CERESiS: ContaminatEd land Remediation through Energy crops for Soil improvement to liquid fuel Strategies

D1.2: Decontamination and separation requirements

H2020-LC-SC3-2018-2019-2020

Contract No: 101006717

APRIL 2021

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101006717

Document control sheet

Project	ContaminatEd land Remediation through Energy crops for Soil improvement to liquid fuel Strategies
Call identifier	H2020-LC-SC3-2018-2019-2020
Grant Agreement N°	101006717
Coordinator	National Technical University of Athens
Work package	WP1 – Definition of requirements for determining integrated solution pathways
Work package leader	NTUA
Related tasks	Task 1.2: Decontamination and separation requirements & methods
Deliverable title	D 1.2: Decontamination and separation requirements
Deliverable nature	Report
Dissemination level	PU
Lead Beneficiary	CERTH
Contributing partners	CNR, KIT
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Version	Final
Total number of pages	67
Issue date	9/4/2021; revised 28/4/2021

Contents

NOMENCLATURE

AAEMs:	Alkali/Alkaline Earth Metal species
AGMD:	Air Gap Membrane Distillation
AO:	Anodic Oxidation
BDD:	Boron-Doped Diamond
BECC:	Brine evaporative cooler/concentrator
COD:	Chemical Oxygen Demand
DCMD:	Direct Contact Membrane Distillation
DEA:	Diethanolamine
DGA:	Diglycolamine amine
deH_2S:	removal/selective separation of H_2S from a gaseous stream
DIPA:	Diisopropanolamine
DSA:	Dimensionally stable anodes
EAOPs	Electrochemical Advanced Oxidation Processes
EC-EO:	Electrocoagulation – Electrochemical Oxidation
ECF:	Electrocoagulation-flotation
ED:	Electrodialysis
EDR:	Electrodialysis Reversal
EDM:	ElectroDialysis Metathesis
EF:	Electro-Fenton
EFC:	Eutectic Freeze Crystalization
FO:	Forward Osmosis
FP:	Fast Pyrolysis process
HMs:	Heavy Metals
HMI:	Human Machine Interface
ICP:	Inductively Coupled Plasma
MD:	Membrane Distillation
MDEA:	Methyl Diethanolamine
MEA:	Monoethanolamine
MED:	Multi-Effect Distillation
MF:	Microfiltration
MGA:	Membrane Gas Adsorption method
MVC:	Mechanical Vapor Compression
NF:	Nanofiltration
OER:	Oxygen Evolution Reaction
PLC:	Programmable Logic Controller
PP:	Polypropylene
PTFE:	Polytetrafluoroethylene
PVDF:	Polyvinylidene Fluoride
RO:	Reverse Osmosis
RSM:	Response Surface Methodology

SCADA:	Supervisory Control And Data Acquisition
SCWG:	Super-Critical Water Gasification process
SEC:	Specific Energy Consumption
SGMD:	Sweeping Gas Membrane Distillation
SHE:	Standard Hydrogen Electrode
TEA:	Triethanolamine
TUR:	Turbidity
UF:	Ultrafiltration
VMD:	Vacuum Membrane Distillation
WAIV:	Wind-Aided Intensified eVaporation

LIST OF FIGURES

LIST OF TABLES

1 EXECUTIVE SUMMARY

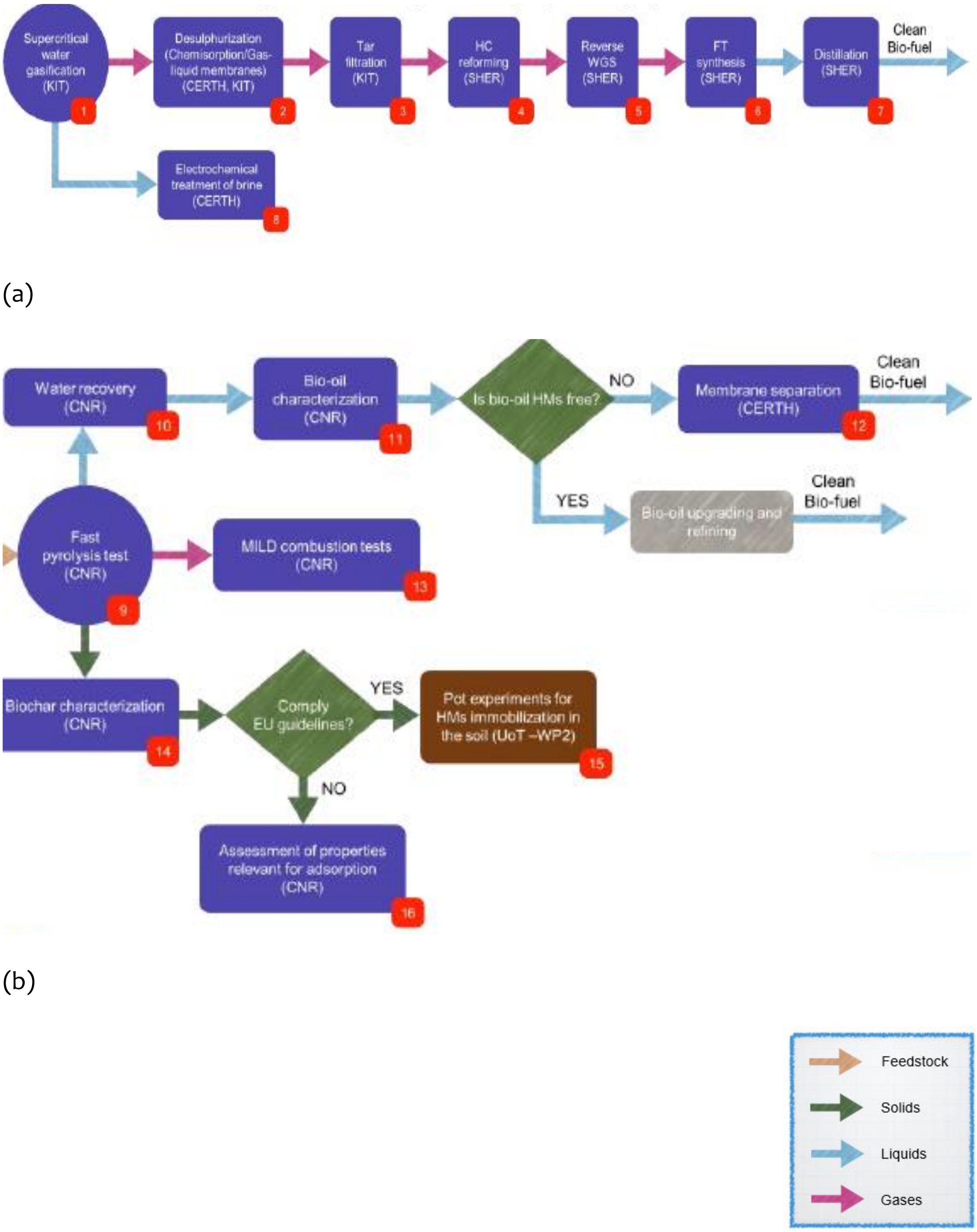
The purpose and scope of this deliverable is to define the requirements, constraints, limitations and boundary conditions of the decontamination and separation/cleaning methods and processes that are necessary to be incorporated into the integrated approaches defined by the two technological pillars of the project; namely the Super-Critical Water Gasification (SCWG) and Fast Pyrolysis (FP) based concepts (see Fig. 1-1 below). The information produced here forms a solid basis for the design, to a certain degree, of experimental studies to be performed in the framework of WP3 and provides input to WP3/Task 3.1.

Naturally, the methods chosen and defined here aim at the removal of harmful impurities and contaminants contained in the gaseous and liquid streams produced by the two aforementioned processes and their downstream steps. The streams that need to be treated are:

- The gas product of the SCWG biomass processing route: this stream contains H_2S that needs to be removed because it poisons the catalysts of the downstream processes (reforming, reverse water gas shift and Fischer-Tropsch), ultimately resulting to the production of bio-fuel.
- The liquid (brine) stream produced by the SCWG route: this aqueous stream contains all (primarily heavy) metals incorporated into the contaminated biomass. These metals are present in the form of salts.
- The bio-oil stream recovered from the liquid (water + oil) effluent of the FP biomass processing route: this stream needs to be purified from entrained fine (char) particles and the water contained in it.

The following sections include a concise description of SCWG and FP processes with emphasis on the streams to be purified/decontaminated, detailed literature reviews of the chosen purification/decontamination methods to be applied to those streams, a reference to main advantages and disadvantages of the chosen methods and concluding remarks directly related to the general implementation plan of the methods which function as starting basis for WP3 workplan. The purification/decontamination methods chosen are:

- The **Membrane Gas Adsorption (MGA)** method for the removal of H_2S from the gaseous SCWG stream.
- The **electrochemical treatment (electrocoagulation (EC) – electrochemical oxidation (EO))** of the liquid brine stream derived by the SCWG process.
- The **microfiltration (MF)/membrane separation** process referring to solid particles, containing heavy metals (HM) and alkali/alkaline earth metal species (AAEMs), removal from the bio-oil stream derived from the liquid product of FP process. Naturally, such particles can be detrimental for further refining operations.



(a)

(b)

Fig. 1-1: The two technology pathways of CERESiS for contaminated biomass treatment and exploitation: (a) The Supercritical Water gasification pathway; (b) The Fast Pyrolysis based pathway.

2 OVERVIEW OF BASIC PROCESSES AND THEIR STREAMS TO BE PURIFIED/ DECONTAMINATED

This section includes a brief description of the SCWG and FP processes and their main operational parameters. Emphasis is given on the properties and characteristics of streams/products to be decontaminated/purified. More details will be provided as a result of WP3/Task 3.1 activities and will be included in the associated deliverable D3.1 (due in M9).

2.1 The SCWG process and its products

Biomass, in appropriate preconditioned form (e.g., biomass-water slurry) and mixed with salts (e.g., $KHCO_3$) which enhance the gasification reaction, is fed into the reactor as an aqueous slurry (typically 10wt% in solids but other contents are possible). A simplified sketch showing the operation of the SCWG reactor, its associated peripherals and the flow of produced streams is depicted in Fig. 2-1. Reaction conditions are above the critical point of water, typically at 650 °C / 280 bar. Reaction products include a gaseous and 2 liquid streams (marked as R and S in Fig. 2-1). Considering the somewhat high-level consideration of WP1/Task 1.2, the stream R is considered directly re-usable/recyclable as process water. The stream to be purified is liquid effluent S that contains substantial amounts of salts and organics/HMs that need to be efficiently removed before the water of this stream can also be recycled to the SCWG reactor. Whether both streams will actually need to be treated or even combined and treated together prior to recycling is not in the scope of this deliverable and relevant decisions will be made in the course of WP3 experimental evaluations. Further analysis on these streams and their differences/first indication on the need of separate or combined treatment or no treatment at all for stream R as currently considered will be included in deliverable D3.1.

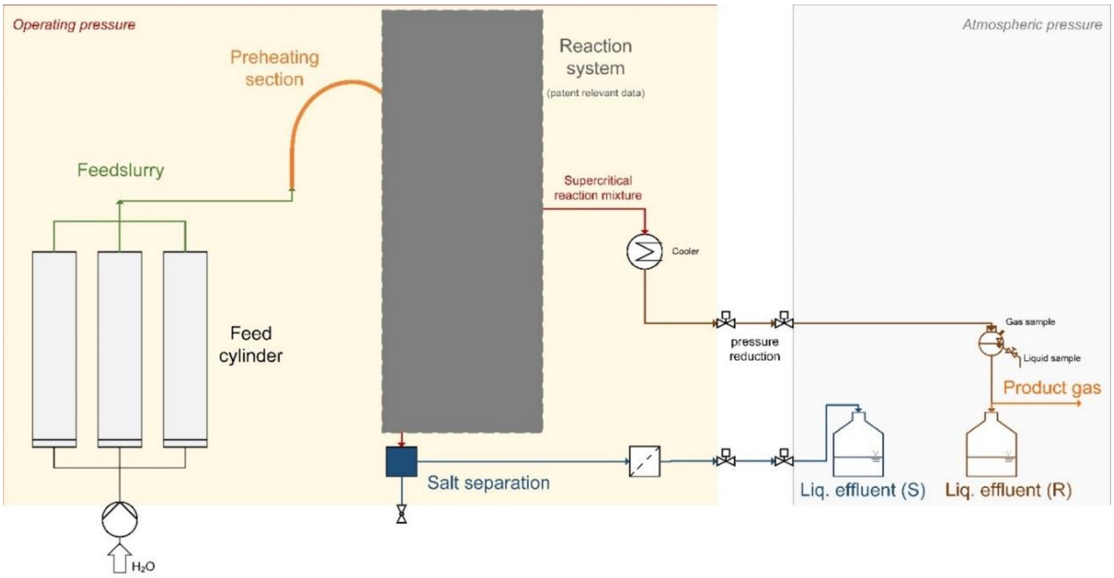


Fig. 2-1: Simplified flow diagram of KIT's SCWG reactor and peripheral components.

2.1.1 The SCWG gas stream

The production rate of the gaseous product depends on the biomass feed rate, the dry matter content and the presence of catalyst (i.e., salt) in the slurry. The product gas has to be cooled down sufficiently, typically at 25°C, for H_2O separation in liquid form. Naturally, the gaseous phase is saturated with H_2O at the P, T conditions of the phase separation. If the temperature during pressure release drops down, then H_2O will again condense. In other process layouts (not applicable to CERESiS) at higher temperature and without cooling, substantial presence of steam in the product gas is possible. Table 2-1 below provides an overview of the main properties of the SCWG gas product.

