

Review

Membrane and Electrochemical Based Technologies for the Decontamination of Exploitable Streams Produced by Thermochemical Processing of Contaminated Biomass

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Abstract: Phytoremediation is an emerging concept for contaminated soil restoration via the use of resilient plants that can absorb soil contaminants. The harvested contaminated biomass can be thermochemically converted to energy carriers/chemicals, linking soil decontamination with biomass-to-energy and aligning with circular economy principles. Two thermochemical conversion steps of contaminated biomass, both used for contaminated biomass treatment/exploitation, are considered: Supercritical Water Gasification and Fast Pyrolysis. For the former, the vast majority of contaminants are transferred into liquid and gaseous effluents, and thus the application of purification steps is necessary prior to further processing. In Fast Pyrolysis, contaminants are mainly retained in the solid phase, but a part appears in the liquid phase due to fine solids entrainment. Contaminants include heavy metals, particulate matter, and hydrogen sulfide. The purified streams allow the in-process re-use of water for the Super Critical Water Gasification, the sulfur-free catalytic conversion of the fuel-rich gaseous stream of the same process into liquid fuels and recovery of an exploitable bio-oil rich stream from the Fast Pyrolysis. Considering the fundamental importance of purification/decontamination to exploit the aforementioned streams in an integrated context, a review of available such technologies is conducted, and options are shortlisted. Technologies of choice include polymeric-based membrane gas absorption for desulfurization, electrooxidation/electrocoagulation for the liquid product of Supercritical Water Gasification and microfiltration via ceramic membranes for fine solids removal from the Fast Pyrolysis bio-oil. Challenges, risks, and suitable strategies to implement these options in the context of biomass-to-energy conversion are discussed and recommendations are made.

Keywords: supercritical water gasification; fast pyrolysis; decontamination; membrane gas absorption; electrocoagulation; electrochemical oxidation; microfiltration

1. Introduction

Available soil contamination surveys indicate that there are about 2.8 million potentially contaminated sites just across the EU-28. Although 650,000 sites have been registered, only 1 in 10 have so far been remediated [1]. The management cost of European contaminated sites is estimated at €6 billion annually. The main types of contaminants are potentially toxic elements (including heavy metals), followed by petroleum. Aromatic, poly-aromatic, and chlorinated hydrocarbons, along with other organic compounds, account for over 50% of all contamination [2]. Meanwhile, meeting the global challenge of

feeding growing populations while still reducing greenhouse gas emissions would require less land used for dedicated bioenergy crops [3]. Therefore, there is a pressing need for land decontamination.

Phytoremediation is a promising emerging technology for restoring contaminated soils back into arable land. The approach uses suitable resilient plants that efficiently absorb soil contaminants. The harvested contaminated biomass can be further thermochemically converted to liquid and/or gaseous energy carriers/chemicals linking soil decontamination to a biomass-to-energy concept within the frame of circular economy [4]. Two promising thermochemical processes, i.e., Supercritical Water Gasification (SCWG) and Fast Pyrolysis (FP), have been considered in the framework of the EU-funded collaborative CERESiS project for the production of biofuels and key biofuel precursors, suitable for further upgrading, starting from harvested contaminated biomass [5]. Other types of thermochemical processes, although very promising, have not been considered in the frame of this review. The interested reader can find more information about these processes in recent, excellent review studies [6–8].

However, the use of biomass from phytoremediation sites raises concerns about the risks for the emissions of potentially toxic elements moved from soil to plant and then potentially to the air or aquatic environment through the use of the fuels obtained from the thermochemical conversion processes. Moreover, transferring contaminants from plants to gaseous and liquid effluents poses a number of technical problems due to the presence of inorganic contaminants, especially heavy metals and H₂S, acting as poisoning agents of the catalysts used in some stages of the thermochemical route. Thus, applying specific purification methods right after the initial thermochemical treatment is necessary, prior to any added value post-processing.

The current study, after a brief overview of the products obtained from SCWG and FP, provides a critical review of state-of-the-art membrane and electrochemical-based technologies for the decontamination of exploitable streams produced by thermochemical processing of contaminated biomass, thereby allowing the efficient operation of downstream processes and the eventual production of contaminants-free fuels and chemicals. In Section 2, a very brief introduction to the two thermochemical processes which are under review, i.e., SCWG and FP, is provided. Section 3 is the main part of this review study, where three different decontamination technologies are analyzed: (i) Membrane Gas Absorption for desulphurization of the SCWG gas effluent, (ii) electrocoagulation and electrochemical oxidation for the removal of inorganic and organic contaminants (including heavy metals, toxic hydrocarbons, nutrients, and other chemical and biological contaminants) from SCWG liquid effluent and (iii) membrane microfiltration/ultrafiltration for the removal of fine metal-laden char particles from the FP liquid effluent (i.e., bio-oil). In this section, the abovementioned methods are assessed compared to state-of-the-art decontamination technologies, aspects relevant to materials and process design parameters are discussed and detailed surveys of the relevant literature for similar applications are conducted to provide a comprehensive analysis to the reader. Finally, in Section 4, the main conclusions of the current review study are retrieved and some recommendations for further research in these fields are proposed.

At this point, it must be noted that the selection of decontamination methods to be reviewed does not necessarily imply that these methods are the best available decontamination technologies for the considered gas and liquid effluent streams. The main target of the current study is to analyze and critically discuss the selected novel and promising methods.

2. Thermochemical Processing of Contaminated Biomass

SCWG and FP represent the initial stages of different thermochemical pathways leading to liquid biofuels. To identify the possible contaminated liquid or gaseous streams derived from these two thermochemical treatments which need further purification, a brief overview of the two processes and their main products are provided in the next subsections.

2.1. The SCWG Process and Its Products

Hydrothermal technologies are an excellent approach for valorizing (waste) biomass, especially materials with a high moisture content [9]. In the framework of the present work, only the process of gasification in supercritical water has been considered. The SCWG process exploits the special features of supercritical water, which comprise a low viscosity and density as well as a non-polar behavior, promoting mixing and reaction with organic compounds. This requires high operating pressures (>221 bar; typically, 250–300 bar) and temperatures (>374 °C; typically, >600–700 °C) [10]. SCWG is a technology particularly suited for small-scale and even mobile processing facilities, avoiding the need to dry the biomass while having the potential to eliminate carbon-based contaminants during the conversion process. Inorganic contaminants (incl. alkali salts and also potentially heavy metals) are known to form salts under supercritical conditions [11,12] and can thus be separated and concentrated in a brine stream [13,14]. Furthermore, the main part of bounded organic carbon will be found in the gaseous phase. This enables effective downstream purification and production of high-value products, like liquid hydrocarbons, via Fischer–Trops synthesis. A simplified sketch showing the SCWG laboratory reactor as it is realized at the Karlsruhe Institute of Technology (KIT) and the process streams, respectively, are depicted in Figure 1. The valuable product of the process is the energy-rich SCWG gas (9 in Figure 1). The liquid effluent contains the largest part of the process water and accounts for up to 90 wt% of the total mass of the biomass fed (8 in Figure 1). The salt brine is an important side product of the process and contains salts and Phosphorous in a much higher concentration than the original biomass (6 in Figure 1). In simplified process layouts, the salt brine is mixed with the liquid effluent. The decision to separate a salt brine depends on the amount of salts contained in the biomass.

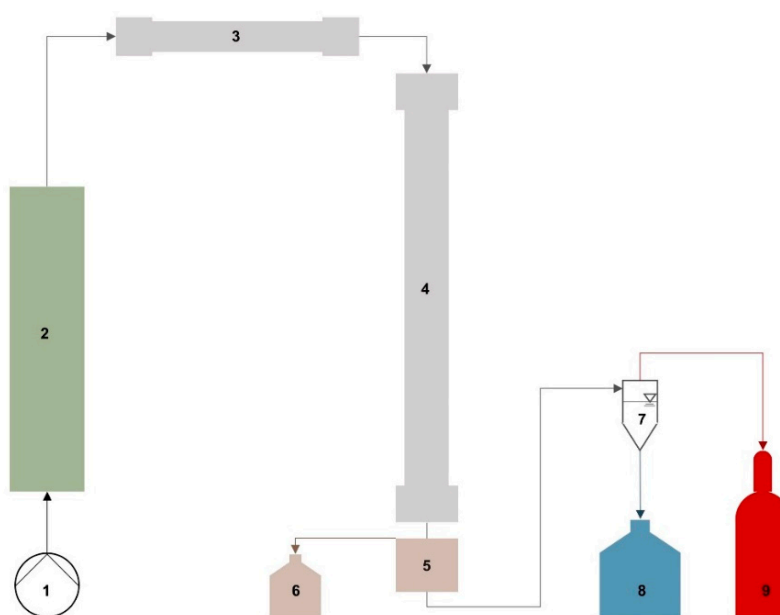


Figure 1. Schematic flow diagram of SCWG reactor and peripheral components. (1): pump, (2): biomass feed cylinder, (3): preheating section, (4): reactor, (5): salt separation, (6): salt brine, (7): gas-liquid phase separation, (8): reactor effluent, (9): product gas.

The gaseous product of SCWG is a mixture consisting mainly of H_2 , CH_4 , and CO_2 [15]. It also contains heavier hydrocarbons (mainly C_2H_6) as well as low amounts of CO [10]. The exact composition of gaseous effluent varies significantly, depending on the type of biomass, process conditions, type of catalyst, etc. Table 1 shows a range of compositions per main constituent that is to be expected.

Table 1. Typical composition range of the SCWG gaseous product.

Component	Typical Composition *
H ₂	20–35% (v/v)
CH ₄	20–25% (v/v)
CO ₂	35–40% (v/v)
C ₂₊ (mainly C ₂ H ₆)	7–10% (v/v)
CO	0–1% (v/v)
H ₂ S	<1000 ppmv

* 5–12% biomass dry matter content, 650 °C, 280 bar, K⁺ as homogeneous catalyst.

The main contaminant in the gaseous product is H₂S, coming from the sulfur content of the biomass. Therefore, efficient de-H₂S technologies need to be considered before any gas upgrading post-treatment process, considering that such processes are typically catalytic and sulfur constitutes a known poison with a potentially detrimental effect.

The vast majority of Potential Toxic Elements (PTEs) are expected to be transferred into the liquid effluents, and thus, the application of specific purification methods is necessary prior to any value-adding post-processing. The liquid streams produced by SCWG are aqueous streams containing non-decomposed organic material and salts (typically NH₄⁺ & K⁺ -salts) as well as (primarily heavy) metals that were extracted from the contaminated biomass. It has been suggested that during SCWG, with increasing temperature, heavy metals are immobilized in solid deposits [16–18], like salts and char that will be contained in the aqueous process streams. Considering the process flow diagram depicted in Figure 1, the reactor effluent is typically less contaminated than the produced salt brine. The contaminants concentration and composition depend on the feed material (nature and concentration of nutrients and organics), the gasification efficiency, and the salt separation strategy [10]. Most of the time, both streams need to be purified, either separately or combined in one stream, so that the water can be recycled back into the SCWG reactor, thereby minimizing the effluents of the process. In this respect, efficient purification methods need to be considered.

