a few straightforward limitations could be sought. At first, increasing the number of operating units implies a higher capital cost and maintainability risks. Certainly, two different units would also imply greater demand for installation area in a more energy-intensive process, which directly reflects in a greater environmental impact. Therefore, rather than just considering separated operational units, intensified processes could be proposed aiming for higher energy and recovery efficiencies.

Process intensification (PI) is a subject to which considerable attention has been given in the past few years. Among several different definitions available, Stankiewicz and Moulijn [7] first defined PI as “*any chemical engineering development that leads to a substantially smaller, cleaner, safer and more energy-efficient technology*”, which encompasses emerging equipment, markedly known for their small area requirement and operational methods for process plans improvements. From a PI point of view, significant advancements are still required while dealing with the mining industry, wastewater treatment, and by-product recovery. To mention a few, the lack of proper knowledge on modular systems and the lack of standard equipment and techniques represents a major impasse and needs to be overcome while proposing an intensified process.

2 Objective

2.1 General objective

Investigate the processes of solvent extraction and membrane distillation intended for reuse water, sulfuric acid (H_2SO_4), and copper recovery from gold mining wastewater.

2.2 Specific objectives

The specific objectives, along with the premises and hypotheses that lead to their definition, were presented in Table 1.

Table 1. Premises, hypotheses, and specific objectives of the research project.

#ID	Premises	Hypotheses	Specific objectives	Chapter
1	Industrial facilities, including those related to the mining industry, are designed with unit operations, according to which a process would be divided into a series of individualized steps.	The state-of-the-art points to emerging and integrated technologies that aimed to by-products recover, but still do not have a sufficient degree of maturity for large-scale implementation.	Appraise, through a critical literature review, the use of membrane distillation, solvent extraction, and membrane contactors, as well as its integration with other processes, aiming at by-products recovery.	CHAPTER 2 - 3
2	The continuous improvement of chemical processes is a criterion for economic competitiveness, which can be achieved through the optimization of operating variables.	The molecular structure of different extractants and their chemical interaction with the by-products significantly interfere with extraction efficiency.	Define the contribution of different extractants and operational conditions for H_2SO_4 and copper recovery from MD concentrate in solvent extraction.	CHAPTER 4
3	The scenario of mineral scarcity led to the valorization of mining tailings and mining wastewater, seen as alternatives and potential sources of mineral goods.	MD and solvent extraction, when integrated, represent a competitive strategy to recover water, acid, and copper from mining wastewater.	Assess the performance of MD and solvent extraction for gold mining wastewater valorization.	CHAPTER 5
4	Continuous processes reflect the reality of industrial applications and, therefore, are preferable to batch processes.	Non-dispersive processes will show better recovery efficiencies as they will be able to maintain the driving force for extraction through the continuous	Compare the performance of dispersive and non-dispersive extraction processes for sulfuric acid and copper recovery from MD concentrate.	CHAPTER 6

#ID	Premises	Hypotheses	Specific objectives	Chapter
		regeneration of the organic phase.		
5	Integrated processes are identified as alternatives to industrial wastewater valorization through by-product recovery.	Integrated systems, operating in a steady state, will allow greater valorization of mining wastewater compared to separated units, meeting the principles of process intensification.	Integrate non-dispersive solvent extraction and membrane distillation to simultaneously recover water and sulfuric acid/copper from gold mining wastewater.	CHAPTER 5
6	The practice of mining from wastewater is a promising alternative to the supply of critical and non-renewable raw materials.	The economic feasibility and applicability of the by-products recovered would be conditioned to the recovery degree and purity, and there may be economic and practical equity when compared to products from primary sources.	Certificate the quality of the byproducts recovered according to their application, combined with a marked prospection for their potential commercialization.	CHAPTER 4-7

3 Document structure

The thesis was divided into chapters; the structure is commonly used in the research group to facilitate their publishment as individual research papers. Efforts were made to make them concise, however, whenever necessary, aspects related to the introduction, methodology, and results that were considered important, although similar between each chapter, were repeated. Chapter 1 is a brief introduction to the theme and contains the objectives and the document structure; Chapters 4 to 7 address the specific objectives 2-6, respectively. The economic feasibility described in the sixth specific objective is a common objective for chapters 4-6 and was appraised individually in each one. Finally, chapter 8 contains the final considerations, and Chapter 9 the references for all previous chapters.

4 Thesis contribution expectations

In 2021, the mining industry in the State of Minas Gerais (Brazil) showed the highest revenue growth, 87% compared to the previous year, higher than the national average growth (51%). The results presented by the National Ministry of Mines and Energy also point out that the sector was responsible for guaranteeing a positive balance in the Brazilian trade balance. The relevance of the extractive industry is not restricted to Brazil, and its importance and presence are observed all over the world. Despite this, it is a sector recognized for its environmental impacts, especially related to accidents with waste containment structures (tailing dams) [8].

Aware of this, it is expected that this Ph.D. thesis will contribute to the advancement of the mining industry sustainability, in addition to strengthening the country as a mineral power worldwide. By investigating new treatment routes, the project advances in aspects beyond treatment for disposal, but for wastewater processing, minimizing the waste disposal by the sector. From an environmental point of view, the research will contribute to the valuation of by-products that constitute mining wastewater, promoting the economy of raw materials and the non-generation of waste, which would minimize the risks associated with disposal in tailings dams. Concerning economic benefits, the following can be mentioned: introduction of new products in the mining production chain, reduction of production costs, and increased competitiveness of mining industries with greater insertion of its products in the market. In terms of social aspects, one can highlight the life quality improvement and the recognition of socially responsible companies.

Furthermore, the project addresses topics that are at the knowledge frontier and presents a great contribution to scientific and technological advancement regarding the processing of industrial wastewater. The project is not restricted to wastewater from gold mining, but also others with equal potential for processing. No less important, it is also expected that the thesis to be developed will contribute to the development and training of the student as a researcher and future professor.

CHAPTER 2 – MINING FROM WASTEWATER: PERSPECTIVES AND CURRENT PRACTICES OF MEMBRANE CONTACTORS FOR METALLIC COMPOUNDS VALORIZATION

Complete articles published in journals:

[1] **Moreira, V. R.**, ..., & Amaral, M. C. S. (2021). Acid and metal reclamation from mining effluents: Current practices and future perspectives towards sustainability. *Journal of Environmental Chemical Engineering*, 9(3), 105169.

[2] **Moreira, V. R.**, ..., & Amaral, M. C. S. (2021). Mining from wastewater: Perspectives and current practices of non-dispersive solvent extraction for metallic compounds valorization. *Chemical Engineering Journal*, 425, 130711.

[3] **Moreira, V. R.**, ..., & Amaral, M. C. S. (2022). Enhancing industries exploitation: Integrated and hybrid membrane separation processes applied to industrial effluents beyond the treatment for disposal. *Chemical Engineering Journal*, 430, 133006.

1 Introduction and theoretical background

Between 1970 and 2010, the demand for mineral goods grew from 23.7 to 70.1 billion tons driven by population growth and changes in terms of consumption patterns [9]. This increasing demand for mineral resources has motivated the mining sectors to pursue not only alternative sources but the implementation of novel beneficiation processes, that assure their competitiveness in a global economic scenario. Although the future expectations are positive for the mineral resources market, a few trends will be decisive for the sustainable growth of these industrial segments. The mining sectors are responsible for half of the global carbon emissions, in addition to a 90% loss (on average) of local biodiversity, going against the current political and economic scenario geared towards increasingly sustainable processes of lower environmental impact [9].

In this context, the concept of “Precision Mining” was first introduced by Crane & Sapsford [10] as an analogy to processes already developed for other industrial segments such as “precision medicine” and “precision agriculture”. Briefly, the idea consists of different approaches for *in situ* exploration that aims at selective recovery of certain compounds directly from the mineral deposits, avoiding, therefore, the indiscriminate generation of complex wastewater composed of several toxic substances. As pointed out by Naidu et al [11], and due to the complexity that mining wastewater presents [12], [13], the costs related to its remediation in abandoned mines located in North America hover around US\$ 10 billion. Additionally, the Canadian Mine Environment Neutral Drainage Program estimates that the total environmental liability costs due to acid mine drainage (AMD) could reach values between CAD\$ 2 to 5 billion [14], [15]. The previously mentioned studies evidenced a high operational expenditure in AMD treatment (conventionally a sedimentation stage preceded by a precipitation process), in addition to making impossible the recovery of most metallic compounds.

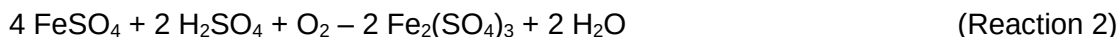
On the other hand, the Precision Mining concept is under the desire for sustainable mining industries, which in turn encompasses concepts of wastewater recycling. In this chapter, we first introduce the idea of “mining from wastewater (MfW)”, in which the wastewater derived from mining sectors represents a potential source of mineral goods to be further beneficiated. Based on the scarcity of mineral resources and aligned with the requirement for effective and economically viable recycling routes, an appropriate and selective technique for these compounds’ recovery is required.

1.1 Gold mining wastewater

Gold, as well as most ores, is not used directly as it is mined and requires further physical and chemical processing. These steps are essential to achieve higher recoveries since most gold ores are occluded in a matrix composed mainly of pyrite (FeS_2), arsenopyrite, and pyrrhotite ($\text{Fe}_{(1-x)}\text{S}_{x(x=0-0.2)}$) [16]. This sulfur-rich matrix lowers the gold recovery in conventional cyanide leaching and requires a prior oxidation treatment to promote the rupture of their crystalline structures [17], [18].

The pressure oxidation (POX), or pressure hydrometallurgy, of refractory gold ores, is a hydrometallurgical process and one alternative available. It is responsible to promote the dissolution of gold from its ore at high temperatures and pressures. In an acid autoclave (pH <2) operated at temperatures greater than 175 °C and high pressures (~21 atm), the following reactions (1-3) may occur and are responsible to produce free-acid levels leaving the autoclave

normally in the range of 10 to 25 g/L H_2SO_4 [19]. The lower pHs solubilize the metals remaining in the ore, resulting in complex wastewater.



The water consumption and subsequent volume of wastewater generated, in gold ore processing by the hydrometallurgical process depend on the plant capacity. For the facility under study, there are estimations that 63 m³/h of aqueous wastewater is continuously produced. The acidic wastewater is conventionally treated by neutralization [20], a process responsible to increase the wastewater pH and thus precipitate metals. Most residual sludge produced after neutralization is disposed of in tailing dams, a practice of concern given its environmental impacts [8]. For that reason, alternative processes for acidic wastewater management are being sought.

1.2 Opportunities for wastewater valorization

Different technologies are being developed for wastewater valorization, which was recently summarized by Naidu et al. [21] and Moreira et al. [22]. Mention a few are electrochemical systems (e.g.: electrolysis, electro reduction, and electrodialysis), ion exchange resins, membrane separation processes, activated charcoal, biological systems, and solvent extraction (SX). As a consolidated technology and already applied in full-scale operations, SX presents itself with an interesting potential for MfW applications [22]–[24]. The technique consists of a selective separation process of a given compound based on its solubility in two different streams, usually an aqueous (containing the compound of interest) and an organic phase (responsible for the extraction of the compound of interest and therefore the process selectivity). However, a major drawback related to the technique is the formation of emulsions, and therefore losses and cross-contamination of the organic phase, as it requires the dispersion of the liquid phase into the organic one.

It is possible to carry out SX without the need for dispersion from one phase to another, which allows, among other things, higher process efficiency. These are referred to as non-dispersive solvent extraction (NDSX) processes and use a membrane contactor (MC) to accomplish a liquid/liquid mass transfer between the aqueous and organic phases that flows on opposite sides of a microporous membrane [25] (Figure 1).

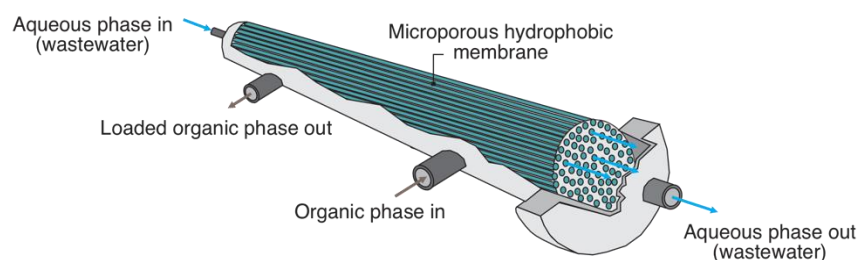


Figure 1. Hollow fiber membrane contactor representation. ©

The term membrane contactor (MC) is conventionally used for processes that aim to establish contact between two distinguished phases in which the membrane is used as a physical interface [26]. In this case, the membrane does not act as a filter medium as in other conventional membrane separation processes (ultra-, micro-, nanofiltration, and reverse osmosis), and does not present selectivity to the constituent being separated.

In these processes, one of the phases is immobilized in the membrane pores so that the fluid/fluid interface is located at the opening of each pore [27], [28]. As for conventional SX, it is possible to combine extraction (aimed for metals uptake), scrubbing (aimed for impurities removal and higher selectivity), and stripping (aimed at organic phase regeneration) MCs to achieve a higher recovery and selectivity for the by-products in the target. The separation principles in all three stages are similar to those from SX. They were elucidated in a previous study [22] and were illustrated in Figure 2.

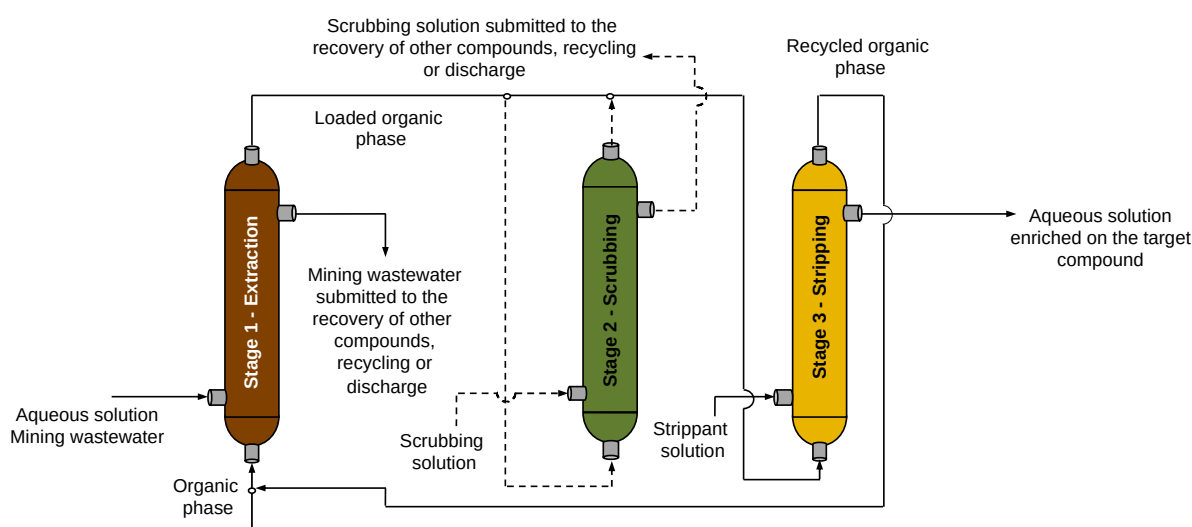


Figure 2. Diagram for by-product recovery by non-dispersive solvent extraction comprised of extraction, scrubbing, and stripping processes. Adapted from Moreira et al. [22]

The major advantages over the traditional form of SX are the (i) possibility of operating with relatively close density phases, (ii) the ability to provide several extraction stages in a single module, (iii) prevents emulsion formation, and (iv) allows operation at different flows between the organic and aqueous phases without the limitations of flooding a dispersive solvent extraction column. These advantages favor the application of NDSX to by-product recovery from different aqueous solutions and gaseous streams, which include but are not limited to mining wastewater and metallic compounds [29].

Microporous membranes are commonly employed in MCs systems, presenting either a hydrophilic or hydrophobic character. They can be manufactured both as hollow fibers and flat sheets. In either case, a higher surface area is obtained when compared to conventional solvent extraction, providing a greater mass transfer efficiency per unit volume. Indeed, MC typically offers 500 times more contacting area than what is obtained in liquid/liquid extraction columns [30]. As a result, MCs present higher energy efficiency, and the fact that it is a modular process enables an easier scale-up of the process [31]. Among the available MCs modules configurations are the plate and frame, spiral wound, rotating ring, and hollow fiber.

The driving force for extraction relies on the chemical potential difference between the solutions being contacted, in which the compound of interest is transferred by a diffusion phenomenon

[30], [32]. In despite of the advantages previously mentioned, it is important to point out the addition of the new resistances opposing the mass transfer deriving from the aqueous phase boundary layer, the membrane, and the organic phase boundary layer, wherein the concentration profile is shown in Figure 3. In addition to an increase in mass transfer resistance, and as in other membrane separation processes, MCs are subject to fouling and have a finite life span, which should be taken into consideration while estimating their acquisition, operational costs, and life cycle environmental impacts. Apart from the additional resistances to mass transfer, it is still possible to achieve high recovery rates by NDSX, with values greater than 90% as will be further presented in Table 2. Therefore, if the operating conditions are properly established, the advantages of non-dispersion and greater contacting area achieved by MCs should overcome the limitations posed by boundary layer effects and membrane resistance.

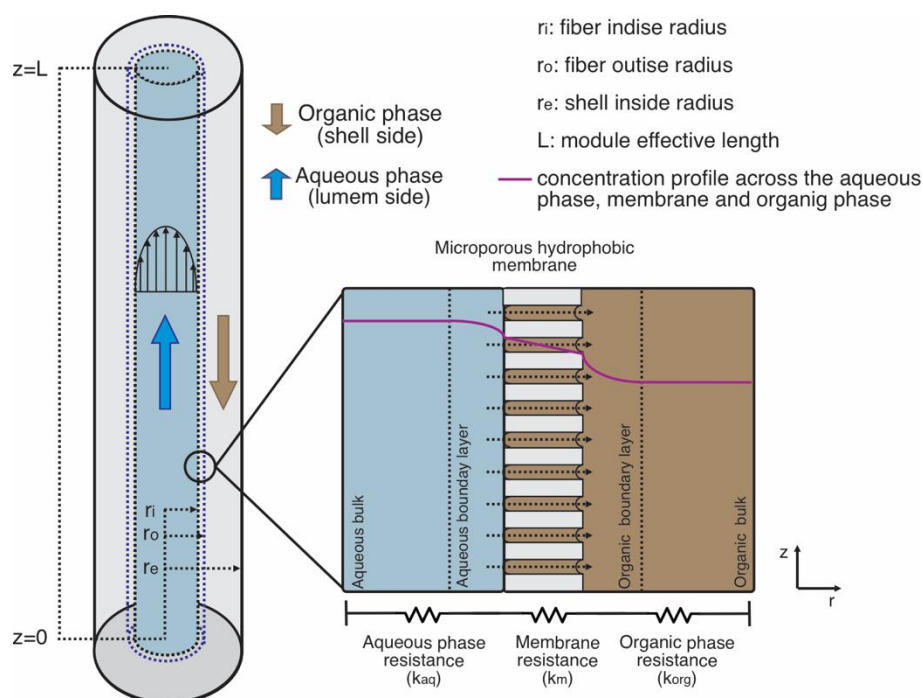


Figure 3. Concentration profile and mass transfer resistances in a single hollow fiber.

A concise literature review is presented in the current chapter, summarizing the recent advancements in MCs for by-products recovery from wastewater by NDSX. The databases and search engines Scopus, Web of Science, Science Direct, and Google Scholar were consulted for the literature review, in addition to the keywords “membrane contactors”, “by-products”, “non-dispersive solvent extraction”, “hollow fiber membrane contactors”, and “solvent extraction”. Over 150 research papers were consulted from 1979 – 2020, being reported those focused on pilot- and bench-scale studies whose results demonstrated a process with the potential to be scaled up to full-scale facilities.

2 Opportunities for metals beneficiation

Concerns about the geological reservoirs' depletion and the long-term availability of metals have led to speculations about their requirement in a near future. The copper demand was estimated until 2100 in research developed by Schipper et al. [33]. The authors highlighted that the current demand for copper would result in its depletion unless higher recovery rates

are achieved. Among all sectors, industrial, commercial, and consumer represent the major contributors to copper consumption in the next years. The authors still pointed out that secondary copper production requires only 20% of the energy used for primary copper production, which reinforces the benefits of pursuing alternative sources for the metallic compound. The shortage in metals supply shortly led to a list of critical raw materials developed by the European Union (EU), which has motivated other countries to take similar action. The first list was presented by the EU in 2011, comprised 14 critical raw materials, and were updated every 3 years since then. The latest report available includes 30 elements [34].

Rather than employing conventional physical and chemical treatments for wastewater treatment, it is possible to beneficiate the wastewater from different industrial sectors, which would represent an additional source of value-added compounds capable to attain a future demand for mineral goods. Figure 4 were summarized the wastewater composition derived from the main mining activities, as these wastewaters stand out among the others in terms of metal concentration. These, in turn, vary according to the geological characteristics from which the ore is extracted and also the beneficiation process [12]. However, it is noteworthy the high concentrations of certain metals with a high added-value, such as aluminum (0.9 – 1878 mg/L; average: 341 mg/L), copper (0.02 – 1400 mg/L; average: 121 mg/L) and zinc (0.3 – 410 mg/L; average: 68 mg/L), in addition to iron, manganese, and magnesium that, although in high concentrations have a lower economic interest.

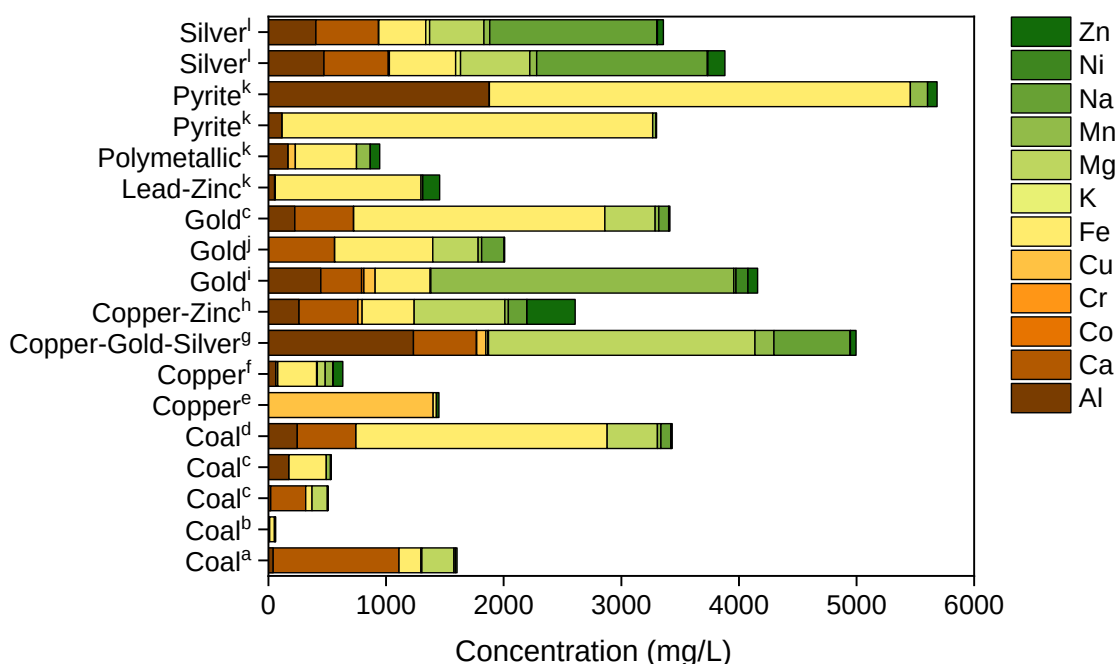


Figure 4. Wastewater composition from different mining sectors. References: ^a[35], ^b[36], ^c[37], ^d[38], ^e[39], ^f[40], ^g[41], ^h[42], ⁱ[43], ^j[13], ^k[44], ^l[45].

3 Modules and membrane materials

In addition to the representation shown in Figure 1, other modules and types of membranes are available and can be applied in MfW processes. In general, it is expected from an MC module to maximize the mass transfer, reduce and allow fouling control, work with low-pressure drops, and ensure constant performance throughout its effective length [46].

Modules that use flat sheet membranes are often used in bench-scale studies due to their operational simplicity, ease of construction, and repair [47]. In this case, a flat sheet membrane is placed between two plates equipped with inlets and outlets through which the aqueous and organic phases must flow (Figure 5a). Modules that use flat sheet membranes still have a few advantages over those that use hollow fiber membranes. In addition to the operational simplicity, the flat sheet modules have the same surface area on both sides of the membrane, and the processes for membrane manufacturing are simpler. Moreover, in some cases, flat sheet membrane modules may have a higher flux of the compound of interest for the same contact area [48].

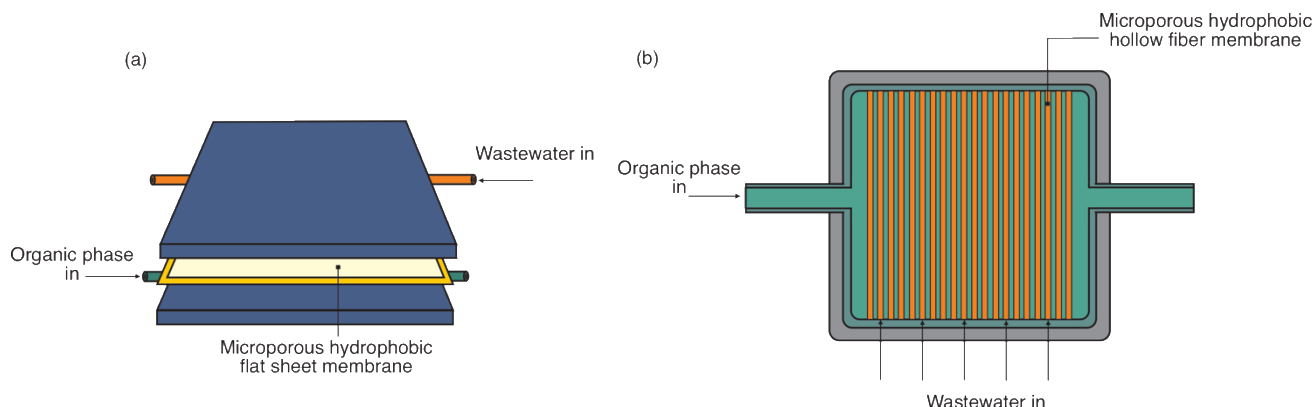


Figure 5. Membrane contactors: (a) flat sheet configuration; (b) hollow fiber transversal flow configuration.

To obtain a module of higher packing density (greater membrane area per volume of module), flat sheet membranes can be rearranged in spiral wound modules. However, most applications that consider this configuration are still restricted to gas-liquid systems, and no recent studies were encountered that investigate its application for metallic compound reclamation.

Conversely, due to their higher packing density compared to the other configurations and applicability to liquid-liquid systems, hollow fiber membrane modules are often preferred in industrial applications [49], [50]. These modules generally have a shell and tube configuration as shown in Figure 1. The choice of which phase, aqueous or organic, flows in the shell- and lumen-side, and how the phase is distributed in the shell side, is decisive as it directly impacts the mass transfer. As a primary example, processes that operate in counter-current have higher mass transfer coefficients compared to the co-current mode of operation, but also have a greater pressure drop [46]. Conversely, parallel flow configurations are more subject to non-uniform distribution, a problem that could be mitigated by the introduction of baffles on the module shell. After baffles addition, it is observed local turbulence, as well as transversal flows in the shell side, responsible to increase the mass transfer coefficients.

Modules that operate with flow rates perpendicular to the fibers (Figure 5b) are another alternative with the advantage of higher mass transfer in the shell side and lower pressure drop compared to parallel flow modules with baffles. Although not as usual as the conventional modules with the parallel flow, the higher turbulence in the shell side results in a thinner diffusion layer and less propensity for preferential paths (flow channeling) formation [51]. From Table 1 it is noteworthy that most recent studies used hollow fiber commercially available modules from Liqui-Cel™. They have a packing density of approximately $\sim 10,000$ fibers/module, presenting an average surface area of 1.4 m^2 for an effective membrane length of 15 cm, with polypropylene (PP) as the base polymer. The membranes are hydrophobic and,

therefore, are wetted by the organic phase. In those cases, and to guarantee greater operational stability, the aqueous phase was admitted inside the fibers (lumen side) at a slightly higher pressure while the organic phase flows through the shell side.

Table 2. Modules and membrane characteristics used for metals extraction from aqueous media. d_i : internal diameter of the fiber; d_o : external diameter of the fiber; S_o : superficial area; ϵ : porosity; τ : tortuosity.

Aqueous phase	Organic phase	Comp. of interest	Membrane material	$d_{i,fiber}$ (mm)	$d_{o,fiber}$ (mm)	S_o (cm ²)	Pore size (μ m)	ϵ	τ	L_o (cm)	Flow arrangement	# Fibers	Manufacture	Q_{aq} (cm ³ /s)	Q_{org} (cm ³ /s)	R(%)	Ref.
Synt. phosphoric acid media	Cyanex 302	Hg ²⁺	PP (C ₃ H ₆) _n	0.28	0.38	29.8	0.2	-	-	2.0	Transversal flow	31	XTO Energy	- (shell side)	- (lumen side)	~55.2	[52]
Synt. phosphoric acid media	D2EHPA	Lanthanides	PP (C ₃ H ₆) _n	0.28	0.38	29.8	0.2	-	-	2.0	Transversal flow	31	XTO Energy	0.4 cm/s (shell side)	- (lumen side)	>13.1	[53]
Synt. aqueous media	D2EHPA	Zn ²⁺ , Cu ²⁺	PP (C ₃ H ₆) _n	0.12	0.15	14000	0.03	0.4	2.6	19.8	Counter current flow	~10,200	Liqui-Cel™	6.0 (lumen side)	6.0 (shell side)	>53.0	[54]
Synt. aqueous media	D2EHPA	Cu ²⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.4	2.6	19.8	Counter current flow	~10,200	Liqui-Cel™	- (lumen side)	- (shell side)	~9.6	[55]
Synt. aqueous media	LIX 973N	Cu ²⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.4	2.5	19.8	-	~10,000	Liqui-Cel™	~1.3 (lumen side)	~0.67 (shell side)	>51.8	[56]
Synt. aqueous media	LIX 84-I	Cu ²⁺	PP (C ₃ H ₆) _n	0.21	0.3	14000	0.03	0.4	2.5	15.6	Co-current flow	~10,800	Liqui-Cel™	7.5 (lumen side)	7.5 (shell side)	95.8	[57]
Synt. aqueous media	LIX 84-I	Cu ²⁺	PP (C ₃ H ₆) _n	0.22	0.3	5800	0.04	0.4	2.5	<12.2	-	7,400	Liqui-Cel™	- (lumen side)	- (shell side)	>83.7	[58]
Synt. aqueous media	TFA	Cu ²⁺	PP (C ₃ H ₆) _n	0.22	0.3	5800	0.04	0.4	2.5	<12.2	-	7,400	Liqui-Cel™	- (lumen side)	- (shell side)	~80.4	[59]
Synt. aqueous media	LIX 662N	Cu ²⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.4	2.5	15.0	Counter current flow	10,200	Liqui-Cel™	~7.4 (lumen side)	~7.6 (shell side)	>98.0	[60]
Synt. nitric acid media	TBP	U ⁶⁺ , Th ⁴⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.4	2.5	15.0	Counter current flow	9,950	Liqui-Cel™	2.5 (lumen side)	2.5 (shell side)	>70.1	[61]
Synt. nitrate media	LIX Reagents	Cu ²⁺	PP (C ₃ H ₆) _n	0.24	0.30	-	0.03	0.4	2.5-3	19	Counter current flow	1680	Liqui-Cel™	*0.73 cm/s	*0.23 cm/s	>29.8	[62]

														(lumen side)	(shell side)		
Synt. nitric acid media	DHOA	U ⁶⁺ , Th ⁴⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.4	2.5	15.0	Counter current flow	9,950	Liqui-Cel™	2.5 (lumen side)	2.5 (shell side)	>54.4	[63]
Synt. aqueous media	Cyanex 272	Co ²⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.4	2.5	15	Co-current flow	9,950	Liqui-Cel™	- (lumen side)	- (shell side)	>99.9	[64]
	Ionquest 801	Co ²⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.4	2.5	15	Co-current flow	9,950	Liqui-Cel™	- (lumen side)	- (shell side)	>99.9	[65]
Synt. nitric acid media	TBP	U ⁶⁺ ,	PP (C ₃ H ₆) _n	1.8	2.25	~381	0.64	-	-	27.0	Co-current flow	20	-	~5.8 (lumen side)	~1.5 (shell side)	>90.0	[66]
Synt. aqueous media	Aliquat-336	As ⁵⁺	PVDF (C ₂ H ₂ F ₂) _n	0.13	0.17	-	0.2	0.8	-	18.0	Counter current flow	3	-	0.47 (lumen side)	1.4 (shell side)	~70.0	[67]
Synt. aqueous media	Aliquat-336	Pu ⁵⁺	PP (C ₃ H ₆) _n	1.8	2.25	~381	0.64	-	-	30	Co-current flow	20	-	5.8 (lumen side)	1.5 (shell side)	>20.1	[68]
Synt. nitric acid media	DNPPA + TOPO	Nd ³⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.4	2.5	19.8	Counter current flow	~10,000	Liqui-Cel™	~1.7 (lumen side)	~0.8 (shell side)	>99.9	[69]
Synt. aqueous media	TBP	Pu ⁴⁺	PP (C ₃ H ₆) _n	1.8	-	~1206	0.64	-	-	27	Counter current flow	20	-	5.83 (lumen side)	1.53 (shell side)	82.2	[70]
Synt. aqueous media	TODGA + DHOA	Nd ³⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.4	2.5	15.0	Counter current flow	9,950	Liqui-Cel™	~5.0 (lumen side)	~8.3 (shell side)	>99.0	[71]
Synt. aqueous media	LIX 79 + TOPO	Au ⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.3	-	-	Co-current flow	10,000	Liqui-Cel™	4.16-15.27 (lumen)	4.16-8.33 (shell side)	>95.0	[72]
Synt. aqueous media	LIX 79	Au ⁺	PP (C ₃ H ₆) _n	0.24	0.3	14000	0.03	0.4	2.5	15.0	Co- and counter-current flow	~10,000	Liqui-Cel™	4.17 - 15.28 (lumen side)	2.78 - 8.33 (shell side)	>99.0	[73]

However, it is important to mention that PP membranes may have their characteristics changed once in contact with aqueous and organic solutions, interfering with the process efficiency in a long-term operation [74], [75]. Barbe et al. [74] examined the morphology and hydrophobicity of PP membranes (Celgard® 2500) by scanning electron microscopy and reported a change in several properties after a contact time of 72 hours with a 30% w/w CaCl_2 water solution. Among them, the author highlighted the increase in the length (from 0.184 ± 0.008 to 0.205 ± 0.004 μm) and area (from 0.0077 ± 0.0009 to 0.0097 ± 0.0004 μm) of the pores, which resulted in membranes of higher porosities (from 0.127 ± 0.014 to 0.188 ± 0.009). This fact was justified by the water meniscus intrusion within the pores, therefore resulting in the enlargement of the entrance.

After contact with different organic solvents, Kamo et al. [75] observed that the membranes showed greater permeability due to an increase in pore size, however a reduction in their length, emphasizing that these effects were associated with the solvents' surface tension. The changes in membrane structure were attributed to the formation of new “liquid bridges” between two fibers during drying, followed by the deformation and adhesion of the adjacent fibers as a result of the solvent surface tension [75]. In addition to morphological changes, the hydrophobicity of the membrane can be severely altered depending on what is adsorbed onto its surface. The results from Lv et al. [76] corroborate with the research previously mentioned, in which a reduction in the membrane contact angle (all $<90^\circ$ after exposure) was observed after exposure to methyl diethanolamine (from 121.6° to 90.8° ; organic phase: 30% methyl diethanolamine; exposure time: 60 days), monoethanolamine and deionized water. As their contact angle reduces, the membranes become more susceptible to wetting by the aqueous phase which might lead to cross-contamination of the organic phase.

Membrane structure and morphology were most affected by solvents with lower surface tensions since they intrude more easily into the membrane pores [77]. Once the hydrophobicity is lowered, and pores became wider, the dispersion of the organic phase onto the aqueous phase would be facilitated, which represents an undesired condition that could imply organic phase losses, emulsion formation, and cross-contamination.

One of the alternatives to overcome these problems, also highlighted by Lv et al. [77], is to increase the membranes' hydrophobicity. Different base polymers have been considered for novel hydrophobic membrane obtainment. When considering their development, it is essential to take into account their contribution to mass transfer resistance since it accounts for a major drawback for non-dispersive solvent extraction. Therefore, thinner membranes would be desirable, in addition to mechanical/chemical resistance for long-term operations.

Among the different polymers available, polyvinylidene fluoride (PVDF) has been extensively investigated since most of its physical properties stand out compared to other materials. Membranes made of PVDF have considerable hydrophobicity, chemical resistance, and high solubility in different solvents, which facilitates their manufacturing process [78]. In addition to PVDF, novel materials have also been proposed for hollow fiber membrane synthesis, and in some cases with lower costs, *i.e.*: polystyrene (PS) and poly (tetrafluoroethylene) (PTFE) [79], [80].

PTFE membranes, for example, have even greater chemical/mechanical resistance and hydrophobicity when compared to PVDF membranes [81], [82]. However, due to their high melt viscosity and insolubility, they are not manufactured by conventional methods (phase inversion process and melting-stretching), requiring alternative processes still under

development *i.e.*: the phase-extrusion method. The main disadvantage to this procedure is the requirement of chemical inputs and the production of membranes with a non-uniform thickness. Alternatively, methods such as emulsion electrospinning have been suggested in recent years and are considered more effective in porous hollow fiber membrane manufacturing. These usually have a greater specific surface area [83], and the process is considered a more environmental-friendly alternative by some researchers [84], [85]. For PTFE membranes, contact angles up to 164° were observed after the incorporation of polyethylene oxide (POE) in its manufacturing process, a contact angle value that exceeds many others observed for modified PVDF membranes.

Even so, these two base polymers (PVDF and PTFE) have low biodegradability, thus hindering their disposal after their lifespan. For that reason, materials with greater biodegradability were also recently considered for hollow fiber membrane manufacturing [86]. This is the case for membranes produced from styrene-butadiene-styrene (SBS), which is also a hydrophobic (contact angle $\sim 132^\circ$ [87]) material with mechanical properties that favor its application in MCs. The contact angle value for membranes made of SBS is comparable to commercial PVDF and PTFE membranes which corroborates its application in extractive processes using MCs [88]. Still, a better comprehension is necessary, especially in terms of SBS' membranes lifespan, and other novel membranes as well, so that their application could be extended to large-scale processes. In summary, recent papers that investigated the synthesis of novel membranes, as well as their main characteristics, are presented in Table 3.

Table 3. Recent advancements in hydrophobic membranes. LEPw: liquid entry pressure of water. PVDF: polyvinylidene fluoride. PP: polypropylene. PTFE: polytetrafluoroethylene. HDTMS: hexadecyltrimethoxysilane. DMP: dimethyl phthalate. NMP: N-methyl-2-pyrrolidone. PES: polyether sulfone. PDMS: polydimethylsiloxane. PMMA: polymethyl methacrylate. PVA: polyvinyl alcohol. PEO: polyethylene oxide. SBS: Styrene-butadiene-styrene.

Membrane	Method	Membrane thickness (um)	Pore size (um)	Porosity (ε)	Water Contact angle (°)	LEPw (bar)	Ref.
Commercial PVDF	-	-	0.75	0.77	136.3 ± 1.0	3.2	[89]
Commercial PP	-	-	0.3	0.4			[90]
Commercial PTFE	-	-	0.22	0.75	~125	0.8	[91]
PVDF (20 wt.%) - HDTMS (1 wt.%)	Non-solvent induced phase-inversion	-	0.04	0.76	143.5 ± 0.5	7.0	[92]
PVDF (20 wt.%) - HDTMS (5 wt.%)	Non-solvent induced phase-inversion	-	0.13	0.73	150.0 ± 0.2	7.0	[92]
PVDF (15 wt.%)	Non-solvent phase separation w/ EtOH (96%)	65.0	0.06	0.62	150.0 ± 1.0	7.0	[93]
PVDF (30 wt.%) - DMP (70 wt. %)	Combined non-solvent and thermally induced phase separation	-	0.17	~0.52	96.0 ± 6.0	-	[94]
PVDF (30 wt.%) - DMP (65 wt. %) - TEP (5 wt.%)	Combined non-solvent and thermally induced phase separation	-	0.20	~0.63	101.0 ± 4.0	-	[95]
PVDF (5 wt.%) - Silica aerogel (3 wt.%)	-	320.0	0.40	0.62	106.3 ± 0.6	0.7	[96]
PVDF (10 wt.%) - Silica aerogel (1 wt.%)	-	255	0.17	0.58	80.1 ± 2.8	1.7	[97]
PVDF - Silica particles (3.6 g)	Self-assembly	134.5	0.58	0.66	159.5 ± 1.1	3.5	[89]
PVDF - Silica particles (0.8 g)	Self-assembly	115.8	0.72	0.75	151.1 ± 1.3	3.3	[89]
PVDF (9 g) - NMP (91 mL)	Non-solvent phase separation	100.1	0.92	0.77	~103.5	0.7	[98]

PVDF (5 g) - NMP (91 mL)	Non-solvent phase separation	99.7	0.69	0.65	~144.3	2.3	[99]
PES	Electro-blowing technique	320	0.91	0.98	~139.3	0.1	[91]
PDMS-PMMA	Dry phase inversion	56.5	6.70	0.65	113.5 ± 2.2	-	[100]
PTFE (6 wt.%) - PVA (1 wt.%)	Electrospinning technique	-	0.56	0.63	136.4 ± 1.7	2.4	[83]
PTFE (6 wt.%) - PVA (1 wt.%) - BA (0.025 wt.%)	Electrospinning technique	-	1.30	0.73	140.2 ± 0.9	<0.2	[83]
PTFE (20 g) - PEO (1.07 g)	Emulsion electrospinning	-	0.48	0.87	164.0 ± 3.0	2.3	[85]
SBS (15 wt.%)	Electrospinning technique	200	0.48	0.81	132.0 ± 2.0	0.81	[88]
PP – nano-silica (0.5 wt.%)	-	-	-	-	~147	-	[101]
PP – nano-silica (2.0 wt.%)	-	-	-	-	~157	-	[102]
PP - SiO ₂ (0.4 wt.%)	Surface microstructure revising			0.06	~146	-	[103]
PP - SiO ₂ (2.4 wt.%)	Surface microstructure revising			0.04	~150	-	[104]

4 Theoretical considerations for mass transfer prediction in hollow fiber membrane contactors

In most research papers, the mass transfer in hollow fiber contactors is described by the resistance in series model (Equation 1-3), in which the overall mass transfer coefficient is a function of the resistances imposed by the aqueous phase, membrane, and organic phase. Depending on the extraction or stripping reaction rate, an additional local resistance may also be considered. These reactions occur inside the membrane pores, where the interface between the two phases is located. For a hydrophobic membrane, wetted by the organic phase, the distribution coefficient (D_A) is associated with the membrane resistance and is estimated according to Equation 2; defined as the ratio between the concentration of the component of interest ($[A]$) in the organic (org) and aqueous (aq) phases.

$$\frac{1}{K} = \frac{1}{k_{aq}} + \frac{d_i}{d_{lm}} \frac{1}{D_A k_m} + \frac{d_o}{d_o} \frac{1}{D_A k_{org}} + \frac{1}{k_i} \quad (1)$$

$$D_A = \frac{[A]_{org}}{[A]_{aq}} \quad (2)$$

$$d_{lm} = \frac{d_o - d_i}{\ln \frac{d_o}{d_i}} \quad (3)$$

Where K is the overall mass transfer coefficient, k_{aq} , k_{org} and k_i corresponds to the aqueous, organic, and local mass transfer coefficients, respectively, d_i to the fiber's inner diameter, d_o to the fiber's outer diameter, and d_{lm} to the logarithmic mean diameter.

The resistance in series model must follow a few assumptions to be considered suitable for mass transfer description. These are: (i) the system is in a steady state; (ii) the pore size and its characteristics are uniform across the membrane; (iii) mass transfer can be described by film-type mass transfer coefficients; (iv) there is no solutes transport through the non-porous part of the membrane; and (v) both aqueous and organic phases are immiscible in each other [105], [106]. Hereafter, a brief description of each mass transfer coefficient would be presented.

The overall mass transfer coefficient (K) is a time-independent parameter and can be obtained empirically while monitoring the concentration of A over time (t) (Equation 4); in which S_o corresponds to the membrane effective area and V the total feed solution volume.

$$\ln \frac{[A]_t}{[A]_0} = -\frac{S_o}{V} K t \quad (4)$$

Aqueous and organic phase mass transfer coefficients, however, are subjected to the process's hydrodynamic conditions. Therefore, although exemplified the most recurrent correlations in the next paragraphs, their accuracy needs to be certified. Several distinct correlations are presented in the literature, being summarized in previous review articles [30], [107], [108]. Due to the differences in module geometry, fiber arrangement, and fluid flow pattern, especially on the shell side, different prediction models have been proposed. The correlations that presented a reasonable adjustment and precision for mass transfer description are shown in Table 4, considering a shell side flow parallel to the fibers as it is the most usual configuration. For demonstration purposes, two of them were presented in the next paragraphs.

The first term to the right of Equation 1 refers to the resistance imposed by the aqueous phase boundary layer. The L  v  que approximation (Equation 5) is a well-known and acceptable model for tube side mass transfer coefficient determination under laminar flow conditions. The expression presents a reasonable accuracy for mass transfer predictions whose Gratz (G_z) number, $G_z = f(Re, Sc)$ – Equations 6-8, are greater than 4, however, overestimate such coefficients in cases in which $G_z < 4$.

In Equation 5, v_{aq} to the average feed velocity; and L to the fiber effective length. D_{aq} corresponds to the diffusivity of the species of interest in the aqueous feed solution (sulfuric acid: $1.97 \times 10^{-9} \text{ m}^2/\text{s}$ [109]), possible to be obtained from the literature or calculated by Wilke-Chang equation (Equation 9) [110]. For Equation 9, D_i was used to represent the diffusivity of solutes in both non-associated solvents ($x = 1$) and water ($x = 2.6$) while $M_{w,i}$ corresponds to the molecular weight of species i (g/mol), T the temperature (K), μ (Pa/s) the dynamic viscosity and V_i (cm^3/mol) the molar volume of species i at normal boiling point [56].

$$Sh = \frac{k_{aq} d_i}{D_{aq}} = 1.62 \frac{D_{aq}}{d_i} \left(\frac{d_i^2 v_{aq}}{D_{aq} L} \right)^{1/3} \quad (5)$$

$$Gz = \frac{D_h}{L} Re Sc \quad (6)$$

$$Re = \frac{v D_h}{\mu_{aq,org}} \quad (7)$$

$$Sc = \frac{\mu_{aq,org}}{D_{aq,org}} \quad (8)$$

$$D_i = 7.4 \cdot 10^{-8} \frac{(x M_{w,i})^{0.5} T}{(\mu \cdot 10^3) V_i^{0.6}} \quad (9)$$

While the correlations for mass transfer in the lumen side are well known, several correlations are proposed for the shell side. As an example, the mass transfer coefficient related to the resistance imposed by the organic phase boundary layer could be given by Equation 10; in which D_h corresponds to the module hydraulic diameter, D_{org} to the diffusivity of the specie of interest in the organic phase solution, and $\emptyset$ the module packing fraction. In this case, the model has good accuracy for $0 < Re < 500$ and $0.04 < \emptyset < 0.4$.

$$Sh = \frac{D_h k_{org}}{D_{org}} = \beta \left[\left(\frac{D_h (1-\emptyset)}{L} \right) \right] Re^{0.6} Sc^{0.33} \quad (10)$$

Finally, the mass transfer coefficient related to the membrane can be obtained by Equation 11, which is inherent to the membrane properties and, therefore, independent of the hydrodynamic conditions. In Equation 11, D_{org} corresponds to the diffusivity of the species of interest in the organic phase; ε the membrane porosity; τ its roughness; and d_o the fiber outside diameter.

$$k_m = \frac{D_{org} \varepsilon}{\tau \frac{(d_o - d_i)}{2}} \quad (11)$$

Once the overall, membrane, aqueous, and organic phases' mass transfer coefficients are determined, the local mass transfer coefficient (k_i) can be obtained through algebraic arrangements of Equation 1. For the stripping process, k_i is considered non-significant to the overall resistance and for that reason is often disregarded. Hence, the global mass transfer coefficient for the stripping stage can be represented by Equation 12; in which D'_A corresponds to the distribution coefficient for the stripping process.

$$\frac{1}{K} = \frac{1}{k_s D'_A} + \frac{d_i}{d_{lm}} \frac{1}{k_m} + \frac{d_i}{d_o} \frac{1}{k_{org}} \quad (12)$$

Table 4. Mass transfer correlations for lumen side, membrane, and shell side coefficients estimation in a parallel flow mode.