Despite initial concerns, almost no tar presence is expected in the specific stream for the CERESIS-relevant operational conditions. Tar is a known by-product of SCWG, but its formation can/will be minimized as much as possible by an appropriate process design or by filtration throughout the course of CERESiS. Thus purification efforts will focus on H_2S removal only. Note that the main emphasis of CERESiS will be on the lab-scale unit/conditions/operating parameters of the SCWG process. Regarding the potential tar issue, this remains open and will be resolved in the framework of WP3/Tasks 3.1-3.2.

Table 2-1 Main properties of the SCWG gaseous product

Expected production rate & composition	Temperature & pressure
Rate: ~20 – 70 NL h^{-1} **Composition:** H_2: 20 – 35 vol.-% CH_4: 20 – 25 vol.-% CO_2: 35 – 40 vol.-% $C_{2\text{-}3}$: 7 – 10 vol.-% (mainly C2H6) CO: 0 – 1 vol.% H_2S (depending on S-content in biomass): ≤ 1000 ppmv	**Lab unit:** Product gas is cooled down to 25°C, atmospheric pressure. **Pilot plant:** phase separation occurs at 280 bar and 25°C

2.1.2 The SCWG liquid product

The main properties of the liquid product (two different streams as described above) are provided in Table 2-2. Since until now no tests with extensively contaminated biomass have been performed, the composition provided is indicative and will need to be carefully re-evaluated after the first test runs for CERESiS (WP3 activity). Naturally, the salt concentration and its composition depend on the feed material (nature and concentration of nutrients and organics) and gasification efficiency. Higher content of inorganic material (i.e., expected to be the case for extensively contaminated biomass of CERESiS) can be a challenge with respect to depositions inside the SCWG reactor and possibly for the downstream separation/decontamination/purification technology, especially when scaled-up conditions (not directly applicable to CERESiS experiments) are considered.

It is anticipated that for CERESiS, salt concentration will be higher compared to a typical SCWG process of uncontaminated biomass.

Table 2-2 Main properties of the 2 SCWG liquid streams

Main characteristics & composition	Temperature & pressure
Mainly (stream R): Organic compounds (TOC > 500mg/L) $NH4^+$ & K^+-salts. Typically 80-90% of liquid product. **Secondarily (stream S):** Non-decomposed organic material, other salts and metals (depending on the feed material). Typically 10-20% of liquid product.	Room temperature & pressure

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 in condensable and incondensable compounds, typically known as bio-oil and pyrolysis gas. The remaining solid carbonaceous residue is known as char or bio-char.

FP represents an alternative approach for treating contaminated biomass since it allows, at the appropriate operating conditions, the fixation of heavy metals (HMs) in **the solid product (biochar)**, thus reducing the volume and weight of contaminated matter while also **producing a combustible liquid product (bio-oil)** containing no or limited amounts of heavy metals. Bio-oil production through FP will 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. A detailed characterization of biochar will be provided to assess its suitability to be used for agronomic purposes. To this respect, the European Biochar Certificate and IBI Biochar Standard criteria and procedures will be carefully considered as guidelines. Subsequently, only the required procedures will be taken into account for the biochar characterization and a selection between the two guidelines will be made.

Although it is not of a high priority for CERESiS, potential assessment of the retained solid particles as catalysts/adsorbents could be investigated as a side activity and in the framework of further reduction of process effluent waste products. For this scope it is necessary, however, to characterize their physical and chemical properties.

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 pivotal to design properly the cleaning of the vapor phase before its condensation and optimize the condensation train. However, it is inevitable that a fine fraction of char will be elutriated and dragged by the vapor phase exiting the reactor. In order to remove this fraction different gas/solid separation systems can be considered, namely cyclones, hot filters and electrostatic precipitators. Based on the separation efficiency reported in the literature, it has been decided to include a cyclone at the exit of the pyrolysis reactor before the condensation train. This gas/solid separation system will prevent the transfer of the bigger particles. This is the reason why a further off-line filtering treatment is required for the condensed bio-oil. Given the low efficiency of the cyclone for particles size < 10 μm, a dry electrostatic precipitator (ESP) will be placed at the end of the condensation train with the aim of capturing part of the finer particles that escape the condensation train.

2.2.1 The bio-oil stream recovered from the liquid product of FP

The produced bio-oil must undergo off-line filtering treatment to remove solid particles with size < 10 μm, since particles > 10 μm are removed during pyrolysis by e.g., hot gas filtration and cyclone separation [1], as stated above. There is currently no well-established technology to remove fine solid particles. In CERESiS, membrane-based separation approaches will be pursued and validated experimentally. It must be noted that the water included in the bio-oil is another critical parameter that affects the separation process design and operational efficiency. It is anticipated that water content will be lower than 20 wt%, however this must and will be validated experimentally in the framework of WP3 activities later in the project. The water content to be determined will, to a certain extent define the design requirements and components of choice for the separation process. In line with this aspect, a fractionated condensation will be performed directly at the exit of the pyrolysis unit in order to tune the water content to proper values suitable for the subsequent separation process (to be determined by relevant parametric analysis of the separation process).

More details on the chosen method and its operational and other main characteristics to address relevant challenges and peculiarities of the necessary purification process, based on a relevant literature review and critical analysis, are provided in the next section.

3 CLEANING/DECONTAMINATION METHODS

3.1 Cleaning of The SCWG gas stream

3.1.1 Review on available methods for sour gas purification (focus on deH$_2$S)

The main technologies for sour gas purification include [2]:

Chemical or physical absorption in packed columns

This can be considered as the state-of-the-art method for sour gas treatment. The principle of the technique is acid gas removal by various absorption/reactive solvents. Then the solvent can be regenerated by the application of heat (typically 110-130 °C for the most common case of amine solutions) and/or mild vacuum to strip the absorbed gases. A typical lay out of the method is shown in Fig. 3-1.

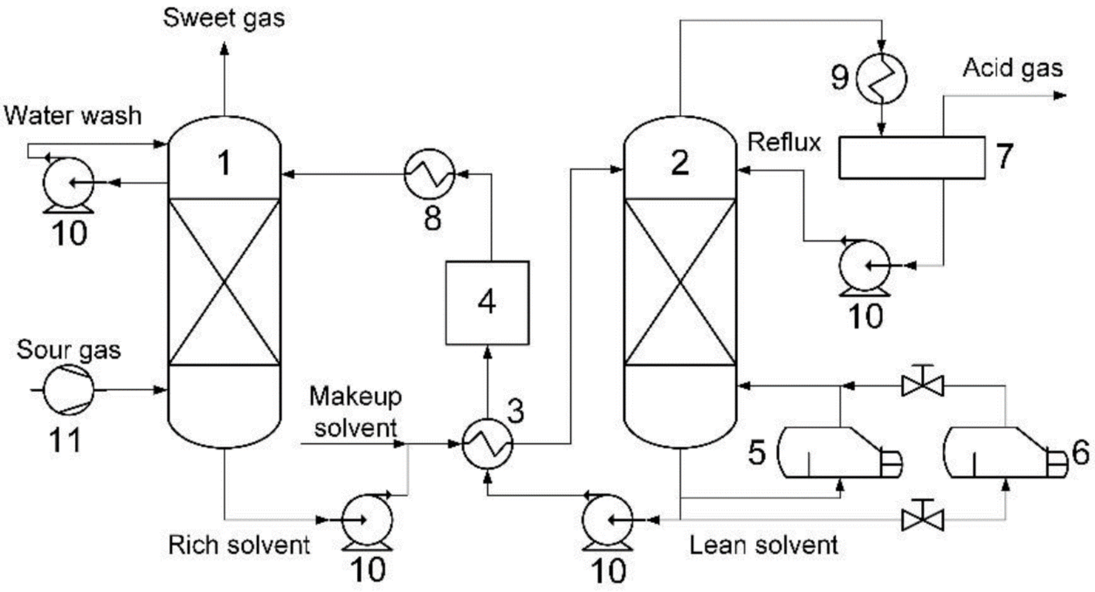


Fig. 3-1: Typical layout of an absorption based sour gas treatment method.

The main solvents that are commonly employed in the process include: i) Aqueous amine solutions (e.g., MEA, DEA, MDEA, etc.) - Chemical absorption, ii) Aqueous alkali solution (e.g., NaOH, KOH, etc.) – Chemical Absorption, iii) Methanol – Physical absorption, and iv) Ionic liquids – Physical absorption.

Adsorption

Adsorptive separation involves the use of a selective and high-capacity solid substrate that shows a preferential affinity for one or more gases of the gas mixture. Similar to absorption, adsorption may also be classified as physisorption and chemisorption, depending on the strength of sorbate–sorbent interactions. Typical adsorbents for H_2S capture from gas mixtures containing CH_4, CO_2, N_2, H_2, and H_2O, include metal oxides (e.g., ZnO, iron oxides, CuO), MOFs, zeolites, carbons, and composite materials. In addition to sorbents' capacity and selectivity, the stability under extreme acid gas environments as well as the performance and structural regenerability are important factors that have to be considered for process design and economic assessment.

Cryogenic distillation

For many chemical separations, distillation has been the most straightforward and often the optimum choice from techno-economic point of view. 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. In the past decade or so, distillation has come again into the frame as a potential option for gas sweetening. However, it must be noted that distillation, in general, is a very energy-intensive process that could find application only in very large plants.

Membranes

The last one- or two-decades R&D activities on membrane technology, as potential alternative to conventional gas separation technologies, have been intensified. 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.

Hybrid processes

An alternative technology that combines the advantages of high surface area per unit volume of membranes 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 compared to the conventional, mostly mature, methods. This technology has been selected for further investigation in the framework of CERESiS project and thus it will be further analyzed in the next section.

Table 3-1 below summarizes the main pros and cons per technology briefly stated above. Selected such advantages and disadvantages will be further analyzed later in the text.

Table 3-1 Main advantages and disadvantages per main sour gas purification method

Packed columns		Adsorption		Cryogenic distillation		Membranes		Hybrid processes (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 decline 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

3.1.2 Detailed description of Membrane Gas Absorption (MGA) technology

Gas-liquid membrane contactors are devices where gas and liquid flow on the opposite sides of a porous membrane, which forms the interface for their contact. Using a hydrophobic membrane, the pores of the membrane are gas-filled and as long as the pressure of the liquid is kept slightly above that of the gas, an immobilized gas-liquid interface is formed at the pores' mouth in the liquid side. Fig. 3-2 shows the operation principle of a gas-liquid contact membrane.

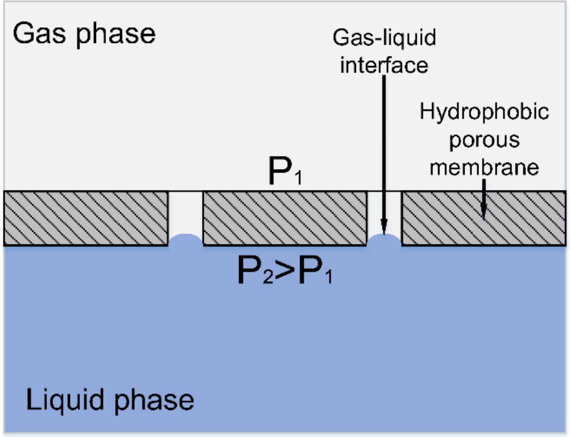


Fig. 3-2: Operation principle of a gas-liquid contact membrane.

Gas–liquid membrane contactors offer several advantages over conventional contacting devices. The one that most often emphasized is the very high specific surface area. Currently, the leading manufacturers of conventional contact devices (e.g., Sulzer) offer structured packings with a specific surface area of up to 1500 m^2/m^3, which is about half of what it can be achieved in a membrane contactor. Table 3-2 shows a comparison of specific surface area for different contact devices [3].

Table 3-2 Comparison of specific surface area for different contact devices.

Contact device	Specific surface area, m^2/m^3
Scrubbers	1-10
High performance unstructured 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 [4]:

- ✓ The available surface area remains undisturbed at high and low flow rates because the two fluid flows are independent. This is useful in applications where the required solvent/feed ratio is very high or very low. In contrast, columns are subject to flooding at high flow rates and unloading at low ones.
- ✓ There are no weeping, foaming, emulsion or entrainment problems because there is no fluid/fluid dispersion.
- ✓ Scale-up is more straightforward with membrane contactors. Membrane operations typically scale linearly, so that a predictable increase in capacity is achieved simply by adding membrane modules.
- ✓ Modular design also allows a membrane plant to operate over a wide range of capacities.
- ✓ Interfacial area is known and constant a priori, which allows performance to be predicted more easily than with conventional dispersed phase contactors.
- ✓ Substantially higher efficiency (as measured by the height of a transfer unit or HTU) is achieved with membrane contactors than with dispersive contactors.
- ✓ Solvent holdup is low, an attractive feature when using expensive solvents.

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

- ✗ The membrane introduces another resistance to mass transfer not found in conventional operations: the resistance of the membrane itself. However, this resistance is not always important, and (design + operational) measures can be taken to minimize it.
- ✗ Partial membrane wetting with time can potentially increase the process' mass transfer resistance. Careful selection of membrane materials, solvents and process conditions are needed to avoid this phenomenon.
- ✗ Membrane contactors are subject to shell side bypassing, which results in a loss in efficiency. Often bypassing is not a problem in the laboratory but may become an issue upon scale-up to larger contactors. Fortunately, several design improvement have been proposed to address this problem.
- ✗ Membranes are subject to fouling, although this tends to be more of a problem with pressure-driven devices than with concentration-driven ones such as membrane contactors.
- ✗ Membranes have a finite life, so that the cost of periodic membrane replacement needs to be considered. Fortunately, 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 the sealing of the bundle of fibers may be vulnerable to be attacked by organic solvents, considering a long-term operation.