2.2. The FP Process and Its Products

Pyrolysis is a thermochemical conversion process conducted in the absence of molecular oxygen through which biomass is decomposed to form a vapor phase consisting of condensable and incondensable compounds, typically known as bio-oil and pyrolysis gas. The remaining solid carbonaceous residue is known as char or biochar. Optimal ranges of temperature, heating rate, and gas residence time have been defined for the maximization of the bio-oil yield, thus leading to the definition of FP operating conditions: high heating rate (~100–1000 °C/s), very short residence time of hot vapors (~1 s) and temperatures between 400 and 550 °C. FP represents an alternative approach for treating contaminated biomass as, given the low operating temperature, it allows the fixation of heavy metals (HMs) in the bio-char, thus reducing the volume and weight of contaminated matter while also producing a combustible liquid product (bio-oil) containing limited amounts of heavy metals. In any case, the different nature of organic components strongly affects the pyrolysis products yields and composition, as well as the presence of inorganic elements catalyzing their decomposition pathways [7,19,20]. Table 2 shows a typical composition of bio-oils produced by four different commercial systems (BTG, Dynamotive, Ensyn, and Pyrovac) operated under fast pyrolysis conditions [21].

Even though it is possible to tune properly the operating variables of the pyrolysis reactor (feedstock size and moisture, temperature, carrier gas flow rate) for limiting both the water content and the transfer of heavy metals into the vapor phase, it is inevitable that a fine fraction of char will be elutriated and dragged by the vapor phase exiting the reactor [22,23]. Bio-oil production through FP needs to be integrated with a contaminant separation technology aiming at removing possible, solid particles (contaminated and not) transferred/entrained from the biomass to the bio-oil during the thermochemical

conversion process [24]. To remove this fraction, different gas/solid separation systems can be considered, namely cyclones, hot filters, and electrostatic precipitators. A simplified sketch showing the process flow diagram of a typical FP unit is depicted in Figure 2. However, these gas/solid separation systems typically only prevent the transfer of the bigger particles (higher than about 10 μm). For this reason, an additional off-line filtering treatment is required at the end of the condensation train to remove fine solid particles (size < 10 μm). Among the peculiar properties of bio-oil, water content and viscosity, typically around 20–30 wt% and 15–40 mm^2/s , respectively [25], strongly affect the filtration process design and its operational efficiency, as it will be clarified in Section 3.3; thus, they must be carefully considered and taken into account [26].

Table 2. Typical concentration of compounds included in bio-oils derived from 4 different commercial plants [21].

Chemical Category	Typical Concentration (%wt)
water	16–30
major carbohydrates	9–17
minor carbohydrates	0.9–1.5
furans	1–1.6
phenols	0.4–1.4
guaiacols	2.6–6
phenols	0.3–2.2
benzene	<0.01

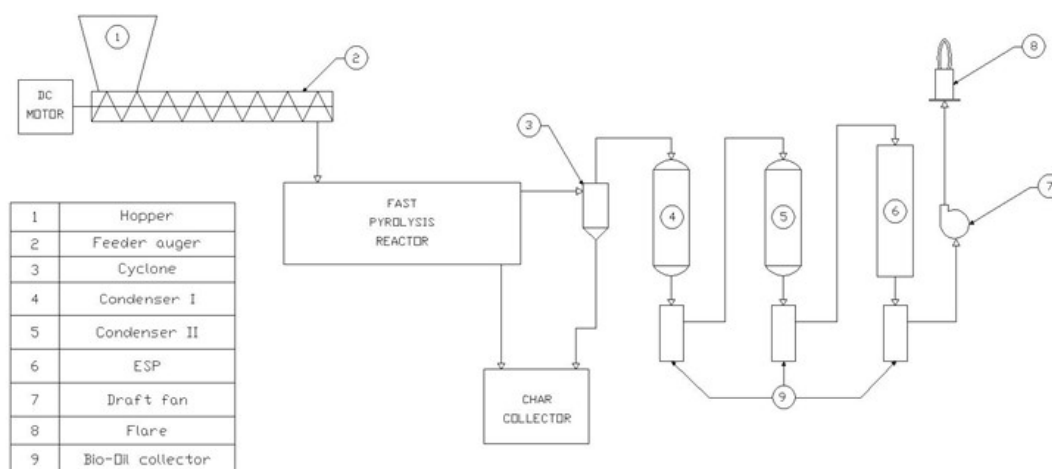


Figure 2. Simplified flow diagram of a typical FP unit.

3. Decontamination Technologies of Gaseous/Liquid Effluents

3.1. SCWG Gas Effluent Treatment

The main target in SCWG treatment is the removal of H_2S and, depending on the downstream processes, the potential simultaneous removal of CO_2 or a part of it. This falls in the general category of sour gas treatment/purification, which mainly includes the technologies described in brief below [27].

3.1.1. Methods for Sour Gas Purification

Chemical or Physical Absorption in Packed Columns

This can be considered the state-of-the-art method for sour gas treatment. The principle of the technique is acid gas removal by various absorption/reactive solvents, as briefly stated below. Then the solvent can be regenerated by applying heat (typically 110–130 $^\circ\text{C}$ for the most common case of amine solutions) and a mild vacuum to strip the absorbed gases. The main solvents that are commonly employed in the process include: (i) Aqueous amine

solutions (e.g., MEA, DEA, MDEA)—Chemical absorption, (ii) Aqueous alkali solution (e.g., NaOH, KOH)—Chemical Absorption, (iii) Methanol—Physical absorption, and (iv) Ionic liquids—Physical absorption.

Adsorption

Adsorption processes employ high-capacity solids which selectively adsorb one or more gases of the gas mixture. Depending on the type of solid-adsorbate interactions, adsorption can also be classified as physisorption or chemisorption. Typical adsorbents for H₂S capture from gas mixtures include metal oxides (e.g., ZnO, iron oxides, CuO), Metal-Organic Frameworks (MOFs), zeolites, carbons, and composite materials. Except for sorbents' capacity and selectivity, other important factors that need to be considered for process design and economic assessment include sorbents' stability in harsh environments as well as their regeneration potential.

Cryogenic Distillation

Distillation is, quite often, the optimum choice, from a techno-economic point of view, for many chemical separations, especially in the petrochemical industry. Although this technology has been studied extensively, mainly in the 1950s, it has not been the preferred option, probably because there was always a better choice available. However, in the last decade, distillation has come again into the frame as a potential option for gas sweetening, although it is very energy-intensive and it seems that it only could be applied in very large plants.

Membranes

In the last two decades, R&D activities on membrane technology, as a potential alternative to conventional gas separation technologies, have been intensified due to some distinct advantages of the membrane technology, such as low energy consumption, simplicity of operation, cost-effectiveness, high specific surface area, small footprint, easy and modular scale-up, and environmental friendliness. Membranes serve as a selective barrier between two compartments (i.e., the feed-retentate and the permeate compartments) which allow the permeation of gas molecules at different rates. Thus, the permeate is enriched to more permeable components of a gas mixture while the retentate to the less. Polymeric membranes are at a higher technology readiness levels (TRL) and have a higher potential for application in gas separation applications compared to inorganic ones due to their much lower cost and the ease of fabrication of large areas and compact membrane modules. In fact, membranes have been commercialized for natural gas sweetening applications, where they seem to be a promising option, especially for small and decentralized applications [28,29]. George et al. [30] conducted a detailed literature survey on polymeric membranes for acid gas removal. They concluded that although a high number of different polymeric membranes have been studied in the literature, only a limited number of these membranes have been tested for the simultaneous removal of CO₂ and H₂S. The membranes' permeability, selectivity, and mechanical stability are the key parameters that determine the overall efficiency of the process. Among the different polymeric membranes considered in that review, the membranes that exhibited higher potential for combined acid gas removal were mainly polyetherurethane urea, polyether block amides, supported ionic liquid membranes, modified cellulose acetate, and polybenzimidazole (PBI) composite membranes. However, in a recent work, Alqaheem [31] studied the potential application of polymeric membranes for treating Kuwait's sour gas. He pointed out a well-known shortcoming of membrane technology related to the typical tradeoff between purity and recovery. For the case of sour gas treatment, this means that when deep desulphurization of the feed gas is needed, along with the covetable H₂S and CO₂ removal, some methane will inevitably also move from the feed to the permeate side due to the finite selectivity of the membrane. This, most of the time, leads to significant methane losses when only one membrane stage is considered. On the other hand, when more complex cascade schemes

are considered, although the overall recovery and purity could be increased significantly, the process' economics are inversely affected.

Membrane Gas Absorption (MGA)

An alternative hybrid technology that combines the advantages of the membrane with that of absorption technology is Membrane Gas Absorption (MGA), i.e., absorption in membrane contactors instead of packed columns. This is a very promising new technology, with interesting advantages and further developmental potential, which has been increasingly studied in the last few years, especially for CO₂ capture applications [32]. Moreover, although most of the above-mentioned technologies are more mature and have been discussed several times in the literature. On the other hand, the review articles about MGA technologies for H₂S removal are limited. For these reasons, although this does not necessarily imply that it is the best available technology, it has been selected for more detailed analysis in the framework of this work.

As a first general conclusion, Table 3 below summarizes the main pros and cons per technology briefly stated above.

3.1.2. Detailed Description of Membrane Gas Absorption (MGA) Technology Theoretical Background

In a gas-liquid membrane contactor, the membrane is the barrier between the two phases, which flow on their opposite sides. In this formulation, the membrane, except for separating and preventing the mixing of the two phases, actually provides the interface for their contact. Specifically, if a hydrophobic membrane is employed, its pores are filled with gas, and as long as the pressure of the liquid is slightly higher than that of the gas, an immobilized gas-liquid interface is formed at the pores' mouth on the liquid side. Figure 3 shows a schematic representation of the mass transfer phenomena in a gas-liquid contact membrane, along with the relevant mass transfer resistances for a hydrophobic membrane.

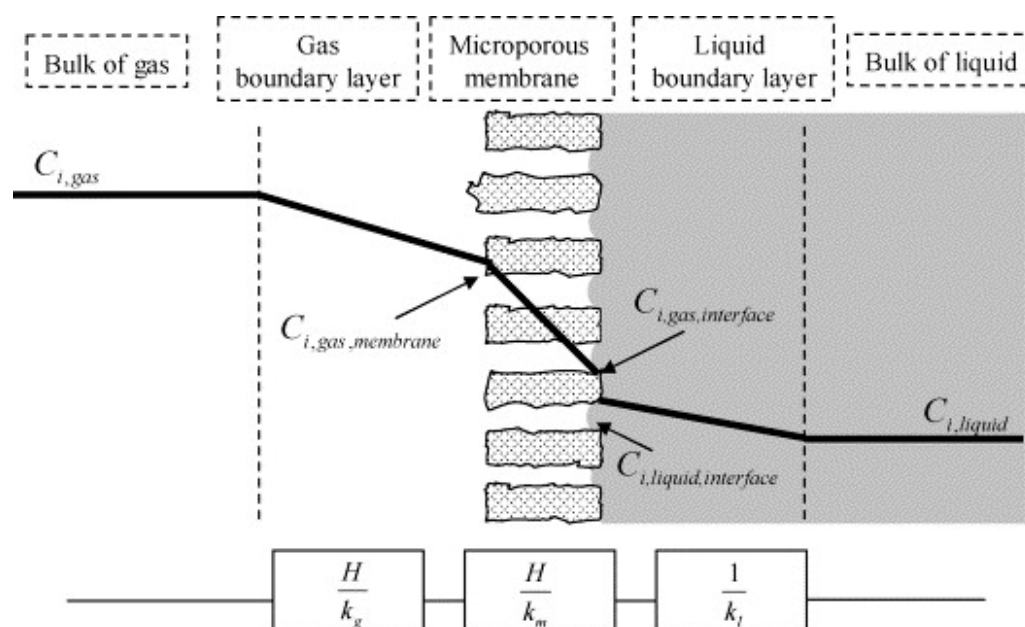


Figure 3. Mass transfer process of a gas-liquid contact membrane (Reprinted with permission from Ref. [33], 2022, Elsevier.)