	Equation	Assumptions	Reference
Lumen side flow	$Sh = 1.62 \left(\frac{d_i^2 v}{LD} \right)^{1/3}$	Reasonable accuracy when $G_z > 4$, but overestimates them for $G_z < 4$	[111]
	$Sh = 0.55 Sc Re \left(\frac{d_i}{L} \right)$	Recommended when $G_z < 6$	[112]
Membrane	$k_m = \frac{D_{org} \varepsilon}{\tau \frac{(d_o - d_i)}{2}}$	Valid if unhindered diffusion takes place through the pore of the membrane	[113]
Shell side flow	$Sh = Af(\phi) \left(\frac{d_h}{L} \right)^\alpha Re^\beta Sc^\gamma$	The shell-side mass-transfer coefficient can be predicted by using general correlations, in which A , α , β , and γ are empirical constants; (ϕ) is a function of the packing density.	[112]
	$Sh = \beta \left[\left(\frac{D_h(1-\phi)}{L} \right) \right] Re^{0.6} Sc^{0.33}$	$\beta = 5.8$ for a hydrophobic membrane and $\beta = 6.1$ for a hydrophilic membrane; Reasonable accuracy for $0 < Re < 500$ and $0.04 < \phi < 0.4$	[114]
	$Sh = 1.25 \left(\frac{Re d_e}{L} \right)^{0.93} Sc^{0.33}$	Reasonable accuracy for $0.5 < Re < 500$ and $\phi = 0.03$	[115]
	$Sh = 0.019 G_z$	Proposed for close-pack fibers and $G_z < 60$	[116]
	$Sh = (0.53 - 0.58\phi) Re^{0.53} Sc^{0.33}$	Proposed for cases in which remixing and splitting of fluids occurs, which constantly presents the membrane surface with fresh fluid	[117]
	$Sh = (-0.458\phi^2 + 0.400\phi - 0.048) Re^{(4.01\phi^2 - 4.43\phi + 1.56)} Sc^{0.33}$	Accurate for $10 < Re < 143$ and $0.406 < \phi < 0.612$	[118]
	$Sh = 1.45 \left(\frac{d_o}{L} \right)^{0.33} Re^{0.33} Sc^{0.33}$	Accurate for $20 < Re < 75$ and $0.05 < \phi < 0.45$	[119]
	$Sh = 1.615(0.6 + 1.7\phi) \left(\frac{d_o}{L} \right)^{1/3} Re^{1/3} Sc^{1/3}$	Accurate for $3 < Re < 78$ and $0.05 < \phi < 0.45$	[120]
	$Sh = 1.89(0.42 + 0.90\phi)(1 - \phi)^{1/3} \left(\frac{d_o}{L} \right)^{1/3} Re^{1/3} Sc^{1/3}$	The model presented a reasonable accuracy for laminar flow and packing density between $0.05 < \phi < 0.45$	[121], [122]
	$Sh = 0.09(1 - \phi) Re^{(0.8 - 0.16\phi + 1.56)} Sc^{0.33}$	The model presented a reasonable accuracy for $0 < Re < 10$ and packing density between $0.05 < \phi < 0.45$	[123], [124]

$Sh = 8.17 \left(\frac{d_o}{L} \right) Re^{0.74} Sc^{1/3}$	Accurate for $0.16 < Re < 7.30$ and $\phi = 0.3024$	[125]
$Sh = 17.4(1 - \phi) \left(\frac{d_h}{L} \right) Re^{0.06} Sc^{0.33}$	Accurate for $1 < Re < 100$ and $0.25 < \phi < 0.48$	[126], [127]
$Sh = 5.85(1 - \phi) \left(\frac{d_h}{L} \right) Re^{0.60} Sc^{0.33}$	Accurate for $0 < Re < 500$ and $0.04 < \phi < 0.40$	[114]
$Sh = 1.25 \left(\frac{d_h}{L} \right) Re^{0.93} Sc^{0.33}$	Accurate for $0.5 < Re < 500$ and $0.02 < \phi < 0.33$	[128]
$Sh = 1.76 Re^{0.82} Sc^{0.33}$	Model proposed for mass transfer in Liqui-Cell® Extra-flow modules	[129]
$Sh = 0.52 Re^{0.62} Sc^{0.33}$	Model proposed for mass transfer in Liqui-Cell® Extra-flow modules	[130]
$Sh = 0.8 Re^{0.47} Sc^{0.33}$	Model proposed for mass transfer in multi-baffled and multi-compartment modules. Flow range: $0.1 < Re < 10^4$	[131]
$Sh = 0.055 Re^{0.72} Sc^{0.33}$	Accurate for $0.1 < Re < 250$ and $0.32 < \phi < 0.45$	[112]

As in any chemical process, extraction efficiencies in hollow fibers are subjected to several operational conditions. Now that the basic principles of MC have been presented, the main process variables and how they affect metals recovery will be discussed in the next subsections.

5 Operating principles for membrane contactors

There is a consensus that processes operated in countercurrent mode present a higher overall mass transfer coefficient as it maximizes the driving force gradient throughout the fibers. For this reason, this configuration is selected in many studies summarized in Table 2. An additional observation regarding the studies presented in Table 2 refers to the trend to admit the aqueous phase on the tube side while the organic phase flows on the shell side. This configuration is commonly adopted in studies that use hydrophobic membranes and allows for greater operational stability, in addition to lower pressure drop if compared to cases in which the organic phase is admitted into the tubes.

As solute concentration and pH are parameters not controlled in wastewater generation, their effect will not be discussed in depth in the next subsections. However, in general, the mass transfer resistance imposed by the aqueous phase would be greater in cases of low concentrations of the compound of interest, high pH values, and high extractant agent concentrations. Conversely, the membrane and organic phase resistance becomes an important factor opposing the mass transfer in exactly opposite conditions [124].

5.1 Effect of flow rate on the extraction efficiency

To avoid the dispersion between both phases, the flow rate of the non-wetting phase is kept higher (lower residence time distribution – RTD) than the wetting phase (generally aqueous and organic phases, respectively, for processes involving metals recovery from aqueous wastewater). Hence, the aqueous phase exerts a higher pressure on the lumen side and prevents the organic phase from transposing the membrane pores. Aiming for that condition, several authors adopt specific flow rates so the pressure difference between the organic and aqueous phases remains around 0.2-0.5 bar [132]–[134].

The recirculation flow rate effect on the overall process efficiency is often assessed one factor at a time, which means keeping the operating conditions associated with one phase fixed and varying the recirculation conditions of the other. This allows for better comprehension of which phase would be imposing the greatest resistance to mass transfer to the process.

In terms of extraction efficiency, the consequences resulting from an increase in flow rate (lower RTD) are commonly positive, and in most studies more pronounced in the initial stages of extraction. What is perceived is an intensification in hydrodynamic conditions, also seen by the Sh number discussed in section 2.2, which is positively related to the recirculation velocity. Thus, the increase in recirculation flow rate would imply a reduction in the boundary layer thickness and, therefore, resistance to mass transfer. In this sense, the feed flow rate may increase to values in which the local resistances (aqueous or organic) may become negligible to the process, increasing its overall performance for the metallic compounds' recovery [134]. In this scenario, the process efficiency would be limited to the membrane characteristics – translated into the membrane resistance (k_m), which once again highlights the importance of developing modules and membranes that have the smallest possible k_m . Furthermore, the mass transfer is more efficient for a lower RTD of the aqueous phase because their concentration driving force is higher than the organic phase [135].

However, there are cases where the effects of increasing the flow rate may be insignificant on extraction efficiency, or even negative [56], [136]; which suggests that the limiting resistance may not be related to that corresponding phase [56]. Similar behavior is expected for those cases in which the extracting agent is in excess in the organic phase. In addition, a reduction in the residence time by increasing the recirculation flow rate was associated with an incomplete carrier loading [137], which led to a lower overall mass transfer coefficient.

5.2 Effect of extractant concentration on the extraction efficiency

A high concentration of the extractant agent in the organic phase, among other variables, favors emulsions development in dispersive solvent extraction processes. However, as membrane contactors are dispersion-free devices, emulsions between aqueous and organic phases will only occur when the pressure exerted by the organic phase exceeds the breakthrough pressure. Therefore, the configuration of an NDSX makes it possible to work with higher concentrations of the extractant agent in the organic phase, hence achieving greater recovery efficiencies [138], [139]. This statement is better represented after considering the equilibrium reactions involved in extraction processes. As an example, a generic extraction equilibrium reaction for a given metal (M) by D2EHPA (in which $(HR)_2$ represents the dimeric form of D2EHPA) is presented below (Reaction 4; Equation 13). Increasing the concentration of $n(HR)_2$ shifts the equilibrium towards the metallic complex formation ($MR_2(HR)_2$), therefore favoring the process.



$$K_{ex} = \frac{[MR_2(HR)_2][H^+]^n}{[M^{n+}][(HR)_2]^n} \quad (13)$$

However, the positive effects on overall mass transfer could be constrained by other aspects that must also be taken into consideration. For those processes in which the membrane resistance limits the overall extraction, increasing the extractant agent load would simply shift the limiting resistance to the aqueous phase, and may not result in significant changes in the overall mass transfer coefficient. Depending on the extractant agent used, higher concentrations imply greater acidity after extraction, which commonly disfavors the distribution coefficient of the compound of interest in the organic phase. Finally, the researcher may be aware that an increase in the extractant content also leads to an organic phase of higher viscosity [140], which may disfavor the mass transfer.

Once again, the dimensionless numbers presented at the beginning of section 2.2 reveal an inverse relationship between the viscosity and mass transfer coefficient. An increase in organic phase viscosity would be associated with lower Re values and lower diffusivity coefficients as can be seen in Equations 9-10. The phenomenon was reported by Alonso et al. [141] when estimating the effect of Aliquat 336 concentration in Cr (VI) extraction, in which an increase in extractant concentration (from 1 to 10 vol.%) led to a reduction in the mass transfer coefficient from 2.22×10^{-7} to 8.08×10^{-8} m/s.

It is worth mentioning the research developed by Oskay & Mul [142], which becomes clear both the positive and negative effects of the increment in extractant agent concentration. The authors simultaneously evaluated the effect of the extractant concentration on the extraction and subsequent recovery in a stripping module by a factorial design. As mentioned previously, copper recovery was initially favored at higher concentrations of the extractant, with little effect on the stripping stage. Further increases led to a condition in which the organic phase viscosity hampered the copper diffusivity and prevailed over its recovery efficiency. Thus, an optimum value for its concentration was observed and reported, affecting not only the stages of recovery but also re-extraction since a lower concentration of the extractant agent would result in longer and excessive operating time for achieving the same recovery rate of copper. The results obtained underscore the necessity to assess simultaneously the effect on both the extraction and stripping processes.

5.3 Effect of temperature on the extraction efficiency

The increase in the liquid phase temperature may lead to different effects on extraction efficiency [143]. Although the increase in temperature enhances the diffusivity, the temperature effect is ruled mainly by the changes in the compound of interest solubility. The temperature effect can also be shown thru the Gibbs free-energy change (ΔG_{ex}^0), a thermodynamic parameter – calculated by the Van't Hoff equation (Equation 14, [144]), which is correlated with the standard enthalpy (ΔH_{ex}^0) and extraction entropy (ΔS_{ex}^0) changes (Equation 15).

$$\Delta G_{ex}^0 = -RT \ln K_{ex} \quad (14)$$

$$\Delta G_{ex}^0 = \Delta H_{ex}^0 - T\Delta S_{ex}^0 \quad (15)$$

Rearranging Equation 14 and substituting it into Equation 15 results in the linearized form of the Van't Hoff equation (Equation 16). Thus, a plot of $\ln K_{ex}$ vs $1/T$ gives a straight line with the angular coefficient (or the slope) equal to $\Delta H_{ex}^0/R$ and the linear coefficient (or the intercept) equals to $\Delta S_{ex}^0/R$.

$$\ln K_{ex} = -\frac{\Delta H_{ex}^0}{RT} + \frac{\Delta S_{ex}^0}{R} \quad (16)$$

5.4 Re-extraction and stripping process

More than being able to extract the compound of interest, its recovery in a subsequent stage and the restoration of the organic phase for further reuse are essential. Mass transfer and most factors affecting extraction efficiency apply to the stripping process. However, two additional factors may play an important role in the stripping process efficiency [145], [146].

When deciding on a proper extractant, not only its efficiency in extracting the compound of interest should be taken into consideration, but also how easily it is stripped. Most extractants present strong interaction forces with the compound of interest, which hampers its recovery and purification. Therefore, deciding on the best extractant based on its extraction efficiency solely could be in most cases a misleading decision. For these cases, the choice of an extractant with lower extraction efficiency but higher unload capacity would be more appropriate. There is no consensus in terms of which side (lumen or shell side) the organic phase, and consequently the aqueous phase, should be admitted in a stripping process. A good practice could be the admittance of the aqueous phase in the lumen side whereas the organic phase flows through the shell side, for reasons of operation stability as previously mentioned. However, in most cases, a little improvement is observed when this operational conditional is compared [63], [132], [147].

The second factor relies on the stripping agent. Several stripping agents have been tested but acid solutions have proven to be an efficient stripping agent for metallic species recovery. Patil et al. [132] achieved reasonable efficiencies (~75 %) after 250 min using a 0.2 mol/L HNO_3 for stripping neodymium (Nd) from tetra-n-octyl-3-oxapentane-diamide (TOGDA) as an extractant. Nitric acid has been used in another stripping process, being a recurrent acid in studies devoted to metallic compound recovery [140]. Nd was also quantitatively stripped by 5.5 mol/L H_2SO_4 from di-nonyl phenyl phosphoric acid (DNPPA) [136]. Inorganic salts may also be used due to their ability to form stable complexes with the compound of interest. This is an example of the study conducted by Ansari et al. [63], which used a 1 mol/L Na_2CO_3 solution as the stripping agent for uranium recovery (efficiency: ~50%; from both N, N-dihexyl octanamide (DHOA) and tri-n-butyl phosphate (TBP) extractants). The authors still demonstrated the importance of choosing a proper extractant and its interdependence with the metallic specie. For thorium, recoveries up to 80% were achieved when DHOA was used as an extractant, compared to about 60% stripping from TBP in a 2h recovery process.

The overall stripping efficiency is a time-dependent variable, as well as the extraction efficiency [148]. Likewise, increasing operating time leads to better process performance. As an example, Alguacil and Navarro [56] investigated the combination of LIX 973N (5 vol.%) and a sulfuric acid (180 g/L) solution, presenting an increase from 53.1% to 93.8% when the operating time was respectively 3 h and 9 h. Increasing the organic phase flow rate was also responsible for an increase in overall stripping efficiency for the reasons previously described.

6 Applications and integration with other processes

By-product recovery by NDSX has been previously screened by theoretical studies, which investigated the process by mathematical modeling and simulations [149], [150]. Ghadiri et al. [151] modeled the extraction of tyramine by Cyanex 923/kerosene through hydrodynamics (by continuity and momentum equations) and mass transfer (by diffusion and convection mechanisms and its concentration changes via position variation). The model was validated with empirical tests that revealed that the estimated errors were about 10%. Marjani & Shirazian [152] develop and solve a mathematical model for the prediction of copper extraction in membrane contactors. The governing equations were then solved numerically using CFD techniques and the velocity field was determined using Navier–Stokes' equations. The authors reported that the simulation results matched the experimental data quite well. Confirming that the proposed model is reliable and accurate. Furthermore, in their study, the extraction of copper achieved upwards of 85.5%. Fadaei et al. [153] also explored the modeling of the extraction of copper by membrane contactors. The authors presented a numerical simulation using CFD of mass and momentum transfer in a membrane contactor for laminar flow conditions. Axial and radial diffusions are considered in the equations of mass transfer within the fiber, the membrane, and the shell side of the contactor. The convection was also considered in both tube and shell sides. The results showed a high model accuracy when compared to experimental data. Furthermore, they achieved a calculated extraction of copper of 99%.

The favorable recovery rate and selectivity motivated empirical researchers that validate NDSX, which so far was proven to be a promising technology for the recovery of metals of higher added value, rare earth elements, and even radioactive compounds (Figure 6). In general, recoveries greater than 80% were commonly observed. Interestingly enough, a high selectivity for the compound of interest could be obtained for these systems as demonstrated by Kumar et al. [147]. The authors investigated the use of NDSX for gold recovery and reported that up to 400 mg/L of gold was effectively separated and concentrated in the presence of other metals such as iron, copper, nickel, and zinc, all of lower added value compared to gold.

For greater recovery efficiency and selectivity, it is essential to establish the most appropriate operating variables and organic phase composition, a research topic still worth of investigating. For copper (Figure 6), different compositions of the organic phase have been proposed with recoveries varying from 47%, when a D2EHPA diluted in kerosene was used as the organic phase (initial copper concentration: 990 mg/L; time: 30 min [124]), up to 99% for an organic phase composed of LIX662N (10 vol.%) diluted in kerosene (initial copper concentration: 200 mg/L; time: 30 min [90]). The contribution of the operating variables and organic phase composition (which were previously presented in Table 2) could also be observed for the recovery of cobalt [65], gold [134], [147], neodymium [53], [132], [136] and uranium [63], [140].

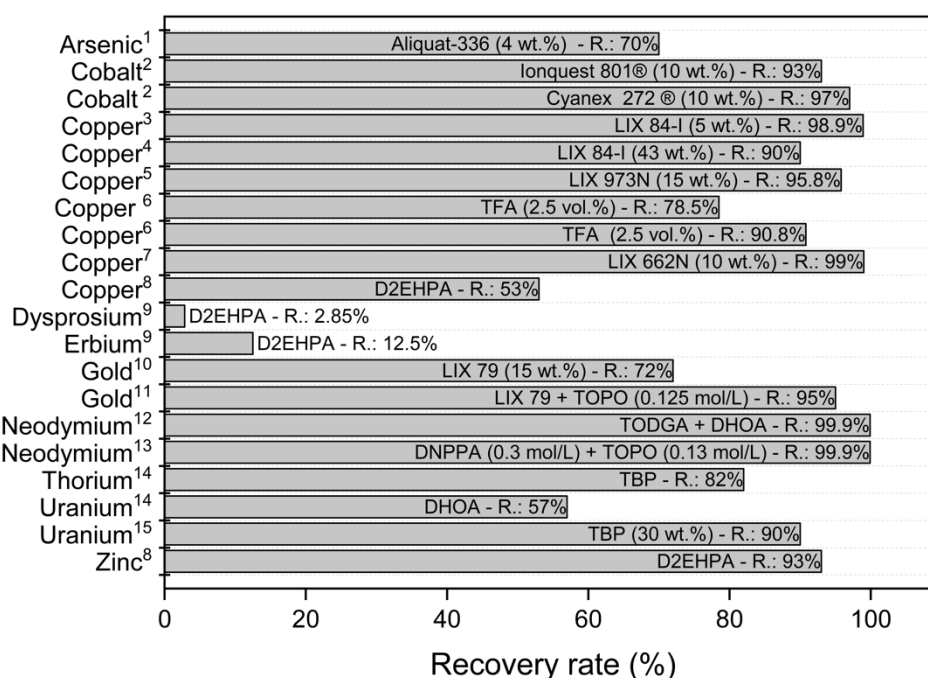


Figure 6. Recovery efficiencies of high-added value metals, rare earth elements, and radioactive compounds. References: ¹[154], ²[65], ³[142], ⁴[155], ⁵[56], ⁶[156], ⁷[90], ⁸[124], ⁹[53], ¹⁰[147], ¹¹[134], ¹²[132], ¹³[136], ¹⁴[63], ¹⁵[140]

The results reported for bench scale investigations have recently encouraged the NDSX scale-up for pilot studies. Arguillarena et al. [157] evaluated the scale-up of membrane-based solvent extraction (wastewater volume up to 91 L; membrane area: 80 m²) aimed at zinc recovery from industrial wastewater in simultaneous extraction and stripping (Figure 7). The authors used tributylphosphate (TBP) diluted in Shellsol D70 and tap water as organic and stripping agents, respectively, in a series of five consecutive pilot-scale experiments that indicated reproducibility of the results, stability of the organic extractant and its adequate regeneration in an NDSX operation, and high selectivity for zinc over other constituents of lower added-value.

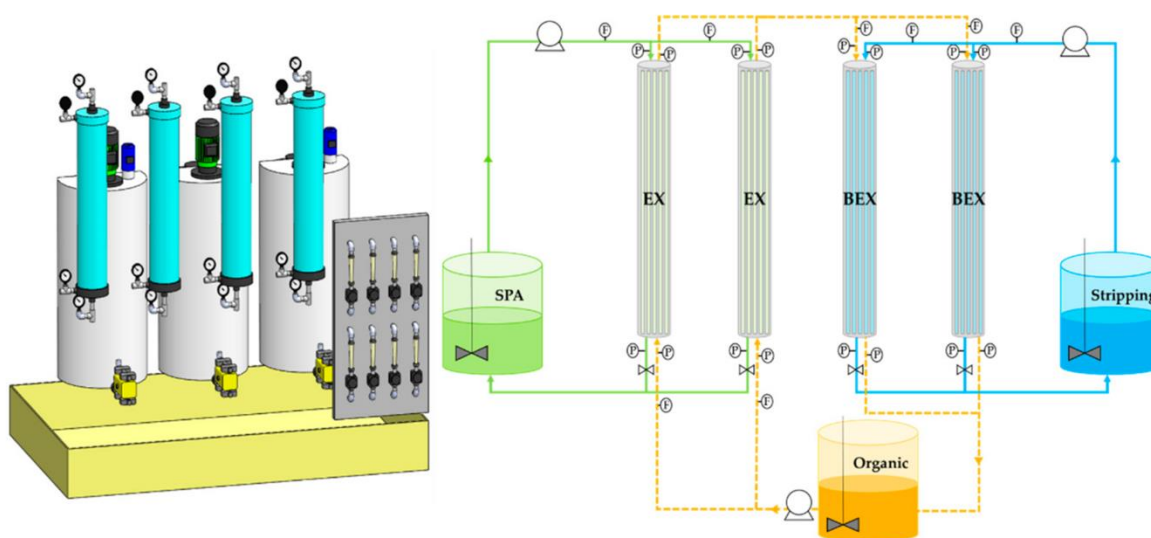


Figure 7. Non-dispersive solvent extraction (NDSX) pilot plant. Withdrawn from Arguillarena et al. [158] under an open-access Creative Common Attribution License CC BY.

Integrated recovery systems may also be anticipated. Kesieme et al. [159] combined both membrane distillation for water reclamation with dispersive solvent extraction for sulfuric acid recovery from its concentrate. Despite the interesting results reported for membrane distillation, it was required a total of three contact stages (comprised of mixing and settling units) to extract 99% of sulfuric acid and a further three contact stages for its stripping from the organic phase. A similar idea was proposed by Pino et al. [160], however integrating nanofiltration membranes with dispersive solvent extraction for AMD treatment and copper recovery from the nanofiltration concentrate. In that case, two contact stages would be required for extraction and one for stripping and copper recovery. Based on the advantages summarized in this chapter, the dispersive SX employed in both studies [159], [161] could be replaced by NDSX processes aiming for higher by-product recovery. Surely, the integration of these processes could represent operational gains. Foureaux et al. [5], which utilized a membrane distillation process for gold mining wastewater treatment, emphasized that sulfuric acid and metallic compounds from the feed wastewater were the main contributors to membrane wetting and its degradation. Due to that fact, the process was constrained to a distillate recovery of approximately 35%. Nonetheless, it is presumable that a simultaneous recovery of sulfuric acid and metals, besides water reclamation, in an integrated system, may extend the recoveries achieved by membrane distillation. Even so, such system design (membrane separation process combined with NDSX) seems to be a research gap to be further explored in future research.

CHAPTER 3 – RECENT PROGRESS IN MEMBRANE DISTILLATION CONFIGURATIONS POWERED BY RENEWABLE ENERGY SOURCES AND WASTE HEAT

Complete articles published in journals:

*[1] **Moreira, V. R.**, ..., & Amaral, M. C. (2023). Recent progress in membrane distillation configurations powered by renewable energy sources and waste heat. *Journal of Water Process Engineering*, 53, 103816.*

1 Introduction

Membrane distillation technology arises as an alternative to solve water scarcity, a subject that comprises quality and quantity issues. The first paper discussing large-scale MD applications was published in 1987 [162], with an increasing trend in the number of papers available since then. One reason for the scenario described is the demand for technologies capable of producing water with high quality and a relatively low energy requirement, characteristics that are consistent with membrane distillation and constitute an advantage over conventional desalination processes.

In membrane distillation, higher water productivity is frequently accompanied by decreased thermal efficiency, which is related to factors such as severe heat loss, a drop in average driving force, and a larger scale of membrane area. These are undesirable aspects that deserve special attention from the scientific community. Still, the integration with renewable energy sources and waste heat, considered abundant and clean, seems to be a crucial step to increasing the efficiency of water reclamation by membrane distillation.

The 71st edition of the Statistical Review of World Energy made available by the British Petroleum Company shows an increase in energy generation in the past years. Compared with 2020, the 2021 growth rate of solar energy was higher than wind energy in North America (25.5%, compared with 11.1%), South America (43.5%, compared with 27%), Europe (11.6%, compared with -1.6%), and Middle East (20.4%, compared with 10.8%). Despite the increase, solar energy production in 2021 was lower in all continents with an exception for Europe and South & Central America (Figure 8a). Conversely, Asia (24.9%, compared with 35.9%), Africa (3.1%, compared with 14.9%), and the Commonwealth of Independent States (21.1%, compared with 84.7%) noticed a larger expansion in wind energy generation compared with the solar one. Asia, North America, and Europe led in renewable energy production in 2021, whereas South and Central America, Africa, the Middle East, and the Commonwealth of Independent States contributed in minor proportions to the total amount produced [163] (Figure 8b).

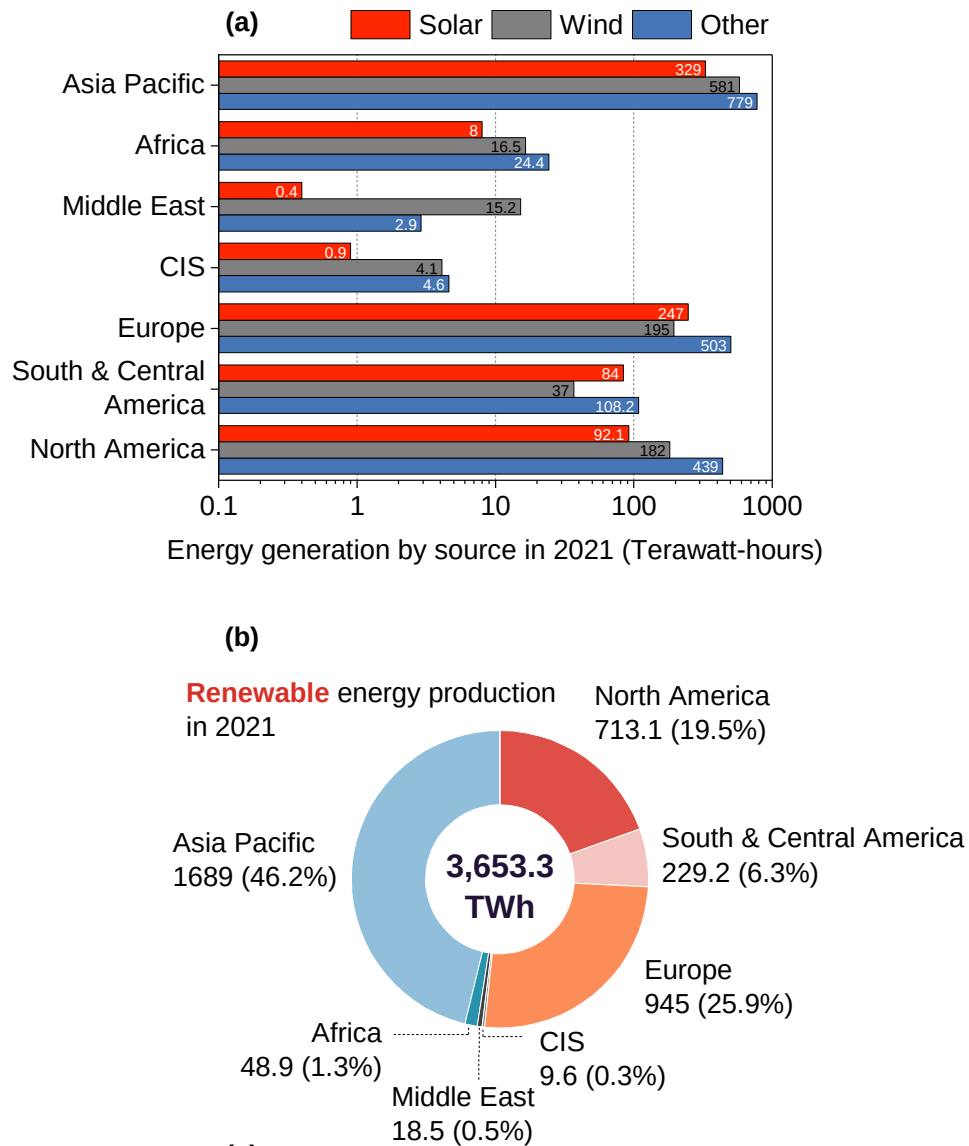


Figure 8. (a) Renewable energy generation by source in 2021. Other renewables: geothermal, biomass, and others not already itemized. (b) Worldwide renewable energy production. [163]

The lower growth rate of solar energy sources may be related to the technological maturity already achieved in these regions, with the opportunity to develop new technologies in complement to the existing ones. It can be observed that the same regions lead in full-scale and pilot systems of membrane distillation powered by solar energy or residual heat (Figure 9), validating the technological maturity of both technologies.

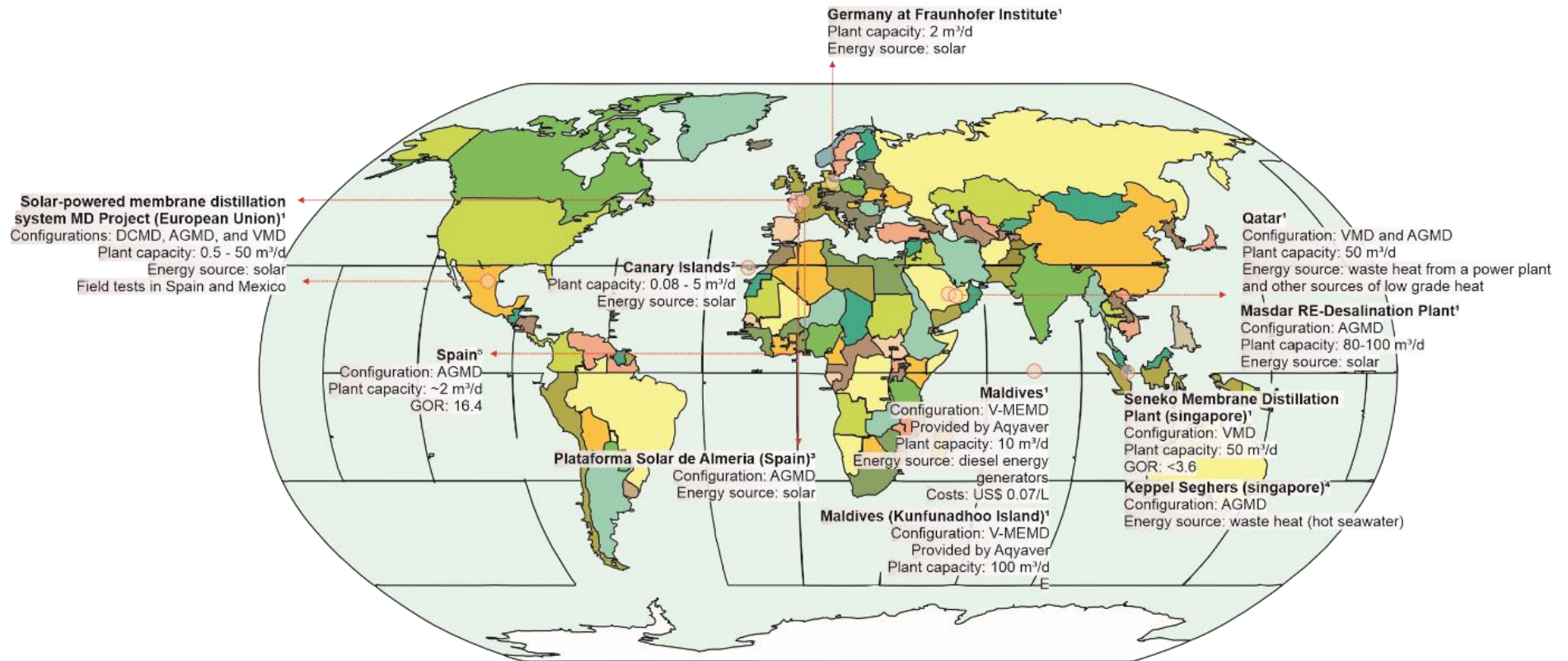


Figure 9. Examples of full-scale membrane distillation systems. References: 1. [164]; 2. [165]; 3. [166]; 4. [167]; 5. [168].

The opportunity to integrate membrane distillation with renewable energy sources and waste heat could contribute to its expansion to full-scale plants. Currently, the technology is in part limited by the energy requirements to maintain the temperature difference required for distillation. Feed heating and distillate condensation require high energy inputs, and efforts have been made to improve energy efficiency in membrane distillation including optimization of operational conditions, membranes modification, and changes in modules configuration [169], [170]. Hence, this work covers the state-of-art of different renewable energy sources and waste heat integrated with membrane distillation to extend its application. It is presented and critically discussed the different engineered configurations powered by renewable energy sources and waste heat, besides the parameters related to energy efficiency were presented and gaps that still limit the use and integration of membrane distillation were identified and critically discussed.

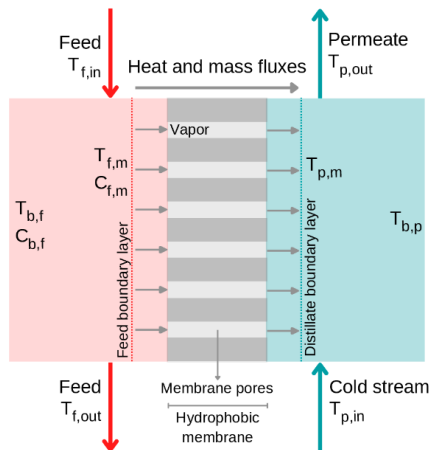
2 Membrane distillation overview

In membrane distillation (MD), high-quality water is recovered as a vapor driven by the pores of a hydrophobic membrane by the action of a vapor pressure difference between the feeding and the distillate [171], [172]. Compared to other membrane separation processes such as reverse osmosis, MD has a lower fouling potential due to its operation without hydraulic pressure [171], [173]. In addition, the use of a hydrophobic membrane prevents the liquid phase from penetrating, ensuring a theoretical retention efficiency of 100% for non-volatile components in the feed [5].

The technology can be subdivided into four main configurations that impact, essentially, how the driving force is established, called: direct contact (DCMD), sweep gas (SGMD), air gap (AGMD), and vacuum (VMD) (Wang and Chung, 2015). The simplest and most applied configuration is DCMD, a configuration in which the heated feed passes through one side of the hydrophobic membrane, and a cooling fluid flows from the other side to directly condense the permeated vapor. In this case, the driving force is established by the temperature difference of the currents. The air gap distillation also condensates the permeate inside the module, but the presence of stagnant air is imposed between the membrane and the condensation surface, which is cooled by a refrigerant that does not come into contact with the distillate [174]. The VMD and SGMD processes work with the permeate current in the gaseous state, which returns to the liquid state outside the distillation module, in a condenser. In the first, the vacuum helps to increase the driving force and, consequently, the distillate flux; in the second, the mass transfer is made possible by the presence of a drag gas that takes the permeated vapor to the condenser [174]. Figure 10 represents the different configurations mentioned including their advantages and limitations.

Ullah et al. [170] demonstrated that membrane distillation can become attractive in energy terms by working with a low-temperature gradient and with various energy sources, such as solar or waste heat. On the other hand, it may present high heat losses depending on the configuration and it is necessary to weigh the advantages and consequences of each available method, aligned to develop increasingly sustainable and efficient production chains. With that in mind, the integration with alternative energy sources is often considered clean, low-cost, and abundant uprisers as an interesting alternative. Table 5 summarizes different studies involving membrane distillation and its integration with alternative energy sources. Parameters related to energy efficiency and the main outcomes were included, and the data summarized will be discussed and analyzed specifically in the following sections.

(a)

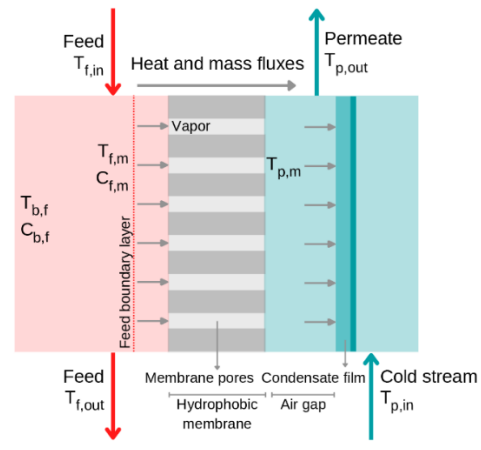
**Advantages**

Simplicity; higher permeate flux; no need for an external condenser;

Limitations

Low thermal energy efficiency; high heat conduction loss

(b)

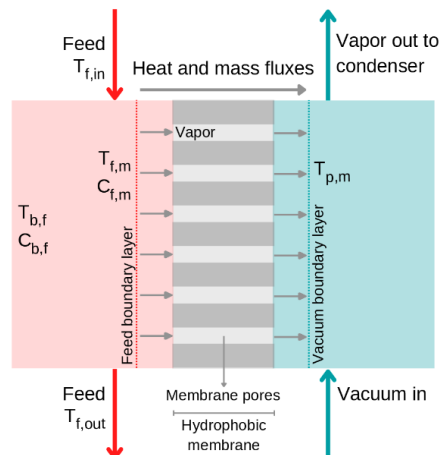
**Advantages**

High driving force; high permeate flux; high thermal energy efficiency

Limitations

Process complexity; high risk of membrane pore wetting

(c)

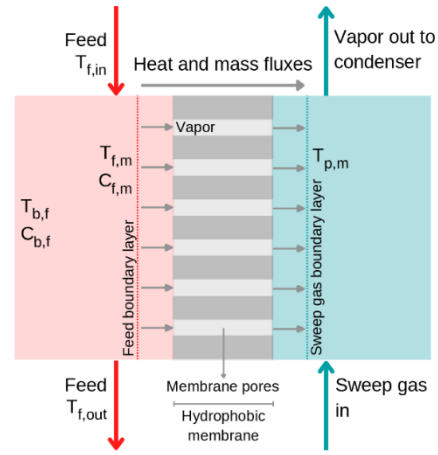
**Advantages**

Low heat conduction loss; high heat recovery; low risk of temperature polarization

Limitations

Lower permeate flux due to mass transfer resistance

(d)

**Advantages**

Higher permeate flux than AGMD; low heat conduction loss

Limitations

Complexity; high cost; temperature polarization; difficulty in heat recovery

Figure 10. (a) Direct contact membrane distillation (DCMD), (b) vacuum membrane distillation (VMD), (c) air gap membrane distillation (AGMD), and (d) sweep gas membrane distillation (SGMD). $T_{f,in}$: temperature of feed stream entering the system, $T_{f,m}$: feed temperature at the membrane surface; $C_{f,m}$: feed concentration at the membrane surface; $T_{b,f}$: bulk feed temperature; $C_{b,f}$: bulk feed concentration; $T_{f,out}$: temperature of feed stream leaving the system, $T_{p,m}$: permeate temperature at the membrane surface, $T_{b,p}$: permeate bulk temperature, $T_{p,in}$: temperature of permeate stream entering the system, and $T_{p,out}$ the temperature of permeate leaving the system. Adapted from: [174]

Table 5. Summary of membrane distillation studies that considered waste heat and renewable energy sources. AGMD: air-gap membrane distillation, DCMD: direct contact membrane distillation, PGMD: permeate gap membrane distillation, VMD: vacuum membrane distillation, V-MEMD: vacuum-multi-effect membrane distillation, WGMD: water-gap membrane distillation, GOR: gain-output ratio, TP: temperature polarization, NA: not available.

Country	Configuration	Scale	Energy source	Main objective	Membrane material	Membrane area (m ²)	Module configuration	Feed temperature (°C)	Distillate flux (L/m ² .h)	GOR	TP	Reference
Brazil	DCMD	Bench	Conventional electric source	Pharmaceutically active compounds removal	PTFE	NA	Flat sheet	60	17.14	NA	NA	[175]
Brazil	DCMD	Pilot	Conventional electric source	Phenolic compounds removal from surface water	PTFE	0.3	Flat sheet	60	2.2	NA	NA	[176]
Turkey	AGMD	Bench	Geothermal	Water treatment	PP, PTFE, and PVDF	0.0044	Flat sheet	50 – 70	~3 – 21.7	NA	NA	[177]
Turkey	AGMD	Bench	Geothermal	Water treatment	PVDF + PTFE	0.0044	Flat sheet	70	20.2 – 35.8	NA	NA	[178]
Different countries from Latin America	Different conceptual models	Full scale	Geothermal	Water treatment	NA	0.33 - 198	NA	<92	25 – 45	NA	NA	[179]
Turkey	AGMD	Bench	Geothermal	Water treatment	PVDF + reduced graphene oxide	0.0044	Flat sheet	60	20.5 – 30	NA	NA	[180]
Malaysia	VMD	Bench	Geothermal	Water treatment	PVDF	0.0024	Flat sheet	60	Up to 9.28	NA	NA	[181]

China	DCMD	Bench	Geothermal	Desalination	PVDF	15	Hollow fiber	52 - 92	14	8.15 – 13.63	NA	[182]
China	DCMD	Bench	Geothermal	Desalination	PVDF	7.48	Hollow fiber	50 – 80	3 – 15	Up to 12.7	NA	[183]
Qatar	V-MEMD	Full scale	Immersion heaters	Desalination	PTFE + PP	6.4	NA	25-35	5	NA	NA	[184]
Qatar	AGMD	Full scale	Immersion heaters	Desalination	PTFE + PP	4.6	NA	25-35	6.1	NA	NA	[184]
Australia	DCMD	Bench	Solar	Freshwater production	PTFE	0.1074	Flat sheet	29 - 43	1.8 - 5.7	0.1	0.34 - 0.38	[185]
China	VMD	Bench	Solar	Desalination	PP	0.25	Hollow fiber	56 - 57.8	4	NA	NA	[186]
China	VMD	Bench	Solar	Desalination	PP	0.09	Hollow fiber	15 - 22	3.09 - 8.03	NA	NA	[186]
Tunisia	V-MEMD	Bench	Solar	Desalination	PVDF	4	Hollow fiber	60 - 80	5.5	1 - 1.11	NA	[187]
Saudi Arabia	V-MEMD	Small scale	Solar	Desalination	PTFE	0.32	Hollow fiber	60 - 90	1.5 - 2.6	NA	NA	[188]
Spain	AGMD	Pilot	Solar	Desalination	PE	24	Spiral wound	55 ^b	1.2	7	NA	[189]
Spain	AGMD	Pilot	Solar	Desalination	NA	9	Flat sheet	60 - 80	0.3 - 5.1	NA	NA	[167]

Spain	AGMD	Pilot	Solar	Desalination	PTFE	2.8	Flat sheet	80 - 90	6.5	NA	NA	[190]
Saudi Arabia	DCMD	Pilot	Solar	Desalination	PP	1.4	Hollow fiber	46.3 - 60.5	5.62 - 8.87	NA	NA	[191]
Brazil	DCMD	Pilot	Solar	Ammonia recovery from landfill leachate	PP	0.18	Hollow fiber	43	0.01	NA	NA	[192]
China	VMD	Pilot	Solar	Water treatment	PVDF	0.1	Hollow fiber	63	6.26	NA	NA	[193]
Spain	AGMD	Bench	Waste heat	Desalination	PTFE	0.025	Flat sheet	70	6.73	NA	NA	[194]
Brazil	DCMD	Bench	Waste heat	Water, mineral acid, and copper recovery	PTFE	0.0042	Flat sheet	60	5.51	NA	0.62	[195]
Brazil	DCMD	Bench	Waste heat	Wastewater treatment	PTFE + spacer	0.0042	Flat sheet	60	6.82	NA	0.67	[5]
Brazil	DCMD	Bench	Waste heat	Wastewater treatment for sulfate removal	PTFE	0.0042	Flat sheet	60	14	NA	NA	[196]
Italy	DCMD	Bench	Waste heat	Wastewater treatment	PE	0.05	Flat sheet	48 - 70	1.04 - 10	NA	NA	[197]
Spain	WGMD	Bench	Waste heat	Desalination	PTFE	0.025	Flat sheet	75	13	0.5	NA	[198]
Australia	DCMD	Pilot	Waste heat	Wastewater treatment	PTFE-PP	0.67	Flat sheet	<40	NA	NA	NA	[199]

United States	DCMD	Pilot	Waste heat	Desalination	PP	0.66	Hollow fiber	90	50	NA	NA	[200]
United States	DCMD	Pilot	Waste heat	Desalination	PP	0.66	Hollow fiber	92	33	NA	NA	[200]
China	VMD	Pilot	Waste heat	Desalination	PP	12.3	Hollow fiber	55	5.4	NA	NA	[201]
Italy	PGMD	Full scale	Waste heat	Desalination	PTFE	10	Spiral wound	65 - 75	NA	2.4	NA	[202]
The Netherlands	DCMD	Full scale	Waste heat	Desalination	PTFE, PP, and UHM-PE	300	Flat sheet	77.9	2.81	17-10	NA	[203]

3 Brief introduction to Energy efficiency parameters

Most energy consumed in membrane distillation is for water evaporation, also known as latent heat. From a molecular perspective, the latent heat reflects the energy required to break the hydrogen bonds between water molecules and depends on the medium salinity and the medium temperature [204]. Its recovery from condensation processes is one of the alternatives to improve the energy efficiency in desalination processes. The latent heat of condensation stored in the permeate could then be recouped to warm up the feed stream by heat exchange. Based on the idea of heat recovery, it has been proposed the concept referred to as the gain output ratio (GOR).

3.1 Gain output ratio (GOR)

The GOR is defined as the ratio of heat associated with the water vapor transfer and the total heat input. In cases where the latent heat is not recovered, $GOR \leq 1$. However, if the latent heat is recouped for feed solution preheating, higher GOR can be obtained. For these cases, Shaulsky et al. [205] interpreted the GOR as the “number of times” the latent heat of condensation is being reused. One alternative to estimate the GOR is presented in Equation 17, in which $\dot{m}_{dis}$ corresponds to the distillate mass flow rate, $\dot{m}_f$ is the heated stream flow rate, and λ_{fg} is the latent heat of vaporization, $T_{f,in}$ and $T_{f,o}$ the inlet and outlet temperature of the heated stream, and $c_{p,f}$ the heated stream heat capacity.

$$GOR = \frac{\dot{m}_{dis} \lambda_{fg}}{\dot{m}_f c_{p,f} (T_{f,in} - T_{f,o})} \quad (17)$$

The GOR served as a basis to estimate the energy efficiency in direct contact membrane distillation in the study conducted by [206]. The first conclusion made is that higher membrane area and feed temperatures should lead to higher energy efficiencies; however, the energy source is a concern if membrane distillation systems are to be economically viable. The authors still mentioned that the GOR increases with the increase in both feed and permeate velocities and recommended operating the desalination system at the feed velocity as high as possible from the concern of the GOR enhancement.

GOR values in solar-driven systems varied from 0.49 [207] to values greater than a unit (1.25; [208]). To increase the gain output ratio in membrane distillation, Abdelgaied et al. [208] considered two additional units in their setup, an energy storage medium, and an evaporative cooler. Their results suggested that the thermal storage materials improve the accumulated productivity and the gain output ratio of their system.

At a constant flux and same condenser area, the GOR values in different membrane distillations follow the order: air-gap membrane distillation < direct contact membrane distillation < and conductive gap membrane distillation. As an example, the GOR associated with direct contact membrane distillation would only exceed the GOR for conductive in a system where the heat exchanger area is 7 times greater than the membrane area. Swaminathan et al. [209] still suggested that the GOR increases linearly with thermal efficiency (η ; Equation 18), but more rapidly with effectiveness in heat recovery (ϵ ; Equation 19).

3.2 Thermal efficiency and heat recovery

Thermal efficiency (η) could be understood as the energy portion transferred from the hot side by mass transfer, being a parameter commonly considered in studies with little or no

condensation energy recovery. Equation 18 could be used to estimate the thermal efficiency, in which $\dot{Q}$ represents the heat transfer rate (“mass” associated with vapor transport through the membrane and “cond” to the conduction heat, B the membrane permeability, Δp_{vap} the vapor pressure difference, h_f the enthalpy of vaporization, k_m is the effective conductivity of the membrane, δ_m the membrane thickness, and $T_{f,m}$ and $T_{p,m}$ are the feed and permeate temperatures at the membrane surface.

$$\eta = \frac{\dot{Q}_{mass}}{\dot{Q}_{mass} + \dot{Q}_{cond}} = \frac{B \cdot \Delta p_{vap} h_f(T_{p,m})}{B \cdot \Delta p_{vap} h_f(T_{p,m}) + \frac{k_m}{\delta_m} (T_{f,m} - T_{p,m})} \quad (18)$$

In cases where heat loss does not occur, the energy supplied is solely used for evaporation and does not seep out from the hot to the cold side by conduction. For these cases, the thermal efficiency corresponds to 1 but does not necessarily represent real cases in which heat is conducted through the vapor transport across the membrane [210]. Improving membrane morphology and module design are two possible ways to increase thermal efficiency in membrane distillation processes. With that in mind, future research should be focused on membranes of higher porosity and lower conductivity. In terms of module design, direct contact membrane distillation has the lowest thermal efficiency (η : 0.5 – 0.85) whereas the air gap configuration leads to the largest values ($\eta > 0.85$) [209], [211].