The above relatively few and non-detrimental disadvantages are often outweighed by the numerous advantages cited earlier in the text. For this reason, membrane contactors have attracted the interest of both academia and industry for a diverse range of applications.

3.1.3 Sour gas treatment with MGA technology

Perhaps the highest number of the studies regarding hollow fiber membrane contactors are dealing with MGA. Although MGA of CO_2 has by far the highest number of studies in the field, there are several others focusing also on H_2S removal, which is the main target compound of the CERESiS removal system. Fig. 3-3 shows the operation principle in a MGA H_2S removal system.

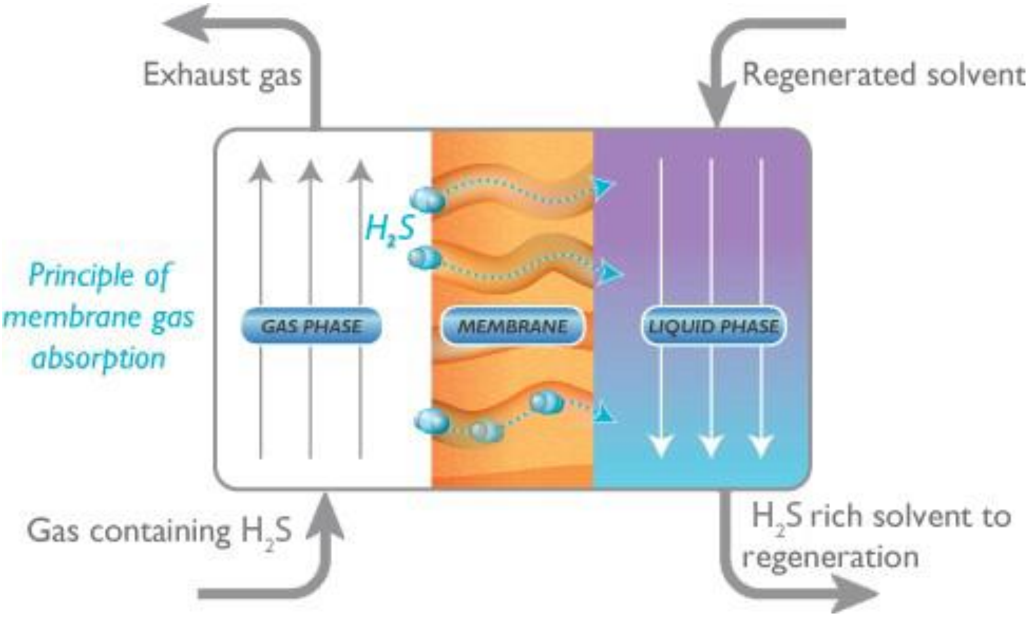


Fig. 3-3: Operation principle of a MGA H_2S removal system.

Bazhenov et al. [5] recently published a very detailed literature review on gas-liquid hollow fiber membrane contactors for different applications. In this study, there is concentrated important information on recent works on H_2S removal systems, which is included in Table 3-3.

Table 3-3 Synopsis of the main results of literature studies on H_2S removal through MGA.

Process	Membrane	Contactor Design	Liquid Phase	Gas Phase	Comments	Reference
H_2S removal from natural gas	PVDF, PSF	Parallel-flow	MDEA, DEA, MEA	$H_2S/CO_2/CH_4$	Increasing MDEA concentration accelerates wetting. Lean MDEA solution is preferred for high H_2S selectivity.	[6]
	PTFE	Counter-flow	Water	H_2S/CH_4	Pseudo-wetting conditions (1–3% of pore filling).	[7]
	PFA	Counter-flow	Water, NaOH, DEA, K_2CO_3	$H_2S/CO_2/CH_4$	Excellent long term operational stability of the PFA membranes under the working conditions.	[8]
	PTFE, PFA	Counter-flow	Water, MEA, DEA, DETA	$H_2S/CO_2/CH_4$	PFA exhibit much higher fluxes (9–10 times) for CO_2 and H_2S than those obtained with the PTFE membranes.	[9]
H_2S removal from biogas	PVDF	Counter-flow	Water, MEA	$H_2S/CO_2/CH_4$	Gas phase resistance plays the most important role.	[10]
	PVDF	Counter-flow	Water, MEA, K_2CO_3, KOH, PS, K_2CO_3/PS	$H_2S/CO_2/CH_4$	The highest H_2S absorption flux is obtained when KOH and K_2CO_3 are used as single absorbents. Gas phase is the dominant mass transfer resistance in the process.	[11]
	PDMS	Fiber immersed to absorption tank	Water, NaOH	$H_2S/CO_2/CH_4$	Moderately high H_2S fluxes (up to 3.4 g/m^2-day) with low CH_4 loss (nearly 5%) achieved	[12]
	PDMS	Fiber immersed to absorption tank	K_2HPO_4,NH_4Cl, $MgCl_2 \cdot 6H_2O$	$H_2S/CO_2/CH_4$	Almost complete H_2S removal (>97%) and high conversion ratio to SO_2 (>74%) achieved.	[13]
H_2S odour control	PVDF	Counter-flow	Na_2CO_3	H_2S/N_2	Overall mass transfer resistance is reduced when the gas mixture is fed in the shell side.	[14]
	PP	Counter-flow	Water	H_2S/air	Up to 89% H_2S removal efficiency	[15]
	PP	Counter-flow	NaOH	H_2S/air	Optimum solvent concentration determined at pH=11	[16]

3.1.4 Review on 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, which typically lead 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 3-4 shows indicative costs for these membrane materials [17].

Table 3-4 Indicative cost of commercial hollow fiber membranes

Membrane type	Price, $/m of hollow fiber	Manufacturer
PP	0.01	Mitsubishi Raynon Ltd. (Japan)
PVDF	0.36	Wenzhou New Century International Ltd. (China)
PTFE	11.5	Sumitomo Electric Fine Polymer (Japan)

3M™ Liqui-Cel™ is the leading manufacturer of membrane contactors. It offers a wide range of membrane modules (from lab to commercial scale), designed for mass transfer applications in gas-liquid systems. Fig. 3-4 and Fig. 3-5 show pictures of some of the commercially available modules designed for small and large scale applications respectively.

Fig. 3-4: 3M™ Liqui-Cel™ membrane contactors for small scale applications (MM series).

Fig. 3-5: 3M™ Liqui-Cel™ membrane contactors for large scale applications (EXF series).

Liqui-Cel® contactors are using porous polypropylene membranes, which are supplied in a fiber mat form with parallel hollow fibers connected to each other by a polymer thread. Such a configuration is designed to allow high packing density of membranes into the specially designed contactor housings. Most of the small scale membrane modules (MM series) are designed for a parallel gas-liquid flow configuration, while the large scale (EXF series) are designed for a transverse flow configuration, which has found to offer higher overall mass transfer coefficients. Fig. 3-6 shows a commercial EXF series membrane contactor with details of the fiber mat, the hollow fiber and the membrane's pores.

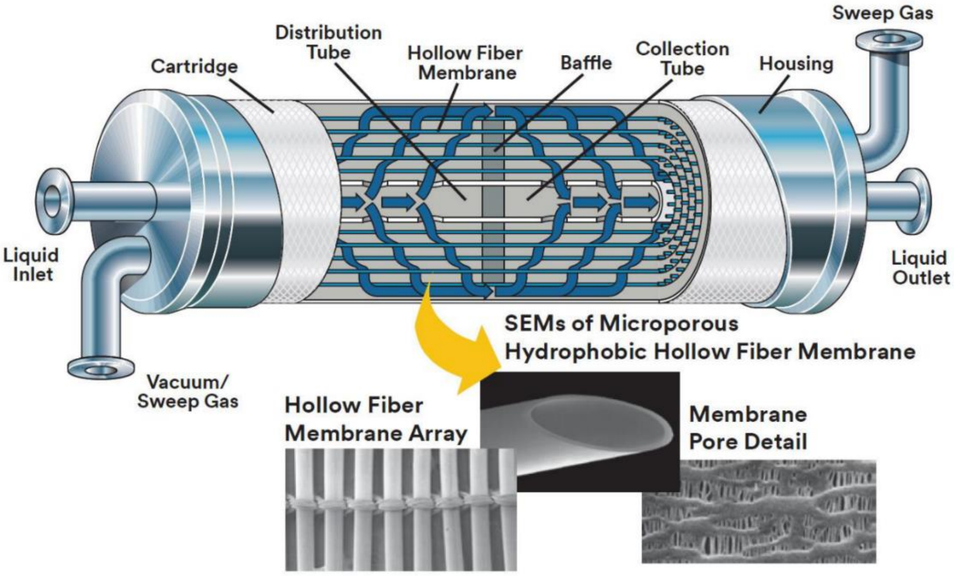


Fig. 3-6: 3M™ Liqui-Cel™ EXF membrane contactor module.

3.1.5 Review on solvents

Solvent selection is probably the most crucial part in any absorption process design and significantly affects the overall system's performance. The identification of candidate solvents to be tested CERESiS MGA process will be based on:

- Operating data for solvents typically used in conventional sour gas absorption processes
- Literature data on solvents compatibility with membrane materials
- Survey on candidate solvents

Survey on candidate solvents

Amines are by far the most commonly employed solvents in sour gas treatment. They have been widely used in the petroleum refining and natural gas processing industries for acid gas removal. 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 [1, 18-20].

The three basic types of amines include: primary amine, such as Monoethanolamine (MEA) or Diglycolamine (DGA), secondary amine, such as Diethanolamine (DEA) or Diisopropanolamine (DIPA), and tertiary amines, such as Methyl Diethanolamine (MDEA). Primary and secondary amines react with H_2S and CO_2 as follows:

$$H_2S + RNH_2 \leftrightarrow RNH_3HS \tag{1}$$

$$CO_2 + RNH_2 + H_2O \leftrightarrow RNH_3HCO_3 \tag{2}$$

The reactions proceed to the right at increased acid gas partial pressures and/or low temperatures (absorption step) and are reversed at low partial pressures and/or high temperatures (solvent regeneration step). In most primary and secondary amine solutions, H_2S and CO_2 react simultaneously with the solution, making selective recovery difficult. Primary and secondary amines react with CO_2 to form carbamate. Carbamate formation limits the solution loading capacity for CO_2 to approximately 0.5 mole of CO_2 per mole of amine. On the other hand tertiary amines cannot react directly with CO_2 to form carbamate. In tertiary amine solutions CO_2 reacts with the hydroxyl ion formed by the dissociation of water to form bicarbonate, and tertiary amines are known to be a catalyst for this reaction. However, CO_2 reaction rate is significantly slower than that of H_2S with tertiary amines; therefore, tertiary amines generally exhibit higher selectivity for H_2S in the presence of CO_2.

The development of aqueous solutions of alkanolamines as absorption liquids for acidic gases started around 1930. Triethanolamine (TEA) was the first alkanolamine commercially used in the first gas-treating plants. Other alkanolamines were subsequently introduced into the market as possible acid-gas absorbents. MEA, DEA, and MDEA are alkanolamines that proved to be of principal commercial interest for gas purification. TEA was found to be less attractive mainly due to its low absorption capacity (resulting from higher equivalent weight), its lower reactivity and its relatively poor stability. DIPA was used to some extent in the Adip process and in the Sulfinol process, as well as in the SCOT process for Claus plant tail gas purification but it was gradually displaced by MDEA in these applications. Table 3-5 summarizes the main advantages and disadvantages of the most common amines.

Table 3-5 Summary of advantages and disadvantages of the main amines

Amine	Advantages	Disadvantages
Monoethanolamine (MEA)	- High alkalinity, which increases the solution effectiveness for acid gas absorption - High solution capacity at moderate concentrations - Contaminated solutions can be reclaimed	- Formation of irreversible reaction products with organic S, which gradually affects the performance of the amine - Higher corrosion rates compared to other amines especially for MEA concentrations exceeding 20% - High heat of reaction with CO_2 and H_2S, resulting in high energy requirements for solvent regeneration - Relatively high vapor pressure, resulting in high vaporization losses in low-pressure operations.
Diethanolamine (DEA)	- The acid gas loading is typically higher for DEA than MEA - DEA forms regenerable compounds with COS and CS_2, thus, partial removal of COS and CS_2 can be achieved without significant solution degradation. - Requires lower energy for solvent regeneration than MEA due to lower heats of reaction - Low solvent vapor pressure makes DEA suitable for low-pressure operations	- The reclaiming of contaminated solutions is more complex since vacuum distillation may be required.
Methyldiethanolamine (MDEA)	- Selectivity towards H_2S. This reduces the total amount of the acid gases removed, thus less solvent is required in case H_2S is the targeted compound. - Low heats of reaction result in low regeneration energy - MDEA is the less corrosive of the amines in question - Low vapor pressure permit its use in high concentrations without vaporization losses - MDEA has high solution capacity, and excellent thermal and chemical stability	- Low ability to remove COS and Mercaptans

In addition to the basic amines, proprietary amines are also offered by many chemical companies, such as UOP (Amine Guard and UCARSOL), BASF (Activated MDEA), or Shell (ADIP-X). Proprietary formulations, usually consisting of mixtures of amines and additives, are used to meet specific gas treating targets such as selective H_2S removal, partial or complete CO_2 removal, high acid gas loading, etc. For example, partially neutralizing an amine (for example, with an acid) can allow very low H_2S levels to be reached in the treated gas.

The selection of an amine solution depends on process conditions, acid gas partial pressures, and targeted purity for the treated gas. Generally, amine processes are suitable for applications with low to medium acid gas partial pressures as the process economic advantage declines with increasing partial pressures of acid gases. The economics of an amine process is also significantly affected by the energy requirements of the solvent regeneration step.

Non-amine solvents have been used to a less 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) is another class of solvents which can be found application in certain cases.