Table 3. Main advantages and disadvantages per main sour gas purification method.

Packed Columns		Adsorption		Cryogenic Distillation		Membranes		MGA	
Pros	Cons	Pros	Cons	Pros	Cons	Pros	Cons	Pros	Cons
Established process Many different solvents can be used depending on the purification targets	Solvent foaming Solvent losses, especially in regeneration Column flooding Voluminous equipment	Established process High performance	Semi-continuous operation Performance declines with time High energy demands for regeneration Spent solvent disposal is an issue	High performance Established process in different applications	High energy demands High cost Voluminous equipment	Use smaller space Modular scale-up Low energy demands Simple operation No wastes	Membrane stability can be an issue Questionable long-term performance Difficult to achieve very low conc. in the treated gas	Combine advantages of membranes and packed columns High specific contact area Compact and modular design No foaming & flooding	Membrane wetting Membrane stability

Advantages and Disadvantages of the MGA Technology

Gas–liquid membrane contactors have some key advantages compared to conventional technologies. The one that is most often emphasized is the very high specific surface area, i.e., available gas–liquid contact area per unit volume of the device. Currently, the leading manufacturers of conventional contact devices offer structured packings with a specific surface area of up to $1500 \text{ m}^2/\text{m}^3$, which is about half of what can be achieved in a membrane contactor. Table 4 compares specific surface areas for different contact devices [34].

Table 4. Specific surface area for different gas–liquid contactors.

Contactors Type	Specific Surface Area, m^2/m^3
Scrubbers	1–10
Random packings	50–250
Structured packings	100–1500
Flat sheet membrane contactors	up to 900
Hollow fiber membrane contactors	1000–3000

In addition to the high specific surface area, membrane contactors have a series of other distinct advantages compared to conventional devices, such as [35]:

- The contact area does not depend on gas and liquid flow rates as the two-fluid flows are independent. This is particularly important in cases where the required liquid/gas ratio needs to be very high or very low. In these cases, the conventional columns could have problems with flooding at high flow rates or unloading at low ones.
- There are no problems that typically come from the gas dispersion into the liquid phase, like weeping, foaming, entrainment, etc.
- Scale-up is more straightforward with membrane contactors as they typically scale linearly. Increased capacities can be achieved simply by adding more membrane modules to a system.
- Modular design also offers flexibility in the operating capacity of a plant.
- The performance of membrane contactors typically can be predicted more easily as the contact area is known and constant a priori.
- The efficiency of membrane contactors (in terms of Height of a Transfer Unit/HTU) is substantially higher, mainly due to their high specific surface area.
- Solvent holdup is typically very low; a feature particularly important when expensive solvents are considered.

On the other hand, membrane contactors also have some disadvantages, such as:

- The membrane introduces an extra resistance to mass transfer between the two phases. However, in many cases, this resistance is small compared to the other encountered in the process, and measures (design + operational) can be taken to reduce its contribution further.
- Partial membrane wetting with time can potentially increase the mass transfer resistance of the process. Careful selection of membrane materials, solvents, and process conditions is needed to avoid this phenomenon.
- Membrane contactors are subject to shell side bypassing, especially at low flow rates, which reduces the efficiency of the system. Fortunately, several design improvements have been proposed to address this problem when scaling up to large-area membrane modules.
- Membranes are subject to fouling. Although this tends to be more of a problem in filtration applications and not in membrane contactors, it must be considered for specific cases.
- Membranes have a limited lifetime. Thus, the cost of periodic membrane replacement must be considered. However, the cost corresponding to membrane materials and

shaping/assembly is by no means prohibitively high to not, at least in principle, allow such a strategy.

- The potting adhesive (e.g., epoxy) used in sealing the bundle of fibers may be vulnerable to attack by organic solvents, considering a long-term operation.

The above relatively few shortcomings are often outweighed by the inherent advantages of the technology. For this reason, membrane contactors have attracted the interest of both academia and industry for a diverse range of applications.

Membranes and Modules

Most of the commercially available membrane materials that are employed in membrane contactor devices are made of hydrophobic polymeric materials such as polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF). Their applications in MGA processes are often restricted by membrane wetting and swelling, leading to reduced performance over time. PP is the most widely used since it can be easily and economically produced and incorporated in large area membrane modules. PVDF and PTFE are more chemically resistant and hydrophobic materials, but their higher cost and limited availability in large area membrane modules are limiting factors. Table 5 shows some indicative costs for these membrane materials [36].

Table 5. Indicative cost of commercial polymeric hollow fiber membranes.

Membrane Type	Price, \$/m of Hollow Fiber	Manufacturer
PP	0.01	Mitsubishi Raynon Ltd. (Tokyo, Japan)
PVDF	0.36	Wenzhou New Century International Ltd. (Wenzhou, China)
PTFE	11.5	Sumitomo Electric Fine Polymer (Osaka, Japan)

In the last few years, ceramic membranes have been studied as membrane contactors for different types of applications due to their inherently higher thermal and chemical stability. However, their development is still in the lower TRL and has significantly higher costs. For these reasons, their potential application in SCWG gas effluent treatment was not considered at the frame of this study.

3M™ Liqui-Cel™ is a leading membrane contactor supplier. It produces a variety of membrane modules (from small to industrial scale), designed for different types of applications (e.g., degassing, carbonation). These membrane contactors are the most well-studied in literature and can be used as a benchmark for assessing systems and processes. They are using porous polypropylene hollow fiber membranes in a shell and tube type of configuration, which ensures a high packing density and specific surface area for the membrane module. Most of the small-scale membrane modules (MM series) are designed for a parallel gas-liquid flow configuration, while the large-scale membrane modules (EXF series) are designed for a transverse flow configuration, which offers higher overall mass transfer coefficients. Figure 4 shows a commercial EXF series membrane contactor with details of the fiber mat, the hollow fiber, and the membrane's pores, as a representative example among the options available in the market.

Other membrane contactor manufacturers, which mainly supply modules for small to large scale degassing applications are Compact Membrane Systems Inc. (Newport, DE, USA), Zena Membranes (Ostopovice, Czech Republic), Pall® (Port Washington, NY, USA), DuPont™ (Martinez, CA, USA), etc.

Survey on Candidate Solvents

Solvent selection is probably the most crucial part of any absorption process design and significantly affects the overall system's performance. The identification of suitable solvents for SCWG gas effluent treatment must be based on

- Operating data for solvents typically used in conventional sour gas absorption processes
- Data on solvents compatibility with membrane materials
- Data related to solvents availability, cost, management, regeneration potential, etc.

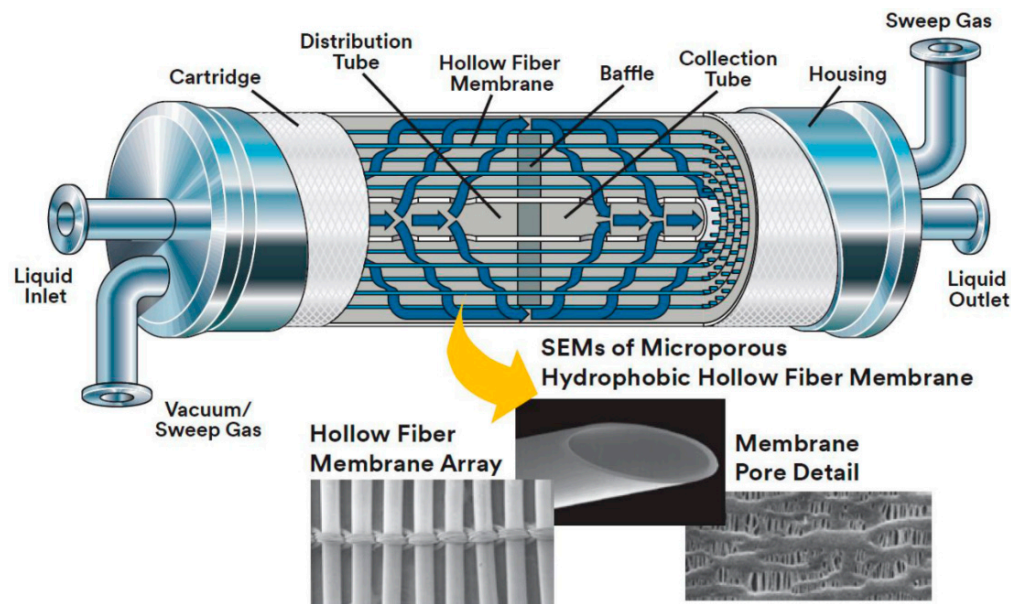


Figure 4. 3M™ Liqui-Cel™ EXF membrane contactor module (Reprinted from [37]).

Amines are by far the most commonly employed solvents in sour gas treatment. They have been commercially applied in the petroleum and natural gas industries for many years. Moreover, amines have also been used to treat synthesis gas from coal gasification units. An analysis of the main characteristics of amine systems is presented below [38,39].

The three basic types of amines include primary (e.g., Monoethanolamine—MEA), secondary (e.g., Diethanolamine—DEA), and tertiary (e.g., Methyl Diethanolamine—MDEA) amines. The absorption step is favored by high acid gas partial pressures and low temperatures. This can be reversed at low partial pressures and higher temperatures (solvent regeneration step). In most primary and secondary amines, H_2S and CO_2 react simultaneously with the solvent, rendering selective H_2S recovery very difficult. On the other hand, tertiary amines react directly with H_2S but not with CO_2 , which reacts with the hydroxyl ion formed by the dissociation of water. Thus, CO_2 absorption kinetics are significantly slower than that of H_2S and tertiary amines are found to be more H_2S selective.

The development of aqueous alkanolamine solvents for acid gas treatment started around 1930. Triethanolamine (TEA) was the first alkanolamine commercially used in gas-treating plants. However, TEA was gradually retracted (due to its low absorption capacity and reactivity and its relatively poor thermal stability) and other alkanolamines were subsequently introduced into the market as potential alternative acid-gas absorbents. Among them, MEA, DEA, and MDEA were found to be of principal commercial interest for gas purification applications. Table 6 summarizes the main advantages and disadvantages of the most common amines.