Equation 19, in turn, could be used to estimate the effectiveness in terms of heat recovery (ε). The variable compares the actual change in the cold stream enthalpy to the maximum possible change in enthalpy of the cold stream. Considering that the specific heat capacity would be constant over the temperature range considered, the equation used to estimate ε could be simplified to the ratio of temperature differences. From what is being presented, $T_{p,in}$ and $T_{p,out}$ are the inlet and outlet temperatures of the permeate stream, and $T_{f,in}$ is the feed inlet temperature.

$$\varepsilon = \frac{h_{c,out} - h_{c,in}}{h_{f,in} - h_{c,in}} = \frac{T_{p,out} - T_{p,in}}{T_{f,in} - T_{p,in}} \quad (19)$$

The parameter ε is an additional variable that could be used to better understand the membrane distillation performance and could complement the discussions provided by GOR and η .

3.3 Temperature polarization (TP)

An increase in feed temperature should favor the GOR but could also lead to a more pronounced temperature polarization (TP). The parameter describes a condition in which the feed bulk temperature differs from the membrane’s interface temperature, which in turn compromises the driving force of membrane distillation processes as the vapor pressure is exponentially related to the temperature. That results in a direct impact on membrane distillation flux and energy efficiency and previous results reported a compromise of 50-80% in water vapor across the membrane due to temperature polarization [212]. It has also been reported that the development of a thermal boundary layer would contribute to an increase in heat loss through the membrane, therefore increasing the energy necessary to maintain a stable permeate flux across the membrane length [170], [213].

Equation 20 could be used to calculate the temperature polarization coefficient (TPC) and expresses the degree of boundary layer resistance versus the total heat transfer resistance

[214]. TPC values approaching 0 suggest that MD is limited by heat transfer in the feed side through the thermal boundary layer, whereas values close to 1 indicate that the process is being limited by mass transfer. In general, TPC values vary from 0.4 to 0.7, as reported in different studies summarized by Anvari et al. [214].

$$TPC = \frac{T_{f,m} - T_{p,m}}{T_f - T_p} \quad (20)$$

Operating conditions and membrane properties influence TPC. Anvari et al. [214] also covered the state-of-art methods for overcoming temperature polarization in membrane distillation. These aspects were detailed in Section 5 and included operational conditions, membrane modifications, flow promoters, and self-heated membranes. An overview of strategies to reduce the temperature polarization in membrane distillation suggests that modification of existing membranes and synthesis of new ones should focus on membranes with improved thermal conductivity, higher permeability, and lower thickness. Flow promoters, in turn, should be considered whenever desired to increase the stream turbulence. In this case, feed spacers, corrugated feed channels/membranes, and the flashed channel could be better alternatives than an increase in flow rates. High flow rates could be energetically unfavorable and may lead to higher internal pressures. In the flow channel, exceeding the liquid entry pressure, and eventually damage the membrane's active layer due to high shear stress [215].

4 Membrane distillation process powered by renewable energy

The main renewable energy sources integrated into the MD process are solar, geothermal, and waste heat.

4.1 Solar

Integrations with solar energy sources are the most common, especially in regions with low availability of centralized energy supply. The fact is also seen in Figure 2 previously presented, in which most full-scale facilities account for this energy source to power the MD systems. In arid environments, where there is less fresh water available, large amounts of salt water, and high levels of insolation, MD integrated with solar energy becomes a competitive option over other methods more used for desalination, such as reverse osmosis [216].

The literature suggests that the most common integration with solar energy is through flat plate collectors (FPCs), evacuated tube collectors (ETCs), compound parabolic concentrators (CPCs), salt-gradient solar ponds (SGSPs), or solar stills. These different technologies sought to heat the feed stream and are classified according to the existence or absence of solar concentrators in their structure. Concentrators are reflective surfaces that converge the sun's rays, reaching higher temperatures. However, this technology presents greater complexity due to the demand for sun-tracking devices [217]. For the supply of electrical energy necessary to drive pumps, solar energy can be obtained through photovoltaic modules associated with direct current batteries and electric current inverters [218].

As the membrane distillation process does not require high temperatures, options that do not have solar concentrators are preferred due to the greater simplicity of installation and operation. Examples of collectors that do not include solar concentrators are solar ponds, flat-plate collectors, or evacuated-tube collectors.

4.1.1 Salt Gradient Solar Ponds (SGSP)

In a solar pond, thermal energy is stored through the retention of solar radiation incident on a volume of water, which in turn has a vertical gradient of salinity. One of the most significant advantages of this method for energy conversion is the low cost of construction and operation when compared to photovoltaic modules [216]. The difference in salinity divides the solar pond into distinct regions with specific characteristics and denominations, as shown in Figure 11.

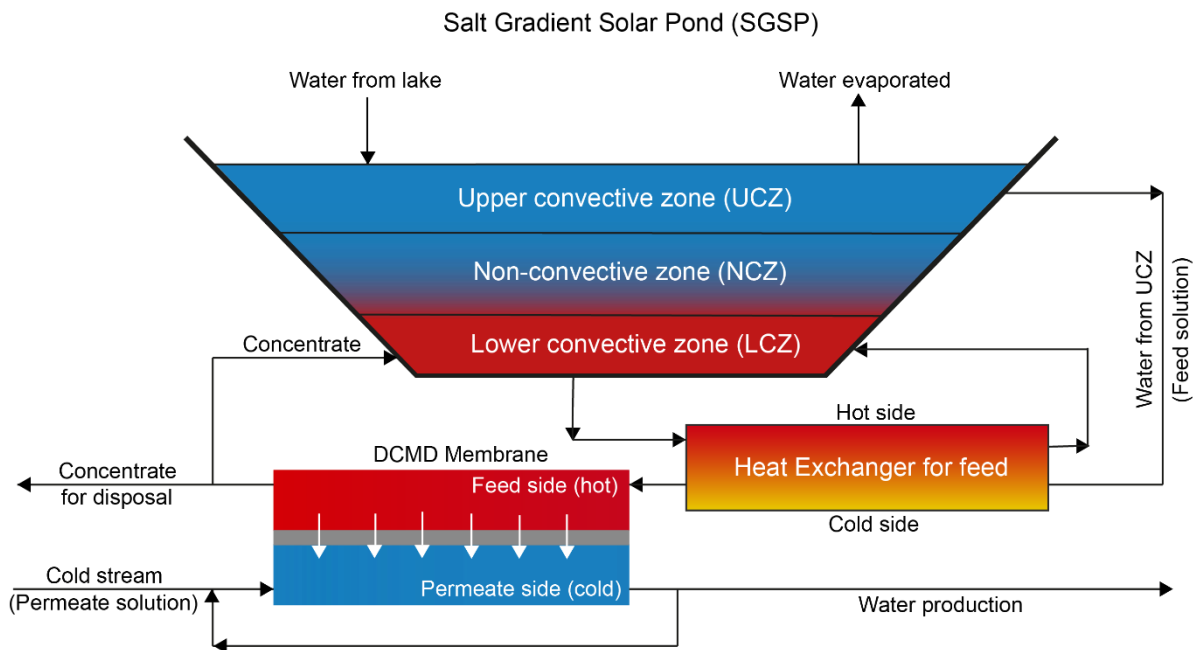


Figure 11. A DCMD module powered by an SGSP. Adapted from Suarez et al. [218].

The upper layer, close to the surface, is called the upper convective zone (UCZ), the middle layer is the non-convective zone (NCZ), and the deepest layer is known as the lower convective zone (LCZ). The salt saturation promoted in the deeper layers (LCZ) changes the convection dynamics, preventing the water from the bottom from rising to the surface due to the reduction in density, a consequence of the heating of a liquid. The retention of hot water at the bottom makes it possible to integrate the water from this region into a heat exchanger and use the thermal energy in other processes.

Suárez et al. [218] describes the integration between a direct contact membrane distillation system (DCMD) and saline gradient solar pond (SGSP) applied to desalination. His work indicates that approximately 70% of the energy extracted from the solar pond was used for thermal desalination, with half of this energy used to transport water through the membrane. The remaining energy was lost by conduction through the membrane, a heat loss characteristic of the direct contact configuration. In addition, 20% of the energy not used for the desalination process was lost in the plumbing system and by conduction through the heat exchanger, the feed storage, and other system components. This experience suggests the need to pay attention to the insulation of the plumbing system to reduce heat losses.

4.1.2 Flat Plate Collectors (FPCs) e Evacuated Tube collectors (ETCs)

A solar collector works as a heat exchanger, converting solar radiation into thermal energy. Two common configurations are flat plate collectors (FPCs) and evacuated tube collectors. The first one consists of an arrangement of tubes coupled to a flat plate with properties that favor solar rays absorption and their conversion into thermal energy (Figure 12a). The absorbed heat is then transferred to the fluid. According to Sakhaei and Valipour [219], the factors that interfere with the efficiency of FPCs are the thickness, the glass cover material, and coating, the absorption material, usually made of copper or aluminum, and the space between the absorption plate and glass cover adopted to reduce convection heat transfer between them.

As FPCs, evacuated tube collectors (ETCs) are also stationary solar collectors (Figure 12b). They have in their structure a vacuum region around the tubes through which the fluids pass, allowing a significant reduction of heat losses by conduction and convection, also providing an increase in thermal efficiency and the heating of the fluid to higher temperatures. A comparative study developed by Sandid (2021), addressing the integration of the vacuum membrane distillation module (AGMD) into the two types of solar collector technologies, showed favorable results for ETCs. The module integrated with the ETCs presented higher permeate fluxes and a cost 22.48% lower than the AGMD connected to the FPC system [219].

There are two ways to connect to the membrane distillation system: single-loop system and two-loop system, as illustrated in Figure 12c. In the single-loop system, the solar collector is directly connected to the membrane module, while in the two-loop system, two circulation paths are structured and connected by a heat exchanger.

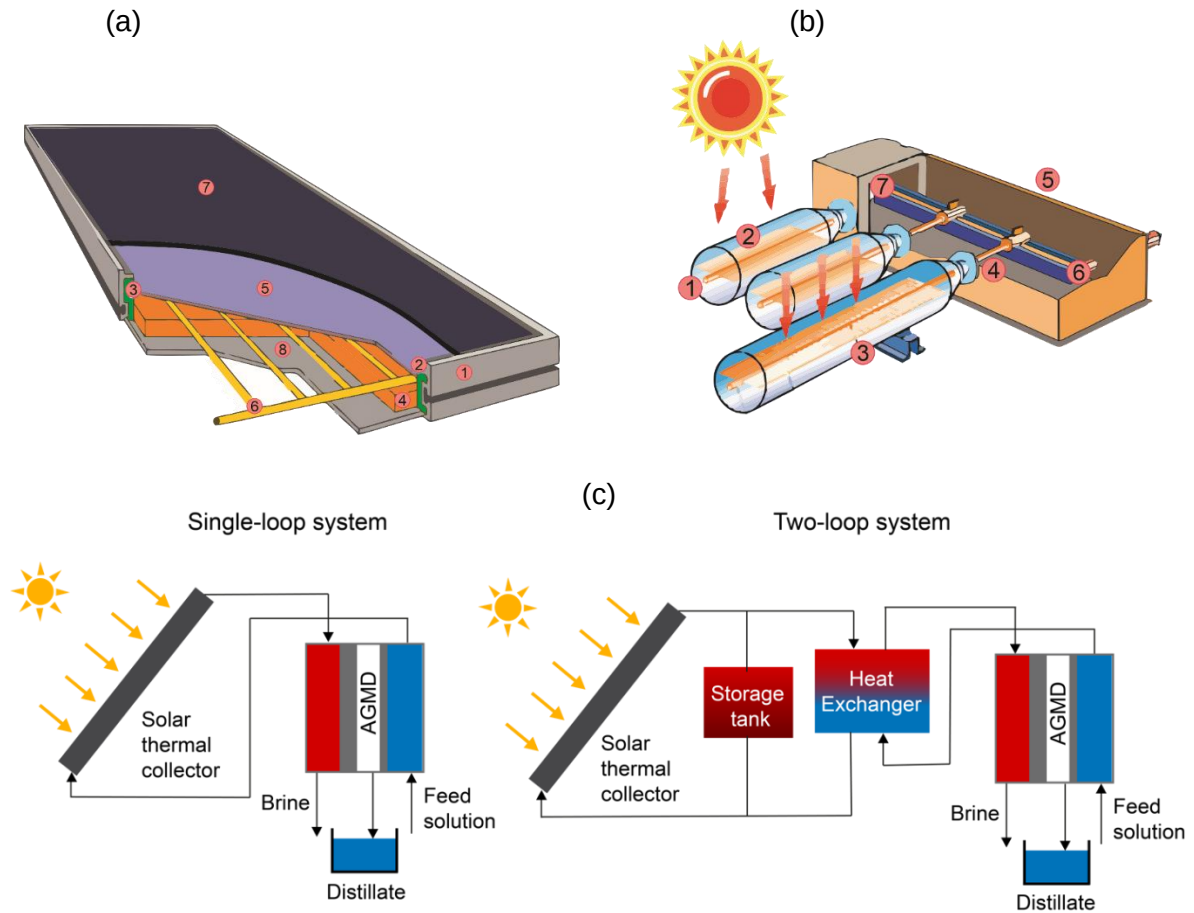


Figure 12. (a) Structure of a flat plate collector: 1. Aluminum frame, 2. Silicone seal, 3. Thermal sidewall insulation, 4. Thermal insulation, 5. Glass, 6. Aluminum or copper tubes, 7. Absorber, 8. Aluminum back. (b) Structure of an evacuated tube collector: 1. Heat pipe, 2. Absorber plate, 3. Individual evacuated tube, 4. Heat transfer, 5. Copper manifold (heat exchanger), 6. Cold water in, 7. Hot water out. (c) Single-loop solar-powered MD systems and two-loop systems Adapted from [218].

The single-loop system is indicated for compact systems with low thermal energy demand, since the flow and temperature of the feed can be adjusted more quickly, without causing relevant transition effects on the distillation process [218]. Another advantage is the possibility of entering the feed at higher temperatures [220], which impacts the transfer rate through the membrane. However, when applied to desalination, the single-loop system requires attention to the materials used, to avoid equipment corrosion, since the saline water is recirculated in the system [218].

In the two-loop system, the presence of the heat exchanger as an intermediary for the transfer of thermal energy reduces the maximum possible temperature, affecting the maximum potential of the driving force of the MD. However, it offers advantages in terms of extending the operating time for a few hours after the absence of the sun and reducing the risk of equipment corrosion in the case of desalination [220].

Apart from the advantages, solar-powered systems are subjected to solar radiation, which in turn impacts feed temperature, permeate flux, and energy efficiency. Figure 13 brings results related to the energy performance of a vacuum membrane distillation plant powered by solar energy. The data presented by Milad et al. [187] indicate that the energy performance of the process is strongly linked to solar irradiation. At greater solar irradiations, the greater the feed

temperature, the permeate flux, and the GOR. In contrast, the energy required to produce one cubic meter of water (specific energy consumption, SEC) decreases as the permeate flow increases. Apart from the variations observed, the authors conclude that as long as the VMD is coupled with solar energy, the process could be competitive with industrialized desalination technologies such as reverse osmosis, multistage flash, and multiple effect distillation. Moreover, changes in feed temperature seem not to impact the rejection efficiency of these systems as demonstrated by Shim et al. [221], and the energy supplied by solar radiation could represent up to 95.3% of the total energy required for feed heating in membrane distillation [221].

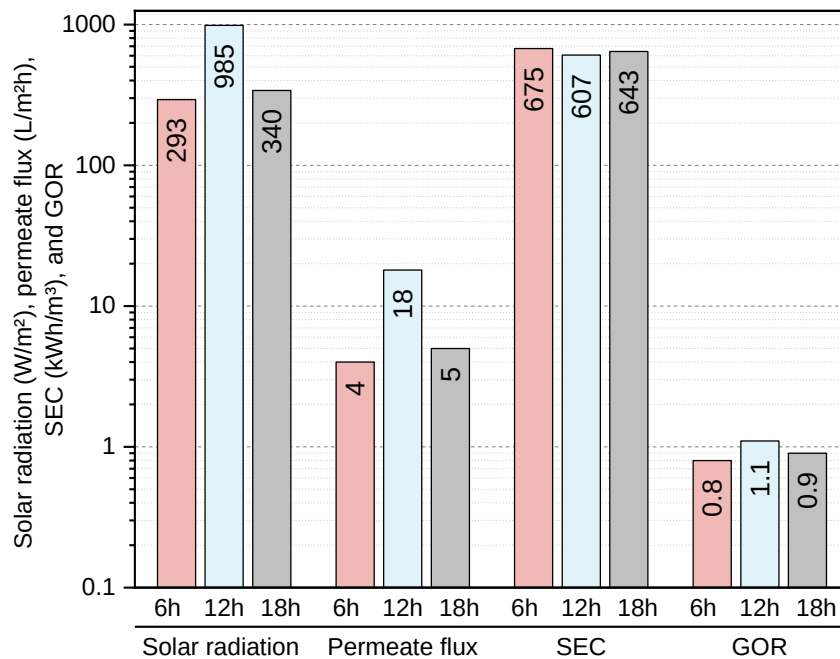


Figure 13. Variations on solar radiation, permeate flux, specific energy consumption (SEC), and gain-to-output ratio (GOR) in a solar-powered membrane distillation system used for seawater desalination. Data source: Miladi et al. [187]. Note: y-axis was presented in a log scale.

One concern while operating at different temperatures is wetting. The current literature suggests that wetting tends to occur at a higher feed temperature [222]. If wetting occurs, the membrane must be completely dried and cleaned before being used again. Mohammed et al. [223] describe some membrane recovery methods, such as drying, chemical cleaning, and backwashing. He et al. [224] reported the inefficiency of the cleaning method with distilled water and subsequent drying due to the deposition of salts inside the membrane, which causes irreversible changes in the structure [224]. The method pointed out by Mohammed that presented the best results in terms of wetting reversion was backwashing, in which the pressurized air causes the salts to be removed from the pores and by chemical or acid washing, by dissolving the salts responsible for the incrustation.

Other configurations of solar collectors include concentrated solar collectors, parabolic trough collectors, and dish collectors. They were summarized in Table 6 along with a comparison between them in terms of advantages and limitations when integrated with membrane distillation.

Table 6. Description and comparison between the advantages and limitations of different types of solar collectors commonly integrated with membrane distillation. References: [225]–[227]

Type of solar collector	Description	Advantages	Limitations
Flat-plate collectors	Most common type is used for air and water heating. Consist of a flat, insulated box, with a dark-colored absorber plate inside, covered with a transparent glass or plastic cover	Generally present lower costs compared with other collectors. They are easily installed and require minimal maintenance. They are capable to convert up to 80% of solar energy into heat	Limited temperature range (80 – 90 °C), lower efficiency in cold climates (especially below freezing temperatures), limited scalability, efficiency is reduced at high temperatures
Evacuated tube collectors:	Instead of a single absorber plate, they have multiple glass tubes, each containing an absorber plate	Due to an evacuated condition, the configuration has lower heat losses due to convection and conduction. Therefore, they are generally more efficient than flat-plate collectors (up to 90%). Better performance in cold climates, higher scalability, and more flexible installation	Costs are generally higher than flat-plate collectors, maintenance is more complex and it has a limited temperature range (80-90 °C). The system is subjected to vacuum failure, which can reduce its effectiveness and requires repair
Concentrated solar collectors:	Use mirrors or lenses to concentrate sunlight onto a small area, increasing the solar irradiation intensity	Lower operational costs, an interesting alternative for remote and off-grid locations	High initial costs and limited scalability, especially for larger-scale membrane distillation systems
Parabolic trough collectors	Use parabolic-shaped mirrors to concentrate sunlight onto a receiver tube running along the focal line of the mirror. The	Can achieve high temperatures (up to 400 °C) and convert up to 80% of solar energy into heat. Can be easily scaled up to larger sizes, making them suitable for	Costs are higher than flat-plate and evacuated tube collectors, and generally have a larger footprint which can limit their use in certain locations. Have limited

receiver tube contains a heat transfer fluid that absorbs the concentrated solar radiation and transfers it to the feed water for MD systems

larger MD systems. Can be designed with thermal storage systems, allowing them to store excess heat for use when sunlight is not available

flexibility as they require precise alignment with the sun. Requires periodic maintenance to ensure optimal performance

Dish
collectors

Similar to parabolic trough collectors, but use a dish-shaped mirror to concentrate sunlight onto a receiver located at the focal point of the dish

Can achieve high levels of efficiency (up to 30% of solar energy into electricity and over 80% of solar energy into heat), can achieve high temperatures (up to 1000 °C). Have a compact design, making them ideal for decentralized applications, and can be designed with thermal storage systems.

Are generally more expensive than other types, limited flexibility requires a precise alignment with the sun, and require periodic maintenance, including cleaning and inspection

4.2 Geothermal

The typical temperature range of geothermal sources is around 70°C to 90°C [228]. Variations with lower temperatures (40 - 70°C) can be integrated into desalination processes, such as membrane distillation, solar stills, or multi-effect distillation units, while sources with higher temperatures can be used for electricity generation. [228].

There are many opportunities to integrate geothermal energy sources into membrane distillation. For example, the treatment of geothermal fluids to reduce possible environmental impacts and the reuse of waste heat available in geothermal plants are among the ways of integrating the MD process with geothermal energy. One of the advantages is that this energy source has less intermittence when compared to other renewable energy sources, such as solar, as it does not depend on factors such as the weather or the seasons. In addition, if managed correctly, it can be an inexhaustible energy source.

One of the possible environmental impacts caused by geothermal plants is the contamination of the surface and groundwater by heavy metals found in thermal waters. The most common chemical species in geothermal fluids are B, SiO₂, NH₃, As, and noble gases. Other cations and anions are Cl⁻, K⁺, SO₄, Br⁻, F⁻, I⁻, HCO₃⁻, Na⁺, Li⁺, Ca²⁺, Mn²⁺, Cs⁺, Rb, Mg²⁺ and Fe²⁺ [229]. Regarding this problem, the high efficiency of membranes in promoting the separation of components, due to their hydrophobic property, represents an alternative for treating these thermal waters, reducing contamination rates. One of the reported separation procedures was developed by [229], in which the membrane distillation process (AGMD) was integrated with the waste heat source of a geothermal plant to remove boron present in geothermal fluids.

Gude [230] also suggests that some desalination processes benefit not only from using waste heat from plants as a source of thermal energy but also from the possibility of using the thermal water itself as a feed stream. The concept of thermal water as a heat transmission medium and feed stream was applied to the membrane distillation process and reported by some authors, such as [231] and [232]. Despite being favorable to the MD-Fluished bed crystallizer (FBC) integration for thermal water desalination, the results of the work developed by [231] indicate that only the sensible heat of geothermal wells is not enough to achieve high recovery values. Therefore, it is suggested that increased efficiency can be achieved by complementing the supply of thermal energy through solar heating sources or by integrating it with other membrane processes such as reverse osmosis [231].

[232] researched the application of vacuum membrane distillation (VMD) in the treatment of thermal water from a geothermal reservoir in Malaysia. The authors concluded that it is possible to treat water at levels suitable for consumption and found an energy saving equivalent to 95% by directly using water from the geothermal source.

To summarize, the advantages of considering geothermal energy sources include the potential to reduce energy consumption and increase process efficiency. Their constant temperature and high energy content can result in cost savings and environmental benefits as it departs from the use of conventional energy sources used to heat the feed stream. These sources are generally located near water resources, such as hot springs or geothermal wells, which can be used as feed for membrane distillation and eliminate the necessity for preheating [181].

On the other side, there is a direct limitation in carefully matching the temperature and quality of the waste heat source with the process requirements. If not compatible, additional heat transfer equipment or heat exchangers may be required, which can increase the capital and

operational costs. Geothermal waters are also generally corrosive and have greater potential to cause fouling and scaling on membrane distillation. The materials used and the configuration of membrane distillation systems must, therefore, withstand the corrosive effects of geothermal waters. Another limitation is the limited availability of geothermal energy sources, which may limit the potential for large-scale integration with membrane distillation. Geothermal energy sources are mainly found in specific regions and are not widely distributed, which may limit their use in areas where the MD process is required but geothermal energy is not readily available. Overall, the integration of geothermal energy sources with MD offers an opportunity for sustainable energy production, but careful consideration of the limitations and challenges must be taken into account during the design and operation of the membrane distillation system [181], [183].

4.3 Waste Heat

Waste heat is the heat produced by industrial machinery or processes, which is conventionally released into the environment. By employing waste heat to heat the feed solution during the membrane distillation process, the once misspent energy can be recovered and utilized to increase energy efficiency. Many industrial operations, including cooling circuits, gas turbines, boilers, and condensers, can be the source of waste heat and through the use of a heat exchanger, heat may be delivered to the input solution, which is then supplied into the membrane distillation modules to obtain pure water vapor [218]. In the case of desalination, possible sources are blow-down steam ejectors, blow-down boilers, dump condensers, or flue gas chambers [218].

[233] described the integration of DCMD, on a pilot scale, into boilers of the textile industry for wastewater treatment. In their case, the wastewater tank represented another source of waste heat, demonstrating the importance of analyzing the particularities and steps of each process to recognize the opportunities for integration. Another opportunity for waste heat reuse was presented by [5], [195], which assessed the potential of membrane distillation for reuse water reclamation from gold mining wastewater. In their case, the wastewater is continuously produced at temperatures around 210°C and cooled down to 60°C before being designated for its treatment. The authors still mentioned the opportunity to use process water as cooling water in the distillation process, reducing the operating costs from US\$ 2.62/m³ to US\$ 0.23/m³ [195]. Their results suggest that waste heat integration with membrane distillation has several benefits, including lower energy use and running costs, increased process efficiency, and lower greenhouse gas emissions. Nevertheless, this integration does have some restrictions, namely the intermittent nature and temperature variation of the waste heat source, which can impair the effectiveness of the membrane distillation. To ensure a steady and effective operation of these systems, it is crucial to examine the waste heat source's properties and establish suitable heat storage solutions.

That was an aspect emphasized by Gustafson et al. [234] when analyzing the use of waste heat for feed heating. The authors pointed out the importance of considering the intermittence and temperature variation inherent to this energy source as the temperature variation interfered in membrane permeate flux. Due to the intermittence and a possible absence of energy supply for some periods, the integration generally demands more complex control measures, being required heat storage strategies to supply the periods when the source is not in operation [235].

With that in mind, Gustafson et al. [234] describe two integration proposals with their respective operational results. The first configuration is direct or single-loop integration, in which the heat

exchanger associated with the thermal energy source is positioned between the supply tank and the membrane module, as shown in Figure 14a. The second configuration features two circuits, described as indirect or two-loop, in which the heat exchanger is positioned in a separate circuit, heating the feed tank volume independently of the tank-membrane circulation (Figure 14b) [235].

The direct configuration achieves higher fluxes through the membrane when using a low-intermittency waste heat source due to the higher supply temperature in the MD module. However, the indirect configuration is more indicated when the thermal energy source has a high intermittency rate, due to the heat retention capacity of the feed tank. Therefore, under the same conditions, it permits a greater distillate flux, in a more predictable way than the direct configuration. Analyzing the waste heat source intermittency becomes an important variable when designing the integration of the membrane distillation system to consider the cost-benefit relationship between the predictability and stability of the system, costs, and efficiency.

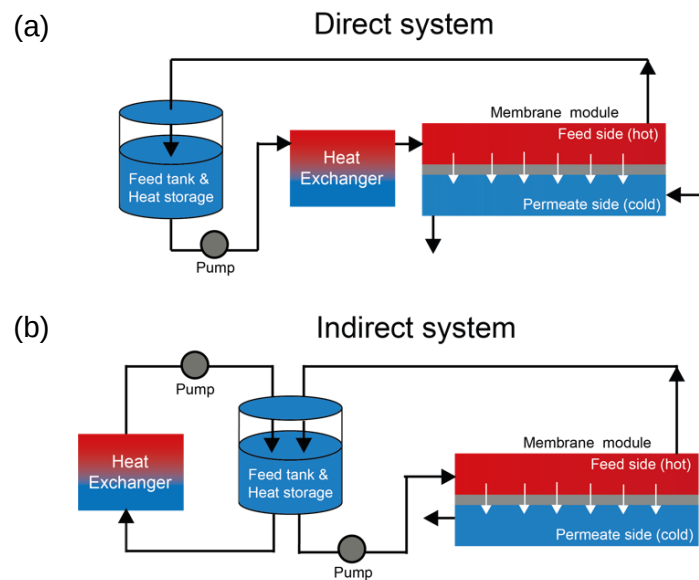


Figure 14. (a) Direct and (b) indirect system arrangements. Adapted from [236]

Possibilities for waste heat integration with membrane distillation can reduce energy consumption and boost process efficiency. Lowering greenhouse gas emissions and conserving natural resources, can lead to financial savings and environmental advantages as well. However, integrating waste heat with membrane distillation has drawbacks and it is not a pushover task. Additionally to the intermittence previously mentioned, it is necessary to properly match the process's requirements with the temperature and quality of the waste heat source. If the waste heat source cannot be used, additional heat exchangers or heat transfer devices may be needed, which may raise capital and operating expenses. Another drawback is that some waste heat sources are intermittent and variable, which might impair the performance and stability of membrane distillation systems [234], [237]. The utilization of waste heat may potentially introduce pollutants or impurities into the system, which could impair the performance of the membrane and cause fouling or other problems. To overcome these difficulties, the system may need to be carefully monitored and maintained. Thus, even though waste heat integration with MD has the potential to have considerable advantages, it is crucial to properly evaluate the waste heat source's compatibility and to design and run the system to reduce any potential damage [237]–[239].

5 Opportunities to improve energy efficiency in membrane distillation

In the membrane distillation process, thermal energy consumption is one of the main limitations pointed out for the scaling up of the technology. From an economic perspective, there is a trade-off between productivity and energy consumption since higher distillate fluxes are obtained at higher temperatures. The economic feasibility analysis shows that the energy cost and the modules investment represent more than 80% of the total cost of the system (Figure 15). If not integrated into alternative energy sources, the costs associated with membrane distillation make it less attractive compared to the already consolidated separation methods [240]. The fact is also seen when the costs for membrane distillation are compared with costs for classic membrane separation processes treating the same wastewater. The total costs reported by Amaral et al. [241] for an integrated process comprised of ultrafiltration, nanofiltration, and reverse osmosis were estimated at US\$ 1.130, which despite the integration of different units was still lower than those reported by [195] for membrane distillation when residual heat is not considered (US\$ 2.62/m³). A direct comparison between membrane distillation and nanofiltration was made by [6], [242], in their case treating wastewater produced at high temperatures. The necessity to adjust the wastewater temperature to attain the limitation of nanofiltration (<40°) implies additional cooling costs that make membrane distillation economically more attractive (a process that would be favored by the wastewater residual heat). That does not diminish the fact that improvements in membranes and modules are still required to reduce the total operating cost of membrane distillation. As demonstrated by [243], the membrane replacement costs can represent the major contributions to the total OPEX, a fact not necessarily observed in classical pressure-driven membranes.

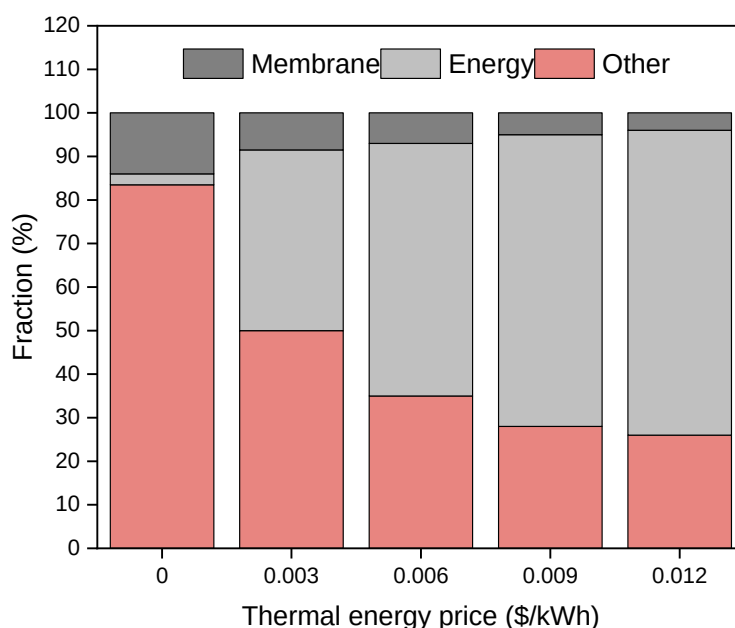


Figure 15: Breakdown of desalination cost under different thermal energy costs with a feed flow rate of 1.5 LPM, a cooling water flow rate of 25 LPM, a hot water temperature of 70 °C, and a cooling water temperature of 25 °C. The relative contributions of membrane and energy cost are subjected to the change in thermal energy price. The integration with renewable energy as waste heat is represented in the first column, in which thermal energy is free (in this case, membrane cost represents more than 80% of the total). Adapted from [244].

Based on the bibliographic research carried out for this work, it was possible to identify some of the main limitations of membrane distillation reported in experiments on a bench, pilot, and

full scale (**Figure 16**). Most studies seek to find the ideal recirculation flow rate, feed temperature, and module configuration to obtain the highest distillate flux. However, it becomes evident the necessity of alternative heat sources given that energy-related issues were the most recurrent limitations reported. In this sense, integration with renewable energy sources represents one of the leading solutions for energy consumption, proving to be a decisive choice for the economic viability of the system, especially in the case of the integration of solar energy and the use of waste heat.

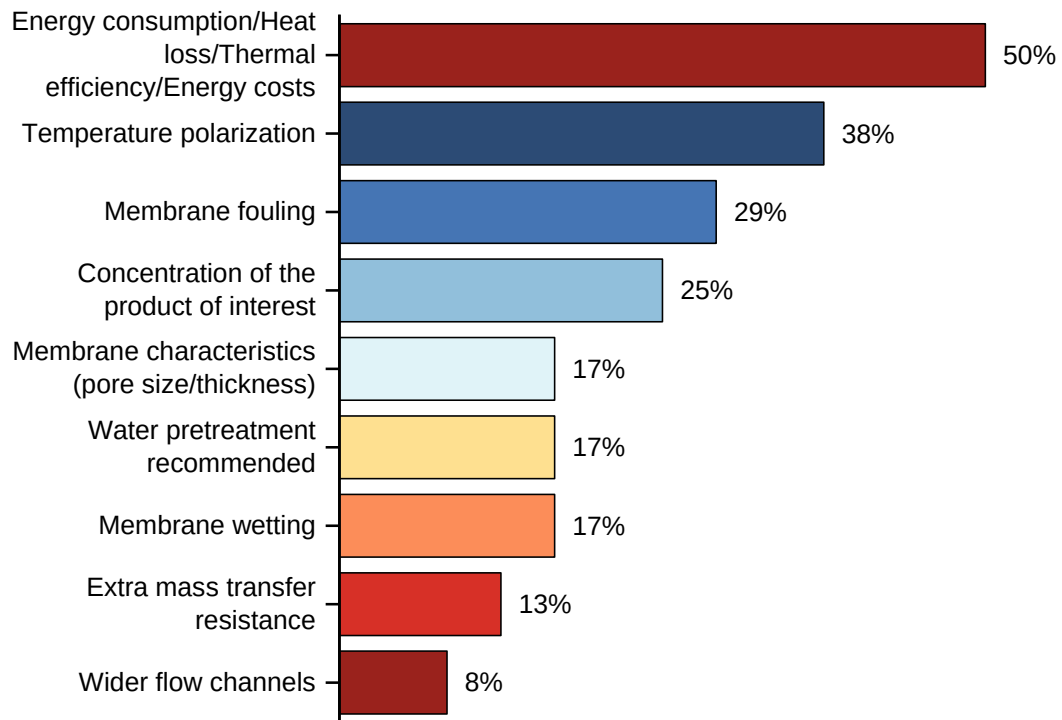


Figure 16. Main limitations reported in membrane distillation integrated with renewable energy sources and waste heat.

Several studies are being developed to improve energy efficiency, aiming to overcome the variations in solar intensity and waste heat intermittence. Regarding renewable sources fluctuation, storage tanks can increase the module's operation period. New proposals for heating are also being tested, integrating the heating source close to the membrane interface. Among these methods are photothermal, electrothermal, microwave, and induction. These methods promote a reduction in the temperature polarization, allow the reduction of heat losses from the storage tank, as well as the transport of the feed through the pipeline to the distillation module [245], and allow an improvement of the results in low flow rates as the heating exposure time is increased.

In parallel with the MD improvements, there are several studies to increase the efficiency of the energy sources themselves, such as the use of nanofluids in the case of solar collectors [246] and improvements to solar ponds, such as evaporation suppression, large-scale numerical simulation, and connection of solar ponds in series [247].

At the current development stage of membrane distillation, thermal efficiency has not yet reached technological maturity and economic viability for large-scale application. However, this scenario allows us to draw a parallel to the development of photovoltaic solar energy in

the last 50 years - a technology known for focusing research on increasing energy efficiency. The expansion of solar energy was due to technical, economic, and environmental factors. Photovoltaic module technology has significantly improved conversion rates, from 15% in 1950 to 28% in 2013 [248]. Though most commercial panels remained between this efficiency, researchers have recently developed photovoltaic cells with efficiencies approaching 50% [249].

However, despite the technical improvement, economic movements were necessary to consolidate its diffusion, such as the cheapening of the components produced on a large scale, as well as the creation of public policies, exemplified by countries such as Brazil, India, Malaysia, Taiwan, Korea, Thailand [248]. In Brazil, for example, the possibility of integrating microgeneration systems in centralized energy distribution encouraged solar expansion due to higher reliability and supply flexibility. Finally, the environmental demand to replace energy matrices based on fossil fuels with low greenhouse gas emission sources has placed solar energy among the primary candidates.

Alternative heating procedures for the feed stream are being sought to improve the efficiency of the membrane distillation process in terms of energy consumption. These techniques focus on heating the surface of the membrane, the region close to it, or the space between the feed and the permeate, reducing temperature polarization and increasing recovery rates [250]. This local heating also allows the reduction of heat losses from the storage tank, as well as the transport of the feed through the pipeline to the distillation module [245]. Some of these methods are photothermal, electrothermal, microwave, and induction heating.

5.1 Photothermal heating

The photothermal effect is a type of photoactivation based on the non-radiative conversion of electromagnetic energy, which increases an object's temperature [251]. This phenomenon is generally addressed in developing devices for converting solar energy into thermal energy. Therefore, one of the fields of improvement focuses on developing materials that increase this conversion rate. According to Wu et al. [251], photothermal materials can be divided into four categories: 1) metallic nanostructures, 2) inorganic semiconductor materials, 3) carbon-based light-absorbing materials, and 4) polymeric materials [251].

The integration of this method into the membrane distillation process can be done by incorporating these photothermal materials into the module structure, close to the feed surface. The intention is to adopt a method of energy absorption that is more efficient than the absorption through a convective fluid and closer to the membrane interface, reducing heat losses [252]

There are variations in the way these photothermal materials are incorporated into the membrane, classified by Gao et al. [253] as 1) Embedding configuration (Figure 17a); 2) Bilayer configuration (Figure 17b); 3) Isolation (Figure 17c) configuration. In the first, the materials are mixed in the membrane structure, while in the second, photothermal material and membrane are incorporated in a dual-layer module. In the third example, in which the photothermal layer and membrane are separated, heat is transferred to the membrane interface through the feed [253].

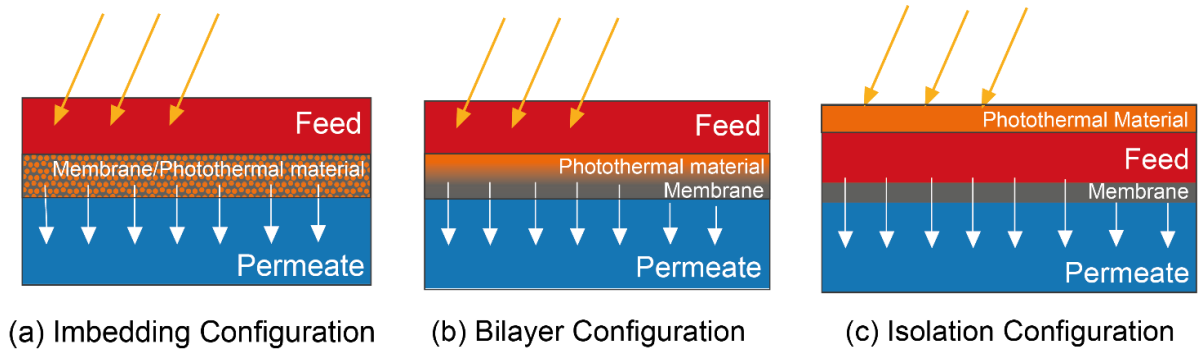


Figure 17: Photothermal membrane distillation arrangements. Modified from [254]

In the conventional MD mode, the feed is heated externally and is then transferred to the membrane distillation module (Figure 18). This transport represents a drop in the temperature of the feed due to heat losses, making the process scaling more complex, as it requires an increase in the feed flow to compensate for the drop in temperature and consequent reduction in the permeate flow. In photothermal heating, the conversion is independent of the size of the system, and the permeate flux is even benefited from the increase in the dimensions of the system [255]. In addition, unlike the conventional MD method, the photothermal membrane distillation process presents better results at lower feed flow rates by increasing the exposure time to the heating source.

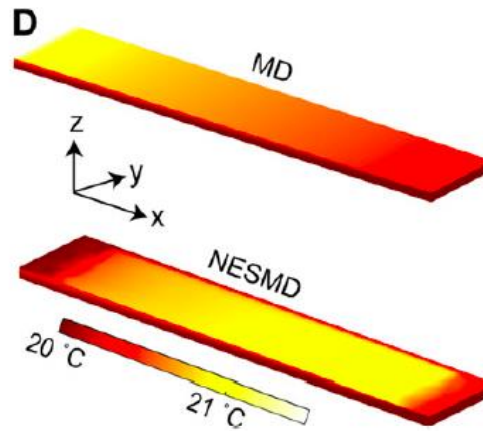


Figure 18: Calculated temperature distributions at the membrane surface for MD (Top) and Nanophotonics-enabled solar membrane distillation - NESMD (Bottom). Adapted from [255].

Applications found in the literature, such as those developed by Li et al. (2020) and Huang et al. (2018), demonstrate that, in addition to achieving an increase in the flow rate through the membrane, there was a reduction in energy consumption through the adoption of photothermal heating. However, Wu et al. [251] suggest that, for applications such as desalination, it is necessary to take into account the properties of the photothermal material adopted, such as stability, corrosion resistance, anti-fouling ability, cost, long-term durability, and possible environmental impacts generated by degradation of the photothermal material. In addition, Dongare et al. [252] suggest integrating heat recovery systems in the feed circulation to improve the process.

5.2 Electrothermal heating/Joule heating

The principle of electrothermal heating is the phenomenon known as the Joule effect, which explains the conversion of electrical energy into thermal energy. When an electric current passes through a conductor, the collisions between the electrons in the current and the atoms that constitute the body cause the system's temperature to increase. The amount of heat generated depends on the current's intensity and the body's electrical resistance.

In the case of MD, this heating method can be incorporated directly into the polymer matrix that constitutes the membrane or can be implemented close to its surface [252]. The main materials used are graphene and carbon nanotubes (CNTs) [256]. The demand for high-quality electrical energy is one of the disadvantages of the electrothermal heating process. This demand can be minimized by combining heating sources, such as using waste heat in the feed tank [256].

Another point reported is the use of electrothermal heating in ionizable environments, such as water, which can cause material degradation. Ways to prevent this degradation are reported, by increasing the frequency of alternating current or changing the position of the photothermal material in the system, so that it is not in direct contact with the external environment [257].

5.3 Microwave heating

When a dielectric material is placed in a microwave field, dipoles are formed, which develop an orientation polarization and change directions at high frequencies. The lag between dipole orientation and the electric field leads to dielectric loss and heat generation [257]. The increase in vibration generated by microwave irradiation favors its application to the MD process by promoting an increase in molecular mobility and an increase in vapor flux through the membrane. In addition, it presents non-thermal effects that contribute to the increase of this flux, such as reducing the activation energy of physical and chemical processes, breaking hydrogen bonds in aqueous environments, and generating nanobubbles at temperatures below boiling [257].

The microwave-induced membrane distillation (MIMD) process to desalination was reported by Roy et al. [257], in which the feed passed through a microwave heater before entering the MD module (Figure 19). As a result, steam flow increased at lower temperatures, higher flow rates, and high saline concentration. Compared to conventional heating methods, energy savings of up to 22% were found using MIMD at low temperatures [257].

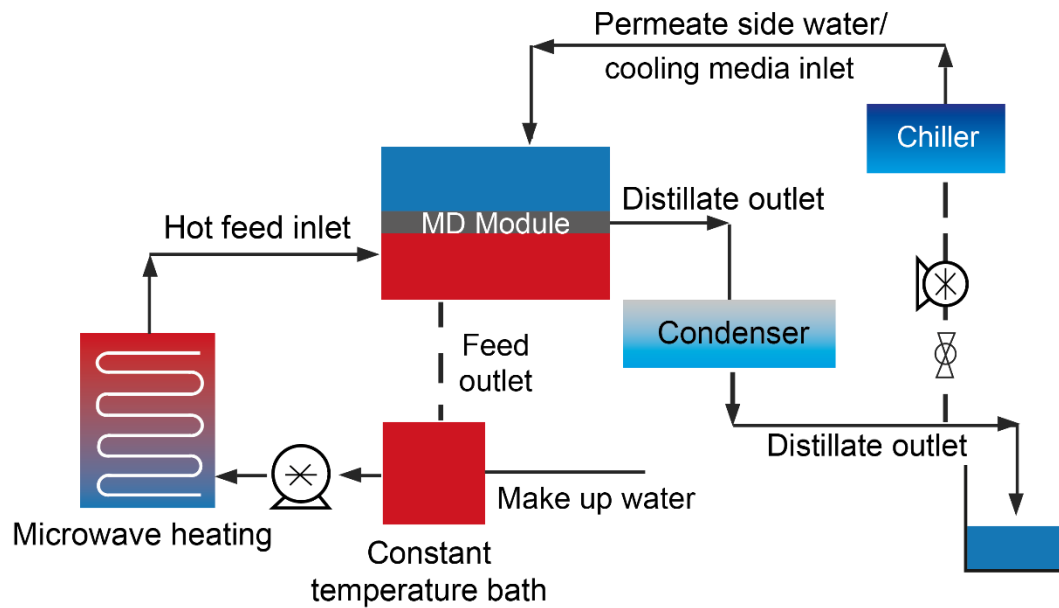


Figure 19: Microwave heating setup. Adapted from [258]

Ji et al. [259] also observed the increase in the mass transfer of the vacuum membrane distillation (VMD) process integrated with microwave heating but also drew attention to another common phenomenon in MD: the crystallization of inorganic salts. It found that MIMD does not contribute to membrane fouling and presents different behaviors regarding sodium chloride or calcium carbonate. For sodium chloride, microwave irradiation decreases the number of crystals deposited on the membrane surface, while the total deposition remains constant and the crystal size distribution becomes more uniform. As for calcium carbonate, microwave irradiation increases the total deposition and the total number of particles and induces crystal growth [259].

5.4 Induction heating

Another heating method used in the industry for smelting metals, which has also been applied in the domestic context and the membrane distillation process, is heating by electromagnetic induction (Figure 20). Applying a high-frequency alternating current to a coil makes it possible to create an alternating electromagnetic field capable of generating a non-contact, directed heating system. This heating is caused by two physical phenomena: eddy currents and magnetic hysteresis. Eddy currents are caused by exposing a body to a magnetic field and are responsible for heating the object through the Joule effect. Magnetic hysteresis is the tendency of ferromagnetic materials to retain their acquired magnetic properties and contributes to body heating.