Solvents-membranes compatibility

A main challenge of the MGA technology is membrane wetting, which sometimes results in significant performance loss over time. The mechanism of membrane wetting is still being debated due to a lack of understanding of membrane–solvent interaction. Several researchers have proposed different explanations for membrane wetting. Some of the prevailing theories include [21,22]:

- Wetting due to possible chemical reactions between the membranes and the solvent which can change the hydrophobic characteristics of the system.
- Wetting due to physical interaction between the membrane pores and solvents (e.g., swelling), resulting in significant changes in the surface morphology.
- Wetting due to changes in membrane surface hydrophobicity by trace impurities and ionic species in the solvent, which can penetrate into the membrane pores via necking phenomena.

Partial membrane wetting by the solvent is something expected, at least to some extent, for any membrane-solvent pair. The partial performance loss many times 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 loss (reaching in 90% flux decline) during the first hours of operation, which apparently inhibits the applicability of the process.

The compatibility of membranes with various inorganic and organic solvents have been studied experimentally mainly for the CO_2 absorption process, but the same remarks also stand for H_2S or combined H_2S/CO_2 removal processes. The main conclusions derived are:

- Inorganic solvents such as deionized water, sodium hydroxide, and potassium carbonate have a high surface tension and do not easily wet common hydrophobic membranes. However, their absorption performance is lower than conventional amine systems.
- Amine solutions are the most commonly used organic absorption liquids in hollow fiber membrane contactors, since they have high absorption performance and regeneration potential. However, the surface tension of the organic solvents is low compared with inorganic solvents and they tend to more easily wet the common hydrophobic membranes.
- Using MEA as absorbent for long-term operations result in dramatic flux declines in all commercial hydrophobic membranes. Their surface morphologies, hydrophobicities and chemical properties are greatly affected by amine attack. DEA and MDEA tend to have milder effects on membranes performance.

In order to avoid membrane wetting, the Netherlands Organisation for Applied Scientific Research (TNO) developed a variety of absorption liquids based on amino acid salts. These advanced absorption liquids had similar absorption performance as alkanolamine solutions and did not significantly wet commercial hydrophobic membranes. Since then, amino acid salts have been widely studied as absorption liquids or promoters in amine solutions for absorption in hollow fiber membrane contactors. In this direction potassium glycinate solution is the most commonly researched amino acid salt for MGA processes since 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 promoter) have also studied for MGA processes with very promising results.

3.2 Purification/decontamination of the SCWG liquid product

Two different options are considered for the separation of the salts (including heavy metals) from the biomass: separation after the pre-heater, at a temperature of 400-500°C and separation after the reaction zone (at 600-650°C). As mentioned earlier in the text (see Section 2), for the needs of a preliminary Task such as Task 1.2, the two brine streams produced by SCWG are treated as one. Depending on the brine composition and HM loading, the two streams will be separately or combined treated by means of a hybrid process which combines two well-known electrochemical techniques, the electrocoagulation (EC) and the electrochemical oxidation (EO). The treatment scheme will be the subject of WP3 activities, also considering the output of Task 3.1 and first experimental studies on SCWG. Both processes take advantage of the high conductivity and the presence of inorganic ions (sulphates, chlorides) in the saline concentrates which result to reduced energy consumption (due to the decreased ohmic resistance of the brine and thus, the low voltage that needs to be applied), and to the in situ production of chemical reagents (coagulants, strong oxidants) for the scope of the separation/elimination of the target contaminants (HMs, organic pollutants).

EC is based upon a process generally referred as "adsorption and co-precipitation". It consists of generating coagulant species in situ by electrolytic oxidation of sacrificial anode materials triggered by electric current applied through the electrodes. The metal ions generated by electrochemical dissolution of a consumable anode spontaneously undergo hydrolysis in water, depending on the pH, forming various coagulant species including hydroxide precipitates able to remove pollutants by adsorption/settling and other ion metal species (HMs). Besides, simultaneous cathodic reaction allows for pollutant removal either by deposition on cathode electrode or by flotation (evolution of hydrogen at the cathode). It is understood that the choice of the appropriate electrode materials is crucial since it determines the reactions that would take place within the electrolytic cell. The main operating principles of the Electrocoagulation-Flocculation (ECF) are shown in Fig. 3-7.

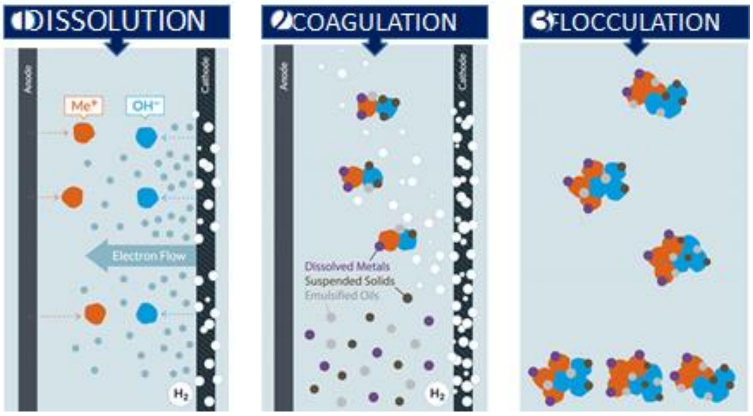


Fig. 3-7: Schematic representation of the ECF operation principle.

The parameters affecting EC effectiveness are related to the operating conditions such as current or voltage and operation time, to the brine features such as pH, alkalinity and conductivity and to the geometry of the EC reactor and the EC electrodes (electrode surface, electrode spacing). **Current density** determines the coagulant dosage at the anode and the hydrogen gas (H_2) evolution at the cathode governed by Faraday's law. The current creates a dynamic physical/chemical environment that governs directly the coagulation/flocculation mechanism and favors the electromigration of ions and charged colloids. The values of the current density range may widely vary according to the features and the amount of pollutants to be removed from the brine. To operate the EC system for a long period without maintenance, current density is suggested to be between 20 and 25 A/m^2.

The **pH** is another key factor influencing the performance of EC, especially the coagulation mechanism because it governs the hydrolyzed metal species generated in reactive media and influences the prevailing mechanisms of EC. **Hydrodynamics** influence both the species transport, orthokinetic flocculation for pollution removal and electrochemical phenomena. As the distance between electrodes becomes lower, more electrochemically generated gas bubbles bring about turbulent hydrodynamics, thereby leading to a high mass transfer as well as to a high reaction rate between the coagulant species and pollutants. In addition, inter-electrode gap defines the residence time between the anode and the cathode for a continuous system and the time of treatment for a batch reactor for reaching a desirable EC efficiency. For a complex electrode arrangement, inter-electrode distance determines also the number of electrodes to place in electrocoagulation cell, once its volume is defined.

Other than the increased current density, the increasing **conductivity** also decreases the treatment time required to reach a given removal yield. Consequently, the energy consumption is reduced. The presence of **chloride anions** in the brine is expected to take part as well in the reduction of the adverse effects of other anions to avoid the precipitation of calcium carbonate in hard water that could form an insulating layer on the surface of the electrodes. For very high current density, chloride anions can also be oxidized to active chlorine forms, such as hypochlorite anions, that can oxidize organic compounds. In order to ensure a normal operation of EC in the brine treatment, it is recommended that 20% of the anions present should be Cl^-.

EC will be coupled with EO towards the total mineralization of the residual organics in the brine stream(s). In EO, hydroxyl radicals can be generated by direct electrochemistry (anodic oxidation, AO) or indirectly through electrochemically generation of strong oxidants in the brine. In the first case hydroxyl radicals ($^{\bullet}OH$) are generated heterogeneously by direct water discharge on the metal anode (M) (Eq. 3) while in the last case strong oxidants are generated in situ indirectly in the bulk (persulfate and active chlorine species by reactions (4–5) thus favoring the oxidation of the organic compounds in shorter time.

$$M + H2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \quad (3)$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (4)$$

$$2Cl^- \rightarrow Cl_2(g) + 2e^- \quad (5)$$

EO requires high oxidation power anodes, i.e., anodes with high O_2 overpotential to minimize the extent of O_2 evolution from reaction (6).

$$2M(^{\bullet}OH) \rightarrow 2M + O_2 + 2H^+ + 2e^- \quad (6)$$

Anode materials such as graphite, Pt, metal oxides, and boron-doped diamond (BDD) are usually preferred. Among the different electrode materials tested in literature, the oxidative action of $M(^{\bullet}OH)$ is much more efficient in the case of BDD anodes. It has been found that operating at a high current, within the water discharge region, reactive $BDD(^{\bullet}OH)$ is produced in much higher quantities than $Pt(^{\bullet}OH)$ and can completely mineralize aromatics and unsaturated compounds such as carboxylic acids. Furthermore, the low adsorption ability of $^{\bullet}OH$ on BDD favors its dimerization to H_2O_2 by reaction (7), whereas the high oxidation power of this anode facilitates the generation of ozone from water discharge by reaction (8) and other weaker oxidizing agents such as $S_2O_8^{2-}$ ion from oxidation of SO_4^{2-} and HSO_4^- ions from reactions (9) and (10), respectively, when sulphate medium is employed.

$$2BDD(^{\bullet}OH) \rightarrow BDD + H_2O_2 \quad (7)$$

$$3H_2O \rightarrow O_3(g) + 6H^+ + 6e^- \quad (8)$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (9)$$

$$2HSO_4^- \rightarrow S_2O_8^{2-} + 2H^+ + 2e^- \quad (10)$$

3.2.1 Comparison of the EC and EO approaches with other state of the art relevant processes

Nowadays, huge amounts of highly saline wastewaters that are characterized by a multitude of inorganic and organic contaminants, including heavy metals (e.g., zinc, lead, manganese, iron, barium), dissolved organics (including toxic hydrocarbons) and other pollutants (e.g., oil and grease, bacteria and nutrients), are typically disposed of in the environment, thus posing environmental and ecological risks [23, 24]. Typical examples are brine wastes that originate from the hydraulic fracturing operations in the oil and gas industries (flowback and/or produced water) [25], landfill leachate [26], acid rock and mine drainage [27], chlor-alkali plant waste [28], chemical manufacturing [29, 30], food processing [31], etc. The removal of heavy metals from brine wastewaters is of great concern due to their toxicity at trace levels and accumulation in the bio-system. Heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Thus, heavy metals (Cu, Cd, Pb, Hg, U, Ni, Cr, and As) are directly or indirectly discharged into the environment increasingly, especially in developing countries, creating serious health and environmental problems [32, 33]. Due to shortage of water resources and safety and health concerns associated with traditional disposal techniques (e.g., underground injection, discharge to streams, rivers, and other surface water bodies, discharge in standard sewage treatment plants, evaporation ponds and land application) [34, 35], treatment and possible reuse of such wastewaters have become emerging needs.

The treatment of polluted saline wastewaters by biological processes (e.g., activated sludge) is not recommended due to the adverse effects of salts and toxic compounds on the bacteria communities and the existence of residual chemicals in the sewage sludge and the discharge water [36]. Conventional oxidation methods, such as chlorination or ozonation could lead to the formation of toxic byproducts [37], while adsorption on activated carbon or other filter media (e.g., zeolites, biochar) present several limitations in treatment cost and handling of saturated/exhausted filter materials [38, 39]. Pressure driven membrane processes (e.g., nanofiltration, reverse osmosis) [40, 41] and other modern membrane technologies (e.g., membrane distillation, forward osmosis) have been also considered for both total dissolved solids (salts, hardness) and dissolved organics removal from high saline wastewaters [42, 43]. However, membrane fouling, due to organic matter, inorganic colloids and micro-organisms (biofouling), is the main disadvantage of these technologies, which necessitates feed pre-treatment, higher pressure requirements during operation and frequent chemical cleanings with obvious negative consequences. Furthermore, pollutants are transferred from one stream to another rather than removed, as chemical content is concentrated in the rejection stream [40, 41].

In regards to heavy metals removal from brine effluents a literature search led to technologies that can be classified into three categories: Physicochemical-based Technologies, Thermal-based Technologies and Membrane-based Technologies, which are discussed in detail as follows.

Physicochemical-based Technologies

Removal of heavy metals from brine wastewaters is mostly based on chemical precipitation processes. Chemical precipitation process is one of the methods which is widely used in brine effluents from industrial treatment containing toxic heavy metals (Pb, Cu, Ni, Cr, Mn, Co, Hg, and Zn) because it is relatively simple and inexpensive to operate. In chemical precipitation process, chemicals react with heavy metal ions, thus forming insoluble precipitates by reducing their solubilities. Then, the precipitates can be separated from the brine water by sedimentation or filtration. Finally, the treated water is decanted and appropriately discharged or reused [32, 44-46].

Heavy metals can be recovered as oxides/hydroxides from brine effluents, by adding chemical reagents such as NaOH, CaO, $Ca(OH)_2$, $CaCO_3$, MgO, $Mg(OH)_2$ and NH_4OH. On the other hand, chemical reagents such as Na_2S, NaHS, H_2S, or FeS precipitate heavy metals such as sulfides, Na_2CO_3 or $CaCO_3$, lead to carbonates precipitates, while apatite or hydroxyapatite to phosphates precipitates. The most widely used chemical precipitation technique is hydroxide precipitation and sulfide precipitation [32, 44-47].