Except for the three basic amines reported above, proprietary amines are also offered by several chemical companies, such as UOP (Amine Guard and UCARSOL), BASF (Activated MDEA), and Shell (ADIP-X). These solvents, typically consisting of mixtures of amines and additives, have been designed for customized applications and specific targets, such as selective H_2S removal, partial or complete CO_2 removal, high acid gas loading, etc. For example, partially neutralizing an amine (e.g., with acid) can allow very low H_2S levels to be reached in the treated gas.

Identification of the optimum amine solvent is a complex task that depends on process conditions, acid gas partial pressures, and targeted purity. Generally, absorption processes with amines are recommended for applications with low to medium acid gas partial pressures, as the process economics decline with increasing partial pressures of acid gases due to the increased energy requirements of the solvent regeneration step.

Table 6. Summary of advantages and disadvantages of the main amines.

Amine	Advantages	Disadvantages
Monoethanolamine (MEA)	High alkalinity, resulting in increased acid gas removal efficiency High capacity, even at low concentrations Contaminated solutions can be regenerated	Formation of irreversible reaction products with organic S, which gradually affects the performance of the amine More corrosive compared to other amines Strong reaction with CO ₂ and H ₂ S, resulting in increased energy demands in the regeneration step High vaporization losses, especially in low-pressure operations
Diethanolamine (DEA)	The acid gas loading is typically higher for DEA than MEA Partial removal of organic S can be achieved without significant solvent degradation Lower energy demands in solvent's regeneration step, compared to MEA Lower vaporization losses due to its lower vapor pressure compared to MEA	Complex regeneration process for the contaminated solvents
Methyldiethanolamine (MDEA)	Selectivity towards H ₂ S. This reduces the total amount of the acid gases removed; thus, less solvent is required in case H ₂ S is the targeted compound Low energy demands in the regeneration step Less corrosive than MEA and DEA Low vapor pressure permits its use in high concentrations without vaporization losses High capacity and excellent thermal and chemical stability	Low ability to remove organic S

Non-amine solvents have been used to a lesser extent. Aqueous solutions of potassium carbonate, alkali solutions, and aqueous solutions of ammonia are some of the potential alternatives. Finally, physical absorbers (e.g., methanol or ionic liquids) are another class of solvents that can be applied in certain cases.

The main challenge of the MGA technology that needs to be taken into account is membrane wetting, which sometimes results in significant performance loss over time. The exact mechanism of membrane wetting has not been fully clarified yet due to the complex nature of membrane–solvent interaction phenomena. Several researchers have proposed different explanations for membrane wetting. Some of the prevailing theories include [40,41]:

- Wetting due to possible chemical reactions between the membranes and the solvent can change the hydrophobic characteristics of the system.
- Wetting due to physical interaction between the membrane pores and solvents (e.g., swelling) results in significant surface morphology changes.
- Wetting due to changes in membrane surface hydrophobicity by trace impurities in the solvent.

Partial membrane wetting by the solvent is something expected, at least to some extent, for any membrane-solvent pair. Many times, the partial performance loss can be counterbalanced by the much higher specific membrane area of membrane contactors with respect to the conventional packed columns. However, there are also references for dramatic performance losses (reaching 90% in flux decline with MEA as solvent) during the first hours of operation, which apparently inhibits the applicability of the process.

The compatibility of membranes with various inorganic and organic solvents has been studied experimentally, mainly for the CO₂ absorption process, but the same remarks also stand for H₂S or combined H₂S/CO₂ removal processes. The main conclusions derived are:

- Inorganic solvents such as H₂O, NaOH, and K₂CO₃ have high surface tension and do not easily wet the common hydrophobic membranes. However, they are typically less efficient than the conventional amine ones.
- Amines are the most commonly employed solvents in hollow fiber membrane contactors and they have high absorption performance and regeneration potential. However, the surface tension of these solvents is typically lower compared with the inorganic ones and they tend to wet the common hydrophobic membranes more easily.
- Using MEA as an absorbent for long-term operations results in dramatic flux declines in all commercial hydrophobic membranes. Their surface morphologies, hydrophobicities, and chemical properties are greatly affected by amine attacks. DEA and MDEA tend to have milder effects on membranes performance.

To avoid membrane wetting, the Netherlands Organisation for Applied Scientific Research (TNO) developed a series of absorption liquids based on amino acid salts. These novel solvents had similar absorption performance as conventional amines but did not significantly wet commercial hydrophobic membranes. Since then, the R&D activities around amino acid salts have been intensified. In this direction, potassium glycinate solution is identified as an amino acid salt with high application potential in MGA processes as it has a surface tension that is higher than water, and aqueous MEA and MDEA solutions, resulting in a lower wetting potential. Moreover, experimental results have shown that it has similar to or better performance than MEA and MDEA for the same process conditions. Several composite solutions based on the glycinate solution (e.g., adding piperazine as a promoter) have also been studied for MGA processes with very promising results.

Literature Survey on Sour Gas Treatment with MGA Technology

The highest number of studies regarding hollow fiber membrane contactors deal with MGA of CO₂. Kim et al. [42] published a very detailed literature review on this subject. The studies focusing on H₂S, which is the pollutant of interest in SCWG gas effluent treatment, or combined H₂S/CO₂ removal are much less. Figure 5 shows the operation principle of an MGA H₂S removal system.

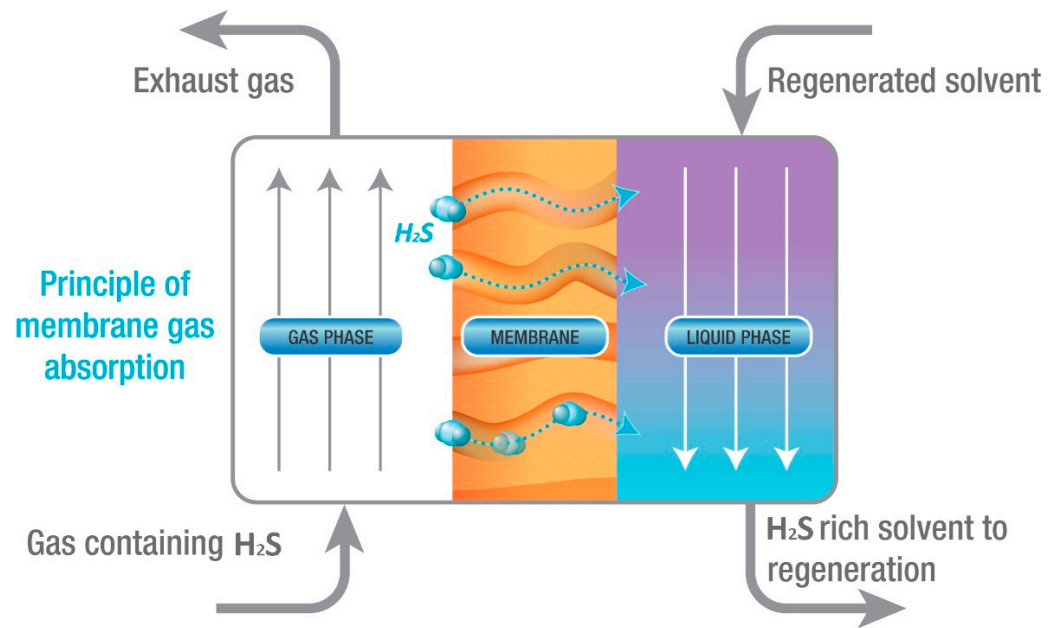


Figure 5. Operation principle of an MGA H₂S removal system (adapted from [43]).

Bazhenov et al. [44] recently published a very detailed literature review on gas-liquid hollow fiber membrane contactors for different applications. In their study, there is concentrated information on works relevant to H₂S removal systems. A summary of the relevant studies, updated with some more recent works, is presented in Table 7.

Table 7. Synopsis of the main results of literature studies on H₂S removal through MGA.

Membrane	Contactor Design	Liquid Phase	Gas Phase	Main Conclusions	Reference
PVDF, PSF	Counter-current Parallel-flow	MDEA, DEA, MEA	H ₂ S/CO ₂ /CH ₄	Increasing MDEA concentration promotes wetting. Lean MDEA solution is recommended for high H ₂ S selectivity.	[45]
PTFE	Counter-current Parallel-flow	Water	H ₂ S/CH ₄	Non-wetting conditions at low-pressure operation. Pseudo-wetting conditions (1–3% of pore filling) at high-pressure operation.	[46]
PFA	Counter-current Parallel-flow	Water, NaOH, DEA, K ₂ CO ₃	H ₂ S/CO ₂ /CH ₄	Excellent long-term operational stability of the PFA membranes under the working conditions (~200 operation hours over a 7-week period).	[47]
PTFE, PFA	Counter-current Parallel-flow	Water, MEA, DEA, DETA	H ₂ S/CO ₂ /CH ₄	PFA exhibits much higher fluxes (9–10 times) for CO ₂ and H ₂ S than those obtained with the PTFE membranes.	[48]
PVDF	Counter-current Parallel-flow	Water, MEA	H ₂ S/CO ₂ /CH ₄	The effects of several operational parameters on the absorption performance and selectivity of H ₂ S were investigated. The results indicated that the gas phase resistance played the most important role in the mass transfer of H ₂ S.	[49]
PVDF	Counter-current Parallel-flow	Water, MEA, K ₂ CO ₃ , KOH, PS, K ₂ CO ₃ /PS	H ₂ S/CO ₂ /CH ₄	The highest H ₂ S absorption flux was obtained when KOH and K ₂ CO ₃ were used as single absorbents. The gas-phase was the dominant mass transfer resistance in the process.	[50]
PDMS	Fiber immersed in absorption tank	Water, NaOH	H ₂ S/CO ₂ /CH ₄	More than 98% H ₂ S and 59% CO ₂ absorption efficiencies were achieved. H ₂ S fluxes (up to 3.4 g/m ² -day) with low CH ₄ loss (~5%) were measured.	[51]
PDMS	Fiber immersed in absorption tank	K ₂ HPO ₄ , NH ₄ Cl, MgCl ₂ ·6H ₂ O	H ₂ S/CO ₂ /CH ₄	The process performance at pH 7 was better than pH 8.5 in terms of H ₂ S removal capacity and selectivity. Almost complete H ₂ S removal (>97%) and high sulfide oxidation (>74%) were achieved.	[52]
PVDF	Counter-current Parallel-flow	Na ₂ CO ₃	H ₂ S/N ₂	Better mass transfer conditions were achieved when the gas mixture was fed into the shell side.	[53]
PP	Counter-current Parallel-flow	Water	H ₂ S/air	Up to 89% H ₂ S removal efficiency was achieved for inlet concentrations of 100 ppmv. The membrane and gas-phase resistance has a significant effect on this mass-transfer process.	[54]
PP	Counter-current Parallel-flow	NaOH	H ₂ S/air	The influence of pH on mass transfer was studied, using sodium hydroxide to control it. A solvent pH of 11 was found to be the most economically attractive.	[55]

Table 7. Cont.