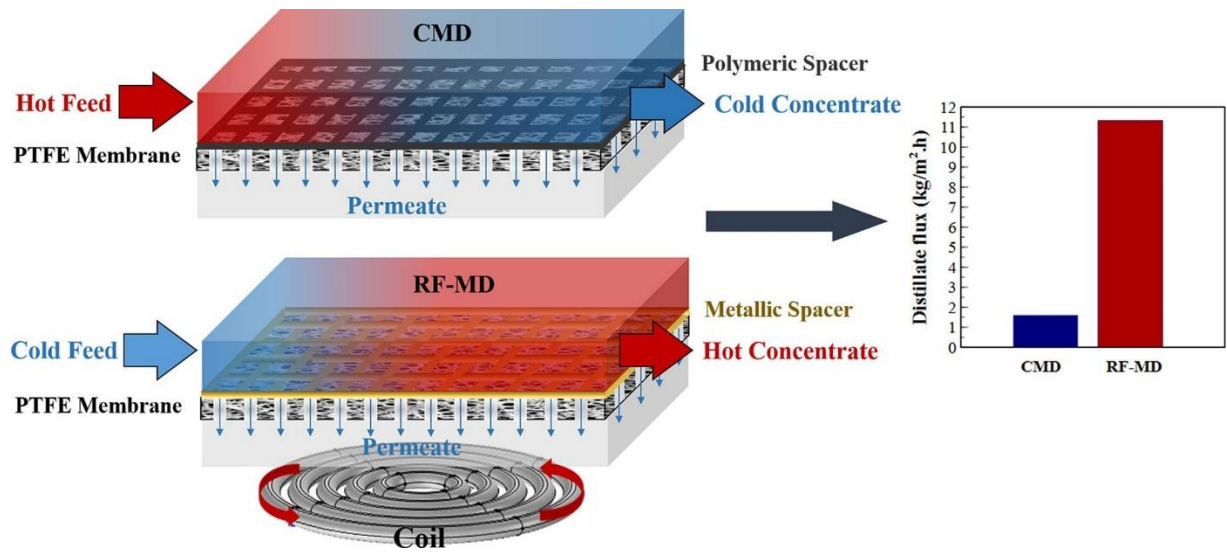


Figure 20: Comparison between Conventional membrane distillation (CMD) and Induced radio-frequency MD (RF-MD). Reproduced from [260]

This heating method was described by Anvari et al. [261] through the incorporation of hydrophilic magnetic iron oxide nanoparticles (FeNPs) into carbon nanotubes (CNT) to a double-layer vacuum membrane (VMD). Compared to traditional heating processes applied to MD, in which better permeate flux results are obtained when higher flow rates are applied, the opposite was observed for the induction heating method. In this case, lower flow rates allowed a longer exposure time to the heating source, causing the permeate flux to be higher due to the contribution of the temperature increase to the permeate flux.

Anvari et al. [261] also reported another factor that impacts the heating and consequently the permeate flux: the thickness of the Fe-CNT layer. A thicker layer resulted in higher heating, resulting in higher permeate fluxes. In addition, a reduction in energy consumption was observed, partly due to the reduction of heat losses caused by temperature polarization and higher permeate fluxes in the treatment of highly saline solutions.

CHAPTER 4 – ONE-STEP RECYCLING OF MINERAL ACID FROM CONCENTRATED GOLD MINING WASTEWATER BY HIGH-TEMPERATURE LIQUID–LIQUID EXTRACTION

Complete articles published in journals:

[1] **Moreira, V. R.**, ..., & Amaral, M. C. S. (2022). One-step recycling of mineral acid from concentrated gold mining wastewater by high-temperature liquid–liquid extraction. *Separation and Purification Technology*, 286, 120447.

1 Introduction

In previous research [5], approximately 34% of high-quality water was recovered from the wastewater produced after POX by membrane distillation (MD). The process achieved rejections greater than 95.7% of inorganic species and 99.9% rejection of mineral acid, which constituted a concentrated stream. One possibility is the recovery of sulfuric acid (H_2SO_4) by solvent extraction techniques. If recovered, sulfuric acid might represent savings for the gold beneficiation plant or additional income from its commercialization. Before the POX circuit, H_2SO_4 is added to the slurry to lower the levels of carbonate below 2 %; otherwise, an excessive amount of CO_2 (a greenhouse gas associated with climate changes) would be produced along with pressure oxidation [262]. The presence of carbonaceous matter is still responsible to adsorb the gold cyanide complex, thus reducing its recovery in a cyanide-based process [263]. Withal, H_2SO_4 is also an important commodity for the chemical and pharmaceutical industries, which market is expected to grow in the next years according to the forecasts made by Mordor Intelligence [264].

Recently, Kesieme et al. [265] reviewed the efficiency of four different extractants applied to hydrochloric, sulfuric, and nitric acid recovery from acidic mining waste solutions. From all of them, Alamine 336, Cyanex 923, and tris-2-ethyl hexyl amine (TEHA) were chosen to be investigated for sulfuric acid recovery from concentrated gold mining wastewater in the current study due to their greater efficiency for acid extraction and stripping. Aliquat 336 and Versatic acid were chosen for similar reasons based on previous research [22], [266].

Despite their efficiency for acidic solutions, selectivity and recovery performance might be affected while dealing with concentrated solutions, in which not only acid but impurities are present at higher concentrations as well. In this chapter, the decision for the most appropriate extractant considered both extraction and stripping efficiencies. The distribution coefficients and selectivity were considered as well. In complement to the decision variables previously mentioned, a preliminary economic analysis was made to estimate the costs for sulfuric acid obtainment by solvent extraction (US\$/kg H_2SO_4 recovered). By that, we hope to extend the applicability of solvent extraction to sulfuric acid recovery from concentrated gold mining wastewater.

2 Materials and methods

2.1 Wastewater sampling and MD concentrate

POX wastewater was sampled in a local mining site (Minas Gerais, Brazil), stored at 4°C after being collected, and brought to room temperature before being concentrated by MD. The experiments considered a PTFE membrane with a spacer, a feed, and a distillate temperature of 60 and 25 °C, both recirculated at 0.3 L/min. The process achieved an average distillate flux of 6.82 L/m²h and a recovery rate of 33.9%, without compromising the distillate physicochemical quality (acid retention: >99.9% and metals retention: >99.5%) [5]. The physicochemical characteristics of raw wastewater and the concentrate obtained after MD were presented in Table 7. All characterization procedures followed the recommendations described in the Standard Methods for the Examination of Water and Wastewater [267].

Table 7. Physicochemical characteristics of POX wastewater and MD concentrate.

Physicochemical characteristics	POX wastewater	MD rejection efficiency (%)	MD concentrate
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pH	1.37 ± 0.27	-	1.10 ± 0.11
Conductivity (mS/cm)	16.8 ± 1.7	99.8	39.4 ± 5.4
Acid (mol/L)	0.072 ± 0.008	>99.9	0.079 ± 0.008
Iron (mg/L)	829.2 ± 21.3	99.8	1541.0 ± 45.3
Zinc (mg/L)	37.6 ± 0.12	99.6	112.0 ± 1.7
Aluminum (mg/L)	484.7 ± 15.0	99.6	950.0 ± 21.8
Copper (mg/L)	171.6 ± 7.1	99.6	285.0 ± 6.0
Magnesium (mg/L)	2662.1 ± 101.9	99.9	5324.2 ± 248.6
Nickel (mg/L)	169.3 ± 2.4	>99.9	370.2 ± 40.6
Cobalt (mg/L)	33.1 ± 0.8	>99.5	66.1 ± 1.9

2.2 Solvent extraction

The five extractants (Alamine 336, Aliquat 336, Cyanex 923, TEHA, and Versatic Acid) were preferably diluted in kerosene (30 vol.%; provided by Dinamica® and used without further purification) and were used as the organic phase in the extraction experiments. In cases where the emulsion was observed, 1-decanol (30 vol.% provided by Fisher Scientific and used without further purification) was used as diluent. Their description and physicochemical characteristics are presented in Table 8.

Table 8. Characteristics of the extractants used for sulfuric acid recovery from MD concentrate.
Reference: [268].

Name	Application	Formula	Density (g/cm ³)	Molecular weight (g/mol)	Melting point (°C)	Boiling point (°C)	Composition (mol/L)
Alamine 336	Used as a phase transfer catalyst and metal extraction reagent	C ₂₅ H ₅₇ N	0.800	353.67	< -20	381	0.74
Aliquat 336	Used as a phase transfer catalyst and metal extraction reagent	C ₂₅ H ₅₄ ClN	0.884	404.16	-20	225	0.72
Cyanex 923	Applications in the solvent extraction recovery of inorganic solutes from aqueous solution	C ₄₂ H ₉₀ O ₂ P ₂	0.880	689.11	-	201 - 202	0.42
Versatic	It is an intermediate in the manufacture of a variety of products, which typically show	R=C ₃ H ₄ O ₂ (R represents alkyl groups)	0.910	174.00	-	243	1.23

		excellent hydrolytic stability and resistance to various chemical					
		Intermediate used in the production of Paint industry and Powder coatings					
TEHA	Tris-(2-ethylhexyl)amine	C ₂₄ H ₅₁ N	0.817	353.7	-46	204	0.762

Both aqueous (17 mL) and organic (33 mL) phases were kept in contact (stirring speed: 300 rpm) in a glass reactor vessel with an organic-to-aqueous ratio of 2:1 for 10 min. The phases were left to settle for 15 minutes and the raffinate was collected for characterization. During the experiments, no organic phase loss was observed which allowed us to estimate its composition by a mass balance. The extraction efficiency was assessed under different temperatures (60 °C, corresponding to the MD concentrate outlet temperature, and ambient temperature – 30 °C).

Analyses of Fourier-transform infrared spectroscopy (FTIR; Shimadzu IRAffinity-1) were made for novel and loaded organic phases in the region of 650–4000 cm⁻¹ with a resolution of 4 scans per second and a total of 20 scans.

The distribution coefficient (D_M) and the selectivity (β_{M_1/M_2}) were estimated by Equations 21 - 22 and were used as response variables related to selectivity. The variables M_{org} (mg/L) and M_{aq} (mg/L) refers to a given compound concentration in the organic and aqueous phases. Selectivity values greater than one suggest that the extraction is possible and it is associated with an organic phase enriched in the compound M_1 , while selectivity values equal to one suggest that extraction is not possible.

$$D_M = [M_{org}]/[M_{aq}] \quad (21)$$

$$\beta_{M_1/M_2} = [D_{M1}]/[D_{M2}] \quad (22)$$

2.3 Organic phase stripping and regeneration

The extracts obtained after solvent extraction were stripped with hot water (60°C; 66 mL). Both aqueous and organic phases were kept in contact (stirring speed: 300 rpm) in a glass reactor vessel with an organic-to-aqueous ratio of 1:2 for 10 min. The phases were left to settle for 15 minutes and the raffinate was collected for characterization. Similarly, the organic phase composition was possible to be determined by mass balance since no organic phase loss was observed. Considering that metals could have been co-extracted, the organic phase was subjected to an additional regeneration procedure using an acid solution (H₂SO₄, 1 mol/L) at similar conditions described for stripping. A summary of the experimental conditions and apparatus used is presented in Figure 21.

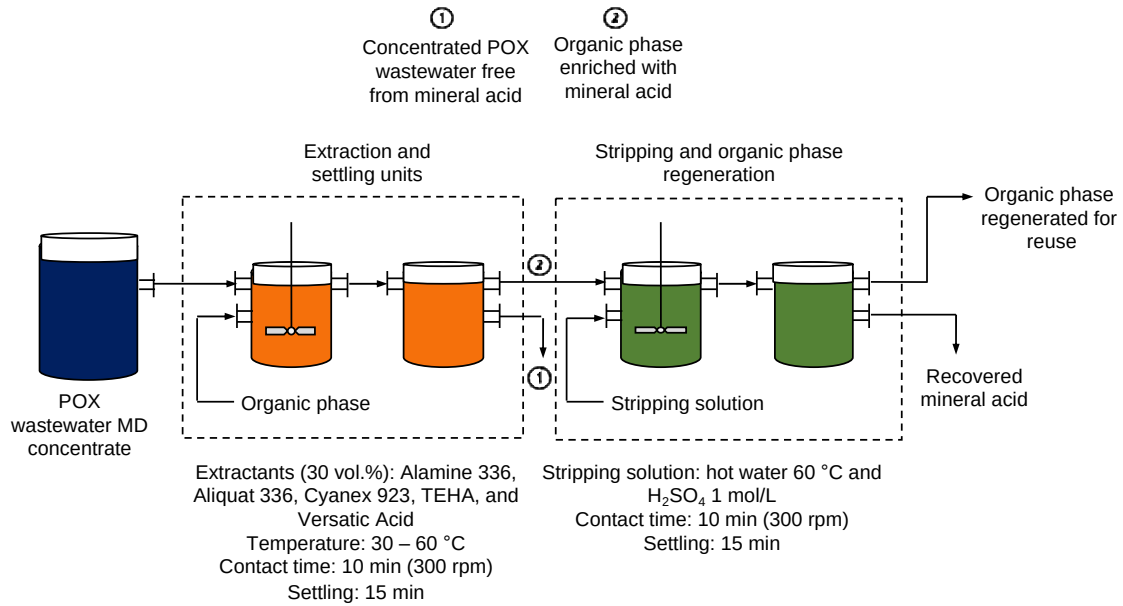


Figure 21. Diagram and experimental conditions for extraction, stripping, and organic phase regeneration.

2.4 Preliminary economic analysis

The capital (CAPEX) and operational (OPEX) costs were estimated considering a wastewater flow rate of 60 m³/h (an average value in which POX wastewater is produced by the local mining site [5]). Equipment costs (C_b) were estimated by Equation 23 along with the respective base variable (S_a), bare module cost (C_a , which accounts for direct and indirect costs associated with equipment purchase and installation) and a factor exponent (n) (Table 9). The costs were updated considering the chemical engineering plant cost index (CEPCI) for 2020 (569.2) and the base year. The amortization costs (AC_f) was calculated by annualizing the capital cost (C_{CapEX}), as shown in Equation 24, where i_r is the investment rate (6.5%) and l the project lifespan (15 years). The maintenance rate was defined as 5% of the capital costs.

$$C_b = C_a(S_b/S_a)^n \quad (23)$$

$$AC_f = C_{CapEX}\{i_r/[1 - (1 + i_r)^{-ls}]\} \quad (24)$$

A replenishment interval of 5 years was considered for the organic phase. This cost, in addition to those related to the extractants, stripping solution, energy for pumps and propellers (efficiency considered: 0.85), amortization, and maintenance were summed up and considered as OPEX, which was normalized by the amount of mineral acid recovered (US\$/kg_{H₂SO₄}).

Table 9. Expenditures considered for capital costs (CAPEX) and operational costs (OPEX) estimation.

*[269], **Values were based on the Chemicals Market Report provided by the Independent Commodity Intelligence Service (ICIS) [270].

Equipment Description for CapEX estimation	Base variable (S_a)	Bare module cost (US\$; C_a)	n^*	CEPCI (base year)	Real variable (S_b)
Floating Head Carbon Steel (m ³) (two units in total)	90	63,524.00	0.6	567.5	120
Propeller (kW) (two units in total)	10	58,384.00	0.5		10

Floating Head Carbon Steel (m ³) (two units in total)	90	63,524.00	0.6	160
Centrifugal, stainless steel shaft power (kW) (four units in total)	1	15,345.00	0.7	1

Chemicals and utilities considered for OPEX estimation	Value**
Alamine 336 (US\$/kg)	7.00
Aliquat 336 (US\$/kg)	10.00
Cyanex 923 (US\$/kg)	5.00
TEHA (US\$/kg)	4.00
Versatic Acid (US\$/kg)	4.00
Kerosene (US\$/kg)	0.71
1-Decanol (US\$/kg)	2.41
Sulfuric acid (US\$/kg)	1.14
Hot water for stripping (US\$/m ³)	0.63
Energy (US\$/kWh)	0.04

2.5 Statistical and data analysis

Microsoft Excel and OriginPro were used for statistical and data analysis. Although the results had a trend for a normal distribution, verified by the Shapiro-Wilk's test and Levene's test for homogeneity, Mann-Whitney U Test was preferred for comparison between two independent groups and correlation, respectively. A confidence level of 95% was set for all statistical analyses performed.

3 Results and discussions

3.1 Solvent extraction

The results for extraction efficiency are presented in Figure 22a, which were classified between low (<50%), satisfactory (50-70%), and high (>70%) values of recovery efficiency. The lowest extraction efficiency was observed for Cyanex 923, although still considered a satisfactory result ($52.4 \pm 0.7\%$) given the physicochemical complexity that MD concentrate presents. Versatic acid, TEHA (diluted in kerosene), and Alamine 336 presented extraction efficiencies greater than 70%.

Cyanex 923 is a commercial mixture of phosphines and extracts the mineral acid mainly by solvation of the neutral species. For that, most water molecules that involve the acid species should be replaced by the extractant, and soluble complexes are formed in the organic phase [271]. That is a complex mechanism, apart from the fact that most H₂SO₄ would be dissociated and not in its neutral form. For that reason, the extractant presented lower efficiency compared with others which enabled a higher extraction rate.

The mechanism related to amine-based extractants (Alamine 336 and Aliquat 336) involves an ion-pair formation since, in general, both amine and the anion of the extracted acid have similar basicities [272]. Anion exchange, H-bond formation, and solvation may occur as well. For experiments using TEHA, for example, extraction seems to be mostly controlled by H-

bonding and solvation and/or undissociated acid molecules [272]. For Versatic Acid, a neutral complex may form via anion exchange principles. To a lower extent, sulfuric acid extraction by Versatic Acid and Aliquat could be a result of ion-exchange mechanisms as well. These mechanisms were summarized in Figure 23.

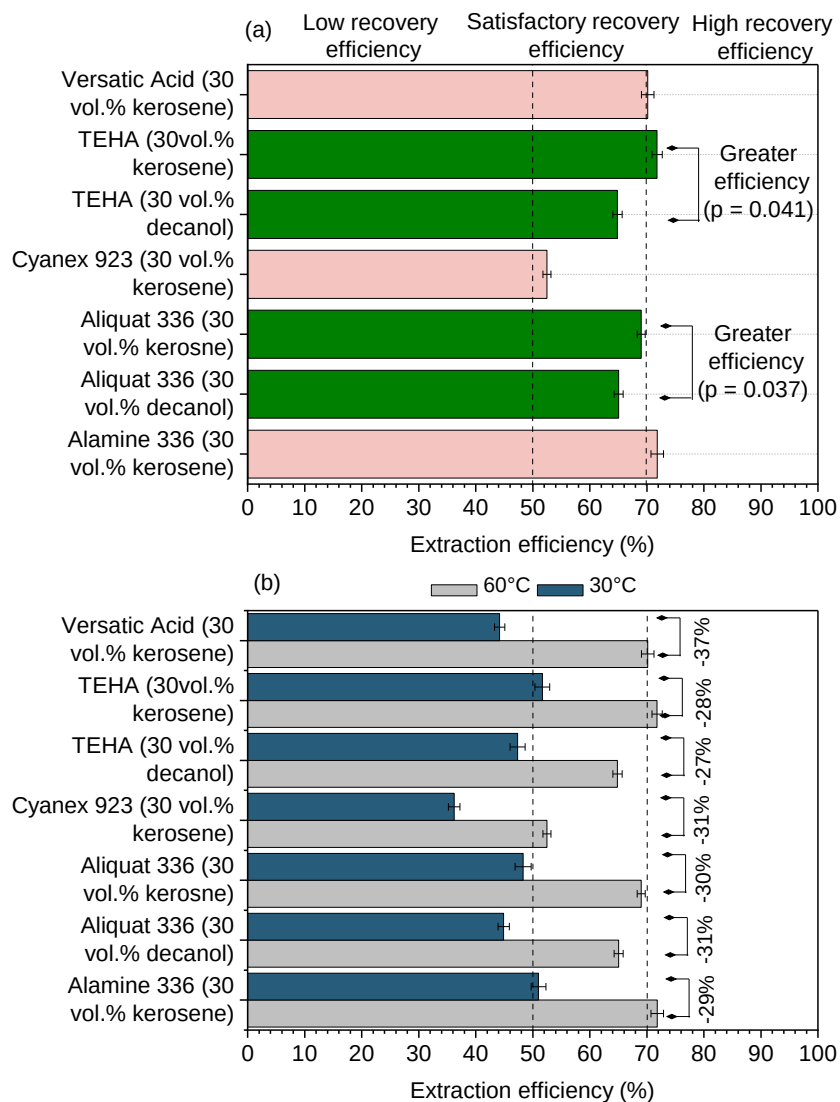


Figure 22. (a) Extraction efficiency of mineral acid for different organic phases. p-values represent significant gains in extraction efficiency when different diluents (kerosene and 1-decanol) were compared as diluents. (b) temperature effect in extraction efficiency. O:A (2:1), stirring speed: 300 rpm for 10 min, settling period: 15 min, temperatures: 30°C and 60°C.

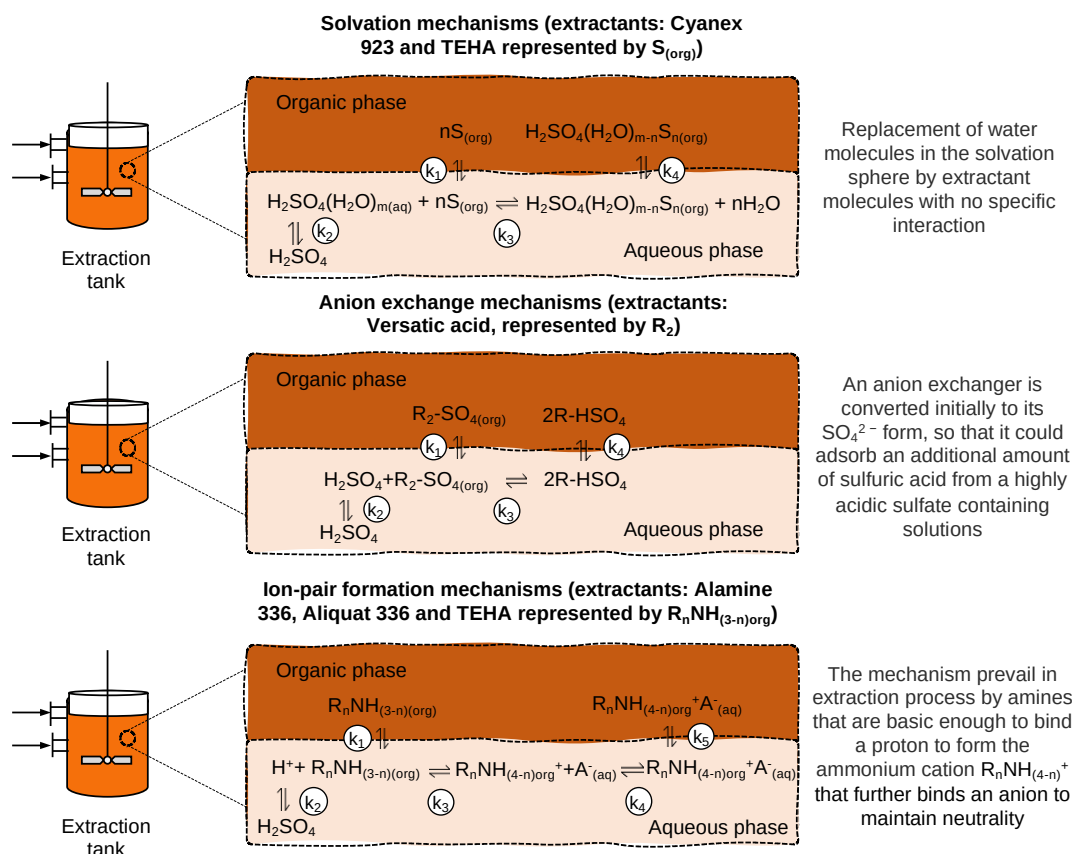


Figure 23. Extraction mechanisms associated with different organic phases and mineral acid recycling. References: solvation [273], anion exchange [274], and ion-pair formation [272]. ©

FTIR analyses (Figure 24) complemented the discussion of mechanisms involved in mineral acid extraction by different organic phases. A general observation of the spectra obtained is that those groups in which the transmittance value remained similar before and after extraction are weakly related to the extraction process. The discussion then focused on groups where the transmittance decreased and/or the peaks shifted from their original wavenumber when spectra before and after extraction are compared.

Bands at 2960, 2410, 1359, 1158, 957, and 902 cm^{-1} have been previously associated with sulfuric acid [275]. Bands at 2852 – 2924 cm^{-1} are associated with vibrations of axial deformation between the atoms of carbon and hydrogen (C-H) in aliphatic molecules. Additional bands at 1430 – 1570 cm^{-1} were attributed to angular deformations of $(CH_2)_n$ – ($n > 3$), confirmed by the appearance of bands in the region around 720 cm^{-1} . For amine-based extractants (Aliquat 336, Alamine 336, and TEHA), bands of weak and medium intensity are observed at 1460 – 1514 cm^{-1} corresponding to angular symmetric deformations of NH_2 and N-H. C-N bonds from aliphatic molecules are also observed in these spectra, characterized by bands observed at 1160 – 1300 cm^{-1} .

In cases of solvation and H-bonding formation, as for Cyanex 923 and TEHA, most bands related to H_2SO_4 appear (e.g.: 2960 and 2952 cm^{-1} ; 1373 and 1377 cm^{-1}) at greater intensities after the extraction process and indicate an organic phase loaded by the non-dissociated form of H_2SO_4 . For the other extractants that involve a complex formation, it is possible to note a reduction in transmittance values after extraction, suggesting that most functional groups previously identified interacted at some point to form complexes with mineral acids.

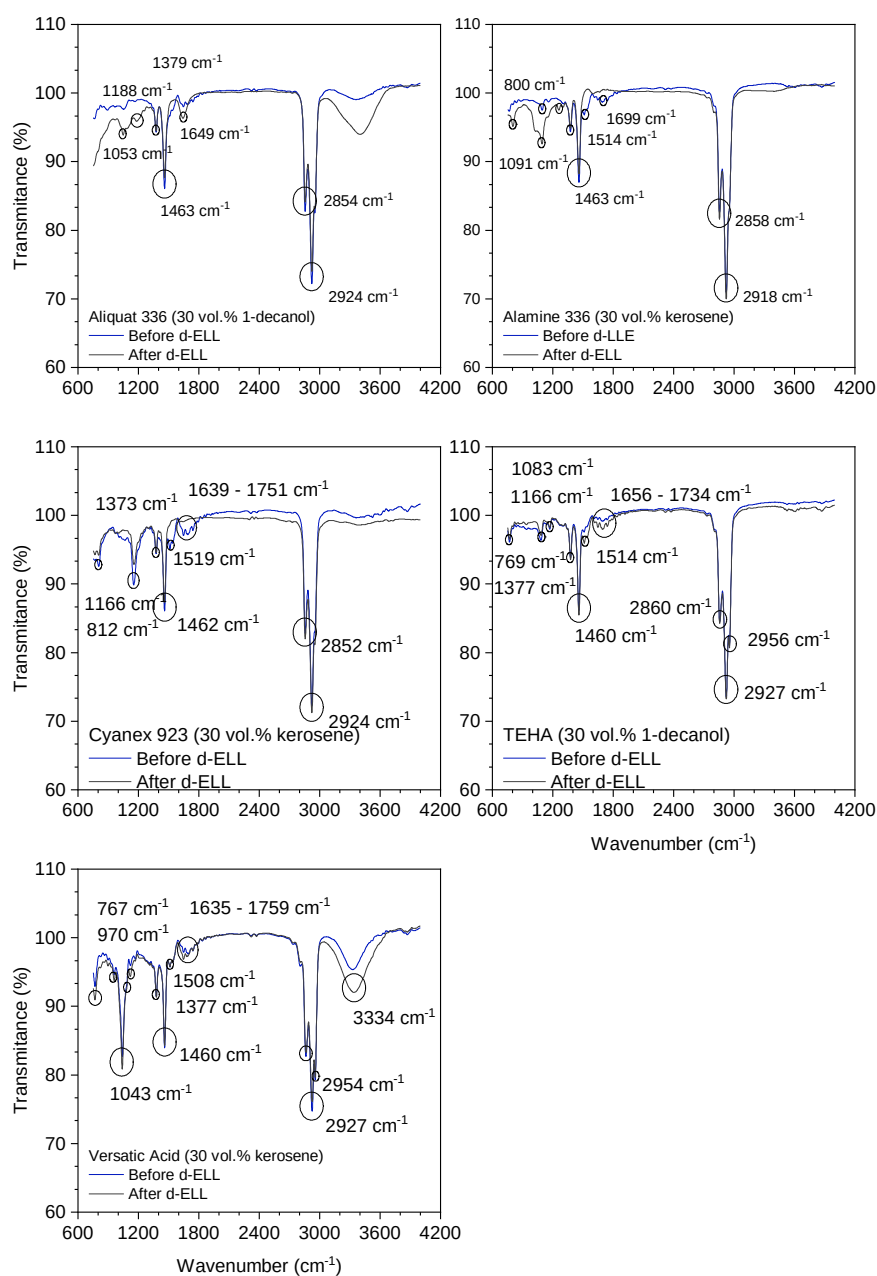


Figure 24. FTIR spectra and functional groups identification for the organic phases before and after the extraction experiments.

From all extractants used, emulsions were observed for Aliquat 336 and TEHA, and for that reason, additional experiments were carried out using 1-decanol as a diluent. The organic liquid has a higher density (kerosene: 0.78 g/cm³ and 1-decanol: 0.83 g/cm³) and surface tension values (kerosene: 23 mN/m and 1-decanol: 28.5 mN/m; both at 20°C) compared with kerosene, which are properties that favors a higher dispersion of the extractants and increases the organic phase coalescence after its dispersion.

However, apart from emulsion prevention, the extraction efficiency decreased significantly for both Aliquat 336 and TEHA ($p < 0.041$), an antagonistic contribution that not necessarily would be observed for other extractants. That is what was reported by Haghshenas et al. [276], who reported that the organic diluent did not affect mineral acids extraction by Cyanex 923.

It is known from current literature that the diluent physical properties such as dipole moment, solubility, dielectric constant, and interfacial surface pressure interfere with extraction rates [277], [278]. If we considered the dielectric constant of both solvents, kerosene has a lower constant ($\epsilon = 1.8$ at 21°C) compared with 1-decanol ($\epsilon = 8.1$ at 21°C), which suggests that 1-decanol would present a higher polarization degree and pronounced dipole moment. Diluents with a high dipole moment, which means a high tendency of the molecules to deviate from the simple intermolecular attraction that is characteristic of spherically symmetrical nonpolar molecules, have a high attraction for the extractant. The high interaction is expected to impose an additional energy barrier for the extractant to leave the diluent environment and later acid or metal extraction.

An important outcome was the temperature contribution (Figure 22b) to extraction efficiency. For all extractants, the operation was considered endothermic, and the higher temperature would be advantageous not only to acid recovery (60°C: 52.4 – 71.8% and 30°C: 36.2 – 51.6%) but also to the integration of MD with solvent extraction. In that case, the concentrate produced after water recovery by MD, which has an average outlet temperature of 60°C, could be directly designated for solvent extraction without being cooled. As in most separation processes, temperature plays a role in solvent extraction as well. Greater temperatures reduce the organic phase viscosity and therefore resistance to mass transfer. On the other side, better control of organic phase loss is required when operated at higher temperatures given that most extractants and diluents have a greater vapor pressure compared with water, and therefore higher rates of volatile loss.

In terms of selectivity (Figure 25), all extractants presented sulfuric acid distribution coefficients greater than one ($D_{H_2SO_4}$: 1.43 – 2.78), except for Cyanex 923 ($D_{H_2SO_4}$: 0.93) which demonstrated unfavorable mechanisms for acid extraction under the experimental conditions. The results indicate that sulfuric acid would be preferably located in the organic phase, whereas other metallic species such as copper, nickel, and cobalt remained in the raffinate ($D_{Cu} < 0.05$; $D_{Ni} < 0.21$, and $D_{Co} < 0.14$). The extraction of these species is not expected considering the extractant used and the medium pH in which they are commonly recovered (Cu: 1.1 – 2.5, Ni: 3.0 – 7.1, and Co: 3.5 – 7.0 [22]). Furthermore, their low extraction rate contributed to the obtainment of a final acid solution of greater purity.

Additional stages of extraction and stripping could be sought for their recovery given their economic value, risk of shortage in a future scenario, and environmental impacts related to their exploration [279]–[281]. As discussed by Kuipers et al. [280], the resource challenge is not only a challenge of meeting future demands but also about trying to mitigate environmental pressures under conditions of cast expansions of resource extraction and processing. According to the authors, shifting away from primary resource extraction towards recycling might be an important step towards a global economy in harmony with the natural environment.

Contrary to copper, nickel, and cobalt, iron, aluminum, and magnesium have a lower-added value, and, considering their high concentration in MD concentrate, it would be interesting to achieve a favorable separation over these compounds as well. They will be referred to as impurities from that moment on. The results were also favorable in terms of mineral acid recovery over impurities ($\beta_{H_2SO_4/Fe}$: 4.95 – 104.96, $\beta_{H_2SO_4/Al}$: 15.26 – 522.45, and $\beta_{H_2SO_4/Cu}$: 10.74 – 64.23). The adverse contribution of 1-decanol as diluent is observed here as well, which significantly decreased the selectivity of mineral acid recovery by Aliquat 336 ($p < 0.02$) and TEHA ($p < 0.02$, except for $\beta_{H_2SO_4/Al}$). Despite the lower selectivity, copper, nickel, and cobalt had a lower affinity for the extractant regardless of the diluent used (Figure 25).

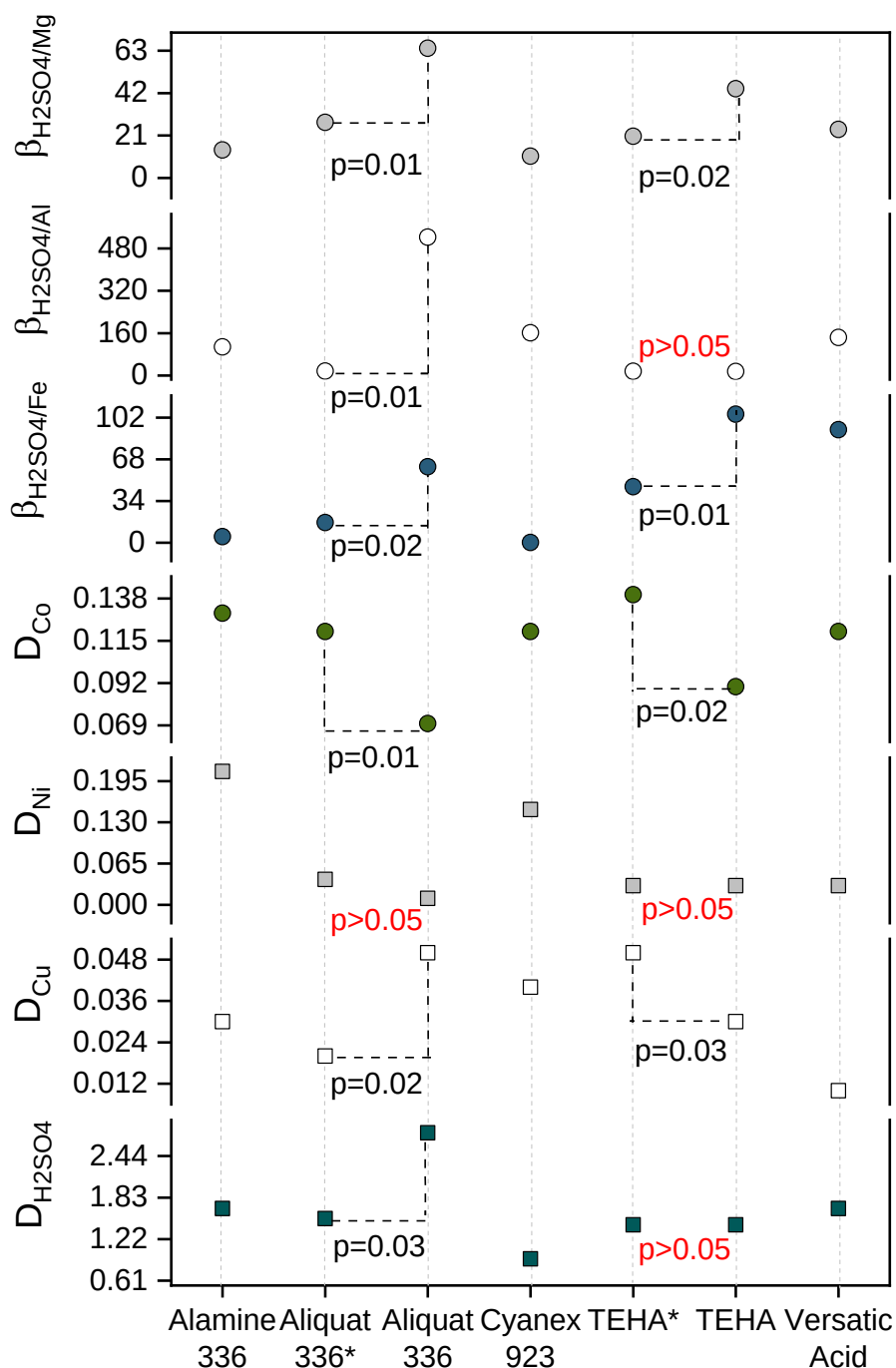


Figure 25. Distribution coefficients (D) and selectivity for sulfuric acid recycling over iron ($\beta_{H_2SO_4/Fe}$), aluminum ($\beta_{H_2SO_4/Al}$), and magnesium ($\beta_{H_2SO_4/Mg}$). Dilution factor: 30 vol.%, O:A (2:1), stirring speed: 300 rpm for 10 min, settling period: 15 min, temperature: 60 °C. *Extractant diluted in 1-decanol.

3.2 Organic phase stripping and regeneration

If stripping is considered, besides the fact that selectivity was not severely affected by the diluent, Aliquat 336 (diluted in 1-decanol), Cyanex 923, and TEHA (diluted in 1-decanol) become the most appropriate organic phases for mineral acid recycling given the greater efficiency for acid recovery from the organic phase (>90%) (Figure 26a). It would be of no use with a high extraction efficiency but low stripping efficiency. In that case, acid and other

impurities will build up in the organic phase and its reuse will become impractical after a few extraction processes.

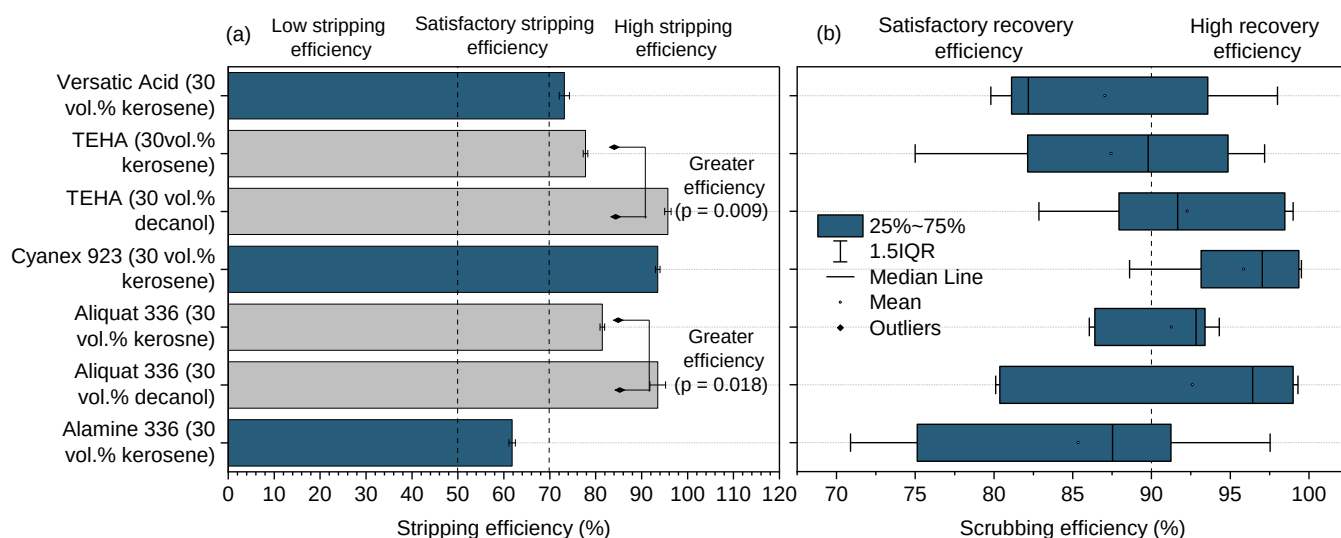


Figure 26. (a) Stripping efficiency of organic phases loaded with mineral acid [O:A (1:2), stirring speed: 300 rpm for 10 min, settling period: 15 min, stripping agent: hot water at 60°C] and (b) scrubbing efficiency of co-extracted species [O:A (1:2), stirring speed: 300 rpm for 10 min, settling period: 15 min, scrubbing agent: sulfuric acid 1.0 mol/L].

A mass balance allowed to estimate the sulfuric acid recovery by these three extractants after stripping, which corresponded to 4.7, 3.8, and 4.8 kg_{H₂SO₄}/m³ of concentrate subjected to extraction by Aliquat 336 (diluted in 1-decanol), Cyanex 923, and TEHA (diluted in 1-decanol), respectively. Despite being easily stripped, the low extraction rates associated with Cyanex 923 yielded a lower overall recovery of sulfuric acid, and the amine-based extractants (Aliquat 336 and TEHA) become interesting alternatives. Although effective for acid stripping, hot water (60°C) was unable to remove the co-extracted species from the organic phase (stripping of co-extracted species: <0.1 – 37.7%). That is a positive outcome considering that the mineral acid would be obtained at a higher purity degree, however, an additional stage would be necessary for organic phase regeneration.

Aliquat 336 and TEHA diluted in kerosene showed slightly lower efficiencies in impurities scrubbing compared with experiments when both extractants were diluted with 1-decanol, or experiments using different extractants such as Cyanex 923 (Figure 26b). Among all extractants, Cyanex 923 was regenerated with greater efficiency in terms of co-extracted species scrubbing (which included all inorganic species from MD concentrate: impurities, copper, nickel, cobalt, and zinc). At this point, it can be reaffirmed that the diluent does not act simply as a carrier but also participates in the extraction process, whether in the extraction of acid or metallic species. For reasons previously discussed in Section 3.1, the use of 1-decanol would imply a lower interaction between the extractant and the acid or metals. When it comes to stripping and scrubbing, the lower interaction would be advantageous to the process as it would facilitate acid recovery and impurities scrubbing. It should be clarified that sulfuric acid as a scrubbing agent, although recurrent in solvent extraction experiments [22], may saturate the recirculated organic phase and may result in the deliberation of acid to the treated concentrated instead of its extraction. For that reason, it is recommended that organic phase scrubbing and regeneration only in cases when decay in acid extraction efficiency is observed,

after successive extraction stages. Besides that, the use of a sulfuric acid solution should not represent a major concern and the scrubbing solution could be, for example, recirculated to the MD feed to avoid additional wastewater generation.

3.3 Economic analysis

A preliminary economic analysis is presented in Figure 27. From all variables considered for OPEX estimation, the costs related to the stripping agent acquisition had the greatest contribution to the total costs. Under the experimental conditions evaluated, the stripping agent would have a flow rate twice as high as the organic phase flow rate, in addition to the fact that it is a heated stream whose costs are higher compared with those practiced for freshwater. Despite that, hot water is often considered for acid stripping given its environmental benefits [282]. If water is used, the mineral acid could be directly used and concentrated if necessary, without the requirement of an additional process for its purification. From a broader perspective and considering the direct acid solution reuse, the costs of stripping agent acquisition would be compensated by the lower requirements of freshwater during POX. In that case, costs would be limited to its heating process, and the solvent extraction OPEX could be reduced.

Complementary studies would be required to validate the acid solution reuse. After extraction and stripping stages, the acid solution had a concentration ranging from 18 – 25 mmol_{H₂SO₄}/L, which might or might not be enough for gold ores acidulation. In general, it is recommended stoichiometric amounts of acid for either a partial or substantial neutralization of the carbonate content of the gold ore [283]. The occurrence of other ions in the acid solution should be evaluated as well. Iron, although present in a low concentration in stripping extracts (<0.001 – 0.14 g/L), can build up on the autoclave circuit and cause processing problems in the subsequent cyanidation. The iron-based compounds formed (e.g.: ferric hydroxide and gypsum precipitates) are stable and alter the rheological properties of the slurry feeding the cyanidation plant, reducing its efficiency for gold recovery. The occurrence of basic iron sulfates also makes it difficult to maintain a pH>10 required to keep cyanide in free cyanide form rather than its toxic form [284]. Chloride ions, although not monitored, also represent a point of concern to be further evaluated. Their presence during POX encourages the formation of sulfur over sulfates and the ultimate consequence is a limited recovery during cyanidation and the formation of soluble gold chloride complexes, commonly lost downstream of the beneficiation process [285].

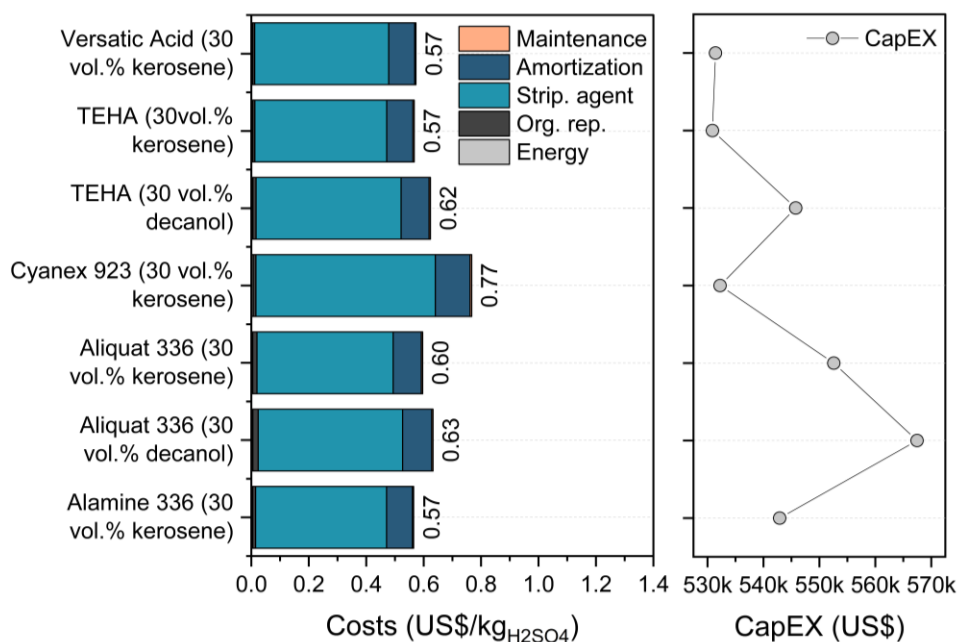


Figure 27. Economic analysis considering the different organic phases. Note: “Org. rep.” stands for “organic phase replenishment” and “Strip. agent” stands for “Stripping agent”.

The high acquisition costs associated with 1-decanol are reflected in a higher contribution of the organic phase replenishment to the total operating costs in processes that used it. Aiming for emulsions prevention, other alternatives could be sought, and their costs evaluated to achieve a better cost-benefit. Kesieme et al. [265] summarized the use of different diluents when sulfuric acid was recovered from acidic mining wastes, which includes octanol, n-dodecane, n-heptane, toluene, and benzol, besides the use of commercial aromatic and aliphatic modifiers of the organic phase. Modifiers are commonly used at low ratios, which could reflect lower costs.

The costs related to the acquisition of 1-decanol for the extraction units' start-up were also responsible for the higher CAPEX observed for TEHA and Aliquat 336 (Figure 27) compared with scenarios in that both extractants were diluted in kerosene.

An important observation made is the impact of acid recovery efficiency on total costs. Cyanex 923, despite being diluted in kerosene and its low acquisition costs compared with other extractants, presented the highest OPEX among all processes given its lower recovery efficiency. Strategies to improve the extraction efficiency could be pointed out and include different diluents, which impact on extraction efficiency was observed in the current study, and an increased concentration in the extractant [265]. The implications of increased extractants concentration should be carefully assessed since higher concentrations should also favor emulsions [265] and increase operating costs. A mixture of extractants is another alternative. In most cases, it is observed a synergy when different extractants are combined and the overall result is a greater extraction efficiency and selectivity. The positive outcomes observed when inorganic species are intended for recovery [286] open up a possibility to consider a synergistic extraction for mineral acid recycling as well. Finally, it is possible to consider multistage operations and appropriate solvent-to-feed ratios. Moreira et al. [195] demonstrated that consecutive stages of extraction using Aliquat 336 (two stages) and TEHA (three stages) enabled a 95% H₂SO₄ extraction (O:A 1:1). Despite the greater CAPEX given the greater

number of extraction units required, the greater recovery rate is reflected in a lower OPEX (US\$ 0.423/kgH₂SO₄).

If we consider the results of extraction efficiency, selectivity, stripping efficiency, and costs, TEHA (30 vol.% in 1-decanol) would be the most cost-effective (US\$ 0.57/kg) alternative for mineral acid recycling from MD concentrate. A summary of the input and output characteristics of the main process streams when TEHA was used as an extractant is presented in Figure 28.