Khosravi and Alamdari (2009) have shown that Cu removal by co-precipitation with $CaCO_3$ reduced the Cu^{2+} concentration in a synthetic sample of oil-field brine from 0.27 ppm to about 0.06 ppm. A Cu removal of 78% required only 1 g of precipitate per 0.15 mg Cu metal [44]. Fazlollahi et al. (2014) have shown that utilization of $CaCO_3$ co-precipitation technique leads to a reduction of Hg content of the contaminated brine from 0.5 ppm to 0.055 ppm which means 89% efficiency of Hg elimination [45]. Habashi et al. (2015) have shown that the Hg, Cu and Pb removal by co-precipitation with $CaCO_3$ reduced the Hg^{2+},Cu^{2+} and Pb^{2+} concentration in the samples of oil-field brine from 0.643 ppm to 0.0514 ppm, 0.270 ppm to 0.06 ppm and 0.98 ppm to 0.07 ppm, respectively [47].

Table 3-6 below summarizes the main pros and cons of the chemical precipitation process.

Table 3-6 Advantages and disadvantages of the chemical precipitation process [48].

Advantages	Disadvantages
- Well-established technology with 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 times, a sophisticated operator is not needed - Easy to monitor	- Chemical precipitation 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 treatment 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

Thermal-based Technologies

Thermal-based technologies for heavy metals removal from brine wastewaters are based on evaporation (mechanically or naturally) and crystallization [49]. A commonly used thermal method for the brine treatment is natural evaporation through the use of evaporation ponds. Evaporation ponds are shallow ponds where water is evaporated from reject brine effluents naturally by the solar energy. As the freshwater has evaporated, the heavy metals in the brine are precipitated into salt crystals, which are periodically harvested and disposed of off-site [50-52].

Wind-Aided Intensified eVaporation (WAIV) is another evaporation method used for brine volume minimization containing heavy metals. This technology relies on the use of vertical wetted packing towers that use wind power for the evaporation of densely packed wetted surfaces. Specifically, pressurized air is diffused via the distribution pipes and is vertically moved to the surface of the brine. Commonly, the evaporation surface consists of woven nettings, non-woven geotextiles or volcanic tuff organized in trays [50, 52, 54].

Brine evaporative cooler/concentrator (BECC) is another thermal technology developed to reduce brine volume wastewater via the principle of evaporative cooling, where the cooling of a stream due to its evaporation, is used for the cooling of a second stream separated from the first by a heat transfer surface [50, 52]. In the work of Cipollina et al. (2011), the brine stream was first cooled (through evaporation) when mixed with a by-pass stream (cold seawater) and then concentrated through contact with atmospheric air. A heat-conductive surface separated the two streams and allowed cooling via recovery of the latent heat of evaporation [56].

Eutectic freeze crystallization (EFC) is a low-temperature thermal technique for the brine treatment and involves simultaneous crystallization of ice and salt, wherein the aqueous solution is separated into pure ice and salt crystals by freezing it down to eutectic temperature. As ice, salt and solution have different densities at the eutectic point, they can be separated by the force of gravity. The brine is cooled down below its freezing point and when it reaches a certain temperature, crystals start to form resulting in a brine/ice crystals mixture. Further cooling increases the salt concentration and the formation of ice crystals. At the eutectic point, no further ice is formed and the salt reaches the saturation and the products (ice and salt) are then separated [35, 49, 51].

Furthermore, the applicability of traditional thermal desalination approaches such as Multi-Effect Distillation (MED) and Mechanical Vapor Compression (MVC) for the treatment of high-salinity reject brines containing heavy metals have been shown by other studies [51]. Multi-Effect Distillation (MED), consisting of multiple cells operating at decreasing levels of pressure, has been used for thermal treatment of RO concentrate, where the steam of one stage heats the concentrate of the next allowing for an increase in recovery depending on the number of effects that can amount up to 93% [49-51].

Mechanical Vapor Compression (MVC), an alternative method for the treatment of highly concentrated wastewater, requires mechanical power as energy input to drive the compressor to produce condensable water vapor and wet salt, minimizing the brine volume up to 92% [49, 51]. This thermal technique presents: 1) simplicity, responsiveness and flexibility of operation, 2) adaptation to production constraints, 3) reliability, 4) low operating costs and 5) it can be driven by renewable energy sources (i.e., solar, wind, etc.) [49, 59, 60].

Table 3-7 summarizes the main pros and cons of the thermal-based technologies discussed above.

Table 3-7 Advantages and disadvantages of thermal-based technologies used for the treatment of brine wastewaters.

Process	Advantages	Disadvantages	Ref
Evaporation ponds	- Low maintenance and little operator attention - Less mechanical equipment except for the pump - Least costly means of disposal, especially in areas with high	- Required for impervious liners of clay or synthetic membranes such as PVC or Hypalon - Potential of contaminating underlying potable water aquifers through seepage from poorly constructed evaporation ponds	[53]

	evaporate rates and low land costs - Easy to construct	- 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)	- This technique minimizes the need for land - It can achieve an evaporation rate up to 90 % compared to evaporations ponds - The method was tested on brines from RO and RO-electrodialysis (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 - WAIV has the lowest SEC (up to 1 kWh/m3) as exploits wind energy for the evaporation and requires only electric energy for the pumps	- Industrial feasibility not proved - Difficult operational control and maintenance - Higher capital and operating costs than evaporation ponds	[51, 52, 55]
Brine Evaporative Cooler/Concentrator (BECC)	- 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, thus reducing the environmental issues related to the desalination process. - Geometrical simplicity	- High cost of tubes (anti-corrosion material) - Fouling and scaling on the tubes 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)	[56]

Eutectic freeze crystallization (EFC)	- 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	- 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	[49, 51, 57]
Multi-Effect Distillation (MED)	- Very low electrical consumption (<1.0 kWh m^{-3}) - Operates at low temperature (<70 °C) and at low concentration (<1.5) - Produces steadily high purity distillate - Does not need complex pretreatment of seawater and are tolerant to variations of seawater conditions - Is highly reliable and simple to operate - Reduces civil works cost - Is simple to install - Has a low maintenance cost - Operates 24 h a day with minimum supervision - Ideal for coupling with power plants - Can be adapted to any heat source - Allows very high thermal efficiencies and savings in fuel costs	- 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	[58]

Membrane-based Technologies

Membrane Distillation (MD) has been largely examined in literature for the removal of heavy metals from brine wastewaters. This method combines membrane filtration and thermal evaporation, where a micro-porous hydrophobic membrane allows water vapor to pass through while blocking the liquid, thus separating the vapor phase from the liquid phase. Vapor pressure created by the temperature difference across the membrane drives this process [35, 46, 61]. There are four MD configurations available, according to the mechanism of the vapor pressure gradient formation across the membrane; Direct Contact (DCMD) [62, 63], Air Gap (AGMD) [64], Vacuum (VMD) [65] and Sweeping Gas Membrane Distillation (SGMD), with DCMD being the most commonly applied in studies because of its ease of application [50-52].

Forward Osmosis (FO) is another membrane-based technology which can be used for the treatment of brine wastewaters containing heavy metals [50-52, 61]. In FO a solution of remarkably high concentration (referred to as the 'draw solution') is used to produce an osmotic pressure gradient across a semipermeable membrane, resulting in the transport of water molecules from the less concentrated feed brine solution to the highly concentrated draw solution. Hence, freshwater and draw solution are separated, with the second being recycled to the FO module [51, 52].

Finally, ElectroDialysis (ED), Electrodialysis Reversal (EDR) and ElectroDialysis Metathesis (EDM) are voltage driven membrane-based technologies that have been commercially successful in brine wastewater treatment [50, 51]. These processes use electric potential to allow the movement of dissolved ions through ion exchange membranes impermeable to water. The cations and anions are allowed to move across the membrane, leaving the water at one side only [50, 51]. EDR operates in the same way as ED except for the fact that the voltage is applied in reverse about three to four times an hour with an overall water recovery of 97%, which can be increased to about 99% through the use of a pretreatment system. EDM is considered to be a zero-discharge desalination process, maximizing water recovery and allowing for the collection of the solid brine salts [51, 52].

Table 3-8 Advantages and disadvantages of membrane-based technologies used for the treatment of brine wastewater.

Process	Advantages	Disadvantages	Ref
Membrane Distillation (MD)	- 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	- The main factors that determine the feasibility of MD as an industrial separation technique still form barriers for commercial implementation - The relatively low permeate flux in	[49, 50, 52]

	- Less susceptible to flux limitations compared to reverse osmosis (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/or a high suspended particle-content at atmospheric pressure and a temperature below the boiling point of the supply	comparison with pressure-based membrane processes - Flux reductions caused by concentration polarisation, membrane pollution - Water loss due to conduction through the polymeric membrane and/or pore wetting - High cost of MD modules and the high thermal energy consumption	
Forward Osmosis (FO)	- It requires less energy consumption compared to RO for the draw dilution step because it is based on natural osmosis phenomenon - 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 FO process suitable for ROC treatment	- 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	[46, 49, 50]
ElectroDialysis (ED) and Electrodialysis Reversal (EDR)	- High salt removal rate - Less susceptible to scaling, especially resistant to silica scaling - Able to achieve high brine concentration (TDS of 150 to 200 g/L)	- Relatively high capital cost	[35, 66]

3.2.2 Electrocoagulation-flotation

Electrocoagulation-flotation (ECF) seems to be a promising treatment method due to its high effectiveness, its lower maintenance cost, less need for labour and rapid achievement of results [67, 68]. ECF treatment has a greater ability to remove COD and suspended solids from effluents in comparison with treatment by conventional coagulation [69]. ECF is characterized by simple and easy operated equipment, short operation time, none or a negligible amount of chemicals and stable and less sludge production [62, 70-72].

The most widely used electrode materials are aluminum and iron since they are readily available, cheap, and very effective. Selecting the proper electrode material is critical since it determines the reactions that would take place. However, studies found that Fe (II) is a weak coagulant if compared to Fe (III) due to its lower positive charge [73]. A lower positive charge indicates that the ion's ability to compress the electrical double layer/destabilize colloids is weaker. In most of the studies, it is generally proven that Al electrodes enhance the efficiency of removing pollutants better than Fe electrodes when the efficiency of the treatment is the only criterion [73]. However, aluminum is more costly [74].

Effect of effluent chemistry on ECF

The operating conditions of ECF are usually dependent on the chemistry of the aqueous medium, mainly the electrical conductivity and solution pH. pH is a key parameter when it comes to electrocoagulation as it affects the conductivity of the solution, zeta potential and electrode dissolution [75]. For better removal efficiency of pollutants, an optimal pH is desirable for any pollutant as it aids the precipitation of the pollutants [74]. pH values above or below the optimal value decrease the pollutant removal efficiency [76].

Effect of time of electrolysis on ECF

The rate of generation of aluminium (II) or iron (II) ions (the electro-coagulants) from aluminium or iron electrodes, respectively, is determined by the time of electrolysis [77]. Generally, the increased electrolysis time increases the reduction of the pollutants. This is due to the fact that the Al and Fe ion concentration and their hydroxide flocs both accelerate the amount of bubble production as the electrolysis period increases [78]. The relationship between the amount of aluminium or iron produced to electrolysis time and current could be explained from Faraday's law. Faraday's law relates the theoretical amount of aluminium or iron ions (M) and hydroxyl ions generated in the reactor to the current flow, $m=(ItM_r)/zF$, where m is the amount of the dissolved anode material (g), I is the current (A), t is the electrolysis time (s), M_r is the specific molecular weight of the anode electrode (Al and Fe) (g/mol), z is the number of electrons involved in the reaction, and F is the Faraday's constant (96,487 C/mol) [79]. Theoretically, the quantity of coagulant is directly proportional to the electrolysis time and current applied, as seen in the law of Faraday.

Effect of temperature on ECF

Increase in temperature improves the solubility of electrodes and the diffusivity of the pollutants [78]. It is noted that at a higher temperature, the electrical energy consumption is significantly reduced in the ECF process [80]. Also, high temperature favoured the formation of large hydrogen bubbles, enhanced the flotation speed, and reduced the adhesion of suspended particles [74]. However, higher temperatures above the optimum usually induce electrodes passivation and cause coagulation instability (increase in the development of protective metal oxide layers), which can reduce anodic dissolution and subsequently contribute to poor performance in the removal of contaminants. Similar observation was seen by Jing et al. (2020) and Tibebe et al. (2019) [81, 82].

Effect of settling time on ECF

The rapid improvement in the efficiency of elimination over time is attributed to either the floc sweep mechanism or the combination with the process of bridging trapping mechanism [83]. When all the coagulated particles have settled and there is no noticeable settling, equilibrium has been reached. Due to the formation of larger and denser flocs (as a result of the attachment of coagulants to the particles), the high settling speed is encouraged [84].

Effect of electrolyte concentration on ECF

The anions concentration in the solution influences the stability of the passive layer of an electrode [74]. Sulphate anions are passivation agents; they can, therefore, reduce the production of metal cations. Chlorides induce the breakdown of the passive layer and pitting corrosion [85]. Some salts can precipitate on the cathodes if the concentration of the salt in water is very high [86]. The conductivity of the solution is an important factor that affects the efficiency and power consumption of EC. The higher the conductivity, the lower the power consumption of EC due to the decreased Ohmic drop, and the higher the pollutant removal [87]. Conductivity allows the current density to increase; thus, it is possible to introduce additional coagulants to the media. To ensure the proper working of ECF in the purification of wastewater, it is recommended that 20% chloride ion should be available among the anions [77]. In the work of Dalvand et al. (2011), the increased NaCl concentration increased the colour (Reactive Red198 dye) removal when using aluminum electrode. It was also found that the presence of chlorine ions effectively contributes to water disinfection [85].

3.2.3 Electrochemical Oxidation

The convenient application of electrical current, instead of chemicals, prompted researchers to develop electrochemical wastewater treatment technologies for the prevention of pollution problems [88-92]. Electro-Fenton (EF) and Anodic oxidation (AO) are major representatives of the electrochemical advanced oxidation processes (EAOPs) that have been proven very effective towards the degradation and mineralization of recalcitrant organics present in saline waters, offering distinct advantages for large scale applications such as versatility, energy efficiency, amenability of automation, the possibility to avoid addition of chemicals, and safety because they operate at mild conditions [93-95]. The main operating principle of EO is schematically shown in Fig. 3-8 below.