PP	Counter-current Parallel-flow	NaOH	H ₂ S/CO ₂ /air	H ₂ S content below 5 ppm and CO ₂ content below 0.01% were achieved in the treated gas, starting from 2% acidic gas content and working at over 7 m ³ /(m ² × h) feed gas capacity.	[56]
PP	Counter-current Transverse-flow	MDEA	H ₂ S/CO ₂ /CH ₄	H ₂ S removal efficiencies of almost 100% were attained with less than 4% of CO ₂ remaining in the retentate stream using feed gas mixtures containing 5000 ppm H ₂ S and 4–12% CO ₂ in CH ₄ . The influence of CO ₂ feed concentration on the H ₂ S removal is not significant.	[57]
PP	Counter-current Transverse-flow	MDEA	H ₂ S/CO ₂ /CH ₄	H ₂ S selectivity increased with the gas flow rate, H ₂ S concentration, and gas/liquid flow ratio but decreased with CO ₂ concentration. The highest selectivity of H ₂ S over CO ₂ (ratio of the respective overall mass transfer coefficients) achieved was 82.7.	[58]

3.2. SCWG Liquid Effluent Treatment

3.2.1. State-of-the-Art of Saline Wastewater Decontamination

The sustainable treatment, safe discharge, and reuse of the highly saline wastewaters produced from various sources, such as flowback and produced water from oil and gas well development processes (hydraulic fracturing) [59], chemical manufacturing [60], food processing [61], and seawater/brackish water desalination [62] are of increasing concern globally due to the significant risks posed to human health and from their disposal into the environment [63,64]. Such effluents contain a variety of inorganic and organic contaminants, including heavy metals, toxic hydrocarbons, nutrients, and other chemical and biological contaminants. The lack of water resources and the issues on health and safety that have emerged with the application of traditional disposal techniques (e.g., underground injection, discharge to surface water bodies or municipal wastewater treatment plants, evaporation ponds, and land application) [65,66], have emerged the research of alternative processes for the treatment and possible reuse of such wastewaters.

Table 8 summarizes the main methods examined in the literature for the removal of heavy metals (such as Pb, Cu, Ni, Cr, Mn, Co, Hg, and Zn) from brine effluents, including their main advantages and disadvantages. These can be divided into chemical-, thermal- and membrane-based processes, each presenting different technology maturity. Among the methods reviewed, chemical precipitation is the most widely applied method because of its simplicity and cost-effectiveness [67–71]. Evaporation (mechanically or naturally) and crystallization [72] methods have also been examined, including the most common evaporation ponds, where water is evaporated from rejected brine effluents naturally by solar energy. Other advanced thermal methods include Eutectic freeze crystallization (EFC) [73], Multi-Effect Distillation (MED) and Mechanical Vapor Compression (MVC) [72,74,75], with the latter two having been largely applied at industrial level for the treatment of seawater reverse osmosis (RO) concentrate.

Pressure driven membrane processes (e.g., nanofiltration, reverse osmosis) [76,77] have been frequently applied for both dissolved organics removal and total dissolved solids (salts, hardness) from high saline wastewaters [78,79]. However, membranes are prone to fouling caused by colloidal particles and solute macromolecules or salts (scaling) deposited or adsorbed onto the membrane pores or the membrane surface. Fouling is the main disadvantage of these technologies, which necessitates the adaptation of fouling mitigation strategies, including pretreatment of influents, optimization of operational conditions, frequent membrane cleanings through physical, chemical, or biological techniques, and higher pressure demands, with obvious negative consequences. In addition, pollutants are not eliminated but rather transferred from one stream to another since the retained pollutants are concentrated in the concentrate effluent [76,77]. Considering the aforementioned drawbacks, researchers have turned their attention to other modern membrane technologies such as membrane distillation (MD), forward osmosis (FO), electrodialysis (ED), etc. (Table 3). Concerning MD, there are four configurations available according to the mechanism of the vapor pressure gradient formation across the membrane; Direct Contact (DCMD) [80,81], Air Gap (AGMD) [82], Vacuum (VMD) [83] and Sweeping Gas Membrane Distillation (SGMD), with DCMD configuration being the oldest and most widely applied due to the ease of handling and the higher fluxes achieved [74,75,84]. In FO, the separation is achieved by utilizing the osmotic pressure difference induced by the solute concentration difference between the feed and ‘draw solutions’ (solutions of remarkably high concentrations which result in the transport of water molecules across a semipermeable membrane from the less concentrated feed solution to the highly concentrated draw solution. Hence, freshwater and draw solution are separated, with the second being recycled to the FO module [74,84]. FO has been examined in literature to treat brine wastewaters containing heavy metals [72,74,84,85] with interesting results; however, the technology is still in rather low TRL. Finally, ED and its alternatives, such as Electrodialysis Reversal (EDR) and ElectroDialysis Metathesis (EDM), are electrically driven membrane processes that have been commercially successful in demineralizing brackish waters [72,74].

Table 8. Advantages and disadvantages of state-of-the-art technologies for saline wastewater treatment.

Technology	Advantages	Disadvantages
Chemical precipitation	<ul style="list-style-type: none"> + Well-established technology with the ready availability of equipment and many chemicals + It has been used effectively for many years + The design of the treatment process can be customized and thus can be used in a variety of situations + Some treatment chemicals, especially lime [Ca(OH)₂], are very inexpensive + Completely enclosed systems are often conveniently self-operating and low maintenance, requiring only replenishment of the chemicals used. Most of the time, a sophisticated operator is not needed. + Easy to monitor 	<ul style="list-style-type: none"> - May require working with corrosive chemicals, increasing operator safety concerns - Large amounts of chemicals may need to be transported to the treatment location - The addition of chemicals, especially lime, may increase the volume of waste sludge up to 50 percent - Chemical reagents need to be procured, energy inputs and manual oversight are required - Not applicable for all cases - Polymers can be expensive
Evaporation Ponds (EPs)	<ul style="list-style-type: none"> + Low maintenance and little operator attention + Less mechanical equipment except for the pump + Least costly means of disposal, especially in areas with high evaporate rates and low land costs + Easy to construct 	<ul style="list-style-type: none"> - Required for impervious liners of clay or synthetic membranes (e.g., PVC) - Potential of contaminating underlying potable water aquifers through seepage from poorly constructed EPs - Large tracts of land when the evaporation rate is low or the disposal rate is high - Weather and climate-dependent
Wind-Aided Intensified eVaporation (WAIV)	<ul style="list-style-type: none"> + This technique minimizes the need for land + It can achieve an evaporation rate of up to 90% compared to evaporations ponds + The method was tested on brines from RO and RO-ED, displaying an evaporation rate 10-fold greater than that achieved through natural evaporation + This method displays potential in the recovery of salts from brine for raw material use + It has the lowest specific energy consumption (up to 1 kWh/m³) as it exploits wind energy for evaporation and requires only electric energy for the pumps 	<ul style="list-style-type: none"> - Industrial feasibility not proved - Difficult operational control and maintenance - Higher capital and operating costs than evaporation ponds
Brine Evaporative Cooler/Concentrator (BECC)	<ul style="list-style-type: none"> + Reducing the temperature of the re-circulating brine with no further energy consumption and without changing its physical-chemical properties + Reducing the temperature and the quantity of blow-down brine to be disposed of, thus reducing the environmental issues related to the desalination process. + Geometrical simplicity 	<ul style="list-style-type: none"> - High cost of tubes (anti-corrosion material) - Fouling and scaling on the tube's surfaces (due to rapid salt formation in concentrated brines) - Difficulty in cleaning the tube surface in tube bundle arrangements - Achievement of a minimum wetting rate (difficult for low brine flow rates)

Table 8. Cont.

Technology	Advantages	Disadvantages
Eutectic Freeze Crystallization (EFC)	<ul style="list-style-type: none"> + In comparison to evaporative thermal methods, EFC offers the possibility of a complete conversion of feed into water (from ice) and salt crystals + Recover water and salts simultaneously + Low energy consumption + Requires no additional chemicals 	<ul style="list-style-type: none"> - High capital costs - High mechanical complexity - This technology hasn't been applied extensively in multicomponent brine solutions - Formation of an ice scale layer in the crystallizer surfaces
Multi-Effect Distillation (MED)	<ul style="list-style-type: none"> + Very low electrical consumption (<1.0 kWh/m³) + Operates at low temperature (<70 °C) and low concentration (<1.5) + Produces steadily high purity distillate + Does not need complex pre-treatment of seawater and are tolerant to variations of seawater conditions + It is highly reliable and simple to operate + Reduces civil works cost + It is simple to install + It has a low maintenance cost + Operates 24 h a day with minimum supervision + Ideal for coupling with power plants + It can be adapted to any heat source + Allows very high thermal efficiencies and savings in fuel costs 	<ul style="list-style-type: none"> - Incompatible with higher temperature heat sources due to scaling issues during spray evaporation - Difficult to scale down to small sizes due to complexity and large numbers of parts required
Membrane Distillation (MD)	<ul style="list-style-type: none"> + Lower working temperature (max 88 °C or 190 °F) compared to conventional separation processes + Lower hydraulic pressure (max 100 psi) compared to pressure-driven membrane separations + Less susceptible to flux limitations compared to RO process + Less expensive membrane compared to reverse osmosis + Ability to use waste heat or solar energy + Simple up-scaling + Simple operations + Possibility for high membrane surface/ volume ratios + Possibility to treat flows with heat-sensitive components and a high suspended particle content at atmospheric pressure and a temperature below the boiling point of the supply 	<ul style="list-style-type: none"> - The main factors that determine the feasibility of MD as an industrial separation technique still form barriers to commercial implementation - The relatively low permeate flux in comparison with pressure-based membrane processes - Flux reductions caused by concentration polarization, membrane pollution - Water loss due to conduction through the polymeric membrane and pore wetting - High cost of MD modules and the high thermal energy consumption

Table 8. Cont.

Technology	Advantages	Disadvantages
Forward Osmosis (FO)	+ It requires less energy consumption compared to RO for the draw dilution step because it is based on the natural osmosis phenomenon	<ul style="list-style-type: none"> - Lack of enhanced and reliable specifically-designed membranes - Energy requirement for the draw regeneration step - Unavailability of effective draw solutions which limit the use of FO for reject brine treatment
	+ There is no need for external hydraulic pressure sources which are energetically intensive	
	+ High-quality product water	
	+ In most cases, FO membrane fouling can be reversed by water flushing, indicating that chemical cleaning may not be necessary.	
	+ High TDS water exceeding 70,000 mg/L can be treated, making the FO process suitable for ROC treatment	
ElectroDialysis (ED) and ElectroDialysis Reversal (EDR)	+ High salt removal rate	<ul style="list-style-type: none"> - Relatively high capital cost
	+ Less susceptible to scaling, especially resistant to silica scaling	
	+ Able to achieve high brine concentration (TDS of 150 to 200 g/L)	

The biological treatment of saline wastewaters (e.g., activated sludge) is limited by the adverse effects of salts and toxic compounds on the microorganisms and the presence of chemical residues in the sewage sludge and the treated water [86]. The applicability and effectiveness of common chemical oxidants such as peroxide, ozone, and permanganate are restricted by the high requirements for handling large quantities of hazardous chemicals and the formation of toxic byproducts [87], while adsorption on carbon materials or other media (e.g., zeolites, biochar) have several constraints including the high treatment cost and the handling of saturated/exhausted filter materials [88,89].