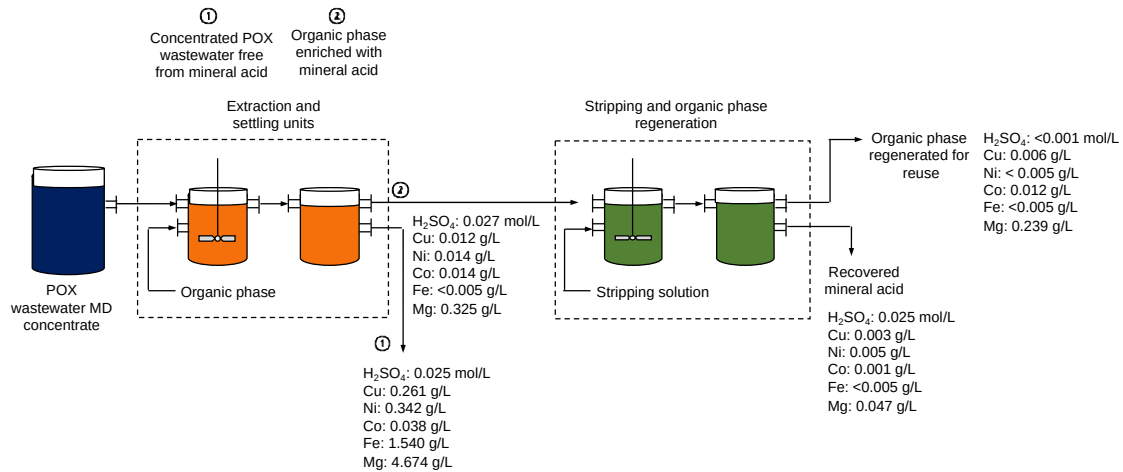


Figure 28. Process flowsheet presenting input and output characteristics of main process streams when TEHA was used as extractant.

**CHAPTER 5 – MEMBRANE DISTILLATION AND DISPERSIVE SOLVENT EXTRACTION
IN A CLOSED-LOOP PROCESS FOR WATER, SULFURIC ACID, AND COPPER
RECYCLING FROM GOLD MINING WASTEWATER**

Complete articles published in journals:

[1] **Moreira, V. R.**, ..., & Amaral, M. C. S. (2022). Membrane distillation and dispersive solvent extraction in a closed-loop process for water, sulfuric acid, and copper recycling from gold mining wastewater. *Chemical Engineering Journal*, 435, 133874.

1 Introduction

Recently, membrane separation processes (MSPs) were applied for mining wastewater treatment on both large-scale [13], [287] and bench-scale [242], [288]. The Emalahleni Water Reclamation Plant, located in the Witbank (South Africa), is an example that combines multiple ultrafiltration and reverse osmosis stages (recovery rates >97%; capacity: 50,000 m³/d) for potable water reclamation from acid mine drainage [289]. Full-scale applications as mentioned were possible after different bench studies that investigated the technologies of ultrafiltration, nanofiltration, and reverse osmosis integrated into different systems. Despite their effective result in terms of water reclamation, they produced a concentrated stream – which has a higher pollution potential than the feed, that is inherent to MSPs. Furthermore, when ultrafiltration and nanofiltration were integrated, the operational costs estimated by Foureaux et al. [242] corresponded to US\$ 2.20/m³ of wastewater treated, a high value driven by the energy requirements for wastewater cooling from 60°C, the temperature of which the wastewater is generated, to 25°C, the operating temperature for nanofiltration.

An alternative to overcome the drawbacks and costs related to cooling requirements is to consider thermally driven technologies for reuse water reclamation, such as membrane distillation (MD). The process relies on phase transitions in which water vapor is transported across a microporous hydrophobic membrane by simultaneous mass and heat transfer. The membrane prevents the liquid phase passes through it, and therefore the process has a 100% theoretical rejection efficiency for non-volatile substances [290]. That should solve the cooling requirements of conventional MSPs, but the generation of a concentrated stream persists. For that, techniques capable of by-product recycling and favored by greater chemical potentials could be considered.

If MD and solvent extraction are successfully integrated, the treatment trail could lower the dependence on primary sources of H₂SO₄ and copper, partially solve the drawbacks related to concentrate generation by MSPs, and ultimately minimize the waste disposed of by mining facilities. Based on that, MD and solvent extraction (in this chapter referred to as d-ELL) were integrated aiming for reuse water, sulfuric acid, and copper recovery from gold mining wastewater. MD was evaluated in terms of distillate flux, fouling, and recovery rate, besides its capability to produce a concentrated stream that was further subjected to d-ELL experiments. The raffinate from H₂SO₄ recovery was subjected to copper recovery in a closed-loop treatment trail. In complement to the decision variables previously mentioned, a preliminary economic analysis was made to estimate the costs for the reuse water (US\$/m³), sulfuric acid (US\$/kg_{H2SO4} recovered), and copper (US\$/kg_{Cu} recovered) obtained by MD-d-LLE.

2 Materials and methods

2.1 Wastewater sampling and characterizations

The wastewater was sampled after a process of pressure hydrometallurgy responsible for the oxidation of sulfides (e.g.: pyrite - FeS₂) that would potentially lower the gold recovery at the subsequential cyanidation leaching. The mining site (located in Minas Gerais, Brazil) produces 60 m³/h of wastewater, which was characterized according to the procedures described in the Standard Methods for the Examination of Water and Wastewater [267]. The same procedures were used to characterize the MD distillate, MD concentrate, and raffinates obtained after d-LLE.

Analyses of Fourier-transform infrared spectroscopy (FTIR; Shimadzu IRAffinity-1) were made for unused and loaded organic phases that presented the highest performance for acid extraction. The data was collected in the region of 650 – 4000 cm^{-1} with a resolution of 4 scans per second and a total of 20 scans.

2.2 Direct contact membrane distillation

MD experiments were carried out with 2 L of wastewater (also referred to as feed–heated stream) and distilled water (also referred to as permeate–cooled stream) that were maintained at a constant temperature and recirculation flow rate (0.3 L/min). The feed temperature was set at 60°C, which corresponds to the wastewater outlet temperature after the process of hydrometallurgy, whereas the distillate was maintained at room temperature (25°C; $\Delta T = 35^\circ\text{C}$). It was used a commercial polymeric membrane made of poly(tetrafluoroethylene) (PTFE) and a spacer (CF042 Low Foulant Spacer, PTFE 31Mil – 0.787 mm), both with an effective area of 0.0042 m^2 and provided by Sterlitech®. The membrane has an average pore size of 0.2 μm , a thickness of 170 μm , 125° of contact angle, and a liquid entry pressure > 4 bar.

The permeate flux (J , $\text{L}/\text{m}^2\cdot\text{h}$; $\rho_{\text{H}_2\text{O}} = 997 \text{ kg}/\text{m}^3$) was estimated with the aid of an analytical scale that monitored the increment in mass at regular intervals of 2 minutes. At the initial stages, the permeate would be diluted by the initial distilled water in the tank, hence, to avoid underestimations, the permeate physicochemical characteristics were adjusted considering the initial distilled water volume. The vapor pressure at the bulk feed (p_f , Pa), membrane surface facing the feed side (p_1 , Pa), membrane surface facing the permeate site (p_2 , Pa) and the bulk permeate (p_p , Pa) were considered to estimate the resistances ($\text{Pa}\cdot\text{m}^2\cdot\text{h}/\text{kg}$) to mass transfer associated with the membrane (ρ_m , Equation 25), permeate boundary layer (ρ_{pb} , Equation 26), feed boundary layer (ρ_{fb} , Equation 27) and fouling layer (ρ_f , Equation 28). The total mass transfer resistance (ρ_t) was estimated by Equation 29.

$$\rho_m = \frac{p_1 - p_2}{J} \quad (25)$$

$$\rho_{pb} = \frac{p_2 - p_p}{J} \quad (26)$$

$$\rho_{fb} = \frac{p_f - p_1}{J} \quad (27)$$

$$\rho_f = \rho_t - \rho_m - \rho_{pb} - \rho_{fb} \quad (28)$$

$$\rho_t = \frac{p_f - p_p}{J} \quad (29)$$

Bulk's equation (Equation 30) was used to estimate the vapor pressures at a given temperature (T , K) given its greater accuracy for vapor pressure estimation compared with Antoine's equation [291]. The p_f was corrected by the feed activity coefficient (α_f), estimated by Pitzer's model and the software "PHREEQC".

$$p_i = 0.61121 \cdot e^{\left[\left(18.678 - \frac{T}{234.5} \right) \left(\frac{T}{257.14 + T} \right) \right]} \quad (30)$$

The feed (T_f, K) and permeate (T_p, K) bulk temperatures were measured by thermostats. The temperatures at the membrane surface facing the feed ($T_{w,f}, K$; Equation 31) and permeate ($T_{w,p}, K$; Equation 32) were estimated by an energy balance at steady-state conditions. Given T_f , $T_{w,f}$, $T_{w,p}$; and T_p it is possible to calculate the temperature polarization coefficient (τ) by Equation 33.

$$T_{w,f} = \frac{h_m \cdot \left(T_p + \left(\frac{h_f}{h_p} \right) \cdot T_f \right) + h_p \cdot T_p - J \cdot \Delta H_v}{h_m + h_f \cdot \left(1 + \frac{h_m}{h_p} \right)} \quad (31)$$

$$T_{w,p} = \frac{h_m \cdot \left(T_f + \left(\frac{h_p}{h_f} \right) \cdot T_p \right) + h_f \cdot T_f - J \cdot \Delta H_v}{h_m + h_p \cdot \left(1 + \frac{h_m}{h_f} \right)} \quad (32)$$

$$\tau = \frac{T_{w,f} - T_{w,p}}{T_f - T_p} \quad (33)$$

In Equations 31-32, incremental ΔH_v (Equation 34) stands for the water vaporization heat and h_m ($W/m^2 \cdot h$), h_f ($W/m^2 \cdot h$, Equation 35), and h_p ($W/m^2 \cdot h$; Equation 35) for the convective heat transfer coefficients of the membrane, permeate, and feed streams. The most appropriate correlations for the Nusselt number (Nu , which considers the module geometry), used for convective heat transfer calculation are described in Equations 36-37 [292], [293].

$$\Delta H_v = 1.7535 \cdot T + 2024.3 \quad (34)$$

$$h_{f,p} = k_{f,p} \cdot Nu_{f,p} / D_h \quad (35)$$

$$Nu_f = 15 \cdot (Re \cdot Pr)^{0.23} (D_h/L)^{0.5} \quad (36)$$

$$Nu_p = 11.5 \cdot (Re \cdot Pr)^{0.23} (D_h/L)^{0.5} \quad (37)$$

In Equations 36-37, Re corresponds to the Reynolds number (Equation 38), Pr to the Prandtl number (Equation 39), $k_{p,f}$ ($W/m \cdot K$) to the permeate or the feed thermal conductivity, c_p to the isobaric specific heat ($J/kg \cdot K$), q (m^3/s) to the volumetric flow rate, d_h to the hydraulic diameter (m), μ ($Pa \cdot s$) and ν (m^2/s) to the water dynamic and kinematic viscosity, and (m) to the pipe's cross-sectional area.

$$Re = \frac{q \cdot d_h}{\nu \cdot s} \quad (38)$$

$$Pr = c_p \cdot \mu / k_{f,p} \quad (39)$$

To estimate the process thermal efficiency (δ_t , %; Equation 40) it was considered the total heat flux (ω_m , kW; Equation 41) across the membrane surface area (s_m , m) and the feed mass flow rate ($m_{f,r}$, kg/s).

$$\delta_t = \frac{J \cdot s_m \cdot \Delta H_v}{\omega_m} 100 \quad (40)$$

$$\omega_m = m_{fr} \cdot c_p \cdot (T_{fb} - T_{pb}) \quad (41)$$

2.3 Solvent extraction

Three of the extractants (Alamine 336, Cyanex 923, and Versatic Acid) were diluted in kerosene (30 vol.%; provided by Dinamica® and used without further purification), whereas Aliquat 336 and TEHA were diluted in 1-octanol (30 vol.%; provided by Fisher Scientific and used without further purification). Preliminary experiments demonstrated that Aliquat 336 and TEHA formed emulsions after extraction experiments when diluted in kerosene. For copper extraction, Lix-84 I was diluted in kerosene (30 vol.%) and was used as an extractant.

Both aqueous and organic phases were kept in contact (stirring speed: 300 rpm) in a glass reactor vessel with an organic-to-aqueous ratio of 2:1 for 10 min. The phases were left to settle for 15 minutes and the raffinate was collected for characterization. The extraction efficiency was assessed under different temperatures (60°C, corresponding to the MD concentrate outlet temperature, 45°C, and 30°C). Extraction isotherms were obtained at a constant temperature (60°C for H₂SO₄ and 30°C for copper) and different O:A ratios (4:1 – 1:4) for the extraction and stripping. Organic phase loading was assessed by four consecutive contacts of the same organic phase with fresh concentrate solutions. During the experiments, no organic phase loss was observed which allowed us to estimate its composition by a mass balance.

The distribution coefficient (D_M ; Equation 42) and the separation factor (β_{M_1/M_2} ; Equation 43) were used as response variables related to selectivity. The variables M_{org} (mg/L) and M_{aq} (mg/L) refers to a given compound concentration in the organic and aqueous phases. Separation factors greater than one suggest that the extraction is possible, and it is associated with an organic phase enriched in the compound M_1 , while separation factors equal to one suggest that extraction is not possible. Iron, aluminum, and magnesium were considered impurities for their low added value.

$$D_M = [M_{org}]/[M_{aq}] \quad (42)$$

$$\beta_{M_1/M_2} = [D_{M1}]/[D_{M2}] \quad (43)$$

The enthalpy change (ΔH) and corresponding free energy change (ΔG) for sulfuric acid and copper extraction were calculated by Equation 44 (Van't Hoff equation) and Equation 45, where R is the universal gas constant (8.314 J/mol·K) and c the integration constant.

$$\log D = \Delta H/2.303R \cdot T + c \quad (44)$$

$$\Delta G = -2.303R \cdot T \cdot \log D \quad (45)$$

2.4 Organic phase stripping and regeneration

For sulfuric acid recovery, the extracts were stripped with hot water (60°C), whereas copper was stripped by an acid solution (H₂SO₄, 1 mol/L). Both aqueous and organic phases were kept in contact (stirring speed: 300 rpm) in a glass reactor vessel with an organic-to-aqueous ratio of 1:2 for 10 min. The phases were left to settle for 15 minutes and the raffinate was collected for characterization. Similarly, the organic phase composition was possible to be determined by mass balance since no organic phase loss was observed. A schematic

representation of the closed-circuit considered for reuse water reclamation, acid extraction, and copper extraction is presented in Figure 29.

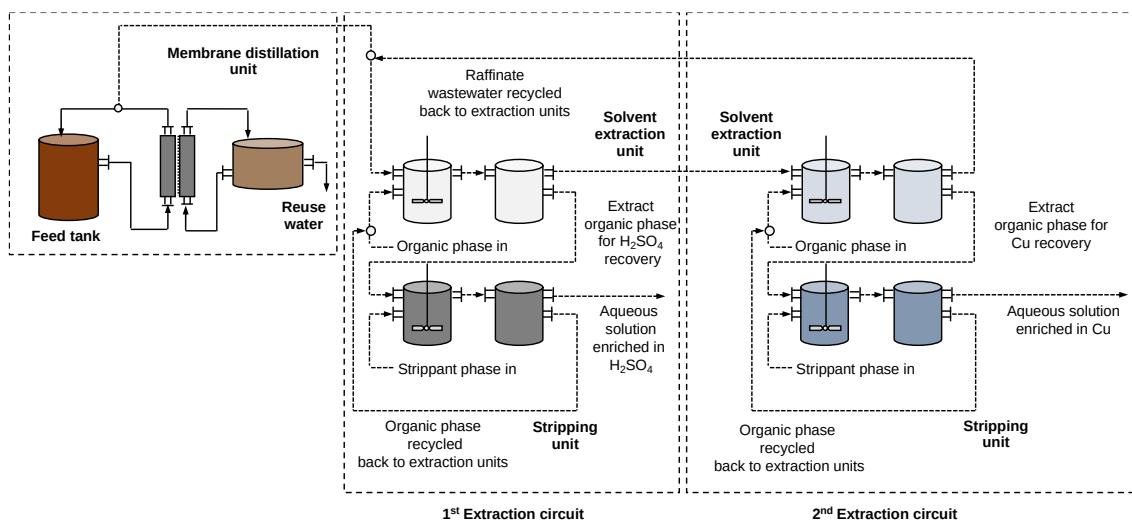


Figure 29. Representation of membrane distillation and dispersive liquid-liquid extraction for gold-mining wastewater beneficiation.

2.5 Economic analysis

The capital (CAPEX) and operational (OPEX) costs were estimated considering a wastewater flow rate of 60 m³/h (the same flow rate at which the wastewater is produced). For equipment costs (C_b ; Equation 46) estimations were considered their respective base variable (S_a), bare module cost (C_a , which accounts for direct and indirect costs associated with equipment purchase and installation) and a factor exponent (n) (Table 10). The costs were updated considering the chemical engineering plant cost index (CEPCI) for 2020 (569.2) and the base year. The amortization costs (AC_f , Equation 47) was calculated by annualizing the capital cost (C_{capEX}), where i_c is the investment rate (6.5%) and ls the project lifespan (15 years). The maintenance rate was defined as 5% of the capital costs.

$$C_b = C_a(S_b/S_a)^n \quad (46)$$

$$AC_f = C_{capEX} \{i_r / [1 - (1 + i_r)^{-ls}]\} \quad (47)$$

It was considered that the MD membranes would operate with a lifespan of 3 years, being cleaned regularly four times a month (cleaning agents' requirement: 0.001 kg/m² - defined empirically). The organic phase replenishment interval was set at 5 years [294]. This cost, in addition to those related to the extractants, stripping solution, energy for pumps and propellers (efficiency considered: 0.85), amortization, and maintenance were summed up and considered as OPEX.

Table 10. Expenditures considered for capital costs (CAPEX) and operational costs (OPEX) estimation. *[269], **Vales were based on the most recent Chemicals Market Report provided by the Independent Commodity Intelligence Service (ICIS).

Operation Unit	Equipment Description for CapEX estimation	Base variable (S_a)	Bare module cost (US\$; C_a)	n^*	CEPCI (base year)	Real variable (S_b)
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MD	Feed Tank: Floating Head Carbon Steel	90	63,524.00	0.6	567.5	60
	Permeate tank: Floating Head Carbon Steel	90	63,524.00	0.6	567.5	60
	Centrifugal, stainless steel shaft power	1	15,345.00	0.7	567.5	1
	Centrifugal, stainless steel shaft power	1	15,345.00	0.7	567.5	1
	Multiple pipe, copper/carbon steel	10	19,515.00	0.6	567.5	10
	MD module	1	4,500.00	0.6	567.5	60
d-LLE	Floating Head Carbon Steel (m ³)	90	63,524.00	0.6	567.5	120
	Propeller (kW)	10	58,384.00	0.5	567.5	10
	Floating Head Carbon Steel (m ³)	90	63,524.00	0.6	567.5	120
	Floating Head Carbon Steel (m ³)	90	63,524.00	0.6	567.5	160
	Propeller (kW)	10	58,384.00	0.5	567.5	10
	Floating Head Carbon Steel (m ³)	90	63,524.00	0.6	567.5	160
	Centrifugal, stainless steel shaft power (kW)	1	15,345.00	0.7	567.5	1
	Centrifugal, stainless steel shaft power (kW)	1	15,345.00	0.7	567.5	1
	Centrifugal, stainless steel shaft power (kW)	1	15,345.00	0.7	567.5	1
	Centrifugal, stainless steel shaft power (kW)	1	15,345.00	0.7	567.5	1
Chemicals and utilities considered for OPEX estimation			Value**			
Aliquat 336 (US\$/kg)			10.00			
TEHA (US\$/kg)			4.00			
Lix 84-I			4.00			
Kerosene (US\$/kg)			0.71			
1-Octanol (US\$/kg)			1.05			
PTFE membranes (US\$/m ²)			12			
Membrane cleaning agent – NaOH (US\$/kg)			0.523			
Membrane cleaning agent – Citric acid (US\$/kg)			9.1			
Hot water for stripping (US\$/m ³)			0.63			
Acid solution for stripping (US\$/kg)			1.14			
Energy (US\$/kWh)			0.04			

2.6 Statistical analysis

Microsoft Excel and OriginPro were used for statistical and data analysis. Although the results had a trend for a normal distribution, verified by the Shapiro-Wilk's test and Levene's test for homogeneity, Mann-Whitney U Test was preferred for comparison between two independent

groups. Mann-Kendall trend tests were made to verify a possible trend for flux decay in MD. A confidence level of 95% was set for all statistical analyses performed.

3 Results and discussions

3.1 Water recovery by membrane distillation

The results for permeate flux were summarized in Figure 30. The process presented an average permeate flux of 5.51 ± 0.14 L/m²·h, without a significant flux decay ($p < 0.001$; $J/J_0 > 0.95$). This is favorable a characteristic of MD, a process that dispenses a constant hydraulic pressure over its membrane (as in conventional MSPs) that would contribute to solutes deposition and fouling. Amaral et al. [241] considered membranes of nanofiltration and reverse osmosis for gold mining wastewater treatment and described an expressive flux decay. The systems operated up to 65% of the recovery rate, however, the final flux for nanofiltration and reverse osmosis membranes were 0.28 and 0.25 times the initial flux.

Membrane resistance was the greatest contributor (76%) to the total mass transfer resistance observed ($\rho_t = 7,852.2$ Pa·m²·h/kg) whereas fouling had the lowest contribution, an expected result given the nonsignificant flux decay. Different from feed and boundary layer resistances, membrane resistance is intrinsic to its morphology and structure and is not lowered by changing the operating conditions. Ideally, MD membranes should have great resistance to wetting (as PTFE membranes) but low resistance to permeate flux; however, these are inversely related properties and an increase in membrane surface hydrophobicity generally leads to the reduction of water vapor flux [295]. That opens up an opportunity for the synthesis of novel MD membranes that, in addition to wetting, could be modified in terms of porosity, equivalent pore diameter, and tortuosity to lower their resistance to permeate flux.

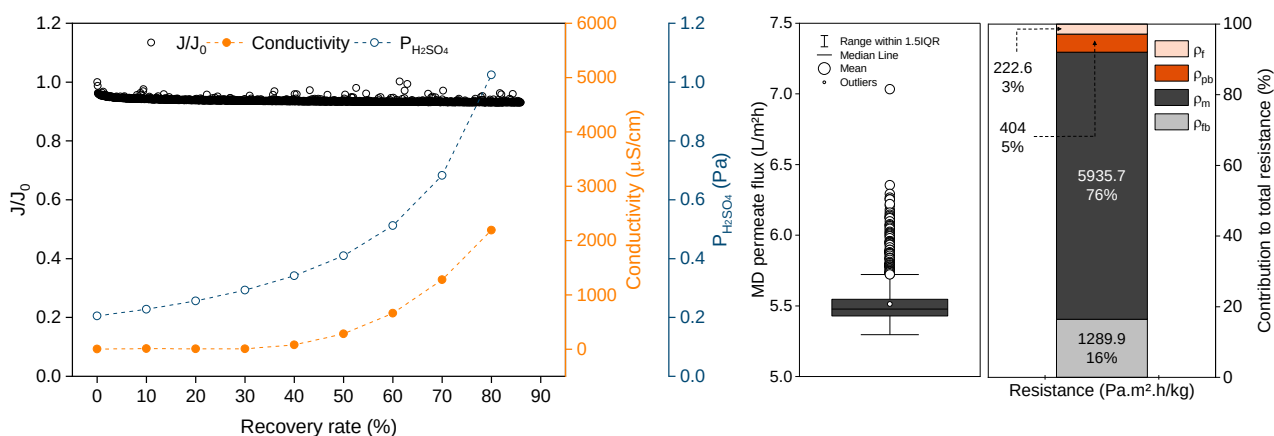


Figure 30. Monitoring data for membrane distillation permeate flux, flux decay, permeate conductivity, sulfuric acid partial vapor pressure, and water recovery rate. Note: Feed temperature: 60 °C, distillate temperature: 25 °C. Recirculation flow rate: 0.3 L/min. The dataset used is available upon request to the corresponding authors.

The temperature polarization coefficient deviated from one ($\tau = 0.62$) and suggested that differences existed between the bulk (feed or permeate) and the membrane surface (facing the feed or permeate). The consequence is a lower driving force for permeation. Besides heat losses to the surroundings, the heat conduction across the membrane is the main responsible for the results obtained. Since the conductive heat across the membrane does not induce

permeate flux, a lower thermal efficiency ($\delta_t = 4.6\%$) was observed as well. Membranes made of PTFE have the highest thermal conductivity and lower thermal resistance compared with other membranes used for MD and are made of polyvinylidene fluoride (PVDF) and polypropylene (PP) [296]. If the wastewater residual heat is considered, the low thermal efficiency would not necessarily imply a greater energy requirement for heating the feed stream; however, the residual heat could be better reused to promote a higher vapor pressure difference across the membrane.

The MD rejection efficiency was greater than 98.7% (Table 11) and the process effectively retained the metallic species that compose gold mining wastewater. Apart from that, the permeate conductivity increased throughout the distillation process (Figure 30) after a recovery rate of 35%. Given that the permeate flux remained stable, membrane wetting was discarded as a possible explanation for the increase in conductivity observed. If wetting is discarded, metallic ions would not transpose the membrane pores and in fact, the highest concentration obtained in the permeate was for magnesium (2.66 ± 0.09 mg/L) and iron (1.65 ± 0.13 mg/L). That leads to a hypothesis that sulfuric acid was permeating through the membrane. In Figure 30 is possible to compare the permeate conductivity and the sulfuric acid vapor pressure along with the process recovery rate, both with a similar increase pattern. As gold mining wastewater is concentrated, sulfuric acid vapor pressure increases, and its propensity to transpose the membrane pores is favored. The phenomenon would then be justified in the permeate final pH, which corresponded to 3.9 ± 0.1 . Despite that, the sulfuric acid recovery by d-LLE would not be compromised given that most acid content from raw wastewater remained in the concentrate. The results were positive in terms of copper retention as well, and the greater concentration of both by-products would favor their recovery by d-LLE. To guarantee high-quality reuse water, the MD recovery rate was then set at 35%.

Table 11. Physicochemical characteristics of POX wastewater and MD concentrate.

Physicochemical characteristics	Raw wastewater	MD rejection efficiency (%)	MD concentrate
pH	1.37 ± 0.27	-	1.10 ± 0.11
Acid (mol/L)	0.072 ± 0.008	98.7	0.079 ± 0.008
Iron (mg/L)	829.2 ± 21.3	99.8	1541.0 ± 45.3
Zinc (mg/L)	37.6 ± 0.12	99.6	112.0 ± 1.7
Aluminum (mg/L)	484.7 ± 15.0	99.6	950.0 ± 21.8
Copper (mg/L)	171.6 ± 7.1	99.6	285.0 ± 6.0
Magnesium (mg/L)	2662.1 ± 101.9	99.9	5324.2 ± 248.6
Nickel (mg/L)	169.3 ± 2.4	>99.9	370.2 ± 40.6
Cobalt (mg/L)	33.1 ± 0.8	>99.5	66.1 ± 1.9

An additional outcome that favors the use of MD is the membrane integrity over longer exposure periods to the wastewater at high temperatures (60°C; exposure period: 240 days). The results summarized in Figure 31 demonstrate that the permeate flux and the rejection efficiency of PTFE membranes were relatively stable, and indirectly suggest that important characteristics of MD membranes (e.g.: liquid entry pressure and wettability) were not severely compromised even under harsh conditions. It is not denied the fact that contact angles and morphological changes might have occurred; however, even when they occur, studies point to the fact that MD performance remains high and stable [297].

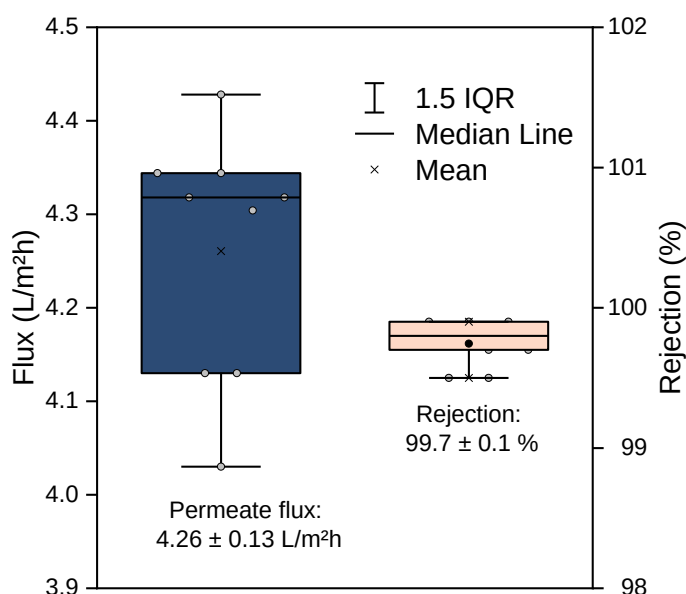


Figure 31. Permeate flux and rejection efficiency of a NaCl (2,000 ppm) model solution of membranes exposed to the gold mining wastewater over 240 days. Note: The membrane integrity was assessed at regular intervals of 30 days. Feed temperature: 60 °C, distillate temperature: 25 °C. Recirculation flow rate: 0.3 L/min. The dataset used is available upon request to the corresponding authors.

3.2 Organic phase selection for acid recovery

Alamine 336 and Versatic acid were the extractants with greater performance for acid recovery from MD concentrate (>70%, Figure 32). The extraction efficiency for the other organic phases varied between 50 – 70% and was considered satisfactory. Among all extractants, Cyanex 923 had a lower efficiency in terms of sulfuric acid extraction. For this system, sulfuric acid preferably stays in the aqueous phase rather than in the organic phase given its distribution coefficient is lower than one. One possible explanation for the lower efficiency of Cyanex 923 is its extraction mechanism of neutral species solvation. For that, most water molecules that involve the acid species should be replaced by the extractant, and soluble complexes are formed in the organic phase [271]. That is a complex mechanism, apart from the fact that most H_2SO_4 would be dissociated and not in its neutral form. For that reason, the extractant presented lower efficiency compared with others.

Versatic acid and Alamine 336 involve an ion-pair formation, besides the fact that anion exchange, H-bond formation, and solvation may occur as well [272]. Both systems had the greatest distribution coefficients suggesting that sulfuric acid preferably stayed in the organic phase rather than in MD concentrate. However, the high interaction rates between sulfuric acid and the extractants Versatic and Alamine 336 impeded an effective recovery after stripping, and the lowest recoveries after stripping were associated with both extractants (Figure 32). Without a proper recovery rate, the organic phase would be saturated, shortening its reuse cycles and requiring early replenishment.

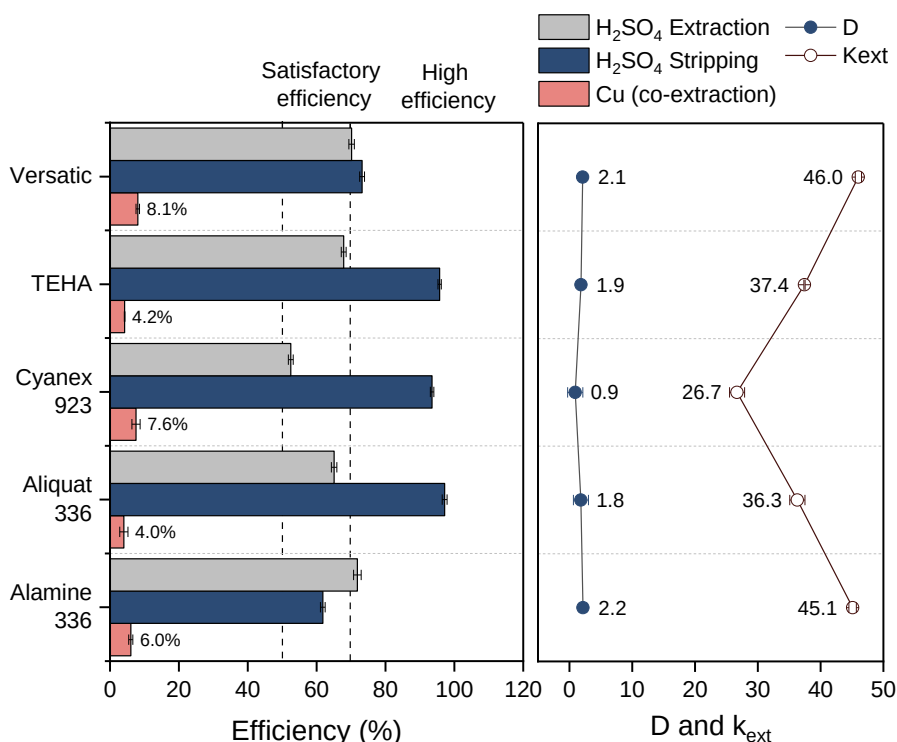
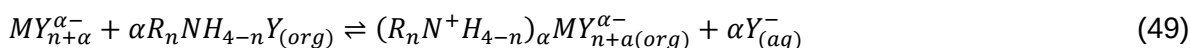


Figure 32. Comparison between different extractants in terms of sulfuric acid recovery, copper co-extraction, and their respective distribution coefficient (D) and extraction constant (k_{ext}). Dilution factor 30 vol.% (O:A 2:1), temperature 60°C, contact and settling time of 10 and 15 min, hot water (60°C) as stripping agent. The dataset used is available upon request to the corresponding authors.

Other alternatives would be TEHA and Aliquat 336, two extractants that presented satisfactory extraction efficiency but high recovery rates after stripping. Moreover, both organic phases had a lower co-extraction of copper compared with the others, which allowed the obtainment of sulfuric acid with higher purity. The use of both TEHA and Aliquat 336 was only possible given that emulsions were prevented when 1-octanol was used. The diluent has a higher density (kerosene: 0.78 g/cm³ and 1-octanol: 0.82 g/cm³) and surface tension values (kerosene: 23 mN/m and 1-decanol: 27.5 mN/m; both at 20°C) compared with kerosene, which are properties that favors a higher dispersion of the extractants and their coalescence after its dispersion. Considering extraction and stripping efficiency, TEHA and Aliquat 336 were chosen for subsequential analysis.

The extraction mechanisms associated with TEHA and Aliquat 336 are similar to those for Alamine 336 since all three extractants are based on amines and ammonium salts. For TEHA ($R_nNH_{3-n(org)}$), the acid ($HY_{(aq)}$) extraction occurs by amine salts formation (Equation 48) whereas the acid ($MY_{n+\alpha}^{\alpha-}$) extraction by Aliquat 336 ($R_nNH_{4-n}(org)$) occurs by ion pairs formation through exchange with Cl (Y , Equation 49), a non-metallic anion that makes up the extractant. In both cases, the extraction efficiency is favored by the acid concentration, which accounts for the advantages of sulfuric acid recovery from MD concentrate rather than raw wastewater.



The mechanisms associated with both extractants were also verified through FTIR spectra, comparing the data before and after d-LLE (Figure 33a-b). Bands at 2920(18), 1384(73), and 1128 cm^{-1} have been previously associated with sulfuric acid [275]. Bands at 2852 – 2924 cm^{-1} are associated with vibrations of axial deformation between the atoms of carbon and hydrogen (C-H) in aliphatic molecules. Additional bands at 1430 – 1570 cm^{-1} were attributed to angular deformations of $(\text{CH}_2)_n$ – ($n>3$), confirmed by the appearance of bands in the region around 700 cm^{-1} . For amine-based extractants (Aliquat 336 and TEHA), bands of weak and medium intensity are observed at 1456 – 1517 cm^{-1} corresponding to angular symmetric deformations of NH_2 and N-H.

In cases of solvation and H-bonding formation, it would be expected that most bands related to H_2SO_4 appear at greater intensities after the extraction. That is confirmed when the bands at 2920(54), 2918, 1460, and 1456 cm^{-1} are analyzed, which indicates that the organic phase was indeed loaded by H_2SO_4 . The hypothesis that complexes may form is also confirmed, in that case by a reduction in transmittance values for the wavenumbers at (e.g.: 1641, 1203, 1126, and 1029 cm^{-1}) after extraction. The spectra and the bands mentioned suggest that most functional groups previously identified interacted at some point to form complexes with sulfuric acid, confirming the extraction mechanisms described.

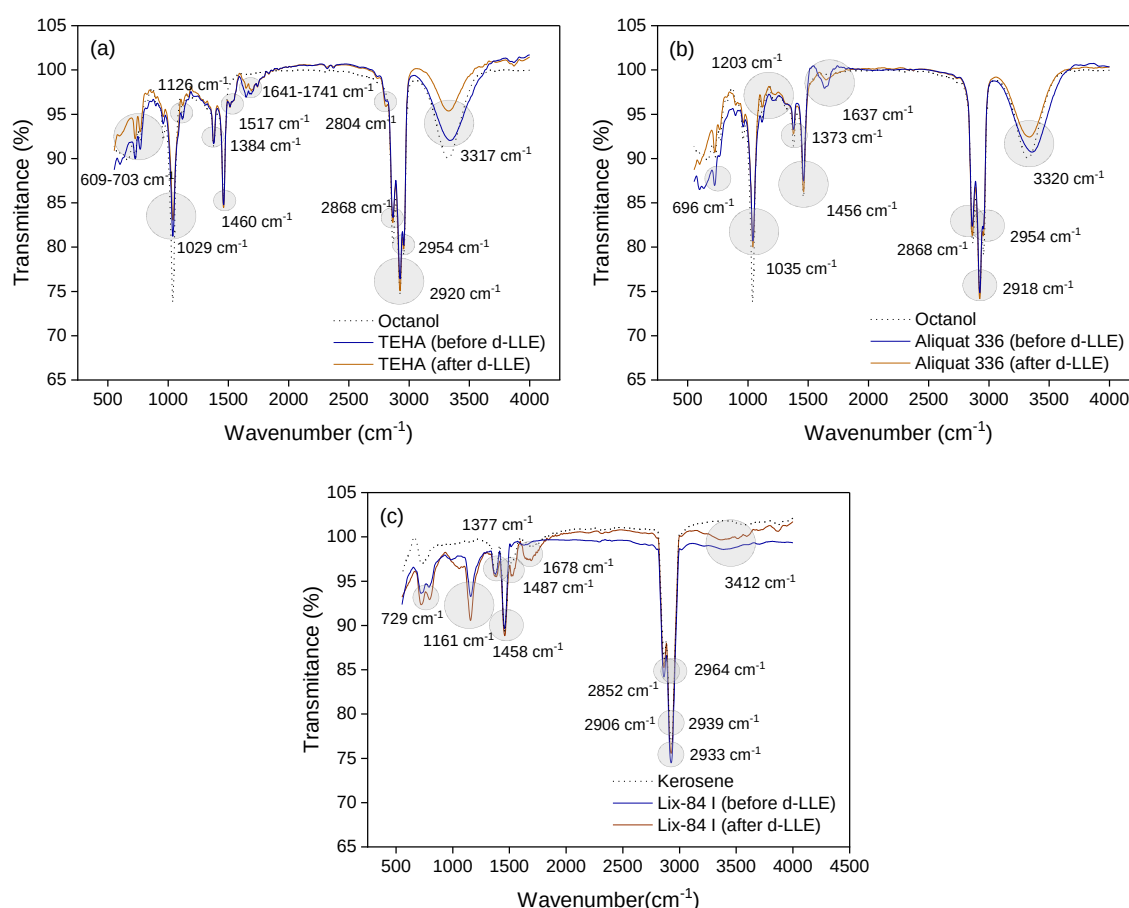


Figure 33. FTIR spectra for (a) TEHA, (b) Aliquat 336, and (c) Lix 84-I before and after dispersive liquid-liquid extraction. The dataset used is available upon request to the corresponding authors.

3.3 Temperature contribution to H₂SO₄ extraction efficiency and selectivity

Results referring to sulfuric acid extraction efficiency and selectivity were summarized in Figure 34. Operations at higher temperatures would in part favor the extraction of sulfuric acid, a process considered endothermic [$\Delta H_{\text{Aliquat 336}}$: 17.9 kJ/mol ($r^2 = 0.999$; $p < 0.01$) and ΔH_{TEHA} : 38.8 kJ/mol ($r^2 = 0.995$; $p = 0.03$)] and spontaneous ($\Delta G_{\text{Aliquat 336}, 60^\circ\text{C}}$: -1.77 kJ/mol and $\Delta G_{\text{TEHA}, 60^\circ\text{C}}$: -2.07 kJ/mol) for both extractants. Given the greater enthalpy value, the temperature would have a greater effect on TEHA extraction efficiency. When the parameter decreased from 60°C to 45°, the extraction performance was lowered by 25.3% for TEHA compared with 11.3% for Aliquat 336. The additional decrease in temperature from 45°C to 30°C was responsible for a reduction of 31.9% (TEHA) and 14.1% (Aliquat 336) in sulfuric acid extraction efficiency. Whereas the extraction of sulfuric acid was considered endothermic, copper co-extraction seems to be exothermic and more pronounced at lower temperature conditions. As demonstrated in Figure 34, copper co-extraction was twice as much when the temperature decreases from 60°C to 45°C for both extractants. An additional advantage of operations at higher temperatures is the shorter phase disengagement times in the settlers, in addition to kinetic and loading advantages [298]. Demopoulos & Gefvert (1984) reported that at room temperature, typical disengagement times are in the range of 8 – 9 minutes, a value that reduces to 5 – 6 minutes at 40-50°C or lower than 4 minutes at temperatures above 60°C.

Overall, the results for sulfuric acid extraction and copper co-extraction are favorable in terms of MD and d-LLE integration considering that MD concentrate is produced at high temperatures (~60°C, MD feed temperature). Given the gains discussed when d-LLE is operated at high temperatures, it would be important to assess the heat transfer and loss that would occur during distillation and d-LLE, and how it would impact the d-LLE performance. On the other side, higher temperatures favored higher co-extraction of magnesium ($\beta_{\text{H}_2\text{SO}_4}/\beta_{\text{Mg}}$) by Aliquat 336 (Figure 34a) and iron ($\beta_{\text{H}_2\text{SO}_4}/\beta_{\text{Fe}}$) and magnesium ($\beta_{\text{H}_2\text{SO}_4}/\beta_{\text{Mg}}$) by TEHA (Figure 34b). When both extractants were compared, TEHA presented higher selectivity given its greater β values. Although it is not expected to recover the species of magnesium and iron after stripping with hot water, which means that sulfuric acid would still be recovered at a reasonable purity, additional scrubbing stages would be required to guarantee that these species would not build up in the organic phase. If not removed, the species of magnesium and iron could saturate the organic phase after multiple contact stages, lowering the acid recovery. For impurities scrubbing, a few agents could be employed as bases, e.g.: NaOH [299], complexing agents, e.g.: EDTA [300], [301], and acids, e.g.: H₂SO₄ [302].

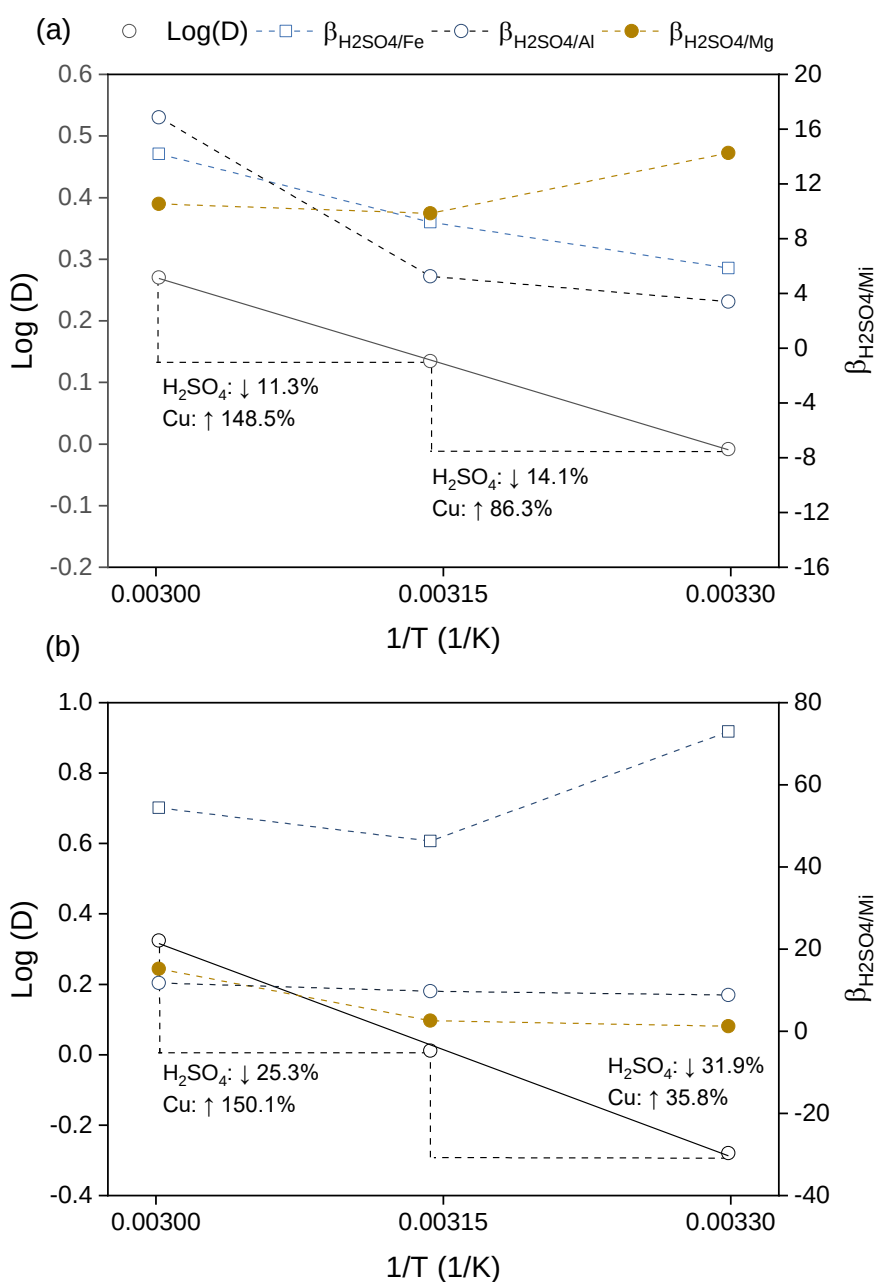


Figure 34. Thermodynamics and selectivity for sulfuric acid recovery by (a) Aliquat 336 and (b) TEHA. Percentages expressed are related to the decrease in sulfuric acid extraction or increase in copper co-extraction. Dilution factor 30 vol.% (O:A 2:1), temperature 60, 45, and 30°C, contact and settling time of 10 and 15 min. Relative standard deviation (RSD) < 2.3%. The dataset used is available upon request to the corresponding authors.

3.4 H_2SO_4 : McCabe-Thiele diagrams and loading capacity

Extraction and stripping isotherms for Aliquat 336 and TEHA were presented in Figure 35 and Figure 36. The greater extraction efficiency of TEHA compared to Aliquat 336 enabled a 95% H_2SO_4 extraction by a lower number of stages (2 and 3 stages, respectively). When it comes to stripping, a single stage was sufficient to recover most sulfuric acid extracted (>95%). To validate the theoretical number of extraction stages, four experimental replicates were made and the raffinate concentrations after the second (for TEHA) and third (for Aliquat 336) stages

were compared with the results obtained from McCabe-Thiele diagrams. The results suggested that the differences observed between theoretical and empirical values (TEHA: 0.005 ± 0.002 mol/L, $p = 0.118$; Aliquat: 0.004 ± 0.001 mol/L; $p = 0.209$) were non-significant.

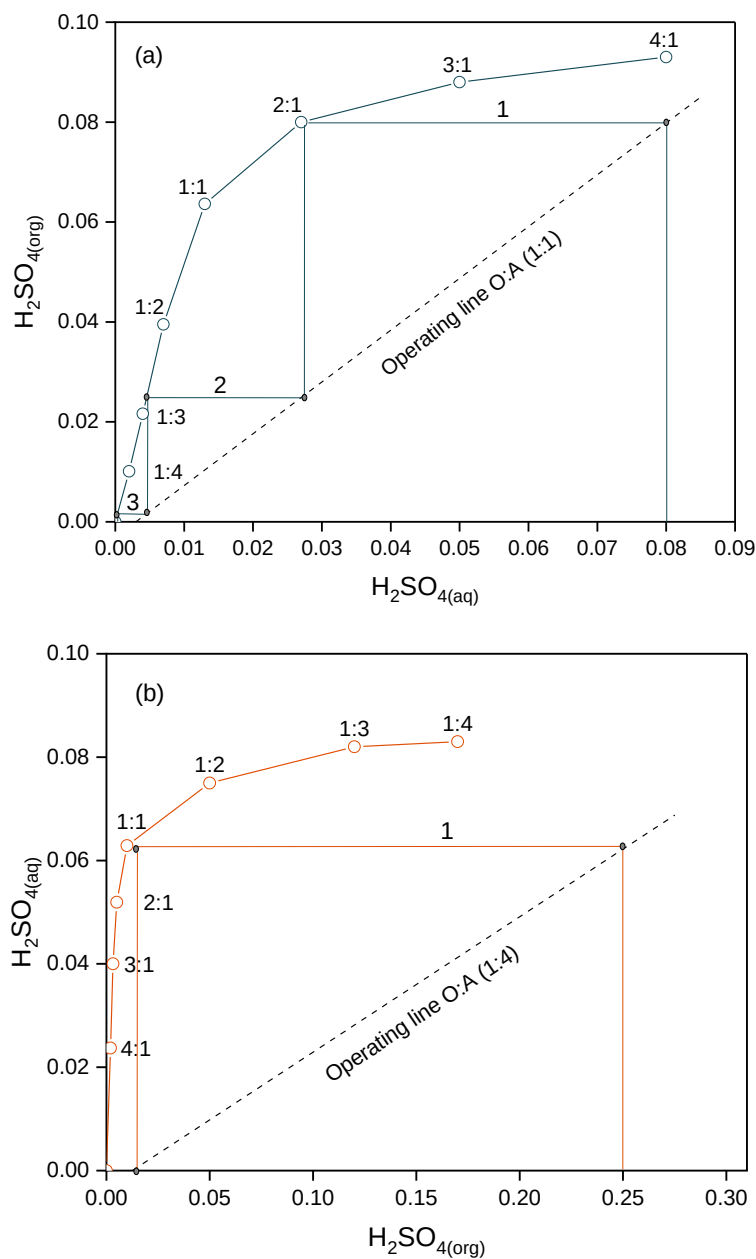


Figure 35. (a) Extraction and (b) stripping isotherms using Aliquat 336 as extractant. Stripping was performed with the extract obtained at an O:A of 2:1. Note: Dilution factor 30 vol.% (O:A 4:1 – 1:4), temperature 60 °C, contact, and settling time of 10 and 15 min. Relative standard deviation (RSD) < 4.1%. The dataset used is available upon request to the corresponding authors.