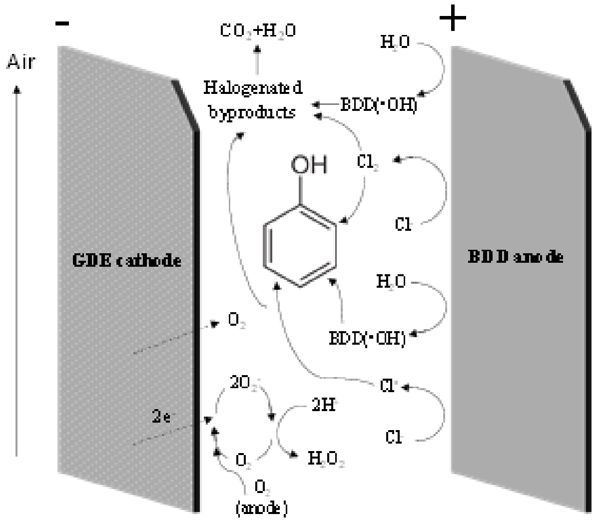


Fig. 3-8: Schematic representation of the EO operation principle (example of phenol oxidation as model organic compound).

Up to now, many researchers have provided a deep overview on the fundamental aspects of electrochemical oxidation (EO) and give updated information on the application of the technology in wastewater treatment [62, 89, 96, 97]. During EO, it is necessary to establish certain indexes including current efficiency and energy consumption for project evaluation and efficiency assessment towards the electrochemical treatment first. Current efficiency (Φ) is generally defined as the percentage of the experimental charge for the oxidation of organic compound to the total charge passed during electrolysis. Despite the fact that different expressions of current efficiency are proposed, the equations most commonly adopted in the literature are determined by Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) using the following relationships [98]:

$$\Phi = \frac{Q_{Exp}}{Q_{Total}} = \frac{COD_0 - COD_t}{8I\,\Delta t}\mathrm{FV} \tag{11}$$

$$\Phi = \frac{\Delta TOC_{Exp}}{\Delta TOC_{theor}} \tag{12}$$

$$\Delta TOC_{theor} = \frac{Itn_c M}{Vn_e F} x10^3 \tag{13}$$

where COD_0 and COD_t are the COD values at times 0 and t (in g O2 / L), respectively, I is the current (A), F is Faraday's constant (96,485 C/mol), V is the electrolyte volume (L), and 8 is the oxygen equivalent mass (g/eq). ΔTOC_{exp} and ΔTOC_{theor} are the experimental and theoretical TOC change values during treatment time (mg/L), respectively, n_e is the number of electrons consumed in the mineralization of organic pollutant molecule, n_c is the number of carbon atoms in organic pollutant molecule, M is the molar mass of carbon (12 g/mol). The specific energy consumption (E_{sp}), expressed in Wh/L (or Wh/kg_{COD}, Wh/kg_{TOC}), is the energy consumed to remove a unit volume (or mass COD, TOC) wastewater and can be calculated using the following relationships [97]:

$$E_{sp} = \frac{U_c I t}{V} \tag{14}$$

$$E_{sp} = \frac{U_c I t}{V \Delta COD_{exp}} \tag{15}$$

$$E_{sp} = \frac{U_c I t}{V \Delta TOC_{exp}} \tag{16}$$

where U_c is the voltage (V), I is the applied current (A), t is the electrolysis time (h), and V is the solution volume (L); ΔCOD_{exp} and ΔTOC_{exp} are the concentrations of the removed COD and TOC (mg/L). In a recent comprehensive review, Brillas and Garcia-Segura (2020) provide a benchmarking framework of novel electrochemical oxidation (EO) processes, based on the oxidation of phenol as model compound, and highlight the engineering challenges that need to be successfully addressed toward novel technology commercialization [99]. Among such challenges, the satisfactory long-term performance in a realistic operational environment critically determines the technology readiness level of these technologies [90]. For example, the EO process, applied to brine wastes characterized by a high chloride content, resulted in improved performance for organic pollutants degradation, due to the formation of reactive chlorine species during electrolysis, thus designated as electrochlorination process (ECL) [100-102].

Electrode materials

Generally speaking, EO essentially proceeds on the electrode/solution interface. Electrode materials, as a key part in the electrolysis process, play a crucial role in the electrochemical oxidation process, which directly concerns the efficiency, selectivity and energy of the process. Table 3-9 lists the anode materials adopted in wastewater treatment according to their types and oxidation power. Active anodes such as IrO_2, RuO_2 or Pt favor the partial and selective oxidation of pollutants, while non-active anodes such as SnO_2, PbO_2 or Boron-doped diamond (BDD) can give the complete combustion. Thus, non-active anodes are regarded as desirable electrodes for the complete oxidation of organics to CO_2 during wastewater treatment. Simultaneously, the degradation of various pollutants has been conducted on different electrode materials, and the merits/demerits have been also well investigated [103] according to actual experimental results.

Platinum (Pt) electrodes with relatively low OEP (i.e., 1.6 V vs SHE in 0.5 M H_2SO_4) have been reported in the oxidation of a wide range of bio-refractory organic compounds in many studies. During degradation of aromatic compounds on Pt, aromatic intermediates were initially formed during the electrolysis process, and the aromatic ring opened subsequently with the formation of aliphatic acids. However, complete TOC removal could not be achieved, and the characters of high price and fouling of Pt electrode further restrict the practical application in the real system.

Dimensionally stable anodes (DSA) [104] coated with metal oxides layers have been extensively employed in many electrochemical industries, such as the chlorine alkali industry, water electrolysis, and metal electrowinning due to their mechanical resistance as well as relatively inexpensive. Meanwhile, successful scale-up has demonstrated the practicability of DSA electrodes in the field of wastewater treatment. However, because they favor the secondary oxygen evolution reaction, DSA-type anodes usually encounter low current efficiency for complete combustion of organic pollutants. The development of PbO_2 anodes for the oxidation of organics has gained great interest in environmental applications because of their good conductivity and relatively large overpotential for oxygen evolution reaction in acidic media, which enables the production of hydroxyl radicals during water discharge. However, practical applications in the oxidation of organics with PbO_2 electrode have been limited due to its relatively shorter service life as well as concerns from the possible release of Pb(IV) ions into the water. The detailed reason could be related to the occurrence of cracks from the increasing internal stress in PbO_2 coating. In order to improve the stability and electrocatalytic activity of PbO_2 electrodes, one common approach being widely investigated is the incorporation of foreign species into the PbO_2 layer [105, 106].

Table 3-9 Classification of anode materials based on oxidation power and potential for OER in acidic media [107].

Anode type	Composition	Electro-catalytic ability for OER	Oxidation potential (V)	Over-potential (V)	Adsorption enthalpy of M-$^\bullet$OH	Oxidation power
Active	RuO_2-TiO_2 (DSA®-Cl_2)	Good	1.4–1.7	0.18	Chemisorption	Lower
	IrO_2-Ta_2O_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_2O_5	Poor	1.9–2.2	0.70		
	BDD	Poor	2.2–2.6	1.3	Physisorption	Higher

The usage of BDD electrodes in chemical destruction of pollutants has received great attention in recent years. High oxygen evolution potential with 2.4 V vs SHE distinguishes BDD electrode from conventional anodes. BDD electrode has been considered as an optimal electrode material for electrochemical oxidation of organic contaminants in aquatic environment [108, 109] and received great attention in the last decades as a new electrode material. Table 3-10 presents the current application of commercial BDD films to degrade varieties of organic pollutants. The results indicate the superiority of BDD electrodes; many commercialization companies have noticed the importance and prospects of BDD anodes.

Generally, the electrochemical incineration mechanism of organic pollutants in aqueous solution is proposed below [98]:

$$\mathrm{BDD} + \mathrm{H_2O} \rightarrow \mathrm{BDD}(^{\bullet}\mathrm{OH}) + \mathrm{H^+} + e^- \quad (17)$$

$$\mathrm{BDD}(\bullet\mathrm{OH}) + \mathrm{R} \rightarrow \mathrm{BDD} + \text{Mineralization products} + \mathrm{H^+} + e^- \quad (18)$$

$$\mathrm{BDD}(\bullet\mathrm{OH}) \rightarrow \mathrm{BDD} + \mathrm{O_2} + \mathrm{H^+} + e^- \quad (19)$$

The initial step involves the formation of $^{\bullet}$OH radical from the discharge of water molecule. Then, organic oxidation is indirectly mediated by the $^{\bullet}$OH radical, which is weakly adsorbed onto the BDD electrode surface and causes the following oxidative degradation due to its extremely high reactivity. The reaction is in competition with the oxygen evolution side reaction generated from the adsorbed $^{\bullet}$OH. Hence, the amount of electrogeneration oxidation radicals, in principle the reactive BDD($^{\bullet}$OH), could reflect the indirect electrochemical oxidation capacity of the electrode materials.

Table 3-10 Performance comparison of commercial BDD film electrodes for various wastewater treatments with electrochemical oxidation in recent application [110].

Commercial BDD	Pollutants	Degradation conditions	Performances	Ref.
BDD from Metakem	Reactive yellow HF	Undivided filter flow press reactor; 64 cm^2; 100–300 mg/L; pH=3	80% color removal and 70% degradation efficiency under 30–50 mA/cm in 120 min	[111]
BDD on Nb substrate from CONDIAS	Hexachlorocyclohexane	Undivided and cylindrical electrolytic cell; 24 cm^2; TOC0=9 mg/L; pH=7	Mineralization degree of 90% under current of 400 mA at 4 h	[112]
BDD film from NeoCoat	Procion Red	Single compartment flow cell; 50 cm^2; 100 mg/L with volume 0.4 L; pH=6	Achieve full dye and COD removal under current density 10–60 mA/cm^2 in 240 min	[113]
DiaCell electrode from	Reverse osmosis concentrate	Electrolytic cell with batch mode; 70 cm^2; flow-rate 10 L/min with volume 2 L	Total micro-pollutant from 149 µg/L to 10 µg/L	[55]

Adamant Technologies			under 100 mA/cm^2 in 60 min	
BDD film by CSEM	Paper mill wastewater	Undivided electrolytic flow cell; 50 cm^2; 100 mg/L with volume 0.3 L; pH=6.8	16.2 kW/m^3 with 2 g/L NaCl under applied current of 0.25–1.5 A	[114]
BDD thin film from Adamant Technologies	Pharmaceuticals	One-compartment flow filter press reactor; 69 cm^2; flow rate 360 L/h; pH=4	100% removal with current density 0.72–2.72 mA/cm^2 in 300 min	[115]
DiaCell system from Adamant Technologies	Reverse osmosis concentrate	Batch mode; 70 cm^2; flow-rate 0.01 m^3/min with work volume 2 L	92% removal with current density 20–200 mA/cm^2 in 120 min	[116]

BDD electrodes have been widely applied in the electrochemical oxidation of a diversity of organic contaminants and real wastewater systems. In the recent review work of He et al. (2019) a summary of the literature on the electrochemical oxidation of different organic contaminants on BDD anodes is provided. A complete mineralization of a multitude of contaminants (i.e., phenolic compounds, carboxylic acids, pharmaceuticals, surfactants, dyes) could be conducted on BDD electrodes by the reaction with electrogeneration $^{\bullet}OH$ radicals while maintaining higher current efficiency versus other anode materials, such as SnO_2, PbO_2, and IrO_2 [117, 118]. The researchers speculated that the enhanced oxidation ability of BDD electrodes could be related to the high electrogeneration ability and weak adsorption towards $^{\bullet}OH$, where more $^{\bullet}OH$ could divorce from the anode surface and go into the bulk solution to react with contaminants.

Effect of current density on EO

Among the variables usually altered in electrochemical oxidation processes, current density, which corresponds to the ratio between the applied current and the working electrode surface, may be the most frequently modified as it directly determines the reaction rate. Previous works [117, 119] have demonstrated that higher current density led to the generation of larger amounts of $^{\bullet}OH$, which resulted in higher degradation efficiency for the target pollutant. It should be highlighted that an increase in current density does not necessarily lead to an increase in the oxidation efficiency or oxidation rate for a given anode material: the effect of current density on the treatment efficiency also depends on the characteristics of the effluent to be treated. However, the employment of higher current densities commonly results in higher operating costs due to the increase in energy consumption and opportunity for oxygen evolution side reaction.

Effect of influent pH

The influent pH has been established to be a significant operating factor influencing the performance of electrochemical processes. It is generally acknowledged that the pH value affects the $^{\bullet}$OH generation concentrations and oxygen evolution overpotential, which subsequently concerns the electrochemical oxidation efficiency. Due to the differences in organic structures and electrode materials, the results regarding the influence of solution pH are also diverse and even contradictory. Hence, a review of previous publications does not allow us to reach a conclusion on whether increasing or decreasing pH favors pollutant removal in electrochemical oxidation of wastewaters. Some authors reported that the oxidation process is more favorable in acidic media [120]. In contrast, others indicated that the efficiency of the process was increased in alkaline media [121]. For example, previous studies have found that the electrochemical oxidation was more favorable in the acidic condition because the low pH inhibits the oxygen evolution reaction, leading to the improvement of degradation efficiency. According to the above literature, it can be concluded that the effect of pH strongly depends on the nature of the inspected organics and supporting electrolyte.