3.2.2. Decontamination of Brines by Electrocoagulation

In recent years, the research community has turned its attention to the utilization of Electrochemical Coagulation or Electrocoagulation (EC) for the treatment of waters with elevated temperature and salinity levels, which contain a high percentage of salt and other contaminants, including heavy metals, valuable metals, nutrients (e.g., nitrogen and phosphorus), organic micropollutants (e.g., pesticides, personal care products, pharmaceutical products, and endocrine disruptors), effluent organic matter (e.g., soluble microbial products, partially degraded organics) and pathogens [71,85]. EC seems to be a promising technology for the treatment of the above type of wastewaters (brines) due to its operational and performance advantages: (1) an excellent electric conductivity that could lead to reduced energy consumption, (2) high effectiveness, (3) lower maintenance cost, (4) less need for labor, and (5) rapid kinetics [71,85,90].

Table 9 summarizes the results of recent research on the treatment of RO concentrates by EC and hybrids, according to which alkaline metals, nutrients, and other contaminants of concern are removed effectively with a rather low energy consumption. According to the literature, Al and Fe are the most frequent electrode materials due to their immediate availability, high efficiency, and low purchase price. In addition, the selection of the appropriate electrode material plays a crucial role, as this is directly related to the kinetics and thermodynamics of electron transfer, often determining the success or failure of the process inside the cell. Nevertheless, studies have shown that Fe(2+) is a cation with a weaker coagulation capacity compared to Fe(3+) due to its lower positive charge [91]. Furthermore, it is generally proven that Al-electrodes demonstrate better performance in removing pollutants than Fe-electrodes when the effectiveness of the treatment is presented as the only criterion [91]. However, Al-electrodes are more expensive [92].

Table 9. Summary of recent literature on brine treatment by EC.

Process	Operating Scale	Feed Type	Potential Application	Performance	Reference
EC	Bench-scale	Simulated RO concentrate	Dissolved Si removal from high-efficiency reverse osmosis concentrate solutions	76–89% Si removal	[93]
EC	Bench-scale	Simulated high-efficiency reverse osmosis brine	Reduction of high concentrations of dissolved silicate	Up to 98.9% Si removal Significant reduction in concentrations of Ba, Sr, Ca, and Mg	[94]
EC	Bench-scale	Synthetic RO concentrate & Real RO concentrate	Treatment and recycling of the Saharan groundwater desalination RO concentrate for sustainable management of Albion resource	93% removal of NO_3^- NO_2^- ions and NH_3 were not detected	[95]
EC	Bench-scale	Simulated RO concentrate	Reduction of waste brine salinity	Preferential reduction of Ca and Mg 10% reduction of TDS	[96]

Table 9. Cont.

Process	Operating Scale	Feed Type	Potential Application	Performance	Reference
EC	Bench-scale	Real RO concentrate	Recovery of ammonia from ammoniated high-salinity brine	99% reduction of the NH_3 concentration (13,700 to 190 mg/L N)	[97]
EC—DCMD	Bench-scale	Real HFPW concentrate	Treatment of high-salinity hydraulic fracturing produced water	Water recoveries up to 57% 96%, 91%, and 61% removal of turbidity, TSS, and TOC, respectively	[98]
EC—AOPs (UVA/ TiO_2 or UVC/ H_2O_2)	Bench-scale	Real RO concentrate	Integrated treatment of RO brines to enhance desalination of secondary/tertiary effluents	Successful removal of phosphate (>99%), carbonate (88–98%), and DOM (40–50%) Increased oxidation of micro-pollutants by 3–4 fold	[99]

3.2.3. Organic Destruction in Brines by Electrochemical Oxidation

Electro-Fenton (EF) and Anodic oxidation (AO) are two of the main representatives of the category so-called Electrochemical Advanced Oxidation Processes (EAOPs), which have been recognized as very promising and effective technologies for the degradation and mineralization of recalcitrant organic contaminants present in saline waters. The above two processes offer noteworthy advantages for large-scale applications, such as energy efficiency, flexibility, versatility, readily amenable to automation, the absence of chemical additives, and safety because EF and AO operate under mild conditions [100–102]. The main operating principle of EO is schematically shown in Figure 6 below.

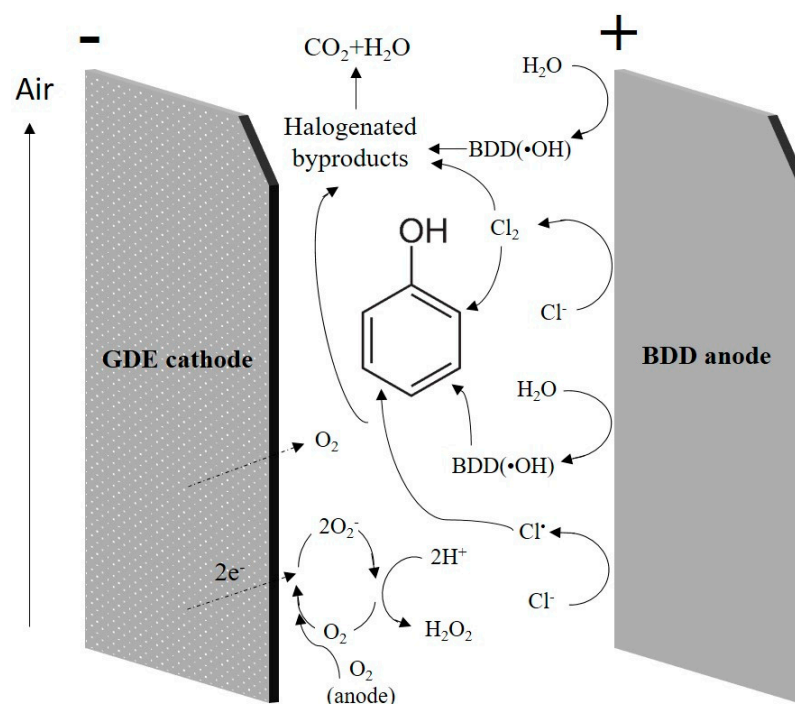


Figure 6. Schematic representation of the EO operation principle (example of phenol oxidation as model organic compound) (Reprinted with permission from Ref. [103], 2022, Elsevier).

Up to the present, many groups of researchers have given an in-depth overview of the fundamentals of electrochemical oxidation (EO), providing up-to-date information on the application of this technology to the treatment of wastewaters [104–106]. In a recent critical review, Brillas and Garcia-Segura [107] implement a benchmark framework of innovative electrochemical oxidation (EO) processes and their recent advances, based on the oxidation of phenol as a model molecule, emphasizing the engineering challenges and difficulties that have to be successfully addressed for commercialization of relevant, innovative technologies. Among such engineering challenges, sufficient long-term performance in a realistic operational environment crucially defines the TRL of these technologies to get closer to commercialization [107]. For instance, the EO process, implemented to brine wastewater streams characterized by a high chloride content, led to improved efficiency for the degradation of organic contaminants due to the production of reactive chlorine species during the electrolysis, designated as the electrochlorination process (ECL) [103,108,109].

3.2.4. Treatment of SCWG Liquid Effluents by EC/EO

As previously mentioned, the SCWG process typically leads to two liquid streams, the reactor effluent and a brine (Figure 1). The composition of the two streams can vary significantly, depending on the feedstock, the process conditions, and the configuration of the salt separation. In case of incomplete gasification, a high amount of organic carbon is expected in reactor effluent (liquid phase: TOC > 1 g/L; unconverted tars), whereas a higher concentration of dissolved inorganic salts (up to 100 mg/L, depending on feedstock) is expected in brine. Concerning the heavy metals (HMs) (Zn, Cu, Cd, Pb, Cr, Ni, Fe, Hg, As, etc.), their distribution may vary significantly among the different parts of the plant. According to the preceding discussion (Section 2.1), during SCWG with increasing temperature, HMs are immobilized in solid deposits, like salts and char. However, their presence in brine and reactor effluent is also likely, since HMs can be dissolved in water in the form of ionic species or as complexes with organic matter. An additional issue to be considered is the possible presence of tar in the reactor effluent. As the reaction mixture is depressurized and cooled down (atmospheric pressure, 25 °C), a large fraction will probably condense and accumulate in the reactor effluent.

Depending on their composition, the two streams can be treated separately or together using a hybrid EC/EO process (Figure 7). Both processes take advantage of the high conductivity and the presence of inorganic ions (sulfates, chlorides) in the two streams, which results in reduced energy consumption (due to the decreased ohmic resistance and thus, the low voltage that needs to be applied), and the in-situ production of chemical reagents (coagulants, strong oxidants) which favor the separation/elimination of the target contaminants (heavy metals, organic residuals of the SCWG process). An analysis of the relevant critical parameters, conditions, materials, components and the choice of suitable methods as part of the CERESiS case study is made below.

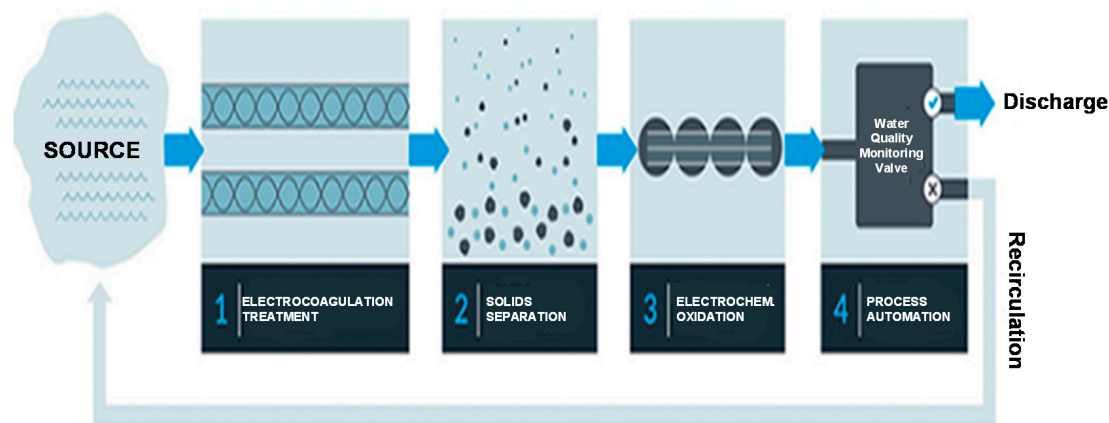
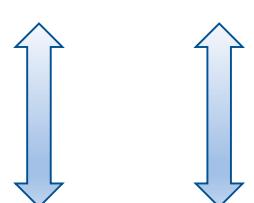


Figure 7. Simplified schematic representation of the EC/EO combined process for SCWG brine treatment.