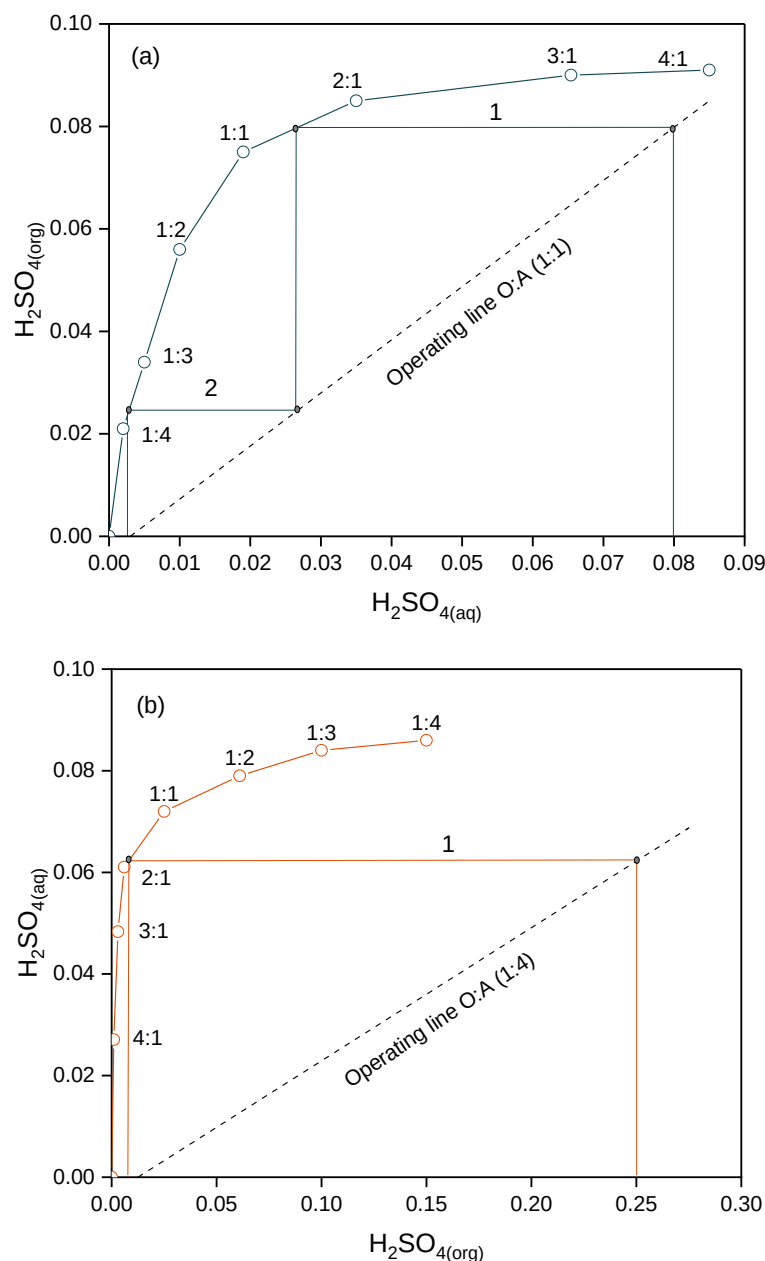


Figure 36. (a) Extraction and (b) stripping isotherms using TEHA as extractant. Stripping was performed with the extract obtained at an O:A of 2:1. Note: Dilution factor 30 vol.% (O:A 4:1 – 1:4), temperature 60 °C, contact, and settling time of 10 and 15 min. Relative standard deviation (RSD) < 3.9%. The dataset used is available upon request to the corresponding authors.

Ultimately, loading capacity was estimated for both Aliquat 336 (Figure 37a) and TEHA (Figure 37b), which remained similar between the first and the second stage given that the amount of sulfuric acid in the organic phase almost doubled (95-96%). That is a positive outcome especially for TEHA, meaning that it would be possible to perform the two contact stages required to achieve a 95% extraction of sulfuric acid (Figure 36a) without an organic phase regeneration by an intermediate stripping process. From the second to the third contact, the amount of sulfuric acid increased by 47% for both extractants and from the third to the fourth contact this value corresponded to 30 – 31%. After four consecutive contacts with a fresh MD concentrate, neither Aliquat 336 nor TEHA became saturated since the amount of sulfuric acid kept increasing. Recent reports suggested that eight consecutive contacts were needed to achieve a condition of organic phase saturation [303], which does not necessarily mean that it

would be practical to perform all eight stages given that the extraction efficiency approaches zero and the gains should not compensate for the additional operational complexity.

Not only acid but the amount of co-extracted species increases with the number of contact stages as well. Nevertheless, compared with their concentration in MD concentrate, the number of species co-extracted by Aliquat 336 and TEHA represented only 1.4 – 1.6% for copper, 0.2 – 0.5% for nickel, and 0.8 – 0.9 for cobalt, and should not compromise their recovery by subsequential extraction stages. Although nickel and cobalt recovery was not covered in the current study, their obtainment from primary sources should be replaced by other alternatives starting from 2025 given that the development and economic competitiveness of different industrial sectors might be threatened by their risk of shortage [304]. Considering the greater loading capacity and lower contact stages for sulfuric acid extraction, the raffinate from the extraction process using TEHA was chosen for copper recovery. The same extractant was considered for economic analysis in Section 3.6.

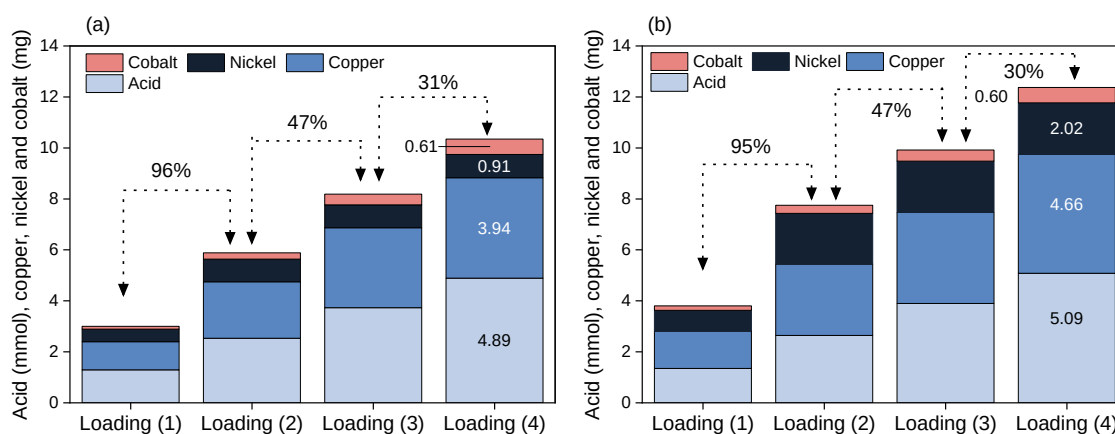


Figure 37. Loading capacity of (a) Aliquat 336 and (b) TEHA. Percentage values represent the sulfuric acid increment in the organic phase. Note: Dilution factor 30 vol.% (O:A 1:1), temperature 60 °C, contact and settling time of 10 and 15 min. Relative standard deviation (RSD) < 1.9%. The dataset used is available upon request to the corresponding authors.

3.5 Copper: Temperature effect, McCabe-Thiele diagrams, and loading capacity

The raffinate from acid extraction by TEHA was subjected to copper recovery by Lix 84 I, in which 99.3% of copper was selectively recovered in a single contact stage ($\beta_{\text{Cu/Fe}} = 4,274$, $\beta_{\text{Cu/Al}} = 176$, and $\beta_{\text{Cu/Mg}} = 1,262$). Equation 46 presents a well-accepted chemical reaction that describes copper ions extraction by Lix 84 I ($RH_{(org)}$), an acid-base reaction in which the extractant would donate protons in exchange for copper ions [305].



As represented, copper extraction would be highly dependent on medium pH and a high concentration of hydrogen ions ($H_{(aq)}^{+}$) would shift the equilibrium towards copper stripping rather than its extraction. That would then justify the first stage of sulfuric acid extraction so that the medium pH (1.89) would fall within the appropriate range that enables higher efficiency and selectivity for copper recovery [22]. H_2SO_4 extraction would still contribute to a lower sulfate content in MD concentrate, responsible to increase the hydrogen ions activity and lower the extraction efficiency [306]. Apart from that, the medium pH and co-existence of other ions

would favor the predominance of divalent protonated species of copper [307], which ultimately would have a higher interaction with the extractant than its complexed form.

FTIR spectrum before and after d-LLE of copper (Figure 33c) presented peaks at 2852 – 2964 cm^{-1} and $\sim 1458 \text{ cm}^{-1}$ that were correlated with C-H of CH_3 and C-H from the benzene ring that composes the extractant. Two distinctive peaks were observed after d-LLE at 1487 and 1687 cm^{-1} most probably derived from complex formation, whereas a shift in stretching vibrations at 759 was correlated to coordination between metal ions with oxygen from C-O [308]. The hypothesis of complex formation was confirmed by the broad absorption band at 3412 cm^{-1} , characteristic of N-OH groups that later disappeared in loaded Lix 84-I due to the intermolecular bonding of copper ions with the oxygen from oxime groups [308], [309].

The process of copper extraction was considered exothermic and spontaneous [ΔH_{Cu} : -23.1 kJ/mol ($r^2 = 0.999$; $p=0.02$) $\Delta G_{\text{Cu},30^\circ\text{C}}$: -12.3 kJ/mol]. At high temperatures ($>40^\circ\text{C}$) and acid conditions, the extractant could undergo deoxidation, therefore lowering its efficiency for copper recovery [310]. Although exothermic, the temperature seems to have a low contribution to extraction efficiency (98.6 – 99.3%), but greater influence over selectivity (Figure 38). Not only copper but magnesium and aluminum had higher co-extracted rates at lower temperatures ($\beta_{\text{Cu/Mg}}$: 1486 – 1262, $\beta_{\text{Cu/Al}}$: 687 – 176; from 60 – 30 $^\circ\text{C}$), whereas iron co-extraction decreases ($\beta_{\text{Cu/Fe}}$: 734 – 4247; from 60 – 30 $^\circ\text{C}$). Despite that, selective copper recovery was not compromised given that the concentration of these species remained low after the extracts obtained at different temperatures were stripped by H_2SO_4 ($<0.33 \text{ g/L}$).

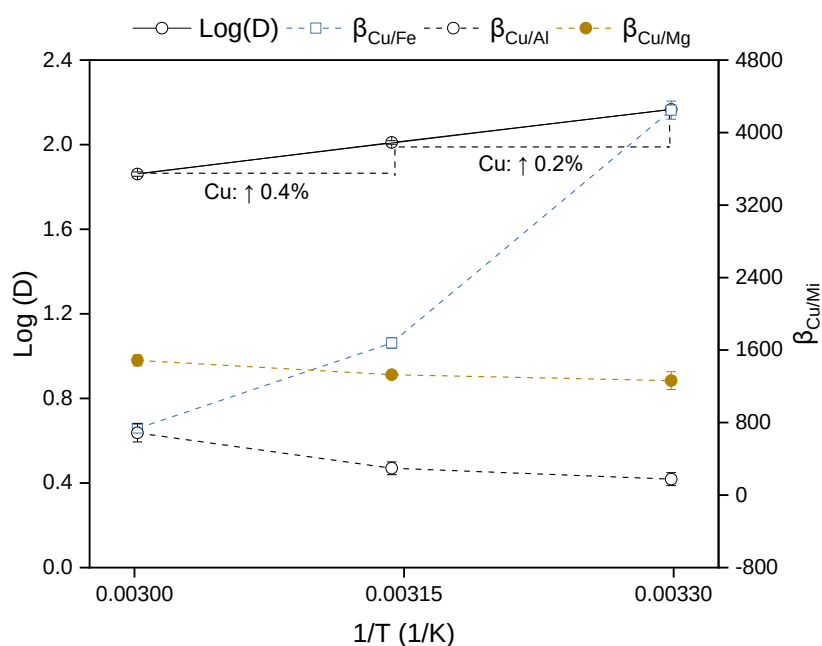


Figure 38. Thermodynamics and selectivity for copper recovery by Lix 84 I. Percentages expressed are related to the increase in copper extraction. Dilution factor 30 vol.% (O:A 2:1), temperature 60, 45, and 30 $^\circ\text{C}$, contact and settling time of 10 and 15 min. Relative standard deviation (RSD) $< 5.1\%$. The dataset used is available upon request to the corresponding authors.

The efficiency for copper extraction and stripping reflected in McCabe-Thiele diagrams, which confirmed an extraction and stripping efficiency greater than 95% after a single contact stage (Figure 39), validated by experimental replicates that had no statistical difference compared with the theoretical values obtained by the diagrams ($p=0.199$). The organic phase selectivity

and affinity for copper also allowed performing four contact stages without a decrease in copper extraction capacity (1st stage: 6.62 mg, 4th stage: 5.93 mg; total: 25.3 mg) and a necessity for the organic phase regeneration. The high loading capacity corroborates the preferable interactions of Lix 84-I for copper compared to other constituents; otherwise, the extractant would be saturated in undesired species and the loading capacity would decrease.

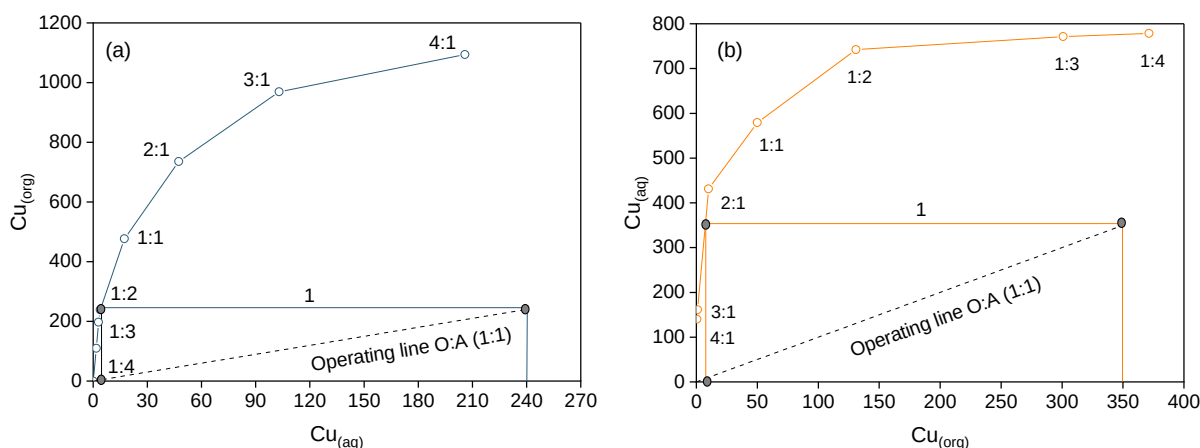


Figure 39. (a) Extraction and (b) stripping isotherms using Lix 84-I as extractant. Stripping was performed with the extract obtained at an O:A of 2:1. Note: Dilution factor 30 vol.% (O:A 4:1 – 1:4), temperature 30 °C, contact, and settling time of 10 and 15 min. Relative standard deviation (RSD) < 2.7%. The dataset used is available upon request to the corresponding authors.

3.6 Economic analysis

For water, acid, and copper recovery, it was estimated a total CapEX of US\$ 1.28 bi, with a greater contribution from the extraction units (MD: US\$ 202k, d-LLE_{H₂SO₄}: US\$ 545k, and d-LLE_{Cu}: US\$ 530k). Greater contributions came from the acquisition of floating head carbon steel tanks, especially for d-LLE in which the tank's volume must ensure a proper hydraulic residence time to achieve the time required for organic and aqueous phase disengagement.

Two different scenarios were considered while estimating the operational expenditures for MD. Without a cooling system for MD distillate, its temperature would increase given the heat transfer from the heated feed stream. That would lower the vapor pressure difference and ultimately reduce the permeate flux. If a cooling system is considered, the cost for water reclamation would be US\$/m³ 2.62, with a greater contribution from cooling requirements (91.9%) (Figure 40). Given the low fouling, cleaning, and maintenance were minor contributors to total MD OpEX. If freshwater or process water is continuously fed in the distillate tank, cooling systems could be in principle discarded. For the second scenario described, the total OPEX would correspond to US\$/m³ 0.23, a value comparable with current prices practiced for freshwater acquisition by industrial facilities (US\$/m³ 0.634). Using the process water as a coolant solution was presented as an alternative by Silva et al. [311], which observed no impact on MD performance when a continuous flow of process water was compared with a refrigerated distillate.

For sulfuric acid, the total OPEX corresponded to US\$/kg_{H₂SO₄} 0.42, with greater contributions from the costs associated with the stripping solution (81.4%). Despite the technical efficiency in H₂SO₄ recovery, the economic results demonstrated that its obtainment by d-LLE would imply a final product with costs greater than currently practiced (US\$/kg_{H₂SO₄} 0.22). Even with

slightly higher costs, the acid recovery would reduce the cost of neutralization and sludge disposal, which could make its recovery feasible when these two parameters are considered in economic analyses.

Copper recovery, though, was both technically and economically viable, with costs of US\$ 4.25 per kilogram of copper recovered (currently practiced: US\$/kg_{Cu} 10.31) (Figure 40). The difference between the OPEX and the commercial copper value would allow additional processes, such as electrolysis, for copper recovery in its solid marketable form, without necessarily compromising the economic viability.

From a closed-loop perspective and considering the technical and economical results, the integrated system opens the opportunity for different scenarios. First, the MD distillate could be used in gold processing units, H₂SO₄ reused to lower the slurry levels of carbonate below 2%, and copper could be commercialization for additional income. A second alternative could be to reuse the water reclaimed by MD as a stripping solution for sulfuric acid, lowering the costs for its obtainment. Besides the reuse of H₂SO₄ to lower the slurry carbonate levels, it could be considered during copper stripping as well. The impacts would go beyond economic gains, but the integrated system should also contribute to lowering the environmental impacts associated with mining industries as well.

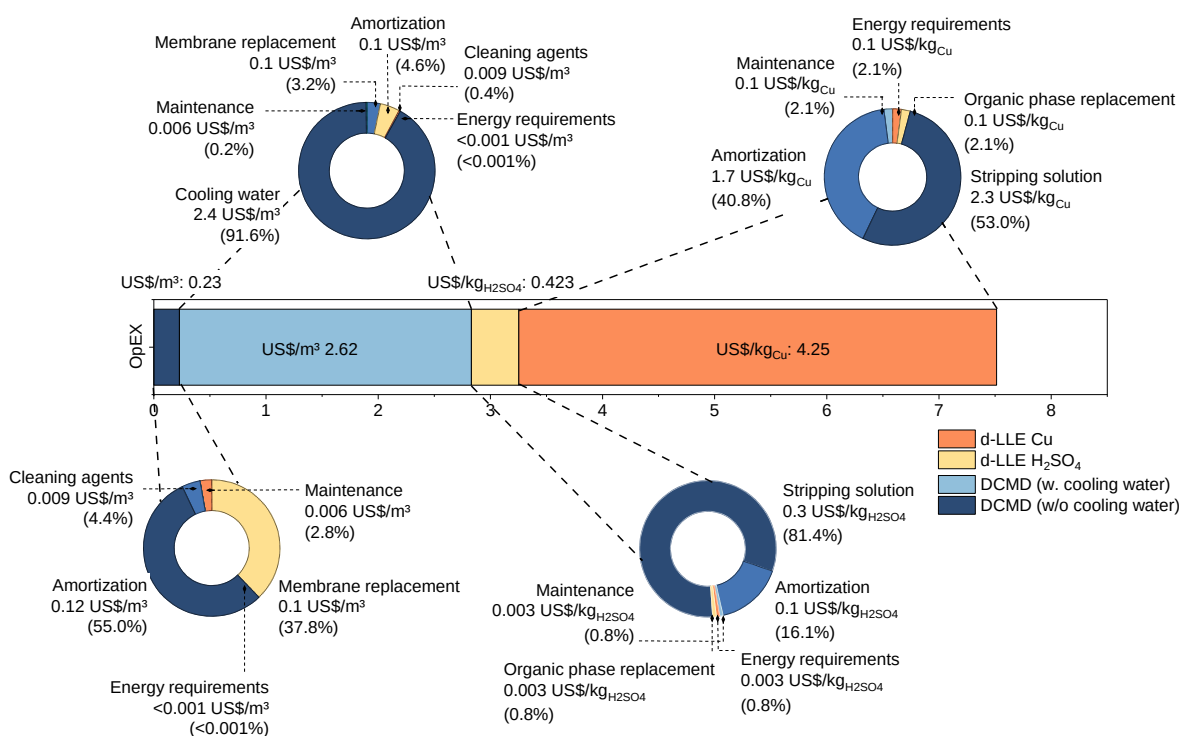


Figure 40. Operational expenditures breakdown for membrane distillation and d-LLE systems.

CHAPTER 6 – NON-DISPERSIVE SOLVENT EXTRACTION AS AN ALTERNATIVE FOR SULFURIC ACID AND COPPER RECYCLING FROM MEMBRANE DISTILLATION CONCENTRATE OF GOLD MINING WASTEWATER

Complete articles published in journals:

[1] **Moreira, V. R., ...**, & Amaral, M. C. (2023). Non-dispersive solvent extraction as an alternative for sulfuric acid and copper recycling from membrane distillation concentrate of gold mining wastewater. *Chemical Engineering Journal*, 144622.

1 Introduction

Mining wastewater treatment represents a challenge due to its complex nature and volume. The high acidity of the wastewater can compromise the integrity of the equipment and hinder the effectiveness of the treatment process [312]. Additionally, trace metals represent serious environmental and human health risks, and their removal requires specialized treatment techniques [312]. One alternative to address this challenge is considering integrated processes, which consist of selecting and connecting different operations to create a treatment flowsheet. Under this perspective, the advantages of each process are summed up to achieve the highest valorization of wastewater, and the final decision on the process design is based on several aspects including efficiency and costs [313], [314].

Amaral et al. [241] integrated different membrane separation processes intended for gold mining wastewater beneficiation. In their case, ultrafiltration membranes acted as a pre-treatment technology for the stages of nanofiltration and reverse osmosis, the first one intended to recover a stream enriched in metals for further beneficiation and the second to recover water and sulfuric acid. The total costs to operate the integrated processes corresponded to US\$ 1.137/m³, from which 71% corresponded to neutralization costs of the ultrafiltration concentrate. A commitment in permeate flux due to fouling was a second aspect reported by the authors, which limited the recovery rates to 40-50% by nanofiltration and reverse osmosis.

Another alternative could be the use of membrane distillation, which can be favored by the wastewater waste heat (temperature after the oxidation circuit: ~60 – 80°C). The waste heat can promote the vapor pressure difference required in membrane distillation, leading to vapor transport across a hydrophobic and microporous membrane from the heated stream (feed) to the refrigerated stream (distillate) [22], [315]. The authors previously investigated the potential of the membrane distillation process in mining wastewater treatment and reported rejection efficiencies greater than 95.7% for metallic species and acid retentions greater than 99.9%, producing a high-quality distillate for reuse purposes.

Even so, the concentrate generation would still represent a challenge. To address it, Kavitha et al. [316] explored the potential of membrane-assisted solvent extraction in the recovery of metallic compounds. The idea consists of the use of an organic phase with a higher affinity for the byproduct of interest compared to the aqueous concentrate stream. In conventional processes, the organic (extractant) and aqueous (wastewater) phases are dispersed in one another to enhance mass transfer and by-product recovery. After dispersion, the system is left to settle for phases' disengagement, and the organic phase is subjected to a re-extraction, or stripping, process for the by-product recovery and simultaneous regeneration [22]. However, the dispersion processes could lead to emulsions and losses of the extractant, which is currently the main shortcoming of conventional processes.

Different from conventional solvent extraction, the membrane-assisted processes dispense the necessity for the organic phase dispersion into the aqueous one. Instead, the use of hydrophobic membranes allows its wetting by the organic phase and the mass transfer interface becomes the opening of each membrane pore. The process account for a higher surface area, providing greater mass transfer per unit volume (~500 times greater than in solvent extraction columns [30]). The process is driven by the chemical potential difference between the wastewater and the extractant and the by-product is transferred by a diffusion phenomenon [317]. Thus, extraction processes applied to concentrated streams might present

a greater performance compared with raw wastewater that was not previously concentrated by a membrane separation process. Still, the existence of a physical medium assisting the extraction also implies greater resistance to mass transfer that derives from the aqueous and organic phases boundary layers and the resistance posed by the membrane itself. For that reason, it is important to properly assess the operating conditions that lower the resistances mentioned and improve the mass transfer in the non-dispersive solvent extraction.

Therefore, the current study intends to experimentally validate the performance of hollow-fiber membrane contactors in sulfuric acid and copper recycling from a concentrated stream obtained from membrane distillation treating a pressure oxidation wastewater. In light of the pH-dependent nature of the extraction process [22], the initial step involved the recovery of sulfuric acid to facilitate the adjustment of wastewater pH to suitable levels for copper extraction (pH~2.0 [22]). Both sulfuric acid and copper exhibit significant potential for reuse within the mining industry, thereby enhancing its overall sustainability. The utilization of acid and copper in the pressure oxidation process plays a pivotal role in reducing carbonate levels within the ore. Additionally, copper demonstrates the ability to augment the oxidation rate of pyrite and arsenopyrite. Consequently, recognizing their potential as valuable by-products, the manuscript will delve further into elucidating the details of their recovery and exploring their extensive possibilities for reuse. Both species were recovered from membrane distillation concentrate after water was recovered for reuse [195].

In addition to extraction efficiency, the paper brings an in-depth discussion of extraction mechanisms and the phenomena of mass transfer at different experimental conditions of organic flow rate, temperature, and organic phase composition. It is also presented a preliminary economic analysis to better support the decision for hollow-fiber membrane contactors beyond the technical results. Thus, it is expected to contribute to the advancement of membrane-based technologies intended to recover by-products from wastewater.

2 Material and methods

2.1 Gold mining wastewater sampling and membrane distillation concentrate

The wastewater was sampled after settling tanks intended to separate the liquid and solid phases leaving the stages of pressure oxidation. The overflow usually achieves temperatures between 60 – 80 °C and is characterized by low pH values and high concentrations of iron, magnesium, manganese, copper, nickel, and cobalt. Once collected, the wastewater was stored at 4°C and brought to room temperature before being concentrated by membrane distillation. The experiments considered a PTFE (poly(tetrafluoroethylene)) membrane with spacer (CF042 Low Foulant Spacer, PTFE 31Mil – 0.787 mm), both with an effective area of 0.0042 m² and provided by Sterlitech. The feed and distillate temperatures were 60 and 25 °C, both recirculated at 0.3 L/min. It achieved an average distillate flux of 6.82 L/m²h and a recovery rate of 33.9%, without compromising the distillate physicochemical quality. These results were presented in detail at [5], and the physicochemical characteristics of raw wastewater and the concentrate obtained were presented in Table 12. All characterization procedures followed the recommendations described in the Standard Methods for the Examination of Water and Wastewater [267] (metal ions: method 3111; pH: method 4500-H⁺; sulfuric acid: methods 4500-H⁺ and 2310; and conductivity: method 2510)

Table 12. Physicochemical characterization for the streams obtained after membrane distillation and non-dispersive solvent extraction processes. Values refer to average $\pm$ standard deviation (n=3). ^{1,2}
Values obtained under the most appropriate extraction conditions.

Parameter	Gold mining wastewater	Membrane distillation permeate	Membrane distillation concentrate	Acid solution	Copper solution*
pH	1.37 ± 0.27	3.90 ± 0.10	1.10 ± 0.11	1.23 ± 0.11	0.13 ± 0.08
Conductivity (mS/cm)	16.8 ± 1.7	20.1 ± 0.3	39.4 ± 5.4	7.7 ± 0.4	-
H ₂ SO ₄ (mol/L)	0.072 ± 0.008	<0.001	0.079 ± 0.008	0.059 ± 0.002	-
Iron (mg/L)	829.2 ± 21.3	0.8 ± 0.2	1541.0 ± 45.3	2.7 ± 0.8	<0.1
Magnesium (mg/L)	2662.1 ± 101.9	1.2 ± 0.2	5324.2 ± 248.6	3.1 ± 0.3	<0.1
Manganese (mg/L)	85.5 ± 2.1	<0.1	154.9 ± 5.8	<0.1	<0.1
Copper (mg/L)	171.6 ± 7.1	<0.1	285.0 ± 6.0	<0.1	269.0 ± 3.9
Nickel (mg/L)	169.3 ± 2.4	<0.1	370.2 ± 40.6	0.3 ± 0.1	<0.1
Cobalt (mg/L)	33.1 ± 0.8	<0.1	66.1 ± 1.9	<0.1	<0.1

*Note: copper was recovered in a sulfuric acid solution of 1 mol/L and the parameters pH, conductivity, and H₂SO₄ concentration do not necessarily represent the contribution of extraction/stripping processes.

2.2 Experiments of non-dispersive solvent extraction

The non-dispersive solvent experiments intended to recycle mineral acid and copper from membrane distillation concentrate. The extractants were chosen based on previous studies that suggested that tris(2-ethylhexyl)amine (TEHA), Aliquat 336, and Lix84-I presented better results in a conventional solvent extraction process, the first two for mineral acid recovery and the last one for copper recovery [195], [318]. The investigations focused on the main variables that affect the efficiency of membrane contactors, assessing the contribution of different flow rates of the organic phase (4 – 12 cm³/s), organic phase composition (5 – 15 wt.%), temperature effect (30 – 60 °C) and equilibrium periods (0 – 1440 min). TEHA and Aliquat 336 were preferably diluted in 1-octanol, whereas Lix-84I was diluted in kerosene, used as received and without further purification. All three extractants were provided by BASF, whereas 1-octanol and kerosene were purchased from Êxodo Científica. The total feed volume and the volume of the aqueous and organic phases were set at 0.2 L. A description of the extractants used is presented in Table 13. Mineral acid was re-extracted from the organic phase by hot water (60°C) and copper by a sulfuric acid solution (1.0 mol/L) at room temperature.

Table 13. Characteristics of the extractants used for sulfuric acid recovery from membrane distillation concentrate. Reference: [268]. N.a.: information not available.

Name	Formula	Density (g/cm ³)	Molecular weight (g/mol)	Melting point (°C)	Boiling point (°C)	Composition (mol/L)
Aliquat 336	C ₂₅ H ₅₄ ClN	0.884	404.16	-20	225	0.720
TEHA Tris-(2-ethylhexyl)amine	C ₂₄ H ₅₁ N	0.817	353.7	-46	204	0.762
LIX84-I	C ₁₇ H ₂₆ O ₂	0.900 – 0.910	262.4	n.a.	n.a.	n.a.

Hollow fiber membrane contactors were used, provided by Liqui-CelTM (membrane material: polypropylene; packing density: ~10,000 fibers/module, the average surface area of 1.4m², and an effective length of 15 cm). The aqueous (lumen side) and organic (shell side) were added in countercurrent mode, both at the same volume (200 mL). The non-dispersion condition was guaranteed by setting a pressure difference of >0.3 bar between the organic and aqueous phases across the membrane, controlled indirectly by the different flow rates of the currents. A schematic illustration depicting the experimental configuration is presented in Figure 2, elucidating the setup employed in this study.

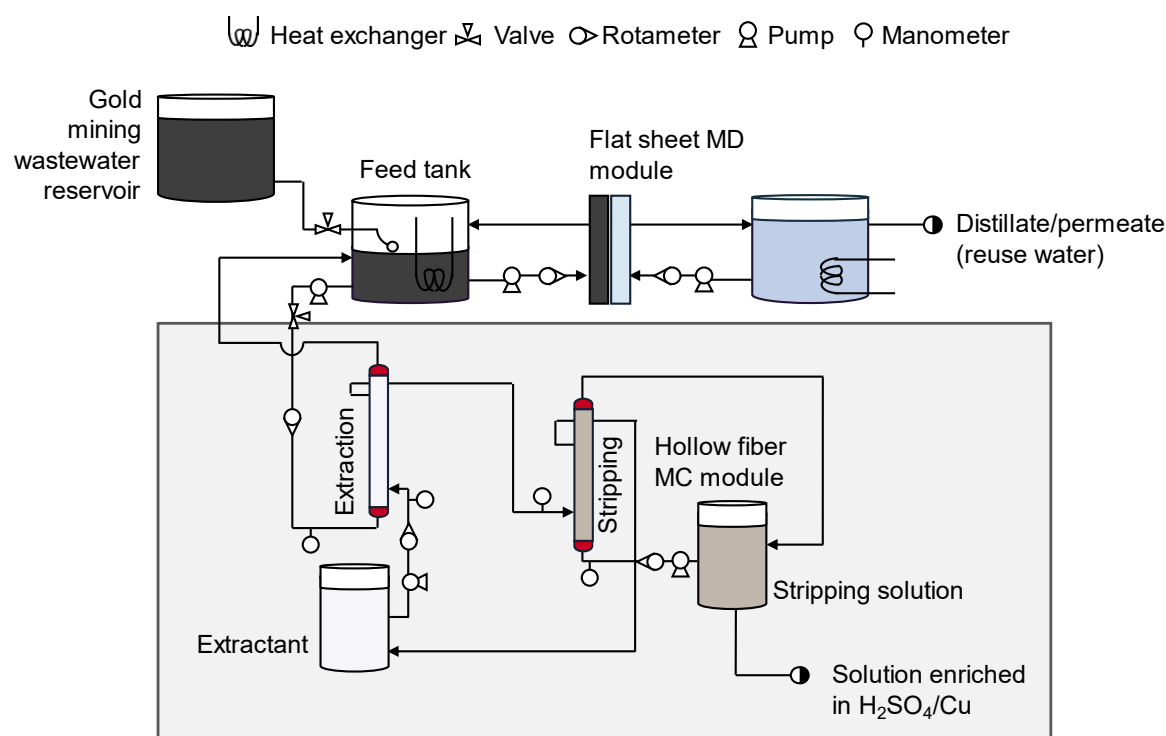


Figure 41. A schematic illustration depicting the extraction system under study.

Two response variables, selectivity for the compound of interest and the recovery efficiency, were monitored during the experiments. These, in turn, are strongly correlated with the mass transfer phenomena, which coefficients should also be appraised for different experimental conditions. The selectivity (β_{M_1/M_2}) is based on the distribution coefficient (H_M), estimated by Equations 50-51. The variables M_{org} (mg/L) and M_{aq} (mg/L) refers to a given compound concentration in the organic and aqueous phases. Selectivity values greater than one suggest that the extraction is possible and it is associated with an organic phase enriched in the compound M_1 , while selectivity values equal to one suggest that extraction is not possible.

$$H_M = [M_{org}]/[M_{aq}] \quad (50)$$

$$\beta_{M_1/M_2} = [H_{M1}]/[H_{M2}] \quad (51)$$

A resistance-in-series (Equation 52) model was considered to assess the mass transfer, which implies that the overall mass transfer coefficient will be a function of the resistances imposed by the aqueous phase, the membrane, and the organic phase. These were represented in Figure 42, along with a brief description of each one and how to calculate it.

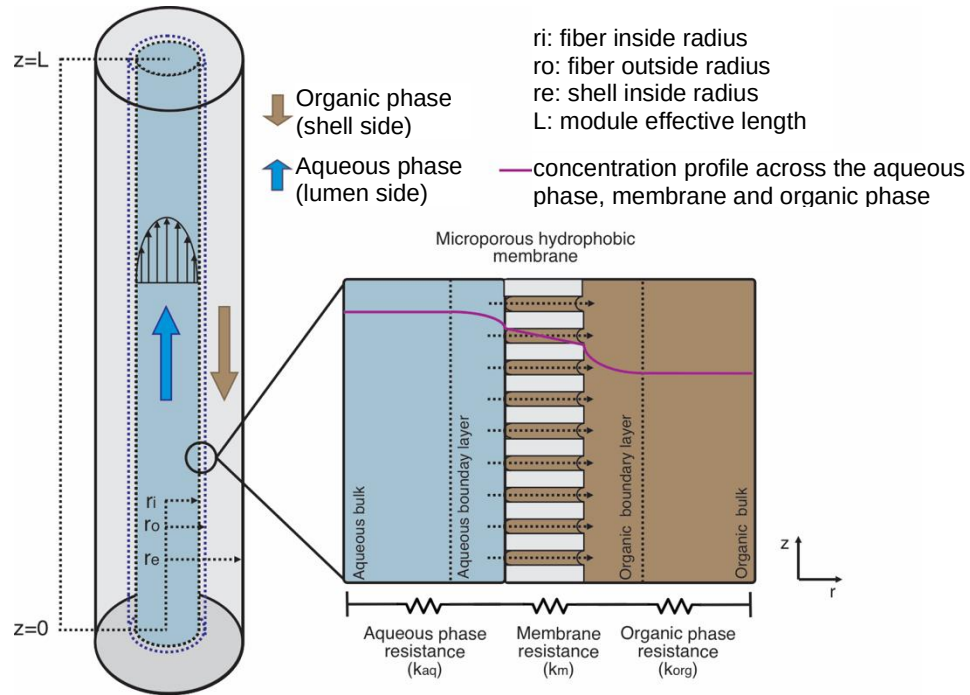


Figure 42. Concentration profile and mass transfer resistances in a single hollow fiber. Reference: [319]

In Equations 52-53, K is the overall mass transfer coefficient, k_{aq} , k_{org} and k_i corresponds to the aqueous, organic, and local mass transfer coefficients, respectively, d_i to the fiber's inner diameter, d_o to the fiber's outer diameter, d_{lm} (Equation 53) to the logarithmic mean diameter, and H_m to de distribution coefficient.

$$\frac{1}{K} = \frac{1}{k_{aq}} + \frac{d_i}{d_{lm}} \frac{1}{H_M k_m} + \frac{d_i}{d_o} \frac{1}{H_M k_{org}} + \frac{1}{k_i} \quad (52)$$

$$d_{lm} = \frac{d_o - d_i}{\ln \frac{d_o}{d_i}} \quad (53)$$

The overall mass transfer coefficient (K) is a time-independent parameter and can be empirically obtained while monitoring the concentration of A over time ($t = 0 \rightarrow t = t$) (Equation 54); in which S_0 corresponds to the membrane effective area and the total feed solution volume.

$$\ln \frac{[A]_t}{[A]_0} = -\frac{S_0}{V} Kt \quad (54)$$

However, mass transfer coefficients related to the aqueous and organic phases are subjected to hydrodynamic conditions. Several distinct correlations are presented in the literature, being summarized in consolidated review articles [30], [112], [129], [319]. Due to the differences in module geometry, fiber arrangement, and fluid flow pattern, especially on the shell side, different prediction models have been proposed. The L  v  que approximation (Equation 55) is a well-known and acceptable model for determining the mass transfer coefficient on the tube side under laminar flow conditions. The expression presents a reasonable accuracy for mass transfer predictions whose Graetz number (G_z) is lower than 6 [$G_z = f(Re, Sc)$ – Equations 56-58; Re : Reynolds number and Sc : Schmidt number]. In Equation 55-59, Sh is the Sherwood number, $v_{aq,org}$ corresponds to the average velocity (aqueous or organic phase); and L to the fiber effective length. D_{aq} corresponds to the diffusivity of the species of interest in the aqueous feed solution, obtained from the literature or calculated by the Wilke-Chang equation [320]; $\rho_{aq,org}$ is the density (aqueous or organic phase); D_h is the module hydraulic diameter; and μ is the dynamic viscosity. In Equation 59, D_i represents the diffusivity of solutes in both non-associated solvents ($x = 1$) and water ($x = 2.6$), while $M_{w,i}$ corresponds to the molecular weight of the solvent (g/mol), T the temperature (K), and V_i (cm³/mol) the molar volume of species i at normal boiling point [56].

$$Sh = \frac{k_{aq} d_i}{D_{aq}} = 0.55 Sc Re \left(\frac{d_i}{L} \right) \quad (55)$$

$$Gz = \frac{D_h}{L} Re Sc \quad (56)$$

$$Re = \frac{v_{aq,org} \rho_{aq,org} D_h}{\mu_{aq,org}} \quad (57)$$

$$Sc = \frac{\mu_{aq,org}}{\rho_{aq,org} D_{aq,org}} \quad (58)$$

$$D_i = 7.4 \cdot 10^{-8} \frac{(x M_{w,i})^{0.5} T}{(\mu) V_i^{0.6}} \quad (59)$$

The resistance imposed by the organic phase boundary layer was calculated by Equation 60; in which D_{org} corresponds to the diffusivity of the species of interest in the aqueous/organic phase solution, ϕ the module packing fraction, and β to 5.8 for a hydrophobic membrane. In this case, the model has good accuracy for $0 < Re < 500$ and $0.04 < \phi < 0.4$. Finally, the mass transfer coefficient related to the membrane can be obtained by Equation 61, which is inherent to the membrane properties and, therefore, independent of the hydrodynamic conditions. In Equation 61, ε corresponds to the membrane porosity (0.4) and to its roughness (2.5), which values were informed by the manufacturer.

$$Sh = \frac{D_h k_{org}}{D_{org}} = \beta \left[\left(\frac{D_h(1-\phi)}{L} \right) \right] Re^{0.6} Sc^{0.33} \quad (60)$$

$$k_m = \frac{D_{org} \varepsilon}{\tau \frac{(d_o - d_i)}{2}} \quad (61)$$

2.3 Preliminary economic analysis

The approach for cost estimation consisted of capital (CAPEX) and operational costs (OPEX) assessment based on the wastewater flow rate in the mining facility (60 m³/h). The equipment costs (C_b) were estimated by the ration-and-proportion relationship (Equation 62) which considers the base variable (S_a), the real variable (S_b) the bare module cost (C_a , which accounts for direct and indirect costs associated with equipment purchase and installation), and a factor exponent (n) (Table 3). The costs were periodically updated as needed, taking into account the Chemical Engineering Plant Cost Index (CEPCI) values for 2020 (569.2) and the base year (567.5).

$$C_b = C_a (S_b / S_a)^n \quad (62)$$

The preliminary economic analysis considered the following assumptions: (i) the membranes would operate with a lifespan of 3 years, being cleaned monthly with isopropanol (cleaning agent requirement: 0.06 kg/m² - defined empirically) and (ii) a 5-year interval for the organic phase replenishment [294]. This cost, in addition to those related to the extractants, stripping solution, energy (efficiency considered: 0.85), amortization, and maintenance were summed up and considered as OPEX. The amortization costs (AC_f , Equation 63) was calculated by annualizing the capital cost (C_{capEX}), where i_r is the investment rate (6.5%) and ls the project lifespan (15 years). The maintenance rate was defined as 5% of the capital costs.

$$AC_f = C_{capEX} \{ i_r / [1 - (1 + i_r)^{-ls}] \} \quad (63)$$

Table 14. Expenditures considered for capital costs (CAPEX [321]) and operational costs (OPEX) estimation. *[269], **Values were based on the most recent Chemicals Market Report provided by the Independent Commodity Intelligence Service (ICIS).

Process	Equipment description	Base variable (S_a)	Bare module cost (US\$; C_a)	n*	Real variable (S_b)
Extraction and stripping system	Wastewater tank: Floating head carbon steel	90	63,524.00	0.6	118.5
	Organic tank: Floating head carbon steel	90	63,524.00	0.6	118.5
	Stripping tank: Floating head carbon steel	90	63,524.00	0.6	15
	Centrifugal, stainless steel shaft power (kW)	1	15,345.00	0.7	1
	Multiple pipe, copper/carbon steel (m)	10	19,515.00	0.6	10
	Hollow fiber membrane contactor (m ²)	1.4	725.50	0.5	166,320
OPEX expenses	Chemicals, utilities, and waste disposal	Value			
	TEHA (US\$/kg)	4.00			

Lix 84-I (us\$/kg)	4.00
Kerosene (US\$/kg)	0.71
1-octanol (US\$/kg)	1.05
Isopropanol (US\$/kg)	1.00
Water for stripping (US\$/kg)	0.63
Acid solution for stripping (US\$/kg)	1.14
Energy (US\$/kWh)	0.04
Waste disposal (US\$/m ³)	1.00

3 Results and discussion

3.1 Non-dispersive solvent extraction for acid recycling

The performance of TEHA and Aliquat 336 for acid extraction is shown in Figure 43. The results show a better performance of TEHA, capable to extract higher amounts of mineral acid from gold mining wastewater. The isotherms shown in Figure 43 (a) tend to have minor variations in concentration values after 120 minutes of extraction, suggesting that times greater than that would not necessarily imply a higher amount of acid extracted. The affinity for acid recovery is also seen in Figure 43 (b), which shows the concentration ratio for other species in the experiment with TEHA. The co-extraction of magnesium (9.8%) was the highest among all metallic species, favored by its higher concentration and therefore driving force, while copper tends to remain in the aqueous phase due to its lower affinity for the extractant (co-extraction: 6.1%). The result suggests the opportunity for a selective acid recovery, with the potential for reuse. Similar results were observed for Aliquat 336 in terms of co-extraction, magnesium, and iron presented the highest co-extraction potential (7.8 and 8.1%, respectively), whereas copper and other species remained in the aqueous phase (co-extraction <5.9%).

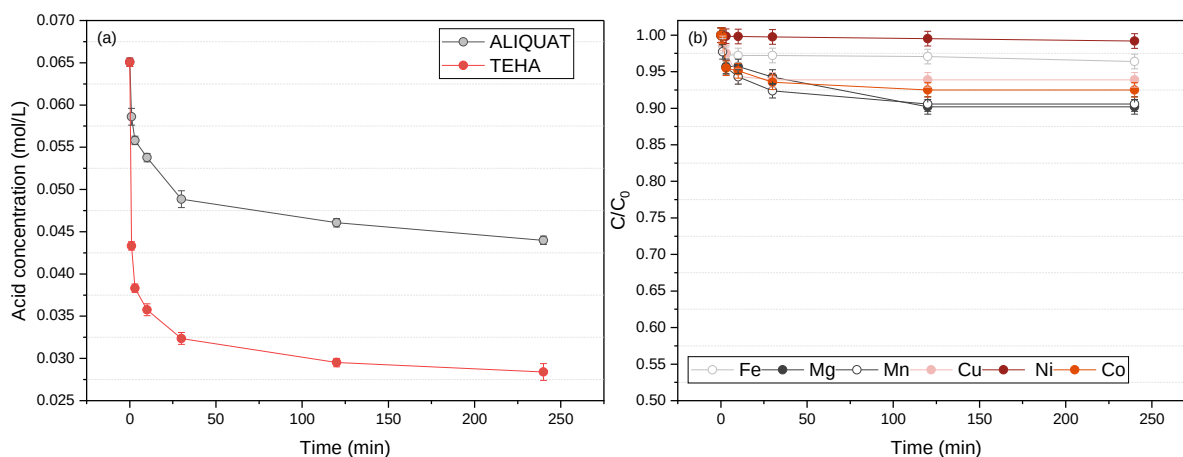
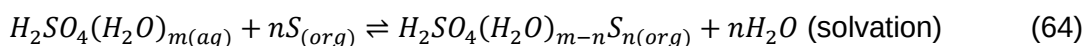


Figure 43. (a) Comparison between TEHA and ALIQUAT 336 in mineral acid extraction and (b) Co-extraction of metals in experiments with TEHA as extractant. Extractant concentration: 10 vol.% in 1-octanol, extraction temperature: 60 °C, Q_{aq} : 36 cm³/s, Q_{org} : 4 cm³/s. Aqueous and organic phase volumes: 200 mL.

The results could be explained by the mechanisms of extraction involving the two extractants. For amine-based extractants such as Aliquat 336 and TEHA, the extraction process relies on an ion-pair formation since, in general, both amine and the acid (in their anionic form) has the same basicity [272], [318]. Depending on their basicity, the extractant can react to form an ammonium cation $R_nNH_{(4-n)}^+$ that further associates with an anion (*i.e.*: a counterion) to maintain neutrality. Complementarily, TEHA could further extract the species of mineral acid by solvation, replacing the water molecules with the extractant molecules in the solvation sphere [272], [273]. These mechanisms were illustrated in Equations 64-65, complemented by an illustration in Figure 44 that also shows the speciation diagram for sulfuric acid under a wide medium pH. Considering that the membrane distillation concentrate pH (1.10 ± 0.11), the prevailing specie being extracted after hydrogen ions would be the bisulfate (HSO_4^-).