Effect of wastewater characteristics

The physicochemical characteristics of the wastewater (nature and concentration of electrolyte and concentration of target pollutants) also affect the electrochemical oxidation process [115, 122]. In this case, the electrolytes play an important role in the process because of the possible formation of side products, which could increase or diminish the efficiency decided for the actual system. Canizares and coworkers (2007) observed that the electrochemical treatment of ethylene glycol in a Na_2SO_4 or Na_3PO_4 medium was more effective than in NaCl. Meanwhile, some researchers discovered that chloride could also be oxidized to form active chlorine (Cl_2, HClO and ClO), which could further promote the degradation of target pollutants. Although no agreement has been reached on the variation mechanisms of the nature of electrolyte on the overall oxidation efficiency, it must be kept in mind that high conductivity of the electrolyte leads to faster electron transport and better degradation rate for organic pollutants, consequently lowering the cell voltage for a given current density and leading to reduced energy consumption.

Last but not least, considering the combination of ECF and EO to achieve complete purification of the liquid SCWG stream/product, a simplified representation is shown in Fig. 3.9 below. More details are provided in section 4, later in the text.

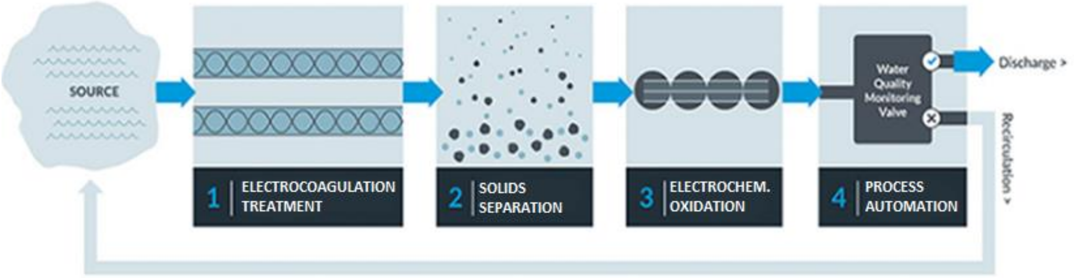


Fig. 3-9: Simplified schematic representation of the ECF-EO combined process.

3.3 FP Bio-oil purification

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 for the removal of char particles from bio-oil, however, these are efficient for solid particles greater than 10 µm [1]. Other conventional technologies, including gravity-driven filtration [123], air floatation [124], coalescence, de-emulsification, coagulation [125], centrifugation, flocculation, metal mesh, hydro-cyclone have been also applied for solid-liquid separations in oily fluids [126]. 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 highly desirable for improving the applicability of bio-oils as engine fuel. Specifically, solid particles in bio-oil can cause corrosion problems and also adversely impact 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 to be converted into gasoline or diesel fuel by hydride oxygenation.

In terms of solid-liquid and liquid-liquid dispersions separation, membrane-based approaches have been proposed and subsequently attracted much attention because of a number of inherent advantages such as lower energy consumption, easy to clean, high purity of permeates, high separation efficiency, modular scalability, recyclability of concentrated flow in crossflow types, and the absence of any requirements for chemical additives or regeneration cycle for spent medial [127, 128].

Different types of pressure-driven membrane operations include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), have been employed to treat oily wastewaters. The primary distinction between these methods is the size difference of membrane pores, but their concepts are essentially the same (see Fig. 3-10). The mechanical sieving acts as a driving force for separation in MF and UF processes, while solution diffusion and capillary force progress the separation by RO and NF membranes. MF and UF are efficient processes with a low-pressure driven force for the oil separation from oily wastewater, confirmed in numerous studies in the last decade [129]. However, their application for the purification of oil-based matrices is rather limited and restricted to only a few studies in the field [130, 131].

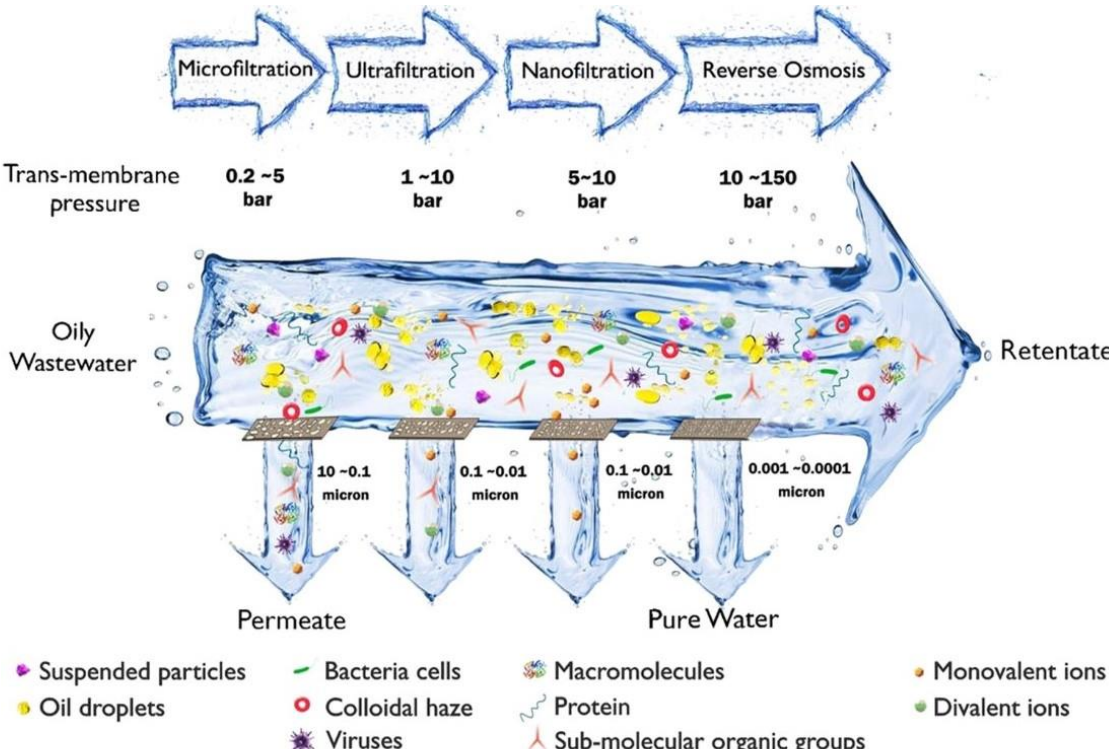


Fig. 3-10: Schematic view of pressure-driven membrane processes (crossflow mode) for treating oily wastewater (retrieved from [129]).

In recent decades, commercial ceramic and polymeric MF membranes have been broadly put into service in industrial separation applications. For water in oil separation, a hydrophobic membrane should be used for selectively blocking the water phase. Recent advances in superhydrophobic and superoleophilic porous membranes have gained also remarkable attention, particularly in selective and efficient water in oil separations [132]. Among the superhydrophobic and superoleophilic porous materials tested, including polymers, cotton/textile, filterpaper, metals, minerals, ceramics, glasses, carbon-based, and composites, the modified and synthesized polymer or ceramic based-membranes have been mostly explored in the specific researches. These materials feature high density, fragility, and incompressibility (their volume is not affected by changing temperature and pressure), compared to the other materials. However, they can be applied in harsh environments due to their excellent thermal stability and erosion resistance [133]. Ceramic membranes feature excellent mechanical strength, high chemical resistance, and exceptional thermal stability [134]. Indeed, the alumina membrane with excellent resistance in the harsh chemical cleaning can be applied in the different ranges of pH and temperature for oil-water separation applications. Yao et al. (2011) fabricated nanostructured alumina membrane through electrochemical anodization in the oxalic-acid electrolyte. In this morphology-dependent technique, a superhydrophobic and superoleophilic alumina films created without using low energy chemicals [135]. Tang et al. (2018) fabricated a superhydrophobic and superoleophilic alumina membrane with PTFE through thermal decomposition (sintering). The modified alumina membrane led to higher than 97% water rejection over four hours of exposure [136].

Although the (super)hydrophobic membranes have found great applications in oil-water separation, such as oil spills and oily wastewater treatment, their application to separate solids in organic solvent solutions or organic-rich aqueous solutions is still at a very early stage (i.e. technology concept formulation level). The fouling performance of these kind of membranes with water-derived fouling is surprisingly missing in oil-water separation applications in the literature. The membrane stability under harsh operating conditions is uncertain while the hydrophobicity can decrease at high temperature conditions. The effects of operating parameters, including temperature, cross-flow velocity, pH, trans-membrane pressure, and the molecular size of solute in separation membranes should not be underestimated, especially in the presence of solid particles that cause rapid fouling.

In the context of CERESiS project, the filtering of the FP bio-oil will be based on a liquid-phase microfiltration (MF) process to remove solid particles down to slightly sub-micron levels. For this scope tubular ceramic membranes of different pore sizes and of different membrane materials (α- Al_2O_3; ZrO_2; TiO_2) will be tested, in their commercial state or a modified one, by altering the hydrophobicity towards an effective water and solid (bio-char) particles separation. 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 MF-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 the development of a new highly innovative technological pathway with applicability in several sectors dealing with waste/byproduct oil-based streams.

4 GENERAL PLAN OF IMPLEMENTATION IN CERESIS

In the present section, a first basis for the implementation of the chosen purification/decontamination methods and processes is provided. Further details addressing precise experimental protocols and matrix per case, final preparatory and adaptation actions of the associated experimental setups and materials/chemicals as well as further important aspects that need to be defined to ensure optimum use of resources right from the beginning of the main experimental phase will be part of WP3/Task 3.1 work and will be provided in deliverable D3.1 (due in M9 of the project).

4.1 The MGA process

A simplified P&ID of the current Membrane Gas Absorption (MGA) process at CERTH is shown in Fig. 4-1. This particular unit will be modified accordingly in order to accommodate tests that will be tailored to the needs, operating conditions and requirements of the SCWG-based route of the project.

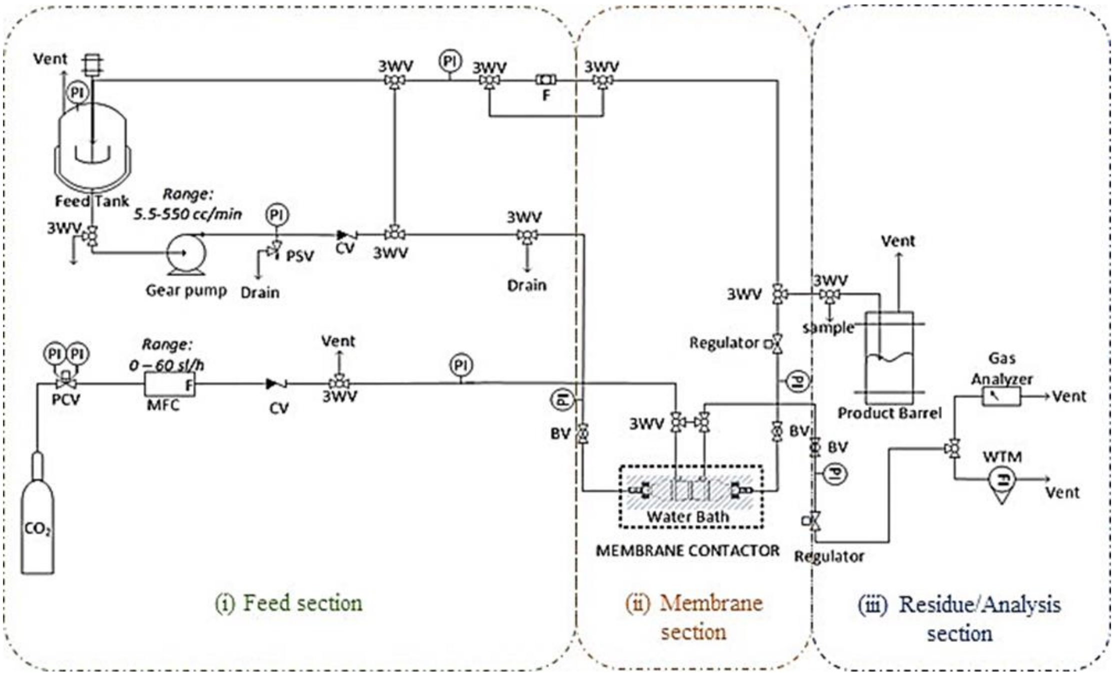


Fig. 4-1: Simplified P&ID of the MGA test setup at CERTH (absorption mode only).

In-principle, the saturated liquid (i.e. the amine/water solution) can be thermally regenerated at atmospheric or sub-atmospheric pressure to ensure re-usability via a closed absorption-regeneration loop. At the experimental level for the needs of the CERESiS project, absorption and regeneration will be studied separately.

A likely peculiarity of the targeted CERESiS-adapted MGA process lies on the fact that gas cleaning should ideally involve complete H_2S removal while at the same time CO_2 capture should preferably be limited or ideally completely avoided. The latter is due to the nature of downstream processes that are designed to convert all or most of the carbon species into a fuel. Thus, removal of CO_2 may have a negative impact on the overall efficiency of the process. It is suggested that no significant CO_2 alteration is considered in the analysis because captured CO_2 is in-principle fully recoverable during the regeneration process and thus can be re-injected to the MGA effluent stream. Moreover, the issue has already been discussed to some extent in section 3.1 and specific mitigation design measures were defined (i.e. choice of suitable solvents).

Below, a concise description of membrane modules and suitable solvents choices is provided. The choice is non-binding and certain adjustments in the course of the experimental campaigns may be necessary on the basis of certain outcomes of WP3 work.