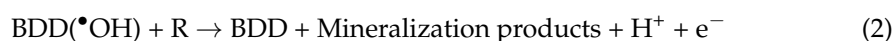
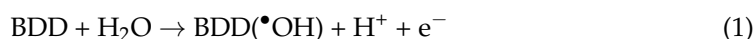
Electrode Materials

Electrode materials play a crucial role in the efficiency, selectivity, and energy of any electrolysis process. Choosing the correct material for the electrode is essential as it affects the chemical reactions that will be performed both on the electrode/solution interface and the bulk. EC can be carried out with several combinations of electrode materials (Fe-Fe, Fe-Al, Al-Fe, Al-Al, SS-SS, Al-SS, and SS-Al), the proper selection of which depends on the performance of the process over the reduction of COD, turbidity and heavy metals. Concerning EO, a number of anode materials can be used, including the “active” and the “non-active” anodes. The first category of anodes includes RuO₂, IrO₂, and Pt, which benefit from the selective partial oxidation of contaminants, while PbO₂, SnO₂, and Boron-doped diamond (BDD) are typical “non-active” anodes which benefit from complete combustion (Table 10).

Table 10. Categorization of anodic electrode materials based on oxidation power and potential for OER in acidic media [110].

Anode Type	Composition	Electro-Catalytic Ability for OER	Oxidation Potential (V)	Over-Potential (V)	Adsorption Enthalpy of M•OH	Oxidation Power
Active	RuO ₂ -TiO ₂ (DSA [®] -Cl ₂)	Good	1.4–1.7	0.18		
	IrO ₂ -Ta ₂ O ₅ (DSA [®] -O ₂)	Good	1.5–1.8	0.25		
	(Ti/Pt)	Good	1.7–1.9	0.30		
	Carbon and graphite	Good	1.7			
Non-active	Ti/PbO ₂	Poor	1.8–2.0	0.50		
	Ti/SnO ₂ -Sb ₂ O ₅	Poor	1.9–2.2	0.70		
	BDD	Poor	2.2–2.6	1.3		

BDD has been recognized as an ideal electrode material for the electrochemical oxidation of a wide spectrum of organic pollutants and systems of real wastewaters. A complete mineralization of a multitude of contaminants (i.e., phenolic compounds, carboxylic acids, pharmaceuticals, surfactants, dyes) could be achieved on BDD anodes by the chemical reaction with electro-produced BDD(•OH) radicals (Equations (1) and (2)), keeping current efficiency at a higher level compared to other materials of anodes, including PbO₂, SnO₂, and IrO₂ [111]. The scientific community hypothesized that the strong oxidation ability of BDD anodes could be correlated with both the high electroproduction ability and weak adsorption towards •OH radicals, where more electrogenerated •OH could separate from the surface of the anode and enter the bulk solution to take place in reactions with pollutants.



Operating Conditions

The operating conditions of both EC and EO are directly related to the aqueous medium chemistry, especially with the pH of the solution and the electrical conductivity. pH plays one of the most significant and critical roles in the EC process as it impacts the solution conductivity, zeta potential, and electrode dissolution [112]. An optimal pH value is desirable for any type of wastewater to achieve a better removal efficiency of contaminants, as pH helps the precipitation of the contaminants [92]. However, values below or above the optimal pH value reduce pollutant removal efficiencies [113].

In the case of EO, it is widely accepted that the value of pH can influence the concentrations of electrogenerated •OH radicals and overpotential associated with the Oxygen

Evolution Reaction (OER), which defines the electrochemical oxidation performance. The results concerning the effect of solution pH are also diverse and even contradictory due to the differences in the structure of organic compounds and electrodes' material. Thus, a review of previous publications does not permit us to conclude whether higher or lower pH values benefit the removal of pollutants during electrochemical oxidation of wastewaters. Some studies have reported that the electrochemical oxidation process is more advantageous in acidic media [114]. On the other hand, other studies have reported that the efficiency of the process was elevated in alkaline media [115]. For instance, previous studies have shown that the electrochemical oxidation of wastewaters was more advantageous in the acidic media due to the inhibition of the Oxygen Evolution Reaction, improving the degradation efficiency of organic pollutants.

The electrogeneration rate of Fe(2+) and Al(2+) cations (the electro-coagulants) from Fe or Al electrodes, respectively, is controlled by the *time of electrolysis* [116]. It is generally proven that the increased time of electrolysis leads to an increased reduction of pollutants. This is correlated to either the sweep flocculation mechanism or the combination of the bridging-entrapment mechanism [117]. The concentration of the Fe and Al cations and their hydroxide flocculants accelerate the amount of bubble generation as the electrolysis time increases [118]. Theoretically, the amount of electro-coagulant is directly proportional to the period of electrolysis and current applied, as presented in Faraday's law. When all the electro-coagulated particles have settled and no considerable precipitation is observed, equilibrium has been reached.

Among the operating parameters commonly affecting the EO processes, the current density is equivalent to the ratio between the applied current in the cell and the surface of the working electrode. Previous studies [119] have proven that higher values of current density led to the production of larger quantities of •OH radicals, resulting in higher degradation efficiencies for the tested pollutant. It should be emphasized that an increase in the value of current density does not necessarily indicate an increase in the oxidation performance or oxidation rate for a specific anode material: the influence of current density on the treatment efficiency also relates to the characteristics of the wastewater to be treated. However, the use of higher values of current density usually leads to higher operating costs due to the increased energy consumption and the possibility of oxygen evolution side reaction.

An increase in temperature improves the solubility of electrodes and the diffusivity of the pollutants [118]. It should be pointed out that at a higher value of temperature, the consumption of electrical energy is notably reduced in the EC process [120]. Moreover, high-temperature values benefit the production of large bubbles of hydrogen, improve the speed of flotation and diminish the adhesion of suspended particles [92]. However, higher temperatures above the optimum value commonly cause electrodes passivation and lead to instability of coagulation (increase in the development of protective metal oxide layers), which can decrease anodic dissolution and consequently the removal of the target pollutants. Similar conclusions were drawn by Jing et al. [121].

The concentration of anions in the solution impacts the stability of the passive layer of an electrode [92]. Sulfate anions are passivation agents; thus, they can diminish the production of metal cations. Chloride anions lead to the breakdown of the passive layer and pitting corrosion [122]. Some salts can precipitate on the cathode surface if the concentration of the salt in the water is very high [123]. The conductivity of the solution is a significant factor that influences the efficiency and power consumption of both EC and EO processes. The higher the conductivity, the lower the power consumption due to the decreased Ohmic drop and the higher the pollutant removal [124]. It is proposed that a 20% chloride anions concentration guarantees the effective operation of an EC system [116]. According to Dalvand et al. [125], the increased concentration of NaCl contributes to the increase of the color (Reactive Red198 dye) removal efficiency when utilizing electrodes of aluminum. Moreover, it was proven that the presence of chlorine anions successfully leads to water disinfection [122].

In the case of EO, the type of the electrolyte plays a crucial role in this process due to the possible generation of side products, which can increase or reduce the system's performance. Cañizares and co-workers [126] reported that the electrochemical oxidation treatment of ethylene glycol in Na_2SO_4 or Na_3PO_4 media was more successful than in NaCl . On the other hand, some researchers proved that chloride anions could also be oxidized to produce active chlorine species (Cl_2 , HClO , and ClO^-), which could further contribute to the degradation of contaminants. High values of the electrolyte conductivity can promote the faster electron transport and lead to a better degradation rate for organic contaminants, diminishing the cell voltage for a specific value of current density and leading to lower energy consumption.

EC Solid By-Product (Sludge) Treatment and Reuse Options

The literature survey on EC treatment of water and wastewaters showed that there are only a few works dealing with sludge treatment and reuse, and to our knowledge, there is no relevant publication on the treatment of SCWG liquid streams by EC. Interesting results were extracted from the works by Xu et al. and Kushwaha et al. [127,128]. In the last study, synthetic dairy wastewater was treated by EC and the produced sludge was dried and characterized by thermal gravimetric and differential thermal analyses; TGA and DTA. The analyses showed that the solid EC byproduct could be utilized to produce fuel briquettes or as fuel in boilers/incinerators. Similar results were obtained by Kumar et al. [129]; generated sludge (heating value 5.3 MJ/kg) from the EC treatment of bio-digester effluent derived from an alcohol distillery could be used to produce blended fuel-briquettes along with other organic fuels. Furthermore, Linares-Hernández et al. [130] reported that the combined use of Fe and Al anodes could lead to significantly better results compared to (less sludge produced and higher removal efficiencies) the utilization of one of the two metals alone.

In the context of the CERESis project, the EC treatment of the SCWG liquid stream(s) will result in the formation of a solid by-product, namely EC sludge, at a mass rate that is expected to be lower than 2–3% ($<2\text{--}3\text{ kg/m}^3$). Considering that sludge can be regarded as a valuable resource because of its high iron or aluminum content (expected to be as high as 50%), a preliminary sludge feasibility analysis will be performed to further reuse the generated EC sludge into useful applications. For this scope, the amount and the composition of that solid waste will be analyzed. Specifically, EC sludge will be collected, dried, and analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Moreover, the heating value, the moisture content, ash, and fixed carbon of the ECF generated sludge will be measured to assess the further application of this solid by-product; i.e., for blending material in coal or for catalysis (in case of high metal content) or in granulated bio ash-based fertilizer products in case, the EC sludge contains notable amounts of phosphorus and nitrogen.

3.3. FP Liquid Effluent Treatment

3.3.1. State-of-the-Art of Bio-Oil Decontamination

One of the key problems associated with the direct use of the FP bio-oil in combustion engines is the high solid content. Several technologies, such as hot gas filtration and cyclone separation, have been applied to remove char particles from bio-oil; however, these are efficient for solid particles greater than $10\text{ }\mu\text{m}$ [26]. Other conventional technologies, including gravity-driven filtration [131], air floatation [132], coalescence, de-emulsification, coagulation [133], centrifugation, flocculation, metal mesh, hydro-cyclone have also been applied for solid-liquid separations in oily fluids [134]. However, there is currently no well-established technology to remove fine solid particles from such fluids.

It is understood that the removal of solid particles in the micron size range is extremely desirable to enhance the applicability of bio-oils as engine fuel. Specifically, solid particles in bio-oil may lead to corrosion problems and negatively affect the ignition process in engines by causing deposition and blocking of the valves. Moreover, they can cause plugging in the

catalytic hydrodeoxygenation reactors if the bio-oil is transformed into gasoline or diesel fuel by hydrodeoxygenation.

In terms of solid-liquid and liquid-liquid dispersions separation, membrane-based approaches have been proposed and subsequently attracted much interest due to an important number of advantages, including simplicity of cleaning, high efficiency of separation, permeates of high purity, modular scalability, reduced energy consumption, and no need for chemical additives or regeneration cycles for spent materials [135,136]. Several categories of pressure-driven membrane technologies, including Micro-Filtration (MF), Ultra-Filtration (UF), Nano-Filtration (NF), and Reverse Osmosis (RO), have been efficiently applied for the treatment of oily wastewaters. The main difference between the above processes is basically the size of the membrane pores; with each different filtration process, a variety of elements get either blocked or pass through with the water (Figure 8). The mechanical sieving is responsible for separation in MF and UF processes, while transport in NF and RO membranes is governed by a solution-diffusion mechanism. MF and UF are effective low-pressure driven processes that have been proven effective for separating oil derived from oily wastewater in many studies over the last decade [137]. However, their application for the purification of oil-based matrices is rather limited and restricted to only a few studies in the field [138,139].