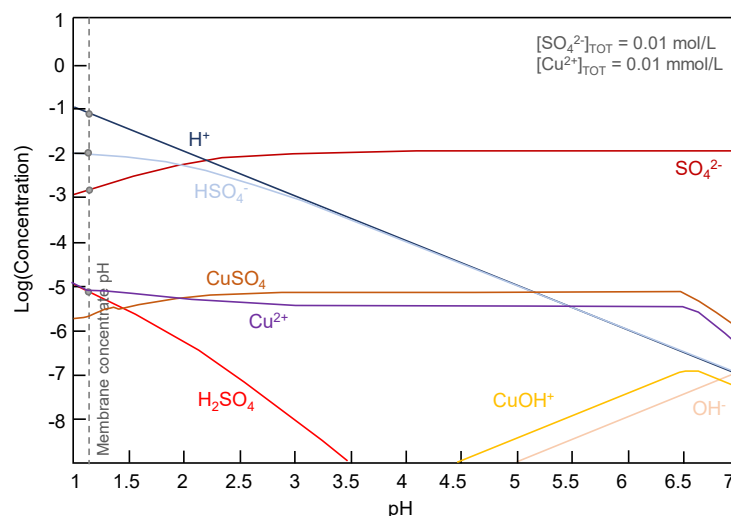
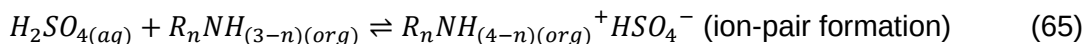


Figure 44. Speciation diagram (Log[Concentration] vs. medium pH) for sulfuric acid and copper.

The molecular structure of the extractant influences its ability to selectively bind to certain species and the interaction with the acid is commonly preferred (see equations 16-17). Additionally, the medium pH can also impact metals recovery, especially copper [22], [268]. The solvent extraction process is often performed under controlled pH conditions. In certain pH ranges, copper may exist in different chemical forms, (Figure 5), which may have reduced affinity for the extractant compared to other species in the medium [22], [268].

The mechanisms are further complemented by the FTIR analysis shown in Figure 45. In general, it is noted that the spectra after and before the extraction process, when compared, remained similar. This is a valuable outcome that attests to the extractant's characteristics even after being exposed to extreme conditions of high temperature and acid wastewater. Depending on the extractant replacement rate, the process could become unfeasible. Bands at 2960 , 2410 , 1359 , 1158 , 957 , and 902 cm^{-1} have been previously correlated with the presence of H_2SO_4 [275]. In cases of solvation and H-bonding formation, mechanisms related to the extraction process with TEHA, most bands related to H_2SO_4 appear (2960 and 2952 cm^{-1} ; 1373 and 1377 cm^{-1}) at greater intensities after the extraction process and indicate an organic phase loaded by the non-dissociated form of H_2SO_4 . The occurrence of these bands, in higher intensities, for the loaded organic phase reinforces the fact that the mineral acid was indeed extracted. Other bands at $2852 - 2924 \text{ cm}^{-1}$ and $1160 - 1300 \text{ cm}^{-1}$ derive from the vibrations of axial deformation between the atoms of carbon and hydrogen (C-H) in aliphatic molecules. Additional bands at $1430 - 1570 \text{ cm}^{-1}$ correspond to angular deformations of $(CH_2)_n$ ($n > 3$), confirmed by bands in the region of 720 cm^{-1} . Considering that TEHA and Aliquat 336 are amine-base extractants, it is expected bands of weak and medium intensity at $1460 - 1514 \text{ cm}^{-1}$, correspond to angular symmetric deformations of NH_2 and N-H. For the other extractants that involve a complex formation (or ion-pair formation), it is possible to note a reduction in transmittance values after extraction, suggesting that most functional groups previously identified interacted at some point to form pairs with mineral acids.

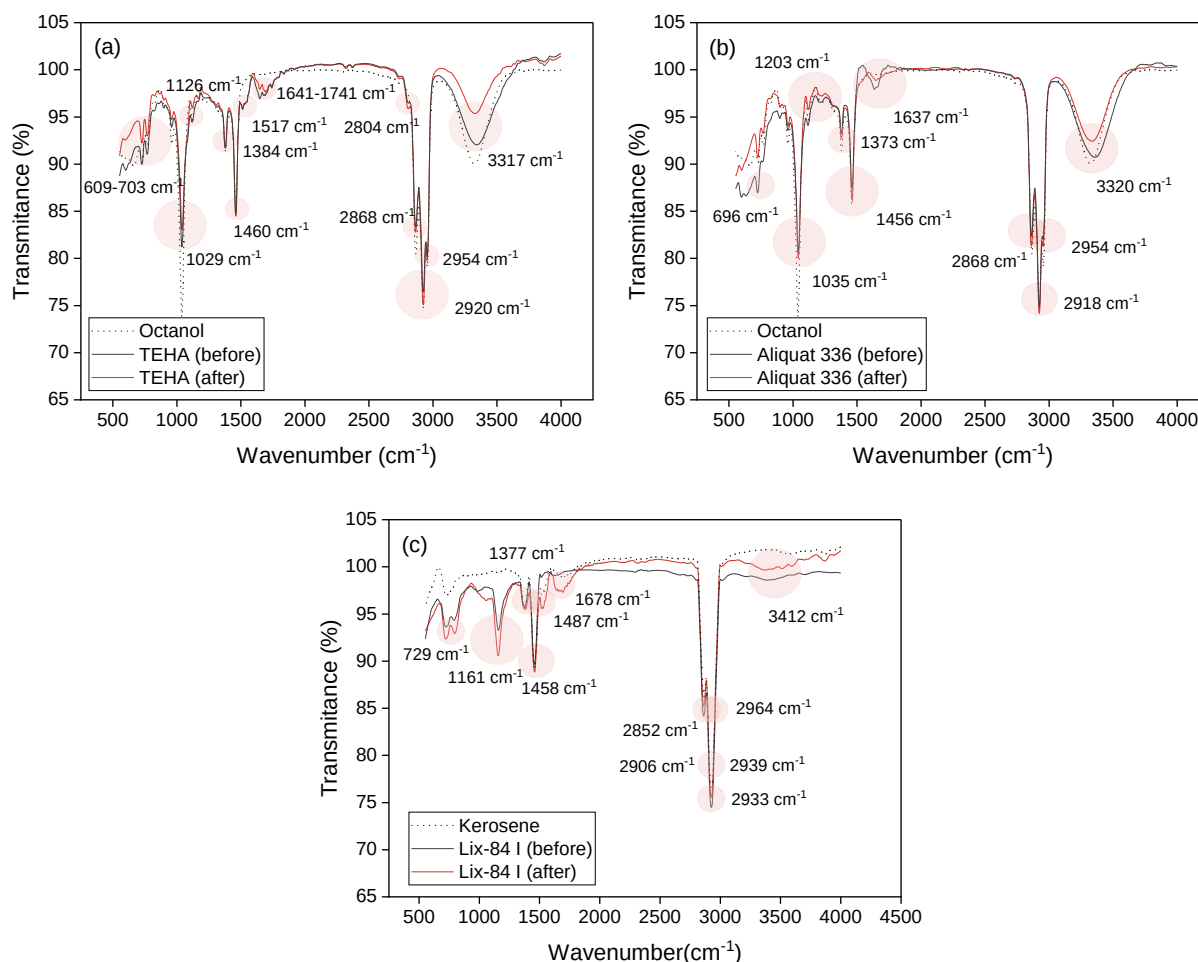


Figure 45. Spectra of Fourier transform infrared spectroscopy (FTIR) for (a) TEHA, (b) ALIQUAT 336, and (c) LIX 84-I before and after extraction experiments.

Due to the greater efficiency in acid extraction and similar co-extraction of impurities and other species, TEHA was chosen for subsequential experiments that investigated different operational variables and their contribution to acid extraction. These results are shown in Figure 46 which shows the results for experiments at different temperatures, organic phase composition, and organic phase flow rate.

The extraction process is favored by higher temperatures (Figure 46 a). When the temperature increased from 30°C to 60°C the acid concentration in the raffinate decreased from 0.0360 ± 0.001 mol/L to 0.0150 ± 0.001 mol/L (extraction efficiency: 54.4% - 81.0%), increasing the acid concentration in the organic phase. It is worth mentioning that the membrane distillation concentrate was generated at elevated temperatures, around 60 °C, which lowers the energy requirement in a scenario where the acid extraction is conducted at higher temperatures to increase its recovery.

At higher temperatures, the viscosity reduces, and the density decreases, variables that are correlated in Reynolds number and that dictate a laminar or turbulent flow. Both variables are inversely related to the Reynolds number and in this case, the reduction in viscosity forces prevails over the decrease in inertial forces, ultimately improving the flow regime. The results could also be interpreted by a reduction in the organic phase boundary layer, which reasons and explanations will be given when the mass transfer coefficients are discussed for

experiments at different flow rates and organic phase composition. In a broader context, a process favored for higher temperatures (60 °C, as assessed in this study) is an interesting outcome considering their integration with membrane distillation into a perspective of process intensification.

Figure 46 (b) brings the results for experiments at 60 °C and different organic phase compositions. Notably, the extraction efficiency is improved at higher concentrations of the extractant. When the composition increased from 5 vol.% to 15 vol.%, the acid concentration remaining in the raffinate decreased from 0.0150 ± 0.0002 mol/L to 0.0002 ± 0.0001 mol/L. The improvement in acid extraction (from 81.1% - 99.7%) suggests that the limiting phenomenon, in this case, was not necessarily the changes in viscosity or density, which resulted from alterations in organic phase composition, but from available sites for extraction. An improved number of available sites prevailed over the increase in viscosity forces commonly observed for organic phases with a higher concentration of extractants. Even at lower concentrations, the non-dispersive solvent extraction processes presented better efficiency in acid recovery compared with conventional liquid-liquid extraction technologies. A review on acid recovery from acidic mining waste solutions using solvent extraction reported similar extraction efficiencies for acid extraction using TEHA (75 – 99%), however for organic phases at higher concentrations of the extractant (50 – 75 vol.%) [265]. One explanation is the greater area provided by hollow fiber membrane contactors for mass transfer, which generally is 500 times greater than in solvent extraction columns [30].

Another indicator that hydrodynamic conditions played a minor role under these experimental conditions is the results from experiments at different organic phase flow rates (Figure 46 c). They were obtained maintaining the temperature fixed at 60 °C and an organic phase composition of 15 vol.%. At 120 min of extraction, the experiments at 12 cm³/s showed slightly better efficiency compared with other conditions, which tend to equalize at longer experimental times. Increasing the flow rate directly increased the organic phase velocity which improves the Reynolds number. Even so, the final concentration of mineral acid in the raffinate, as seen in Figure 46 (c), remained similar and within the standard deviation range.

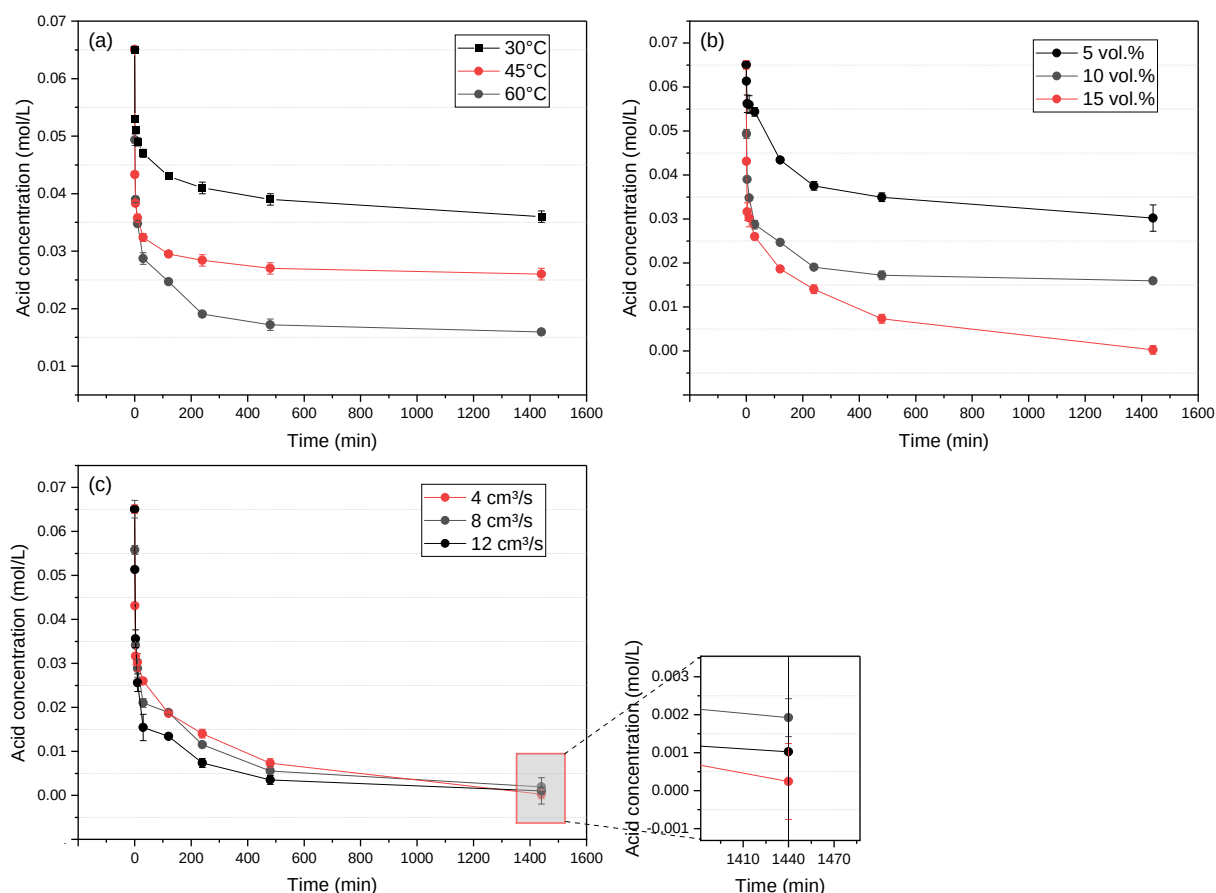


Figure 46. Contribution of different (a) temperatures, (b) organic phase composition, and (c) organic phase flow rate for mineral acid extraction. Aqueous and organic phase volumes: 200 mL.

The results are complemented by the estimations of mass-transfer coefficients, which were made for experiments with different organic phase compositions and flow rates (Figure 47). The results could also be interpreted as resistances, which are inversely proportional to the mass transfer coefficients. The decrease in Reynolds number is quantitatively demonstrated when the organic phase composition is increased, and its flow rate is reduced. In any case, the regime remained laminar with values lower than $Re < 2400$. The Graetz is another dimensionless number useful to explain the results obtained. The number characterizes the flow inside the fibers and indirectly indicates the contribution of mass diffusivity to the solute transport across the fiber walls. The occurrence of slow-flowing regions, favored by a laminar flow, leads to mass transfer boundary layers that extend beyond the hydrodynamic ones. In these cases, Graetz (Gz) numbers are generally proximate to a unit [322], as observed for experiments related to acid extraction ($0.627 < Gz < 1.882$), also explaining the minor contributions of organic phases flow rate to the improvement of acid extraction (Figure 46 c). In cases that the number is lower than 6 as obtained, a limit intrinsic to the equation used for its estimation, the mechanism prevailing is the diffusive transport of the solute into the fluid, across the membrane pores, rather than being carried along by the aqueous phase flow.

The impact on the organic phase is also seen when different extractant concentrations and flow rates are considered. Indirectly, the different experimental conditions also impacted the membrane coefficients that act as a support for the organic phase. In both experimental conditions, from all resistances, the one associated with the organic boundary layer is the greatest (lowest mass transfer coefficients, even under improved experimental conditions of

temperature, composition, and flow rate) whereas the resistance presented by the membrane had minor contributions. The results agree with other studies that also reported minor contributions from the membrane to the total resistance [323], [324]. Asimakopoulou and Karabelas [324], for example, reported contributions lower than 10% while studying the mass transfer in hollow fiber membrane contactors with different packing fractions.

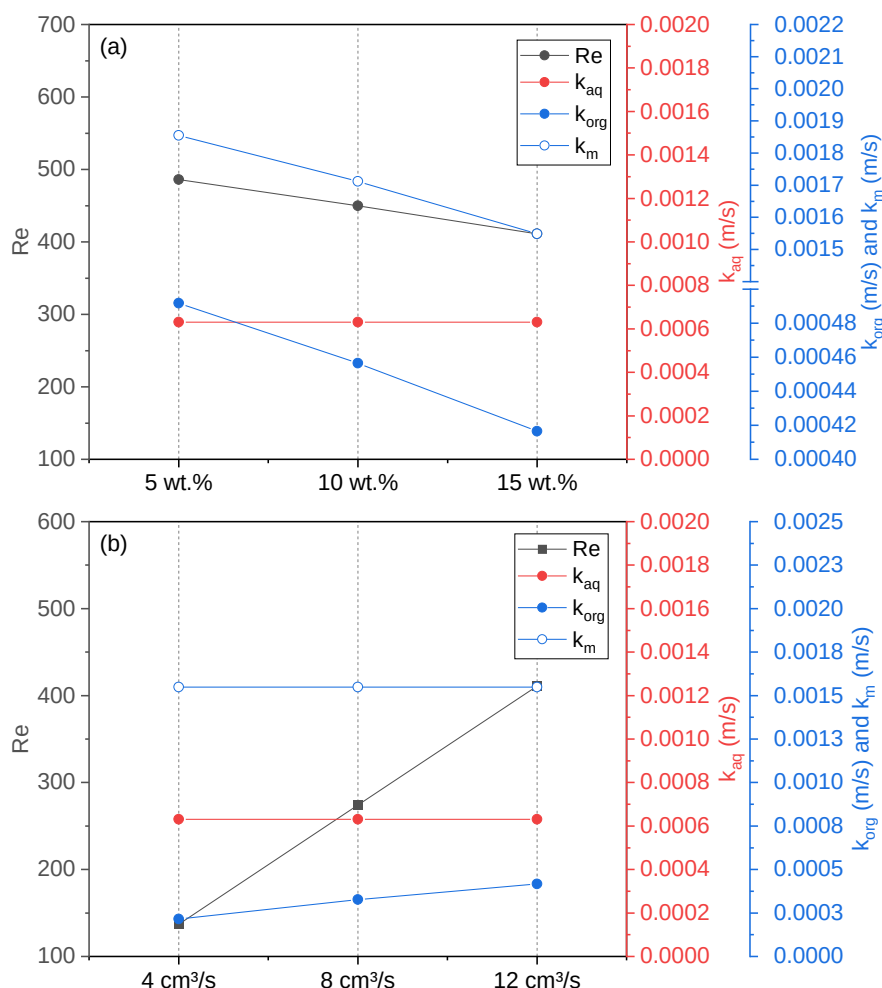


Figure 47. Mass transfer coefficients associated with mineral acid extraction. Re: Reynolds' number, k_{aq} and k_{org} : mass transfer coefficients associated with the aqueous and organic phases, and k_m : mass transfer coefficient associated with the membrane. Note: physicochemical properties were not available at different temperatures (30 – 60°C) and for that reason, the mass transfer coefficients were not calculated.

The positive outcomes related to acid extraction are complemented by the re-extraction results that showed the opportunity for 91.6% of acid recovery from the organic phase (Figure 48). That represents a stream with 5.86 g- H_2SO_4 /L (0.059 ± 0.002 mol/L) and lower contaminants concentration, mainly magnesium, 0.0027 ± 0.0008 g/L, and iron, 0.0031 ± 0.0003 g/L (Table 12), possibly to be reused within the mining industry or commercialized. These results are also seen in Figure 49, which brings the selectivity coefficients for H_2SO_4 extraction over iron, magnesium, and manganese. Among all three species quantified in the wastewater, these three would have the lower added value and their co-extraction would be undesirable. During the experimental time, it is possible to see that selectivity increases due to the increased acid extraction and lower co-extraction of other species. In all moments during acid extraction, the

selectivity coefficient remained greater than one, which reinforces that acid extraction is indeed technically viable.

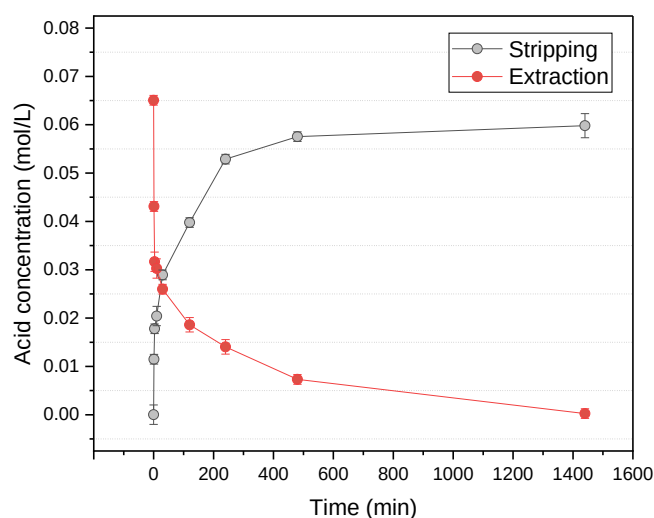


Figure 48. Organic phase loaded at 60°C, Q_{aq} : 36 cm³/s, Q_{org} : 4 cm³/s, and TEHA composition: 15 vol.% in 1-octanol. Stripping agent: hot water (60°C), Q_{aq} : 36 cm³/s, Q_{org} : 4 cm³/s. Aqueous and organic phase volumes: 200 mL.

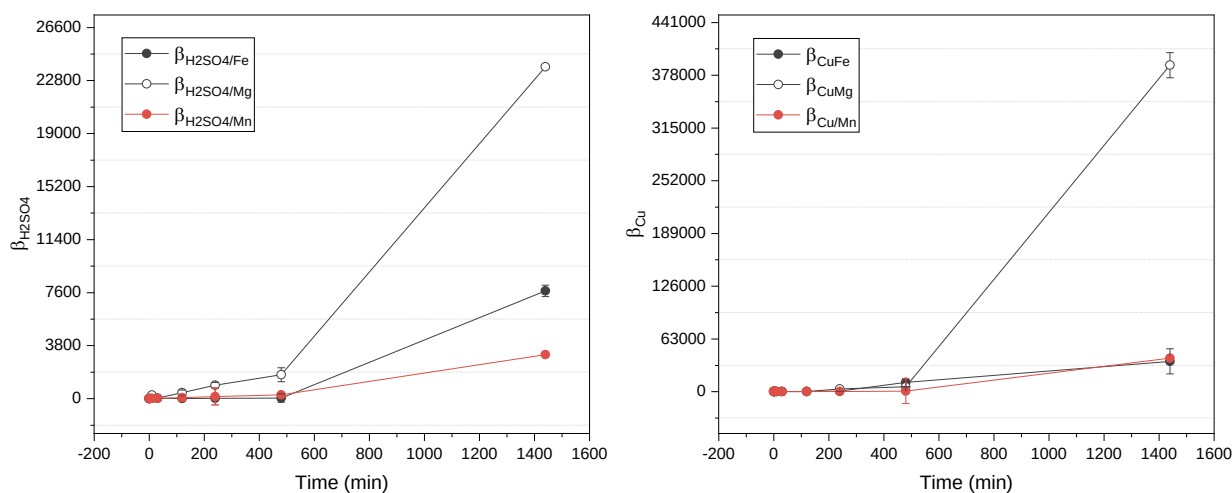


Figure 49. Selectivity for sulfuric acid ($\beta_{H_2SO_4}$) and copper (β_{Cu}) extraction from membrane distillation concentrates. For sulfuric acid, the organic phase was loaded at 60°C, Q_{aq} : 36 cm³/s, Q_{org} : 4 cm³/s, and TEHA composition: 15 vol.% in 1-octanol. For copper, the organic phase was loaded at 30°C, Q_{aq} : 36 cm³/s, Q_{org} : 12 cm³/s, and LIX-84I composition: 15 vol.% in kerosene.

3.2 Non-dispersive solvent extraction for copper recycling

It was also investigated different experimental conditions intended to improve copper recovery by non-dispersive solvent extraction. These experiments considered the raffinate from sulfuric acid extraction for reasons that will be further discussed. Similar to the organic phase used in acid extraction, the one used for copper recovery also maintained its characteristics and stability even after being exposed to acid wastewater (Figure 45 c). That could be seen by the similarity between the FTIR spectra related to the organic phase before and after the extraction. Equation 66 shows a well-accepted chemical reaction that represents the extraction

of copper ions by Lix-84 I ($RH_{(org)}$). It refers to an acid-base reaction in which the extractant would donate protons in exchange for copper ions [305].



The equation shows that the copper recovery is highly dependent on the medium pH and a high concentration of hydrogen ions (H^+) would be unfavorable for its extraction. That is the main reason why mineral acid is primarily recovered from membrane distillation concentrate so that the medium pH would be within acceptable ranges that favor copper extraction. From a perspective of integrated processes, membrane distillation could be first combined with a stage responsible for mineral acid recovery, which in turn could be followed by a stage responsible for copper extraction. The recovery of H_2SO_4 would also alleviate the sulfate content from membrane distillation concentrate. The species are responsible to increase the activity of hydrogen ions, ultimately lowering the extraction efficiency [306]. Under the pH from which copper was extracted (2.15 ± 0.11), the element is present mainly in its divalent cation form, which would have a higher interaction with the extractant compared with its complex forms [307]. The same spectra in **Figure 45** (c) show peaks at $2852 - 2964\text{ cm}^{-1}$ and 1458 cm^{-1} that were correlated with C–H bonds (related to CH_3 and benzene rings) that are present in the molecule of Lix-84 I. After the extraction, peaks at 1487 and 1687 cm^{-1} not previously observed were most probably derived from complex formation between the extractant and the species of copper, a similar explanation for the shift in stretching vibrations at 759 cm^{-1} that most probably derived from interactions between the species of copper and the oxygen from C–O [308]. Another indication that complexes were formed is the disappearance of the broad peak at 3412 cm^{-1} , characteristic of N–OH groups that could have interacted through intermolecular bonding between copper ions and the oxygen from oxime groups [308], [309].

Membrane distillation concentrate is generated at high temperatures, intrinsic to the process. As a reminder, the temperature difference is required to promote the water vapor permeation across the membrane and for that reason, its concentration is characterized by elevated temperatures. For that reason, the temperature effect was assessed during acid extraction, and the first by-product recovered. However, due to heat losses across the units, the raffinate from the first extraction process would eventually reach thermal equilibrium with the room temperature, and the costs associated with a re-heating process would directly compromise its feasibility. Higher temperatures would only be justified in cases where high extraction efficiencies would not be achieved under ambient temperatures. In that case, the additional heating costs could be compensated by the improvement in copper extraction. For that reason, the variables investigated for copper extraction were limited to the organic phase composition and its flow rate as shown in **Figure 50**.

The increase in available sites for extraction also suppressed the commitment in the organic phase viscosity and density, which decreased and increased, respectively, due to high concentrations of the extractant (**Figure 50 a**). When the concentration increased from 5 vol.% to 15 vol.% the extraction efficiency varied between 75.4% and 99.7%. Different from acid extraction the organic flow rate seems to have a greater contribution to copper extraction (**Figure 50 b**). The viscosity forces tend to have a greater contribution in the organic phase flow through the hollow fiber contactors due to its higher viscosity ($\mu_{Lix84-15vol. \%}$: 0.0010 Pa.s , compared with $\mu_{TEHA-15vol. \%}$: 0.0007 Pa.s), and higher flow rates tends to compensate for the inertial forces.

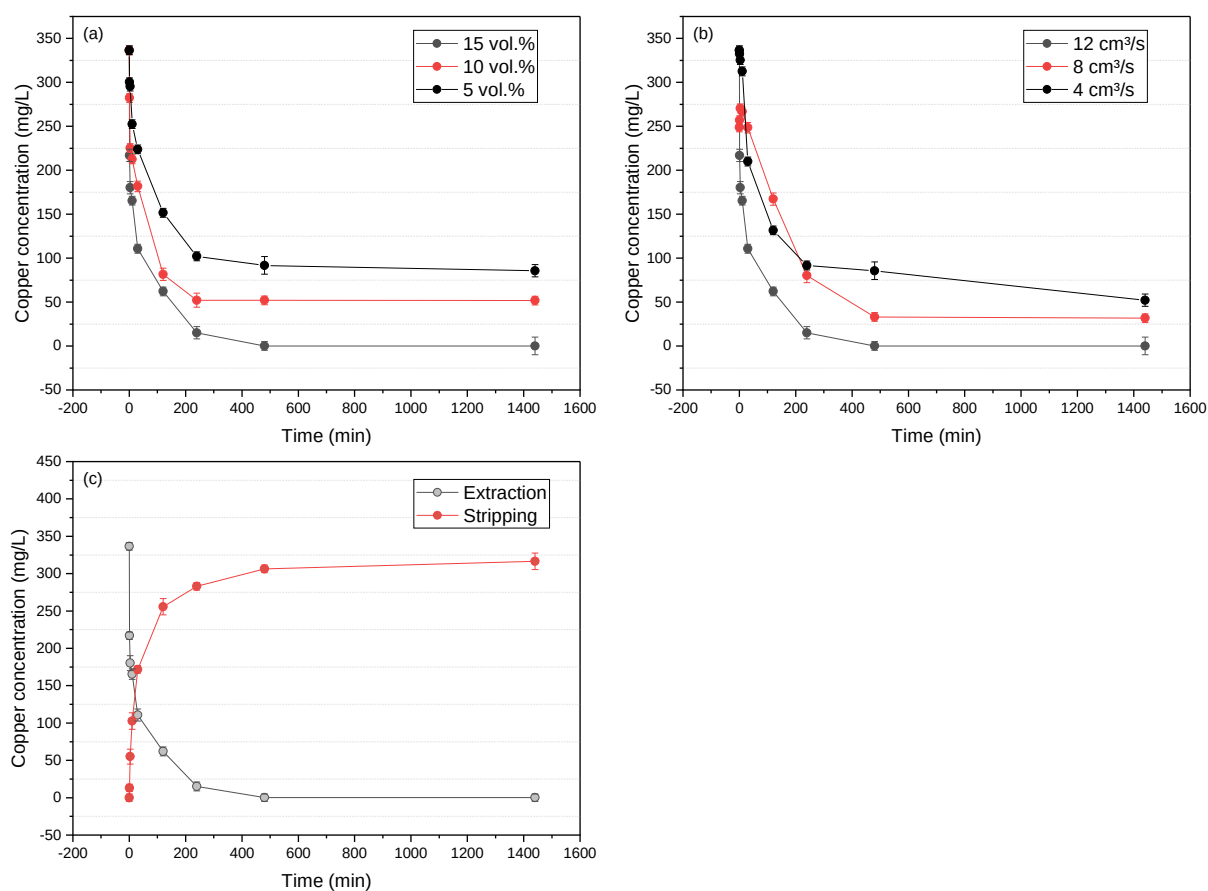


Figure 50. Contribution of different (a) organic phase compositions and (b) organic phase flow rates for copper extraction. (c) Copper concentration during extraction and its stripping from the organic phase. Organic phase loaded at 30°C, Q_{aq} : 36 cm³/s, Q_{org} : 12 cm³/s, and LIX-84I composition: 15 vol.% in kerosene. Stripping agent: H₂SO₄ (1 mol/L). Aqueous and organic phase volumes: 200 mL.

Changes in fluid properties and its flow rate is quantitatively seen through the Reynolds number (**Figure 51**). The number decreases under the higher concentration of extractant and lower organic flow rates. The same figure also shows that for copper extraction, the rate-limiting step would be the solute diffusion across the aqueous boundary layer. As for acid extraction, the Graetz number remained lower than 6, indicating that the mechanism prevailing is the diffusive transport of the solute into the fluid, across the membrane pores, rather than being carried along by the aqueous phase flow. For copper extraction, improvements in the aqueous phase flow rate could be sought to overcome the resistance imposed by the aqueous phase. Although not tested, it could be a better alternative compared with its heating, another option with potentially higher costs. Even so, the resistance did not limit the copper extraction given the high extraction rates reported. The higher extraction rates were followed by high re-extractions during stripping (94.0%). As for acid, copper was also selectively recovered from membrane distillation concentrate in a stream containing solely copper. Other impurities were below the detection limit (< 0.1 mg/L) (**Table 12**). These results are reinforced by the selectivity coefficients obtained during copper extraction, all greater than one suggesting that a selected separation is possible (**Figure 49**).

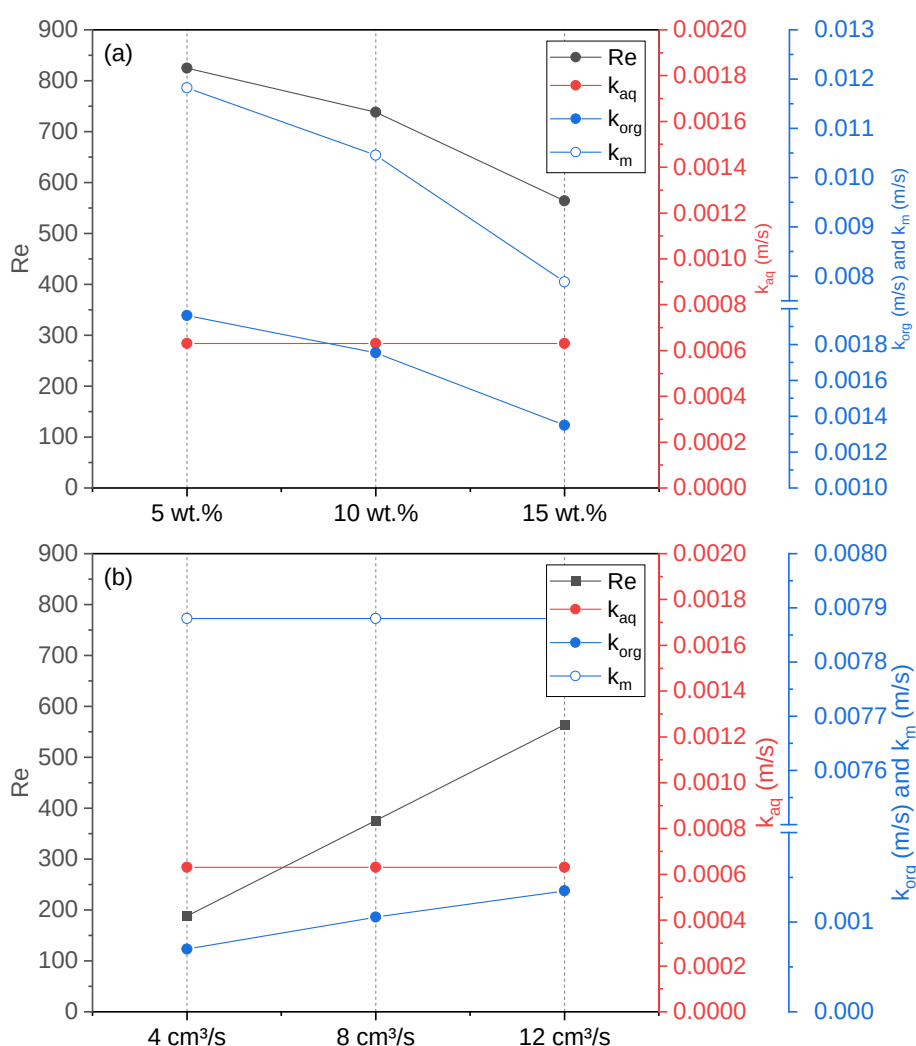


Figure 51. Mass transfer coefficients associated with copper extraction. Re: Reynolds' number, k_{aq} and k_{org} : mass transfer coefficients associated with the aqueous and organic phases, and k_m : mas transfer coefficient associated with the membrane.

3.3 Preliminary economic analysis

Complementary to the technical results presented in the previous section, a preliminary economic analysis was made specifically for acid and copper recovery using non-dispersive solvent extraction and hollow fiber membrane contactors. These results are shown in **Table 15**. The difference in the initial investment costs (CAPEX) is related to the difference in chemicals required for the recovery of each product (mainly the extractant). When it comes to operational costs, apart from amortization of the initial investment, two other variables were the main contributor to the values obtained, the stripping solution and the membrane replacement. Given these results, the reuse of water and sulfuric acid in the extraction process as stripping agents becomes an interesting strategy to reduce operational costs. The total values obtained for acid and copper recycling corresponded to 0.549 US\$/kg_{H₂SO₄} and 11.581 US\$/kg_{Cu}. Compared with a previous study that assessed the performance of conventional solvent extraction processes [195], the prices were higher for sulfuric acid (0.423 US\$/kg_{H₂SO₄}) and copper (4.250 US\$/kg_{H₂SO₄}) recycling. The present study encompassed the expenses related to waste disposal, which accounted for approximately 31% of the overall operating

costs associated with sulfuric acid and copper recycling. This incorporation of waste disposal costs represents an advancement in achieving a more accurate and comprehensive economic analysis. Notably, proper disposal of the organic and aqueous streams presents a variable that necessitates precise consideration in the economic evaluation. The costs for acid extraction were above the commercial prices of metallurgical-grade sulfuric acid (0.027 – 0.110 US\$/kg_{H₂SO₄}). For copper, however, the costs were comparable with those practiced (10.31 US\$/kg_{Cu}).

Table 15. CAPEX and OPEX estimation for mineral acid and copper recycling from membrane distillation concentrate.

Economic variables	H ₂ SO ₄ recycling	Copper recycling
<i>CAPEX</i>		
System acquisition (US\$)	725,671.45	689,050.00
<i>OPEX</i>		
Energy (US\$/kg)	<0.001	0.006
Organic phase replacement (US\$/kg)	0.017	0.134
Stripping solution (US\$/kg)	0.109	2.374
Amortization (US\$/kg)	0.114	2.373
Maintenance (US\$/kg)	0.006	0.118
Membrane replacement (US\$/kg)	0.074	1.619
Membrane cleaning (US\$/kg)	0.055	1.209
Waste disposal (US\$/kg)	0.172	3.754
Total OPEX (US\$/kg)	0.549	11.581

If not commercialized, both elements can be reused to improve the gold recovery. According to Thomas et al. [325], sulfuric acid can be added to the slurry intended to destroy sufficient carbonate (CO₃²⁻) before entering the autoclave circuit. The process referred to as acidulation can reduce the levels to < 2% CO₃²⁻, ultimately reducing the levels of CO₂ produced during the gold ore oxidation. Recycling it from the wastewater could then lower the dependence of mining sectors on the variabilities mentioned, increasing its market competitiveness.

Interestingly enough, the efficiency of gold ore oxidation can also be improved by the addition of copper ions. The results made available by Long and Dixon [326] revealed that the addition of copper, in a concentration of 2 g/L can improve the oxidation rate from 14%, for the oxidation of low pulp densities, to over 50%, for pulps at high densities. The authors explained that the copper catalytic effect probably stems from the fact that its reaction with dissolved oxygen is virtually instantaneous, while that between species of iron and dissolved oxygen is very slow, as demonstrated by the authors themselves [326]. Also, the divalent species of copper acts as a redox catalyst for dissolved oxygen in the oxidation of divalent species of iron [327]. Hence, in the presence of copper, a larger proportion of iron oxidation can occur homogeneously, in the bulk solution rather than at the pyrite surface [326], [327]. Therefore, the integration of acid and copper recycling methodologies can also present a promising approach to advancing mining sustainability and optimizing gold recovery operations.

Compared with other studies summarized in Figure 1, the results obtained in our study demonstrate a reasonable agreement in terms of extraction efficiency, particularly for copper. In Figure 1, copper recovery values varied from 78.5% to 99% in previous research. Notably, superior results were achieved when using extractants such as LIX 662N and LIX 84-I, which yielded extraction efficiencies of 98.9% [142] and 99% [90], respectively. In our current study, we achieved a high extraction efficiency of 99.7% for copper, aligning with the findings of previous studies, indicating the significant potential for copper recovery from wastewater.

In addition to the approach presented in this study, Lebron et al. [328] proposed the use of ion exchange resins as an alternative method for acid and copper recycling from industrial wastewater. Their study reported the opportunity to recover approximately 1.3 g/L of acid from wastewater using Amberlyst A26 resin, representing 13% of the total acid concentration. Although the reported acid recovery was lower compared to our method, the use of ion exchange resins offered the advantage of recovering other elements such as nickel and cobalt (using IRC747 and Dowex M4195 resins). It is worth noting that resins, alongside non-dispersive solvent extraction, fall under the category of active treatment options, which also include adsorption, membrane separation methods, and neutralization. These methods present the potential for byproduct recovery from wastewater and can contribute to the overall sustainability of the mining industry [329]. Each of these methods, however, comes with its advantages and limitations, which must be carefully considered for application in specific contexts.

**CHAPTER 7 – INTEGRATED SYSTEM OF MEMBRANE DISTILLATION AND NON-
DISPERSIVE SOLVENT EXTRACTION FOR GOLD MINING WASTEWATER
TREATMENT**

1 Introduction

Mining stands as a primary economic activity in numerous countries. Its significance has endured for an extended period, but in the current economic and industrial context, it holds immense growth potential. This growth is primarily driven by the escalating demand for metals essential in the production of technological goods and to support increasingly mechanized industrial processes. However, with the mounting prominence of the mining industry, new challenges have arisen that warrant attention.

As the world becomes more focused on environmental impacts and sustainability, urgent measures are required to align the mining-metallurgical system with these demands, as it traditionally lacks long-term sustainability. Mining practices often cause significant physical alterations to landscapes [330], emit greenhouse gases, and generate substantial amounts of liquid effluents [330], [331]. Consequently, exploring alternatives becomes imperative, particularly in reducing and utilizing effluents resulting from the mining process.

Among the major concerns related to gold mining processes are the acid effluents formed during the oxidation of certain sulfide minerals. High volumes of these effluents and their inadequate disposal lead to acidification of natural water bodies and heightened concentrations of various metals, rendering water unfit for consumption or industrial use [332].

Neutralization has been the most employed method to manage acidic effluents. Although effective, this technique can be costly for mining companies [13]. They not only miss the potential benefits of the generated effluents but also incur excessive costs due to the sheer volume produced [319]. Most sludge produced is disposed of in tailing dams, and the history shows various incidents related to their rupture [330]. The waste volume produced varies according to the wastewater characteristics and the alkalizing agent used; however, as a rough estimative, it is estimated that 20 tons of sludge is produced from 1000 m³ of acid wastewater neutralized with lime or limestone [333]. As an alternative to neutralization, reusing and valorizing raw mining effluent presents an opportunity. This effluent contains a high concentration of metals such as copper, nickel, and cobalt, alongside a substantial water content and an acidic nature with a pH ranging from 1.5 to 2.0 due to the presence of sulfuric acid. Therefore, a project aimed at recovering these metals, water, and acid for reuse in the mining process or sale appears to be both viable and scalable.

A promising alternative for treating various industrial effluents is membrane technology. Membranes act as selective barriers enabling separation processes to remove specific components from the effluent being treated. Among these techniques, membrane distillation (MD) stands out. MD relies on a temperature gradient across the hydrophobic membrane walls. The hydrophobic properties of the membranes prevent the passage of the aqueous effluent while allowing the vapor formed by their micropores to pass through [334]. Consequently, heating the effluent at the ideal temperature causes steam to form and pass through the membrane, condensing on the other side. As water is more volatile than the acids and metal ions present in the effluent, it crosses the membrane in the form of steam, leaving the other components trapped within the barrier [195].

Through an integrated approach, the acid and metals can be successfully recovered from the effluent. A method employed for this purpose is non-dispersive solvent extraction (NDSX) [319]. This process employs membrane contactor modules, operating similarly to the MD system used in distillation. The hydrophobic membrane exhibits an affinity for the solvent (or

organic phase), which also possesses hydrophobic properties. Consequently, the organic phase can cross the membrane and, upon contact with the concentrated effluent, carry with it the component it has the greatest affinity for - either copper or sulfuric acid, depending on the organic phase employed [319]. For copper recovery, LIX 84 can serve as the organic phase, while TEHA can be used for acid extraction [335].

Subsequently, the re-extraction step follows a mechanism and strategy closely resembling the extraction step. However, the mass transfer occurs in the opposite direction, aimed at depleting the organic phase of the target compound and simultaneously increasing the concentration of this compound in an aqueous phase known as the stripping solution. This solution exhibits greater affinity than the organic phase for the target compound, ensuring prominent levels of purity.

In this chapter, the main objective is to analyze the efficiency and explore the potential of using an integrated membrane system (MD - NDSX). It is essential to note that employing an integrated system offers the prospect of enhanced wastewater valorization, as it leads to the recoveries of multiple elements simultaneously. By using a continuous process of distillation and extraction, it is expected to lower the wastewater volume to be discharged, as well as its acid and metal content. For that, different polymeric membranes were tested for water, sulfuric acid, and copper recovery, intended to better comprehend how they would impact the performance of the integrated system. The integrated processes may also favor the recovery of other constituents besides sulfuric acid and copper, clearing up the path for the recovery of other constituents such as nickel and cobalt. It is expected to advance in technologies capable of mining wastewater valorization towards a sustainable industry.

2 Materials and Methods

2.1 Gold mining wastewater and characterizations

The wastewater was sampled after settling tanks intended to separate the liquid and solid phases leaving the stages of pressure oxidation. The overflow usually achieves temperatures between 60 – 80 °C and is characterized by low pH values and high concentrations of iron, magnesium, manganese, copper, nickel, and cobalt. Once collected, the wastewater was stored at 4°C and brought to room temperature before the experiments. All characterization procedures followed the recommendations described in the Standard Methods for the Examination of Water and Wastewater [267] (metal ions: method 3111; pH: method 4500-H⁺; sulfuric acid: methods 4500-H⁺ and 2310; and conductivity: method 2510).

2.2 Membrane distillation

The integrated system is presented in Figure 52 and accounts for one module of membrane distillation intended for water recovery and two modules of membrane contactors, the first for sulfuric acid recovery and the second for copper recovery. All units are simultaneously connected to the feed tank, which is continuously fed by the wastewater reservoir.

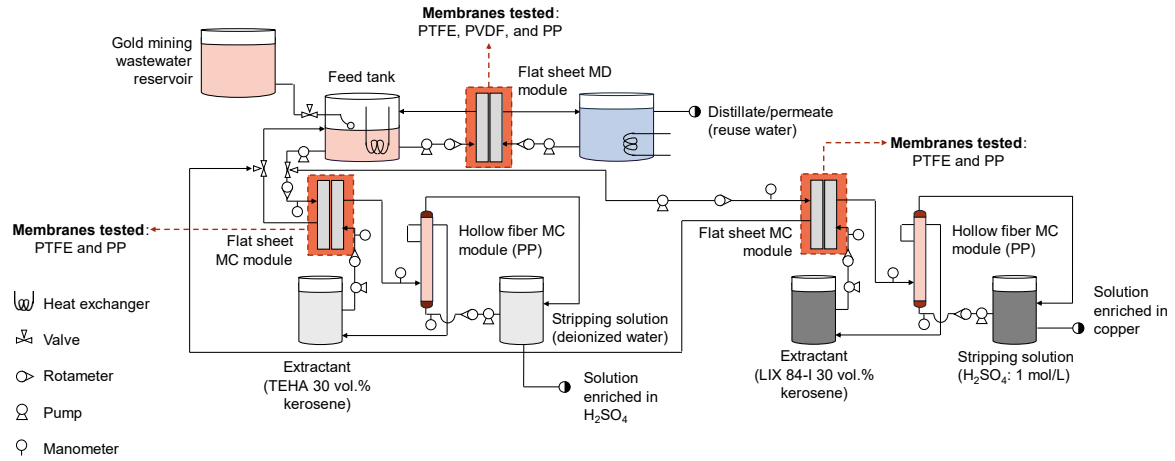


Figure 52. Integrated system of membrane distillation and membrane contactors for simultaneous water, sulfuric acid, and copper recovery from gold mining wastewater. MC: membrane contactor, PP: polypropylene, PTFE: polytetrafluoroethylene, PVDF: polyvinylidene fluoride, MD: membrane distillation.

MD experiments were carried out with 2.5 L of wastewater (also referred to as feed–heated stream) and 1.5 L of distilled water (also referred to as permeate–cooled stream) that was maintained at a constant temperature and recirculation flow rate (0.3 L/min). The feed temperature was set at 60°C, which corresponds to the wastewater outlet temperature after the process of hydrometallurgy, whereas the distillate was maintained at room temperature (25°C; $\Delta T = 35^\circ\text{C}$). The experimental conditions followed the recommendations of a previous study developed in the research group devoted to establishing the most appropriate operating conditions of MD while treating gold mining wastewater [5]. Three commercial membranes made of poly(tetrafluoroethylene) (PTFE), poly(vinylidene fluoride) (PVDF) membranes, and polypropylene (PP), all commercially available and provided by Sterlitech®, with an effective area of 42.09 cm², were compared in these experiments. After each test, the membrane was cleaned once with distilled water (physical cleaning) and with HCl (0.1 %v/v – chemical cleaning). Both cleaning procedures considered a recirculation flow rate of 4 L/min, maintained for 30 min and at 60 °C.

The distillate (or permeate) flux was estimated with the aid of an analytical scale that monitored the increment in mass at regular intervals of 5 minutes. At the initial stages, the permeate was diluted by the initial distilled water in the tank, hence, to avoid underestimations, the distillate physicochemical characteristics were recalculated considering the initial distilled water volume.