Membrane modules selection

In the framework of the CERESiS project, the 3M™ Liqui-Cel™ membrane modules will be the building blocks of contactor devices of choice that will be employed for sour gas purification in the SCWG gas stream route. This selection allows for the direct assessment of the technology at lab scale using commercial devices with standardized and reproducible properties. As soon as the optimum process conditions are identified at lab scale (WP3 work), the process will be directly scaled up at pilot scale by selecting a larger area membrane module. Moreover, the techno-economic assessment of the process will be favored by the relative low cost of polypropylene cf. PVDF and PTFE membranes. However, it must be noted that if any serious issues, related to membrane stability and significant performance loss at the applied process conditions, arise during the experimental test campaigns in the course of WP3, alternative options will be directly considered.

Solvents selection

Based on the conducted survey about acid gas removal solvents, the following solvents have been shortlisted as potential candidates (to be further studied and tested depending on the results of experimental campaign) for the CERESiS MGA process:

- **DEA, MDEA and mixtures of them is the most likely option.**
- Amine salts (e.g. potassium glycinate) and mixtures of them with DEA and MDEA.
- Aqueous alkali solutions (e.g. NaOH, KOH, etc.).

4.2 EC and EO processes

Laboratory-scale experiments will initially be carried out in a new bench-scale EC setup, aiming to assess the performance of different electrodes on HMs removal (e.g., Zn, Pb, Cu, Cd and As). These include aluminum, iron [Fe(II), and Fe(III)] and stainless steel (SS) which are the most commonly used electrode materials thanks to various advantages: their availability, i.e. abundance on the earth and low price, their non-toxicity, as iron and aluminum hydroxides formed by precipitation are relatively non-toxic, and their high valence that leads to an efficient removal of pollutant. The EC setup will be specially designed so as to investigate the influence of different combinations (arrangements) of electrodes on the handling of SCWG brine for COD and heavy metal reductions. Specifically, the research activities will target to evaluate and compare the performance of electrocoagulation-flocculation (ECF) process on the reduction of COD, turbidity (TUR) and heavy metals using Al-Al, Al-Fe, Fe-Fe, Fe-Al, SS-SS, Al-SS, and SS-Al. The design of the experiments (DoE) will depend on the pollutant concentrations and the treatment targets. The organic load is expected to be rather low (< 500 mg C/L) due to their rapid decomposition in the supercritical water, while the concentrations of the HMs will depend on the biomass pollution load and their partitioning in the gasification/condensation streams. Most metals, such as Cd, Sr, Cs, Co, Zn and Cu, shall be retained in the saline concentrate, whereas Hg, the most volatile is more likely to go into the vapour phase and condense together with aerosols in the phase separation system. The impact of various parameters such as initial pH, current intensity, electrolysis time, temperature, settling time and ionic strength on the electrocoagulation process using Al, Fe and SS rods as the sacrificial electrodes will be explored.

Next, experiments will be carried out towards organic abatement using a bench-scale EO setup consisting of a plate-and-frame electrochemical cell (MicroFlow by ElectroCell, Denmark), a DC power supply, anolyte/catholyte circulation tanks, sensors located at the inlet and the outlet of the cell, measuring different operating variables, such as pH, conductivity, temperature, redox and pressure, accompanied by the respective transducers. A Supervisory Control And Data Acquisition (SCADA) system is also included for collection and recording of the measured parameters and for overall control through a PLC unit, a touch screen – Human Machine Interface (HMI), and other expansion electronic modules (Fig. 4-2).

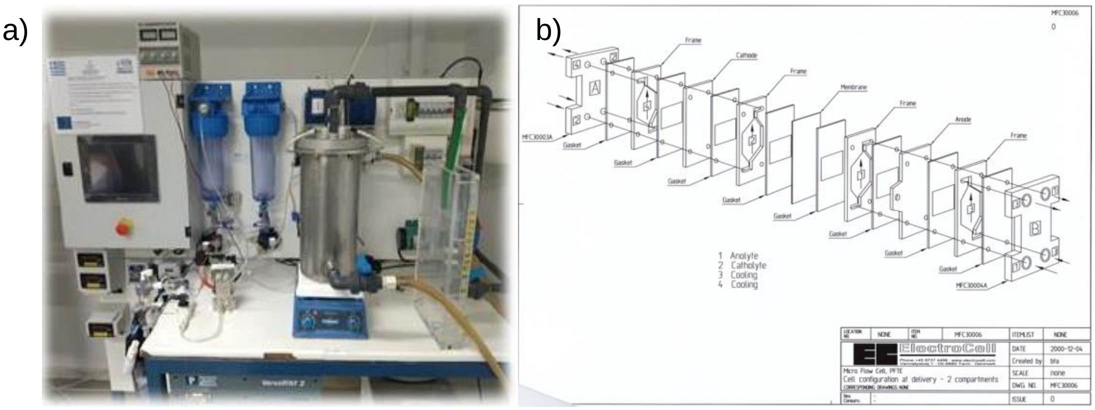


Fig. 4-2: a) Electrochemical treatment bench-scale setup, b) MicroFlow cell by ElectroCell.

A number of high-O_2 overpotential anodes will be assessed for the scope of the project, such as boron doped diamond (BDD) and Ti impregnated with metal oxides (e.g., Ti/IrO_2, $RuO_2–TiO_2–SnO_2$). Operational parameter optimization and modeling using the response surface methodology (RSM) will be performed, for evaluating the effect of key operating parameters. For both EC and EO processes, the major parameters to be optimized are current density (the current per area of electrode), solution's pH, and hydraulic residence time. Other parameters affecting process performance, such as conductivity and presence of ions in the feed solution will be also considered, depending on their ranges in the SCWG brine(s). At this preliminary stage, no estimations on expected HMs concentrations are possible due to complete lack of experience with SCWG of contaminated biomass. This aspect will be clarified upon initiation of first relevant experimental campaigns in WP3.

Finally, EC and EO processes integration will be examined by testing two different cell configurations: a) electrode setups in series, and b) electrodes in parallel connection in a single setup. In the latter configuration the current is divided between the electrodes resulting in a lower potential difference if compared to the electrodes connected in series. The choice of the appropriate electrode configuration will be determined by the removal efficiency and treatment cost.

4.3 The MF process

A microfiltration (MF) membrane separation process will be developed to remove 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. For this scope, a fully automated laboratory pilot MF unit, designed and constructed in-house at CERTH, will be used, testing different commercially available tubular ceramic membranes of nominal pore sizes (e.g., 0.5 to 1 μm), that are stable in a hot, pressurized bio-oil feed. A schematic diagram and images of the pilot unit are included in Fig. 4-3a and b-d, respectively. The system is comprised of the following main components: the MF membrane module (Fig. 4-3c), the feed pump (Fig. 4-3d), the feed tank (Fig. 4-3d), the balance for measuring permeate flow, as well as the measuring/recording and control instruments (Fig. 4-3b). Experiments will be conducted in the cross-flow mode at different temperatures ranges (based on the FP and the primary water recovery process, i.e., 35-45 °C) and at different trans-membrane pressures (e.g., varying from 0.5 to 2 bar). The concentrate of the membrane filtration is recycled back to the feed tank, whereas the membrane permeate is collected in a beaker (permeate tank) through a manual three-way valve. The volumetric flow rate of the permeate is determined by measuring the mass flow with the electronic balance, connected to a PC (by means of GeniDAQ software). 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. 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.

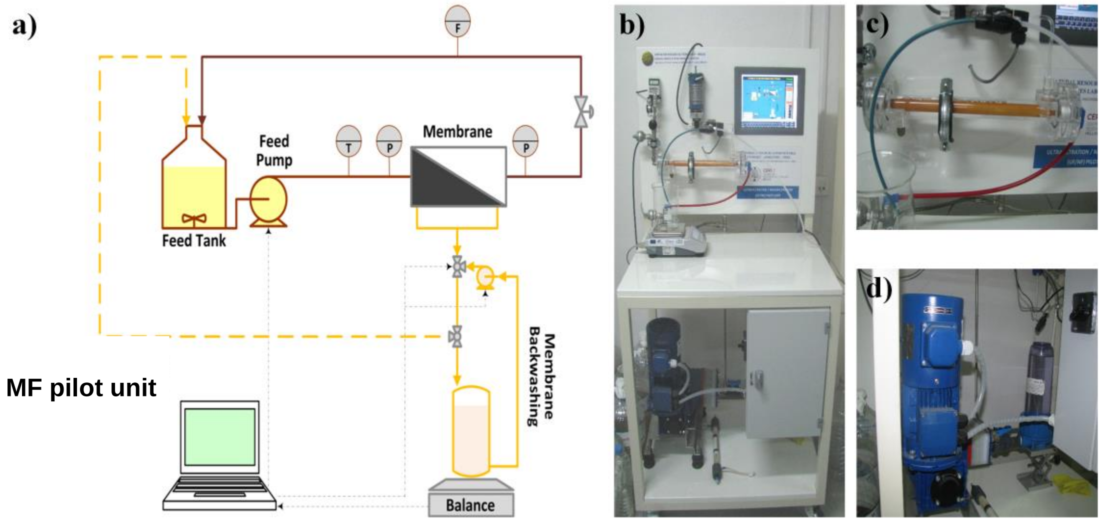


Fig. 4-3: (a) Schematic diagram of the experimental set-up, (b) front view of the MF pilot scale system, (c) membrane module and (d) feed pump and feed/recirculation tank

As already mentioned earlier, the water included in the bio-oil is a critical parameter. Notably, it affects the passage of the bio-oil through the small pores of the hydrophobic MF 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 that has been pointed out as the main phenomena responsible of phase separation, especially with hydrophobic membranes. The optimum water content and viscosity for an effective microfiltration of bio-oil depends 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), since these can have an impact on membrane fouling and to the permeation of bio-oil through the membrane.

In order to define the threshold values of bio-oil water content and viscosity for microfiltration experiments one or more blends reproducing viscosity and water content of a real bio-oil will be used, since, according to the current WP3 planning, the first sample of bio-oil will be available at the end of 2021. The liquid blends will be mixed with a proper amount of solid particles; e.g., activated carbon with a pre-defined/well-known particle size distribution. A literature survey is underway for the identification of the proper surrogate and more details. Decision on the specific grade(s) to be used will be provided/made in the framework of WP3/Task 3.1 and relevant information will be included in deliverable D3.1. Moreover, the results of these preliminary tests will be used in WP3 to define to which extent it is needed to operate a fractionated condensation directly at the exit of the Fast Pyrolysis reactor.

5 CONCLUSIONS & NEXT STEPS

Following a first analysis of main specifications and requirements of selected streams derived by the SCWG and FP thermal treatment processes, the basic design attributes of suitable purification/ decontamination methods have been defined. The choice was based on relevant critical literature reviews, analysis of advantages and disadvantages of chosen and other 'competitive' state of the art methods per case as well as a first approach on required adaptation of methods of choise and general protocols to CERESiS needs and peculiarities. More specifically:

- For the removal of H2S from the gaseous product of the SCWG process, a **Membrane Gas Absorption (MGA)** method will be developed by employing hollow fiber polymeric membrane contactors (3M™ Liqui-Cel™) and a short list of solvents which will be assessed experimentally for the, as much as possible, selective capture of H_2S vs. CO_2; namely DEA, MDEA and mixtures of them, amine salts (e.g., potassium glycinate) and mixtures of them with DEA and MDEA as well as aqueous alkali solutions (NaOH, KOH). It is noted that the potential issue of tars presence in the gas stream is open (as of M6 unclear) and will be investigated and adjustments will be carried out, if needed, in the framework of WP3/Tasks 3.1-3.2.
- For the purification/decontamination of the 2 liquid brine streams (here treated as a unified stream for simplification) of the SCWG process with the aim of water recycling back into the reactor, the choice is **a combination of Electro-Coagulation (EC) and Electrochemical Oxidation (EO)**. This combination ensures adsorption and co-precipitation of contained HMs in the form of hydroxides and almost total mineralization of residual organics via their oxidation.
- For the removal of solids/water and recovery of bio-oil derived by the FP process, **a customized Micro-Filtration (MF) process** will be developed. Experiments, at least initially, will be carried out with the aid of synthetic mixtures emulating the relevant FP product composition.

The work reported here is novel in the sense that it contributes substantially to the definition of tangible integrated processes, as envisaged by the technological pillar of CERESiS, converting biomass to clean biofuel/bio-oil and other useful products while ensuring minimization of effluents and associated environmental impact by producing such effluents in a concentrated form and relatively easy/safe to handle way.

The 2nd phase of the work concluded here will be carried out in the framework of WP3/Task 3.1 (primarily) and also the other Tasks of WP3 (secondarily). The preliminary requirements, specifications, setups and protocols will be further elaborated upon and specified to ensure that launching of experimental campaigns will be carried out in an optimized manner right from the beginning of the main phase of associated experimental campaigns. Specific next steps for the completion of the work initiated by WP1/Task 1.2 and reported here include:

- More accurate definition of streams/mixtures simulating the products of interest in terms of decontamination/purification derived from the SCWG and FP thermochemical processes. Such definitions could/should be revised appropriately, if needed, as soon as the first experimental results from the SCWG and FP reactors become available.

- Procurement of components, materials, chemicals and adaptation of associated setups for the initiation of the experimental activities related to the 3 main purification/decontamination processes defined here. Revision/re-alignment of certain choices may be necessary as the first experimental outcomes are derived.
- Definition of detailed experimental matrices per case to ensure that an adequate number of experiments will be carried out while at the same time redundant tests or excessive use of resources is avoided. It will be important to design the experiments also considering the expected challenges, already identified here to some extent and further elaborated with the completion of Task 3.1, so that mitigation measures and alternative ways, when/if needed, are discussed and applied in time.
- Formation of a first interface with the process simulation pillar/activity to define the kind of data needed from both sides and assess the possibility for a two-way feedback. This is more applicable to the SCWG and FP processes but the possibility to include the decontamination/ purification processes, in the integrated simulation approaches, should also be considered and discussed in the framework of Task 3.1.

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