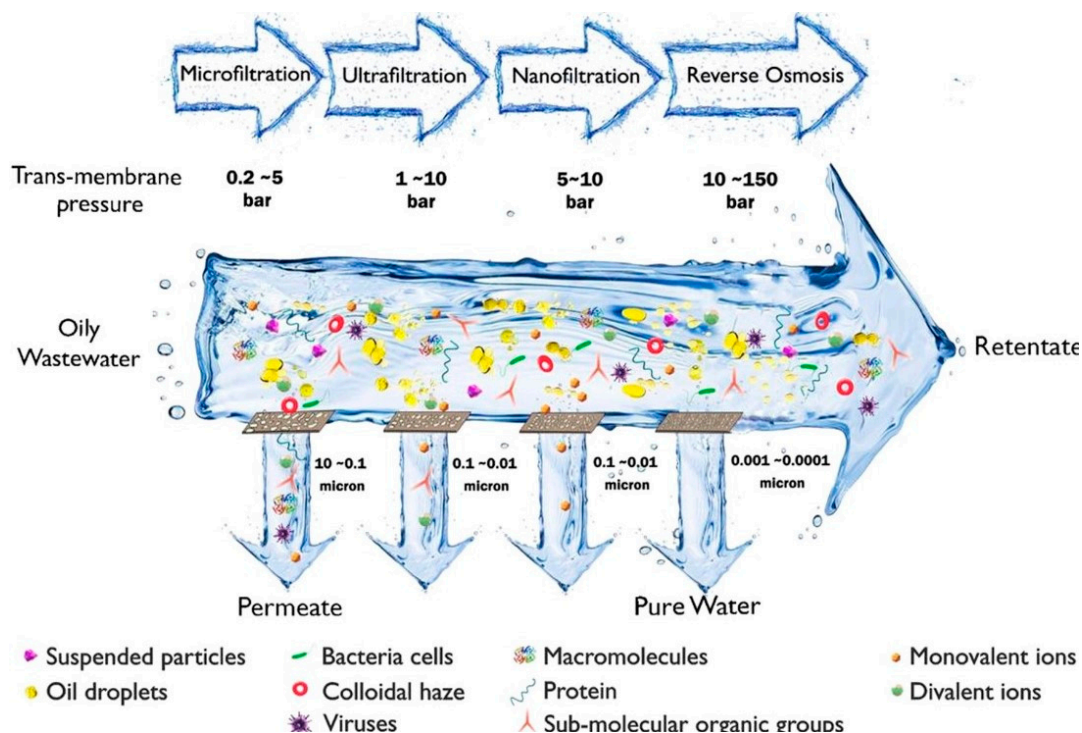


Figure 8. Schematic representation view of pressure-driven membrane technologies (cross-flow mode) for the treatment of oily wastewater (Reprinted with permission from Ref. [137], 2022, Elsevier).

In the latter decades, commercial polymeric and ceramic MF membranes have been widely used in industrial separation applications. For water in oil separation, a hydrophobic membrane should be used to selectively block the water phase. Recent advances in porous membranes with superhydrophobic and superoleophilic surfaces have also received notable attention, especially in selective and efficient water in oil separations [140]. Among the superhydrophobic and superoleophilic porous materials tested, such as ceramics, polymers, metals, minerals, cotton/textile, glasses, filter paper, carbon-based materials, and composites, the fabricated and altered ceramic or polymer based-membranes have been mainly investigated in the specific studies. These materials are characterized by high density, frangibility, and also incompressibility compared to the other materials. However,

they can be applied in harsh environments due to their impressive resistance to corrosion and thermal stability [141].

Ceramic membranes present significant advantages compared to polymeric ones, including high levels of chemical resistance, outstanding mechanical strength, and excellent thermal stability [142]. Actually, alumina membranes are resistant to harsh chemical cleaning processes and can operate in different ranges of temperature and pH values. Yao et al. [143] produced a nanostructured alumina membrane via the anodic oxidation of aluminum in an oxalic-acid electrolyte. In this morphology-dependent method, a superhydrophobic and superoleophilic film of alumina is formed without the addition of low-energy chemicals. Tang et al. [144] produced a superoleophilic membrane of alumina covered with PTFE via a sintering process (thermal decomposition). After four hours of treatment, the modified membrane resulted in higher than 97% water rejection.

Although the (super)hydrophobic membranes have been successful in oil-water separation applications, including oil spills and oily wastewater treatment, their application to separate solids in organic solvent solutions or organic-rich aqueous solutions is still to be investigated (i.e., membrane fouling, membrane stability under harsh operating conditions, alteration of the hydrophobicity at high-temperature conditions). The influence of operating parameters, such as pH, temperature, trans-membrane pressure, cross-flow velocity, and the molecular size of solute should be taken into consideration, specifically in the presence of solid particles that can lead to rapid and irreversible fouling.

3.3.2. Treatment of FP Bio-Oil by Ceramic MF/UF

In the context of the CERESiS project, the filtering of the FP bio-oil (Figure 2) has been based on a liquid-phase MF/UF process to remove solid particles down to slightly sub-micron levels. For this scope, tubular ceramic membranes of different pore sizes and membrane materials (α - Al_2O_3 ; ZrO_2 ; TiO_2) can be used, in their commercial state or a modified one, by altering the hydrophobicity towards effective water and solid (biochar) particles separation.

Membrane hydrophobicity is a crucial parameter that typically affects the overall process performance of a membrane filtration process. Depending on the targeted application, using either hydrophobic or hydrophilic membranes can be advantageous. For this reason, several methods have been proposed in the literature to turn either hydrophobic polymeric membranes into hydrophilic [145] or hydrophilic ceramic membranes into hydrophobic [146]. In this case, considering the importance of the membrane hydrophobicity on the effective blockage of the water phase from the bio-oil, efforts should be focused on increasing the ceramic membranes' hydrophobicity. The review of the different methods applied in literature for the production of superhydrophobic ceramic based-membranes showed that the immersion process is the most broadly utilized due to its simplicity, while the Chemical Vapor Deposition (CVD) process is a promising potential alternative that has not been widely assessed in the literature [147]. In both processes, grafting occurs via condensation reactions between the hydroxyl groups found in the membrane and the Si–O–alkyl groups of the silane. Considering the attributes of these techniques, CERTH recently developed a silane grafting protocol through either immersion or CVD techniques for the hydrophobic modification of tubular ceramic membranes. In these techniques, hexyltrimethoxysilane was employed as a potential economic alternative, with similar properties, to 1H,1H,2H,2H-perfluorodecyltriethoxysilane, which is considered the “gold standard” in the literature. Initial experimental results revealed that although both methods are, in principle, effective for creating hydrophobic membranes, the CVD method is more effective and suitable for a uniform hydrophobic coating on complex membrane geometries [148].

As already mentioned, the water content of the bio-oil is a critical parameter. Notably, it affects the passage of the bio-oil through the small pores of the hydrophobic porous membrane. Specifically, the water content determines the size of the oil-water droplets, the shear rate, the surface tension, and the oil in water viscosity ratio. In addition, water

can affect the agglomeration and coalescence of oil droplets, which have been pointed out as the main phenomena responsible for phase separation, especially with hydrophobic membranes. The optimum water content and viscosity for effective filtration of bio-oil depend on the membrane characteristics (hydrophobicity, pore size), the stability of the oil/water emulsion, the oil-to-water droplet size to pore diameter ratio, and the operational parameters (transmembrane pressure, temperature, pH) as these can have an impact on membrane fouling and to the permeation of bio-oil through the membrane. In addition, microscopic (membrane autopsy), ICP (HM determination), and ash content analysis of the feed and permeate streams will be conducted to determine the efficacy of the process concerning the removal of the undesirable HM-laden char particles (less than 10 μm in size) from the bio-oil.

The main challenges in this investigation will be (a) to understand, quantify and reduce membrane fouling, and (b) to deal with highly viscous liquid streams. Special attention will be given to fouling analysis from longer runs of bio-oil through the membranes to determine the predominant fouling mechanisms. This will help propose measures for fouling mitigation and overall process optimization. In conclusion, the FP-derived oil purification in CERESiS with the aid of the chosen membrane-based process will be a quite challenging task and it is possible that, in the course of the relevant experimental studies, certain mitigation measures and re-alignment of approaches to tackle the challenges will be needed. On the other hand, this leaves room for developing a new, highly innovative technological pathway with applicability in several sectors dealing with waste/byproduct oil-based streams.

4. Conclusions and Future Recommendations

In this work, membrane and electrochemical-based technologies were examined as potential options for the decontamination of exploitable gas and liquid streams produced by SCWG and FP of contaminated biomass. Applying these technologies is necessary for the efficient operation of downstream processes and the eventual production of contaminants-free fuels and chemicals.

The MGA process was assessed as a potential novel and highly promising method for desulphurizing the SCWG gas effluent stream. A detailed analysis of relevant literature studies indicated that hydrophobic polypropylene membrane contactors operated using MDEA as solvent could be a technically and economically viable option, especially for small to medium scale applications, with many advantages compared to conventional technologies. However, it must be noted that the vast majority of the published experimental works refer to lab-scale tests. Therefore, long-term tests at larger scales are necessary for the final assessment of the technology before moving to commercial applications.

Electrocoagulation and electrochemical oxidation methods were proposed and further assessed for the treatment of SCWG brine to remove heavy metals and organic residuals of the SCWG process. A detailed literature survey on this field indicated that EC using a combination of aluminum and iron(III) electrode materials could effectively remove heavy metals, nutrients, and other contaminants of concern at a rather low energy consumption as a result of the high conductivity of the SCWG brine effluent and the rapid kinetics. Depending on the SCWG brine composition, EC could be coupled with an EO process to totally eliminate the residual organics, using, in the latter case, non-active anodes (SnO_2 , PbO_2 , or BDD) to promote the total mineralization of the effluent in the absence of chemicals. The chemistry of the SCWG brine (pH, anions) can largely affect the process efficiency as it regulates the precipitation of the pollutants and the electro-generation of the strong oxidants ($\bullet\text{OH}$) in the EC and EO processes, respectively. To achieve optimum performance at an affordable cost, optimization of the main operation variables is necessary, including current density, brine flow rate, treatment time, and pH. For both EC and EO processes, the design of the electrochemical cells/reactors and the electrode geometries largely affect the process performance and the respective research remains a hot topic in the field.

Finally, low-pressure membrane processes, such as MF and UF, were assessed for FP bio-oil treatment to remove fine particles contained in the bio-oil. Considering that the water included in the bio-oil is a critical parameter as it affects the bio-oil filtration, a relevant literature survey indicated that ceramic membranes grafted with organosilanes for hydrophobicity enhancement could be a potential solution for this very challenging task. Considering the rather low TRL of the MF/UF process for dealing with highly viscous liquid streams, systematic investigations of the influences of operating parameters, including pH, temperature, trans-membrane pressure, cross-flow velocity, water content, and molecular size of solid particles on bio-oil permeation and the removal of the undesirable fine char particles from the bio-oil, are necessary. The stability of the produced hydrophobic ceramic membranes and the mitigation of the membrane fouling are decisive factors for the practical application of MF/UF for FP bio-oil decontamination.

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