The vapor pressure at the bulk feed (p_f , Pa), membrane surface facing the feed side (p_1 , Pa), membrane surface facing the permeate site (p_2 , Pa) and the bulk permeate (p_p , Pa) were considered to estimate the resistances (Pa·m²·h/kg) to mass transfer associated with the membrane (ρ_m , Equation 67), permeate boundary layer (ρ_{pb} , Equation 68), feed boundary layer (ρ_{fb} , Equation 69) and fouling layer (ρ_f , Equation 70). The total mass transfer resistance (ρ_t) was estimated by Equation 71.

$$\rho_m = \frac{p_1 - p_2}{J} \quad (67)$$

$$\rho_{pb} = \frac{p_2 - p_p}{J} \quad (68)$$

$$\rho_{fb} = \frac{p_f - p_1}{J} \quad (69)$$

$$\rho_f = \rho_t - \rho_m - \rho_{pb} - \rho_{fb} \quad (70)$$

$$\rho_t = \frac{p_f - p_p}{J} \quad (71)$$

Bulk's equation (Equation 72) was used to estimate the vapor pressures at a given temperature (T , K) given its greater accuracy for vapor pressure estimation compared with Antoine's equation [291]. The p_f was corrected by the feed activity coefficient (α_f), estimated by Pitzer's model and the software "PHREEQC".

$$p_i = 0.61121 \cdot e^{\left[\left(18.678 - \frac{T}{234.5} \right) \left(\frac{T}{257.14 + T} \right) \right]} \quad (72)$$

The feed (T_f, K) and permeate (T_p, K) bulk temperatures were measured by thermostats. The temperatures at the membrane surface facing the feed ($T_{w,f}, K$; Equation 73) and permeate ($T_{w,p}, K$; Equation 74) were estimated by an energy balance at steady-state conditions. Given T_f , $T_{w,f}$, $T_{w,p}$, and T_p it is possible to calculate the temperature polarization coefficient (τ) by Equation 75.

$$T_{w,f} = \frac{h_m \cdot \left(T_p + \left(\frac{h_f}{h_p} \right) \cdot T_f \right) + h_p \cdot T_p - J \cdot \Delta H_v}{h_m + h_f \cdot \left(1 + \frac{h_m}{h_p} \right)} \quad (73)$$

$$T_{w,p} = \frac{h_m \cdot \left(T_f + \left(\frac{h_p}{h_f} \right) \cdot T_p \right) + h_f \cdot T_f - J \cdot \Delta H_v}{h_m + h_p \cdot \left(1 + \frac{h_m}{h_f} \right)} \quad (74)$$

$$\tau = \frac{T_{w,f} - T_{w,p}}{T_f - T_p} \quad (75)$$

In Equations 73-74, incremental ΔH_v (Equation 76) stands for the water vaporization heat and h_m ($W/m^2 \cdot h$), h_f ($W/m^2 \cdot h$, Equation 77), and h_p ($W/m^2 \cdot h$; Equation 77) for the convective heat transfer coefficients of the membrane, permeate, and feed streams. The most appropriate correlations for the Nusselt number (Nu , which considers the module geometry), used for convective heat transfer calculation are described in Equations 78-79 [292], [293].

$$\Delta H_v = 1.7535 \cdot T + 2024.3 \quad (76)$$

$$h_{f,p} = k_{f,p} \cdot Nu_{f,p} / D_h \quad (77)$$

$$Nu_f = 15 \cdot (Re \cdot Pr)^{0.23} (D_h/L)^{0.5} \quad (78)$$

$$Nu_p = 11.5 \cdot (Re \cdot Pr)^{0.23} (D_h/L)^{0.5} \quad (79)$$

In Equations 78-79, Re corresponds to the Reynolds number (Equation 80), Pr to the Prandtl number (Equation 81), $k_{p,f}$ (W/m·K) to the permeate or the feed thermal conductivity, c_p to the isobaric specific heat (J/kg·K), q (m³/s) to the volumetric flow rate, d_h to the hydraulic diameter (m), μ (Pa·s) and ν (m²/s) to the water dynamic and kinematic viscosity, and s (m) to the pipe's cross-sectional area.

$$Re = \frac{q \cdot d_h}{\nu \cdot s} \quad (80)$$

$$Pr = c_p \cdot \mu / k_{f,p} \quad (81)$$

2.3 Non-dispersive solvent extraction

The first module of non-dispersive solvent extraction has a plate and frame configuration and is equipped with a flat sheet membrane made of PTFE or PP, both commercially available and provided by Sterlitech®, with an effective area of 42.09 cm². This module has an easier set-up, which facilitates the evaluation of different membranes and enables exploration into how their morphology influences mass transfer within non-dispersive solvent extraction processes. The second module employed for extraction is a hollow fiber membrane contactor, provided by Liqui-Cell™ (membrane material: polypropylene; packing density: ~10,000 fibers/module, the average surface area of 1.4m², and effective length of 15 cm). The extraction and re-extraction circuits integrated into membrane distillation were illustrated in Figure 52.

Tris(2-ethylhexyl)amine (TEHA) was used for acid extraction (15 vol.% diluted in kerosene), whereas LIX 84-I (15 vol.% diluted in kerosene) was used for copper extraction. The organic flow rate for acid extraction was set at 4 cm³/s, and the aqueous flow rate was set at 36 cm³/s. For copper, the organic flow rate was set at 12 cm³/s, and the aqueous flow rate was set at 36 cm³/s. Mineral acid was re-extracted from the organic phase by hot water (60°C; 500 mL) and copper by a sulfuric acid solution (1.0 mol/L; 500 mL) at room temperature. In both experiments, the aqueous and organic were fed into the extraction module in countercurrent mode. In the hollow fiber module used for stripping, the aqueous phase was fed into the lumen side and the organic phase into the shell side. The non-dispersion condition was guaranteed by setting a pressure difference of >0.3 bar between the organic and aqueous phases across the membrane, controlled indirectly by the different flow rates of the currents. The concentration of acid and copper was monitored in the feed tank and the stripping solutions to validate the performance of the extraction units.

3 Results and discussions

3.1 Water recovery by membrane distillation

The results of distillate flux for membrane distillation were summarized in Figure 53 for all three membranes tested. The average values for PTFE, PVDF, and PP membranes corresponded to 0.37 ± 0.34 , 0.10 ± 0.09 , and 0.67 ± 0.32 L/m²h, respectively. Notably, a flux decay was observed for all three processes when initial and final values of distillate flux are compared, being more pronounced for the experiments with the membranes of PTFE and PP. Due to the greater distillate flux, experiments with PP membranes achieved a recovery rate of 85%, greater than the values obtained for PTFE (64%) and PVDF (14%).

The results obtained are better comprehended if the membrane's properties are considered. Vapor transport through the pores relies on its size and mean free path for transport (membrane thickness). From all three membranes tested, PTFE and PP membranes have a similar pore size of 0.2 μm ; however, they differ in terms of membrane thickness which is greater for PTFE (170 μm) than for PP (100 μm) membranes. PVDF membranes would have an intermediate thickness of 121 μm , however the smallest pore size of 0.1 μm , suggesting that pore size would have a greater effect on vapor transport across the membrane compared with its thickness. The membranes' morphology would then explain the results for distillate flux obtained, being classified as $J_{\text{PP}} > J_{\text{PTFE}} > J_{\text{PVDF}}$. The impact of membrane morphology was also observed for the resistances calculated, which results were summarized in Table 16.

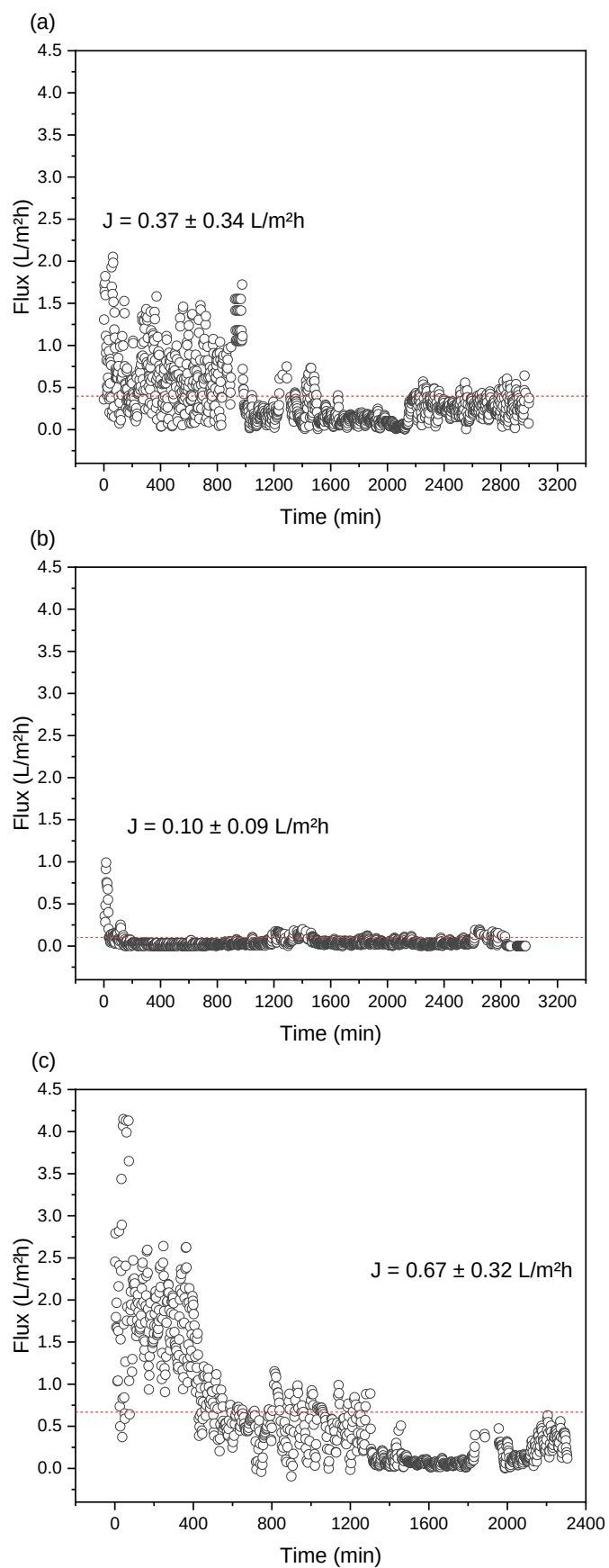


Figure 53. Distillate flux in membrane distillation for different membranes: (a) PTFE, (b) PVDF, and (c) PP. J: distillate flux.

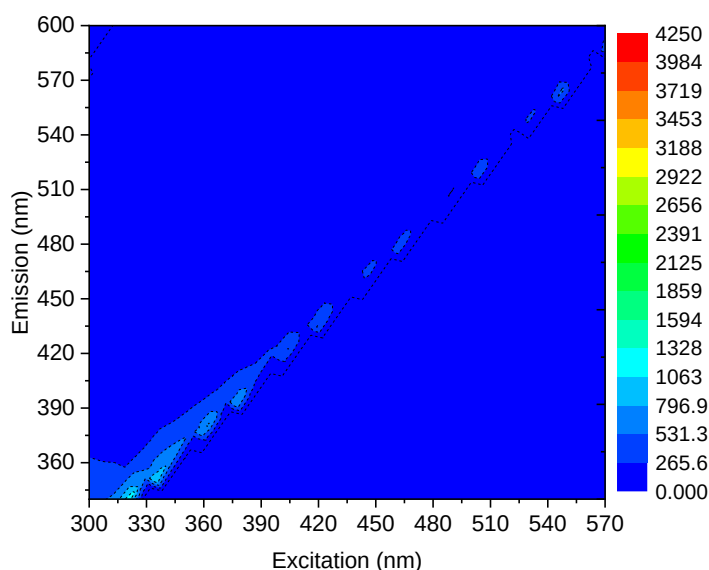
Table 16. Resistance to distillate transfer in membrane distillation process using PTFE and PVDF membranes. In parentheses, the contribution of each one to the total resistance estimated.

Resistance (kPa.m ² .h/kg)	PTFE	PVDF	PP
Feed side (bulk)	290.6 (15.4%)	334.8 (17.7%)	176.2 (18.7%)
Membrane	40.6 (2.1%)	144.3 (7.6%)	15.1 (1.6%)
Distillate side (bulk)	89.7 (4.7%)	106.2 (5.6%)	56.6 (6.0%)
Fouling	1,463.5 (77.6%)	1,299.1 (68.9%)	694.1 (73.6%)
R _{total}	1,884.5	1,884.5	942.2

The contribution of PP membranes to the total resistance to mass transfer corresponded to 1.6% (15.1 kPa.m².h/kg), which was lower compared with PTFE and PVDF membranes (Table 16). Comparatively, the PVDF membrane had the greatest resistance of all three (144.3 kPa.m².h/kg) and a greater contribution to the total mass transfer across the membrane (7.6%); all results following the values of distillate flux previously presented. Following the contributions to total resistance, the one imposed by the feed side and by the fouling layer formed into the membrane surface were the greatest ones.

Despite the greater flux, temperature polarization was more pronounced for experiments with PP membranes, in which $\tau_{PP} = 0.758$. For PVDF and PTFE membranes, the values corresponded to $\tau_{PVDF} = 0.771$ and $\tau_{PTFE} = 0.803$. The temperature polarization results from a simultaneous heat and mass transfer across the membrane, which creates a boundary layer located adjacent to its surface. The result is heat resistance and temperature polarization effects, and the values obtained represent the fraction of the total thermal driving force that contributes to the mass transfer. At high heat transfer rates in the liquid phase, τ approaches the unity and the process is controlled by the transmembrane mass-transfer resistance. Conversely, in cases where τ approaches zero, the process is controlled by heat transfer resistances in the liquid phase. The results of temperature polarization agree with previous observations reported in the literature. Ricci et al. [336] suggested that associated with higher fluxes is also a more pronounced temperature polarization resulting in an increased temperature gradient in the boundary layers.

In membrane distillation, fouling is not expected and tends to be lower than in classical membrane separation processes. That results from its operation mode, which dispenses a hydraulic force over its surface to promote permeation. However, all resistances and the results of distillate flux suggested the opposite. Due to the low pH values and the predominance of inorganic species, there is a low expectation that they would precipitate onto the membrane surface. However, it was observed during the experiments that droplets of the organic phase from the extraction system transposed their pores toward the wastewater feed tank. The hydrophobic nature of the organic phase and the membrane used in MD experiments would favor their interaction, leading to a complete pore blockage and reducing the membrane's effective area for distillation. The presence of organics on the membrane surface was further validated by EEM matrices, which results were shown in Figure 54 for PTFE membranes. From all three, this was the one in which fouling seemed to be more pronounced based on the results of flux decay and for that reason was chosen for analysis.



(b)

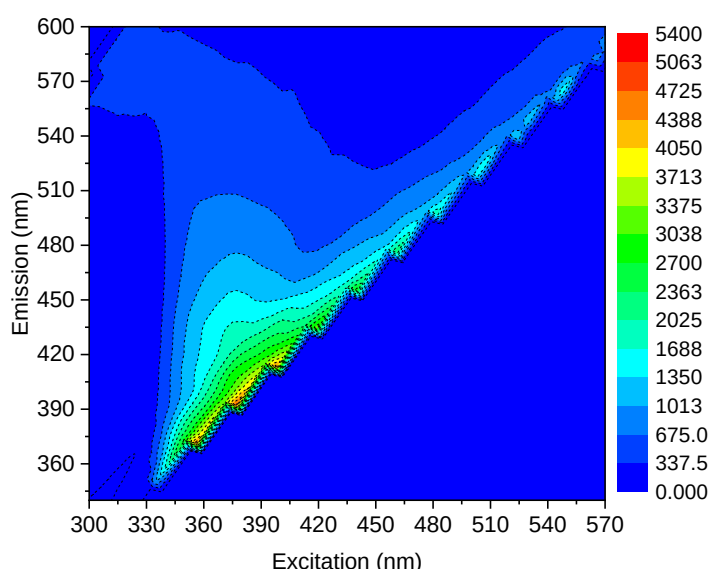


Figure 54. Excitation emission matrices of (a) pristine and (b) fouled membranes of PTFE.

The matrix for the pristine membrane (Figure 54a) reveals the absence of regions of high intensity, different from what was observed in Figure 54b for a sample of the fouled membrane of PTFE. The latter exhibits compounds at λ_{exc} : 360 – λ_{emi} : 370 nm, λ_{exc} : 390 – λ_{emi} : 390 nm, λ_{exc} : 400 – λ_{emi} : 420 nm. It corresponds to a region that was previously correlated with kerosene [337], [338] (the diluent used in NDSX experiments), confirming the organic phase presence on the membrane surface. Organic fouling in membrane distillation was observed in previous studies with a significant flux decline of up to 65% [339], [340]. While assessing the fouling behavior of mineral oils in membrane distillation, Boo et al. [341] suggested that the aqueous solution does not remain on a hydrophobic surface, thereby allowing effective contact between the organic phase and the hydrophobic membrane. The mineral oil readily adsorbed and penetrated the membrane pores, a behavior favored by its low surface tension (~ 30 mN/m). That is a surface tension value close to the surface tension of kerosene (23 – 28 mN/m [ref.: md-ell]), suggesting that a similar behavior could have occurred in the system under study. Even so, the authors demonstrated that the rejection was monitored to be $>99.8\%$ (NaCl) in

distillation experiments, and the change in MD membrane performance was solely attributed to the deposition of foulants on the membrane surface or pore blocking.

As for Boo et al. [341], the rejection efficiency remained high in the experiments despite the membrane used. The results for gold mining wastewater composition, distillate obtained by the different membranes, and the raffinate after the extraction of sulfuric acid and copper are shown in Table 17. In terms of quality, the distillate could be classified as PTFE > PP > PVDF, the two latter with iron, manganese, and cobalt at concentration values greater than the detection limit (>0.5 mg/L), which still represented rejections greater than 85%. For the experiment made with a membrane made of PTFE, the rejection efficiencies were greater than 99,2% representing a stream of high quality that could be potentially reused within the facility even in processes that have a stricter requirement for water quality. Another observation is a concentration from Table 17 is that the concentration of sulfuric acid and copper decreased in the raffinate, suggesting that both species were extracted by the modules of NDSX. Other species monitored remained in the raffinate and had their concentration increased. The results may anticipate a necessity for proper raffinate management, whether being its disposal or the recovery of other species of higher added value as nickel and cobalt. In terms of disposal, the lower volume to be disposed of already represents an advantage (both technical and economical). In terms of the recovery of other species, the greater concentrations could be an advantage since most techniques being investigated (*e.g.*: solvent extraction, ion exchange resins, others [335], [342]–[344]) are favored by high concentrations due to their driving force being related to their chemical potential.

Table 17. Composition of the different streams generated by the hybrid system. The extraction and stripping processes used a membrane made of polypropylene.

Parameter	Gold mining wastewater	Distillate - PTFE	Distillate - PVDF	Distillate -PP	Raffinate of gold mining wastewater - PTFE	Raffinate of gold mining wastewater - PVDF	Raffinate of gold mining wastewater - PP
pH	2.13 ± 0.54	4.69 ± 0.03	3.97 ± 0.13	4.35 ± 0.03	4.04 ± 0.03	3.68 ± 0.07	4.00 ± 0.08
H ₂ SO ₄ (mmol/L)	13.62 ± 18.81	0.02 ± 0.01	0.11 ± 0.07	0.03 ± 0.01	0.09 ± 0.08	0.21 ± 0.04	0.10 ± 0.03
Cobalt (mg/L)	56.85 ± 4.00	<0.5	<0.5	0.95 ± 0.02	60.03 ± 0.29	62.90 ± 0.18	152.3 ± 1.67
Copper (mg/L)	211.20 ± 76.23	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Iron (mg/L)	1335.20 ± 674.84	<0.5	191.24 ± 5.93	90.33 ± 4.67	2060.14 ± 11.48	2180.90 ± 12.91	835.10 ± 3.76
Magnesium (mg/L)	443.94 ± 235.15	<0.5	53.8 ± 2.51	8.85 ± 1.92	591.9 ± 2.49	561.14 ± 0.51	728.30 ± 0.74
Manganese (mg/L)	149.35 ± 154.23	<0.5	<0.5	<0.5	164.28 ± 7.79	146.72 ± 0.70	287.70 ± 0.42
Nickel (mg/L)	227.83 ± 198.05	<0.5	<0.5	<0.5	351.3 ± 1.46	473.13 ± 0.21	214.6 ± 0.14

A previous study on membrane distillation and mining wastewater treatment reported higher fluxes, corresponding to 12 L/m².h on average without a flux decay of up to a 25% recovery rate [311]. From that point onwards, the flux sharply declined and achieved values <2 L/m².h (80% recovery rate), mostly due to calcium sulfate precipitation onto the membrane surface. To prevent fouling and guarantee a stable operation, cleaning procedures and synthesis of membranes with anti-fouling properties are recommended. Wang et al. [345] modified a PVDF membrane to obtain an asymmetric wettability, which means that its outer layer was oleophobic, whereas its inner and support layer made of PVDF remained hydrophilic. Their outcomes were promising and suggested that the membrane obtained would be able to deal with hypersaline wastewater with high concentrations of hydrophobic contaminants. While treating a wastewater with such characteristics (1000 ppm oil), the average distillate flux corresponded to 26.1 L/m².h, with a flux decay <10%.

3.2 Sulfuric acid extraction and re-extraction

For sulfuric acid, extraction was tested on two different membranes, one made of PTFE and the other made of PP, and the results were summarized in Figure 55a. It achieved 99.1% and 97.1% of extraction for PTFE and PP membranes, respectively. The recoveries reported are promising, however, achieved in a long-term experiment (2400 min). The time required for extraction most probably relates to the effective area available for extraction in the flat sheet modules (0.0042 m²) since a longer time was required for both membranes used. In previous studies in which the extraction was made with a hollow fiber module with an effective area of 1,4 m², recoveries greater than 90% were achieved at 400 min of experiment [331], a shorter time, and aligned with real case applications. Even so, the decision for a flat sheet module was maintained to better comprehend how different membranes could impact extraction efficiency.

The mass transfer resistance across the membrane relates to the membrane roughness and its pore diameter and is inversely related to the diffusivity of the specie of interest on the organic phase and its porosity. Since the organic phase was the same in both experiments of acid extraction, and both have the same pore diameter (0.2 µm), roughness and membrane's porosity become the main characteristics impacting the efficiency observed experimentally. When PTFE and PP membranes are compared, the first one is more porous (ϵ_{PTFE} : 0.7 and ϵ_{PP} : 0.4) and has a higher roughness (68.9nm compared with τ_{PP} = 51.7 nm [346]). Based on their characteristics, porosity had a greater impact on the extraction efficiency given the higher extraction rates observed in experiments using this membrane

The organic phases used, and the wastewater pH, are unfavorable to the extraction of other species in the gold mining wastewater. As a result, their concentration increased during the experiments as seen in Table 17 when gold mining wastewater and the raffinate are compared. The selectivity and purity of the acid and copper solution recovered were further validated when the composition of the stripping solution was analyzed. Once it was extracted, sulfuric acid was recovered from the organic phase by hollow fiber membrane contactors, and the results for the stripping solution are shown in Figure 56. In both cases, the re-extraction achieved high efficiencies and the results confirm the selectivity given that the concentration of the contaminants in the recovering solution was <10 mg/L. From all compounds monitored in this study, only iron and manganese were observed in the stripping solution and all others remained below the method quantification limit (<0.5 mg/L). Another result summarized in Figure 56 is the copper concentration. Ideally, the element to be recovered in the second extraction system should not be detected in the acid-recovering solution, as observed in both figures.

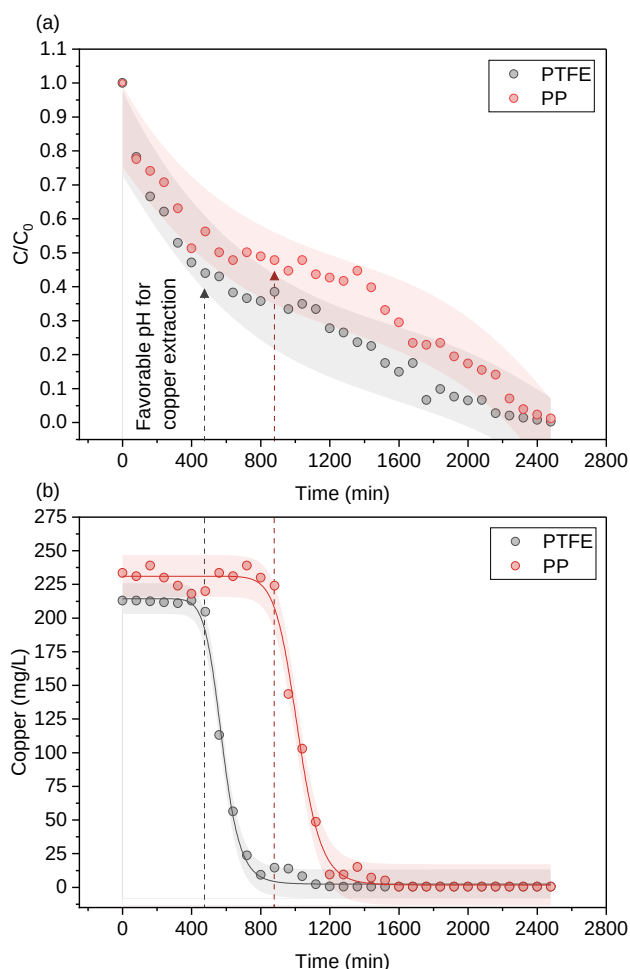


Figure 55. Concentration profile of (a) sulfuric acid and (b) copper in experiments of simultaneous extraction from gold mining wastewater. Initial sulfuric acid concentration corresponded to 40.3 mmol/L and 28.9 mmol/L for experiments with PTFE and PP, respectively.

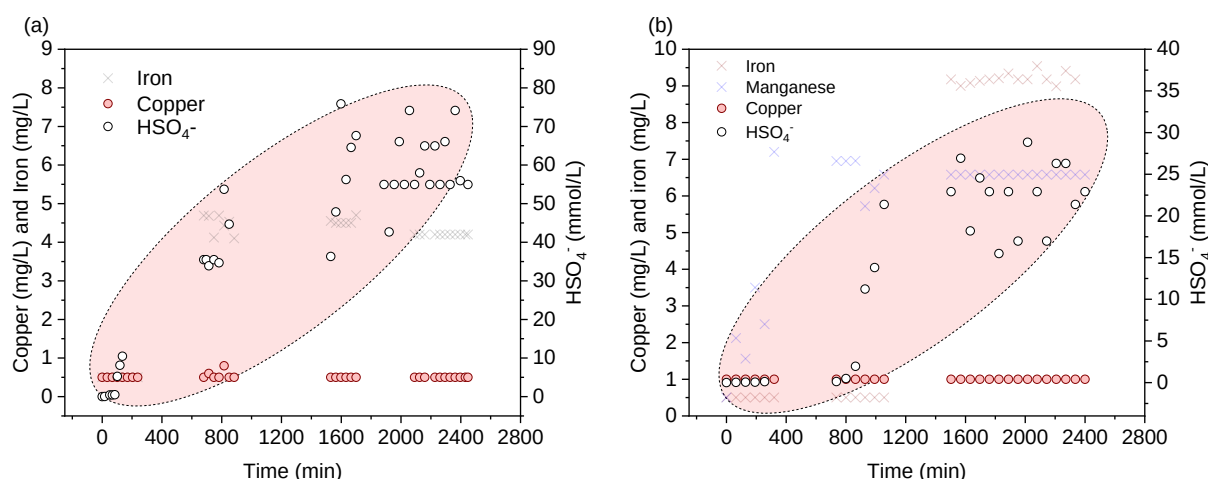


Figure 56. Metals and mineral acid were concentrated in the stripping solution when (a) PTFE and (b) PP membranes were used for acid extraction.

It could be observed that the time required for re-extraction (Figure 55) was similar to that required for extraction (Figure 56). In other words, the acid started to be recovered as soon as

it was loaded in the organic phase; in a perspective of an integrated system, the limiting step for acid recovery would be the extraction. However, the conclusion is only valid for the system under study, in which the extraction and re-extraction membranes had a different area. Once again, the smaller area available for extraction limited its recovery in a shorter period. The final concentration of sulfuric acid in the acid solution was 75 mmol/L (7.35 g/L) in experiments made with a membrane made of PTFE and 29 mmol/L (2.84 g/L) for experiments made with a membrane made of PP. That would represent efficiencies greater than 98.4% of re-extraction and a global recovery of sulfuric acid of 94.0% and 90.7%, for PTFE and PP membranes, respectively. A higher recovery achieved for membranes made of PTFE suggested that its usage for non-dispersive solvent extraction should yield higher efficiencies, prevailing over membranes of PP commonly used in membrane contactors.

3.3 Copper extraction and re-extraction

The results for copper extraction were summarized in Figure 55b. Previous studies suggested that copper is extracted at pH~2 (10 mmol/L) when LIX 84I is used as an extractant, which would explain the low variability in copper concentration in the wastewater tank at the first moments. As soon as the sulfuric acid is extracted and the medium pH achieves values closer than 2, the concentration of copper is reduced in the wastewater tank, being transferred to the organic phase. The concentration profile of copper and sulfuric acid is shown in Figure 55. differs, suggesting that the extraction of copper occurs at higher rates compared to sulfuric acid. Considering that the membranes used were the same, the differences observed could be related to the species' diffusivity and the organic phase's properties. For a better comprehension of the parameters affecting the species diffusion in an organic phase, Wilke-Chang proposed an equation that considers the molecular weight ($M_{w,i}$) and viscosity (μ) of the solvent and the molar volume of the specie ($V_i^{0.6}$), as demonstrated in Equation 82. The diffusivity decreases as the viscosity of the organic phase and the molar volume of the specie increases, and the diffusivity increases as the molecular weight of the solvent increases.

$$D_i = 7.4 \cdot 10^{-8} \frac{(xM_{w,i})^{0.5} T}{(\mu)V_i^{0.6}} \quad (82)$$

Since both extractants were diluted in kerosene and a similar proportion, the differences in the organic phase properties would be related to the extractants used and the species being extracted. LIX 84-I has a lower viscosity, but also lower molecular weight compared to TEHA ($M_{w,LIX\ 84I}$: 262.4 g/mol, $M_{w,TEHA}$: 353.7 g/mol). In addition, sulfuric acid has a higher molar volume compared with copper ($V_{H_2SO_4}$: 53.26 cm³/mol and V_{Cu} : 7.11 cm³/mol). When all variables are considered and considering the Wilke-Chang equation, it is seen that the viscosity and the element volume would be the prevailing parameters governing the diffusion, which are also more favorable to copper than sulfuric acid. That emphasizes the importance of strategies to improve the acid recovery since it would be a limiting step for the recovery of other species by NDSX. Copper was rapidly re-extracted and recovered in the stripping solution, which results are shown in Figure 57. In terms of copper extraction, the overall recovery achieved values of 97.3% and 91.1% when the membranes made of PTFE and PP were used during extraction, respectively.

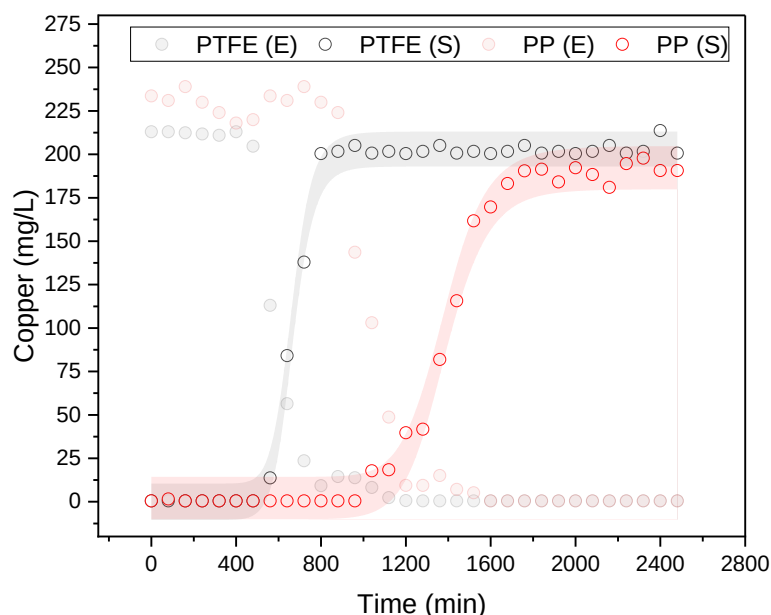


Figure 57. Concentration of copper in the stripping solution when PTFE and PP were used for copper extraction. (E) = extraction step and (S) = stripping step

3.4 Technologies comparisons: integrated or separated, dispersive or non-dispersive extraction?

The primary outcomes of the integrated system have been compared with prior investigations that investigated the efficacy of membrane distillation and non-dispersive solvent extraction as individual processes. In previous studies, membrane distillation was exclusively explored in conjunction with a membrane made of PTFE. Therefore, the findings summarized in Table 18 and Table 19, related to the integrated system, are those obtained in experiments that considered the same membrane.

Table 18 undertakes a specific comparison of the membrane distillation's performance concerning distillate flux, flux decay, temperature polarization, and the recovery rate, as achieved in both the autonomous and integrated methodologies. Conversely, Table 19 summarizes the physicochemical characteristics inherent in all streams obtained during both approaches. This compilation encompasses the distillate, and concentrate, in addition to the acid and copper solutions, recovered.

Table 18. Comparison between the performance of membrane distillation in integrated and separated approaches for gold mining wastewater treatment. ¹[ref], ²[ref]

Variable	Integrated units	Separated units ¹
Distillate flux (L/m ² h)	0.37 ± 0.34	5.51 ± 0.14
J/J ₀	0.12	>0.95
Recovery rate (%)	64%	35%

The integrated units exhibited a reduced distillate flux, a justification rooted in the lower fouling rate identified when assessing membrane distillation in isolation. When comparing the initial and final distillate flux, discrepancies of less than 5% were noticed for the membrane distillation unit operated separately. In contrast, an average deviation of 88% was observed within the integrated approach. Higher recovery rates, if accompanied by preserved distillate quality, are preferred. In this context, the integrated system achieved higher values. Prior research concentrated sulfuric acid during distillation, resulting in a simultaneous increase in its vapor pressure within the feed stream. Due to increased vapor pressure, the compound permeated the membrane pores once recoveries exceeded 35%, thereby acidifying the distillate and undermining its quality. This constraint, encountered when membrane distillation operated solely, was reversed within the integrated process, where acid extraction took place concurrently.

Despite instances of fouling, the distillate quality remained uncompromised during the integrated processes of membrane distillation and non-dispersive solvent extraction. However, it once again emphasized the importance of cleaning protocols to assure the membrane distillation's capacity while treating gold mining wastewater in a system that simultaneously enables acid and copper recovery. The literature suggests additional advantages pertinent to integrated systems, encompassing higher treatment efficiency, simultaneous removal of diverse components, reduced physical footprint – crucial in locales constrained by space for the deployment of wastewater treatment plants - and the opportunity for valuable resource recovery, thus reducing environmental impact. To exemplify, integrated systems would have diminished environmental impact via reduced volumes of concentrate to be discharged.

Table 19 shows the characterization results for distillate, concentrate, acid solution, and copper solution. Both processes demonstrated notable efficiencies in generating acid and copper solutions. Distinctions, however, were observed in terms of distillate and concentrate quality. In terms of metals concentration and rejection efficiency, integrated and isolated systems performed quite similarly; however, the higher pH values of the distillate from the integrated system broaden its potential applications. In addition, the concentrate obtained in the integrated system had also lower concentrations of acid and copper, which indirectly suggests lower costs for further treatment and lower volume of sludge and wastes to be disposed of.

Comparisons are also possible for the extraction technology, whether to consider dispersive (or conventional) solvent extraction or a process assisted by hollow fiber membranes as investigated in this study. In conventional processes, the organic and aqueous phases are dispersed in one another to enhance mass transfer and by-product recovery. After dispersion, the system is left to settle for phases' disengagement, and the organic phase is subjected to a stripping process for the by-product recovery and simultaneous regeneration [335]. However, the dispersion processes could lead to emulsions and losses of the extractant, which is currently the main shortcoming of conventional processes. Different from conventional solvent extraction, the membrane-assisted processes dispense the necessity for the organic phase dispersion into the aqueous one. Instead, the use of hydrophobic membranes allows its wetting by the organic phase and the mass transfer interface becomes the opening of each membrane pore. The process account for a higher surface area, providing greater mass transfer per unit volume (~500 times greater than in solvent extraction columns) [319], [331].

In terms of extraction efficiency, conventional solvent extraction achieved a recovery of 70% of sulfuric acid for the same extractant and diluent used [195], [318]. Better results were obtained in non-dispersive solvent extraction, which resulted in a recovery of 91%. The

advantages of greater surface water for mass transfer were evident for sulfuric acid. For copper, however, higher recoveries were already achieved in conventional solvent extraction (>99%), which was maintained in non-dispersive solvent extraction. The operational costs related to sulfuric acid recovery were positively impacted by higher efficiency. The economic data for both processes were summarized in Figure 58, discarding the costs related to waste disposal previously considered for non-dispersive solvent extraction for a fair comparison between both technologies. The greater contribution of amortization results from higher initial investment costs (CAPEX) given that hollow fiber modules would be costly compared to stirring tanks used in conventional solvent extraction. Membrane replacement and membrane cleaning were two additional variables intrinsic to a system of non-dispersive solvent extraction and summed up to the total operational cost of this approach. Even so, when costs were normalized by the total amount of acid recovered, the extraction approach assisted by hollow fiber membranes achieved lower values and was comparable with commercial prices of sulfuric acid [331].

That would not be the case with copper recovery, in which high efficiencies were already observed in conventional solvent extraction. Therefore, the increased costs of amortization, besides the additional variables related to membrane replacement and cleaning, were not compensated by greater amounts of copper recovered. In both cases, the preliminary economic analysis suggests that the costs would be lower than the marketable price of copper; however, when recovered by the conventional process of solvent extraction, there is greater scope for considering other technologies to recover the metal in its salable solid form.

Table 19. Comparison between the characteristics of the different streams obtained in the integrated and separated units for gold mining wastewater treatment and by-product recovery. ¹ [195], [331], ²[331],

Variable	Distillate (removal rate)		Concentrate (concentration rate)		Acid solution	Acid solution	Copper solution	Copper solution
	Integrated units	Separated units ^{1,2}	Integrated units	Separated units ¹	Integrated units	Separated units ²	Integrated units	Separated units ²
pH	4.69 ± 0.03	3.90 ± 0.10	4.04 ± 0.03	1.10 ± 0.11	1.25 ± 0.21	1.23 ± 0.11	0.12 ± 0.01	0.13 ± 0.02
H ₂ SO ₄ (mmol/L)	<1 (99.8%)	<1 (98.7%)	<1 (0.0%)**	79 ± 8 (10.0%)	54.9 ± 9	59 ± 2	758.5 ± 25*	743 ± 13*
Iron (mg/L)	<0.5 (99.9%)	0.8 ± 0.2 (99.8%)	2060 ± 11.4 (54.3%)	1541.0 ± 45.3 (85.9%)	4.2 ± 0.4	2.7 ± 0.8	<0.5	<0.5
Magnesium (mg/L)	<0.5 (99.8%)	1.2 ± 0.2 (99.9%)	591.9 ± 2.4 (33.6%)	5324.2 ± 248.6 (90.6%)	<0.5	3.1 ± 0.3	<0.5	<0.5
Nickel (mg/L)	<0.5 (99.7%)	<0.1 (>99.9%)	164.2 ± 7.7 (54.7%)	370.2 ± 40.6 (91.6%)	<0.5	0.3 ± 0.1	2.8 ± 0.7	<0.5
Cobalt (mg/L)	<0.5 (99.1%)	<0.1 (>99.5%)	60.3 ± 0.3 (7.1%)	66.1 ± 1.9 (>99%)	<0.5	<0.1	<0.5	<0.5
Copper (mg/L)	<0.5 (99.7%)	<0.1 (99.6%)	<0.5 (0.0%)**	285.0 ± 6.0 (66.1%)	<0.5	<0.1	205.9 ± 4.8	269.0 ± 3.9

*Copper was recovered in an acid solution(1mol/L) and the acid concentration does not reflect the acid content from the wastewater.**The elements were simultaneously extracted in the integrated units, therefore not concentrated.

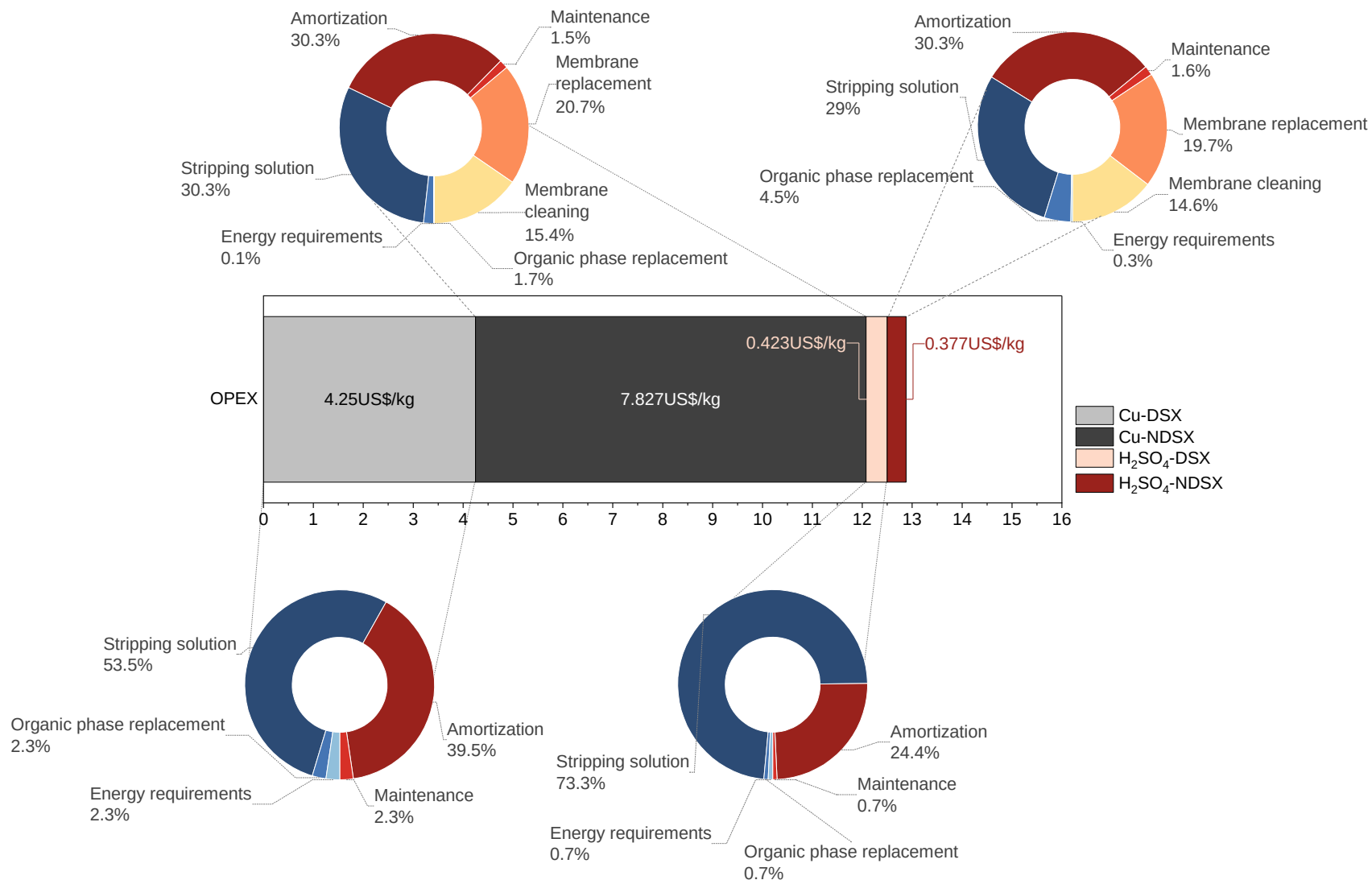


Figure 58. Comparison between operational expenditures (OPEX) for dispersive solvent extraction (DSX) and non-dispersive solvent extraction (NDSX) intended for sulfuric acid and copper recovery from gold mining wastewater. References: DSX [195], NDSX [331].

CHAPTER 8 – FINAL CONSIDERATIONS

The demand for water in mining operations is often substantial due to the extensive water requirements for mineral processing. Addressing the issue of water scarcity in the mining industry is a complex challenge, and various efforts have been made to incorporate sustainable practices, including water recirculation and the adoption of more water-efficient technologies. In the context of this thesis, the membrane distillation process has demonstrated the ability to convert up to 85% of wastewater into high-quality water suitable for reuse. It is noteworthy that the elevated temperatures (80 – 60 °C) at which wastewater is generated are conducive to membrane distillation, as the driving force for this process is indirectly correlated with temperature. The temperature differential across the membrane surface generates a vapor pressure gradient, facilitating vapor transport through the membrane pores, which is subsequently condensed and recovered as distillate. In conventional membrane separation processes, the wastewater would necessitate cooling to meet the restrictions of polymeric membranes, which must operate at temperatures below 40 °C. An intermediate cooling process could lead to increased operational costs, rendering this option unviable. However, the membrane distillation process consistently achieved rejection rates exceeding 98.7% for acids and metals, concurrently yielding a concentrated stream from which sulfuric acid and copper were successfully recovered.

To achieve this, solvent extraction was employed, initially determining the most suitable organic phase for acid and copper extraction and optimizing operating conditions. Simultaneous investigation of extraction and re-extraction processes was conducted to ensure a higher extraction rate followed by efficient re-extraction, as suboptimal re-extraction could undermine the overall process efficiency. For acid extraction, TEHA exhibited superior extraction rates and selectivity for sulfuric acid recovery, while Lix 84-I demonstrated robust copper extraction efficiency, consistent with prior literature findings. However, the formation of emulsions in these experiments led to organic phase losses, necessitating continuous replenishment and resulting in higher operational costs. To address this issue, non-dispersive solvent extraction was considered.

Non-dispersive solvent extraction experiments exhibited superior efficiencies primarily due to enhanced area-to-mass transfer. Copper and acid were simultaneously extracted and re-extracted, achieving overall recoveries exceeding 90%. Specifically for sulfuric acid, this approach led to enhanced acid recovery with reduced operational costs (US\$/kg_{H₂SO₄} recovered), despite additional expenses related to membrane replacement and module maintenance. This marks significant advancements in extraction efficiency and membrane application, positioning them as competitive alternatives to conventional solvent extraction methods, while simultaneously addressing emulsion-related challenges.

The integration of membrane distillation and non-dispersive solvent extraction reaffirmed the potential of both processes for concurrent recovery of high-value products from mining wastewater. Nevertheless, during integration, the organic phase migrated through the pores of the hollow fiber membrane contactors into the membrane distillation system, resulting in membrane fouling. This highlights the need for future research in developing membranes with lower fouling susceptibility towards oils and organics, reduced wettability, and greater resistance to low pH conditions. Additionally, performance improvements can be achieved through the implementation of cleaning strategies throughout operation.

For the mining sector, it is currently recommended that separate units be initially implemented to address operational challenges related to integration and costs. Ensuring non-dispersion conditions demands stringent operational control. For the scientific community, continued

exploration of integration is warranted due to its potential for simultaneous wastewater treatment and by-product recovery. Limitations pertaining to fouling control present a future research opportunity to develop and validate oleophobic membranes or cleaning protocols conducive to stable membrane distillation performance.

With the progress made in this study, opportunities for acid and copper recycling emerge, contributing to sustainability in the mining sector. Both elements can be strategically reused in mineral processing to enhance gold recovery. As discussed throughout this thesis, sulfuric acid can be added to the slurry to reduce carbonate (CO_3^{2-}) levels before entering the autoclave circuit, a process known as acidulation. This reduces CO_2 production during gold ore oxidation. Recycling sulfuric acid from wastewater can reduce the mining sector's reliance on variable market prices (as high as 400% fluctuation) for metallurgical-grade sulfuric acid, which is influenced by fertilizer demand. Furthermore, the efficiency of gold ore oxidation can be improved through the addition of copper ions, enhancing the oxidation rate. Considering reuse opportunities, the recovered water and mineral acid can be incorporated back into the extraction process itself, with the former used for acid stripping and the latter for copper stripping. Potential commercialization opportunities for copper and sulfuric acid can also be explored, dependent on market prices and external variables. As the global population continues to grow, and developing countries modernize their infrastructure, the demand for copper is expected to rise.

It is also conceivable that the system developed and investigated in this thesis can be applied to other industrial wastewaters, not limited to mining sectors but also encompassing acid liquors from industries such as galvanization and glass manufacturing, among others involved in metal processing. Employing membrane distillation and solvent extraction represents a departure from the linear perspective of wastewater generation, treatment, and disposal, instead aligning with reuse practices and attributing value to wastewater, which now emerges as a potential source of significant societal products for development.

In summary, the integration of membrane distillation and non-dispersive solvent extraction presents a promising avenue for addressing wastewater treatment challenges while simultaneously harnessing high-value by-products. This research paves the way for improved sustainability in the mining sector and opens opportunities for resource recovery that can positively impact various industries. As technology advances and costs decrease, integrated systems like the one studied herein hold great potential as alternatives for wastewater treatment and beneficiation in the context of gold mining and beyond.

CHAPTER 9 – REFERENCES

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