CERESiS

ContaminatEd land Remediation through Energy crops for Soil improvement to liquid biofuel Strategies

Advanced membrane and electrochemical decontamination technologies

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23.04.2024

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

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This project has received funding from the Brazilian Fundação de Amparo à Pesquisa do Estado de Goiás under grant number 202110267000220

Fonds Nouvelles frontières en recherche / New Frontiers in Research Fund
Fonds de recherche Société et culture Québec
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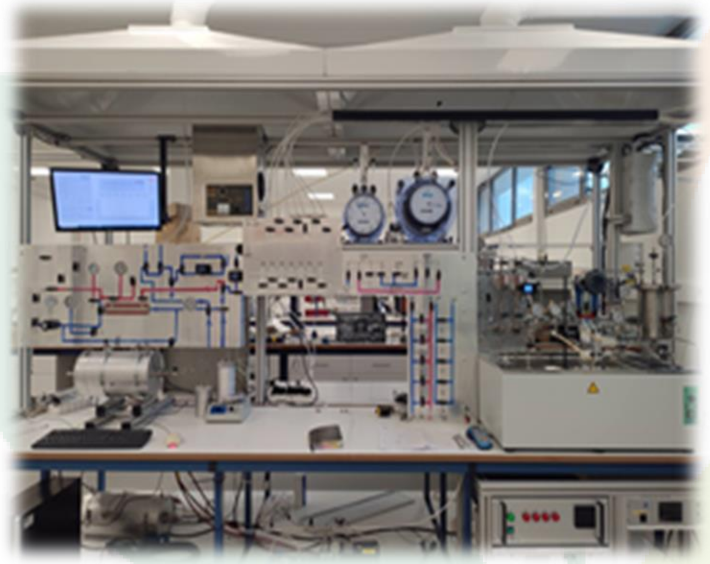
SCWG process



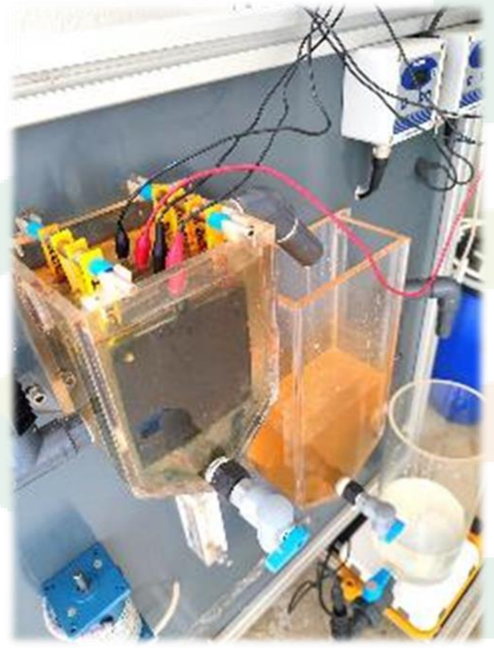
Desulphurization by Membrane Gas Adsorption (MGA)

HC reforming

Supercritical Water Gasification (SCWG)

Tar removal

FT synthesis



Electrochemical decontamination of saline wastewater by Electrocoagulation Flotation (ECF) and Electro-oxidation (EO)

FP process

Mild combustion

Feedstock pretreatment

Fast Pyrolysis (FP)

Water recovery

Char particles separation by membrane Microfiltration (MF)

Adsorption studies / heavy metal immobilization in the soil

Bio-oil upgrading and refining

Feedstock
Liquids
Solids
Gases

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Electrochemical decontamination of SCWG saline wastewater

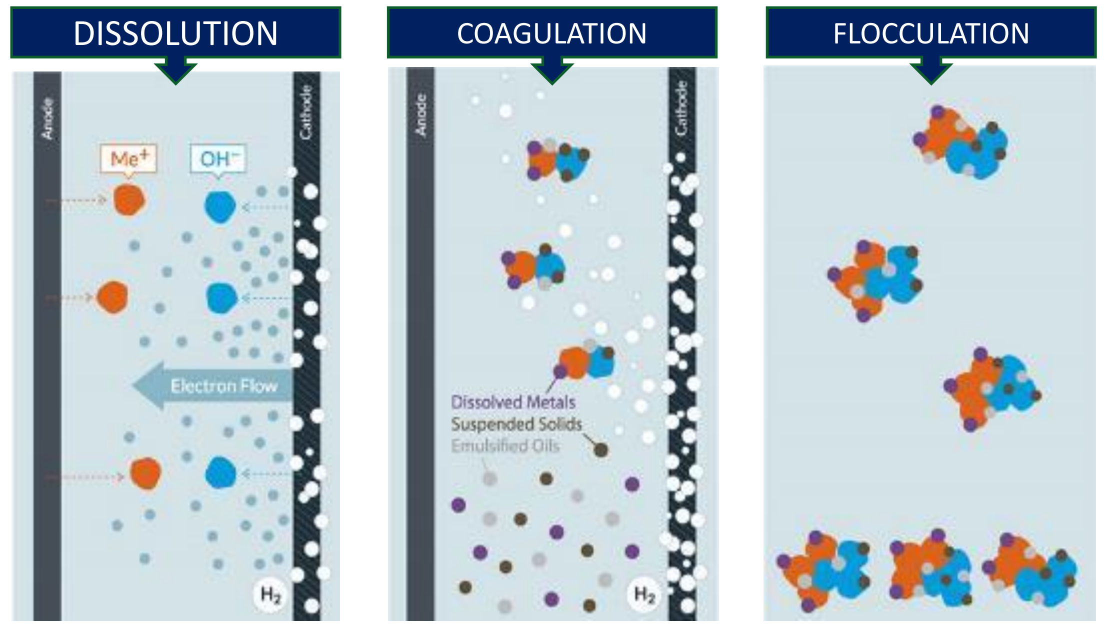
Development of a ***hybrid ECF –EO*** process for effective removal of organics and heavy metals (HMs) from SCWG brine / wastewater

CHALLENGE

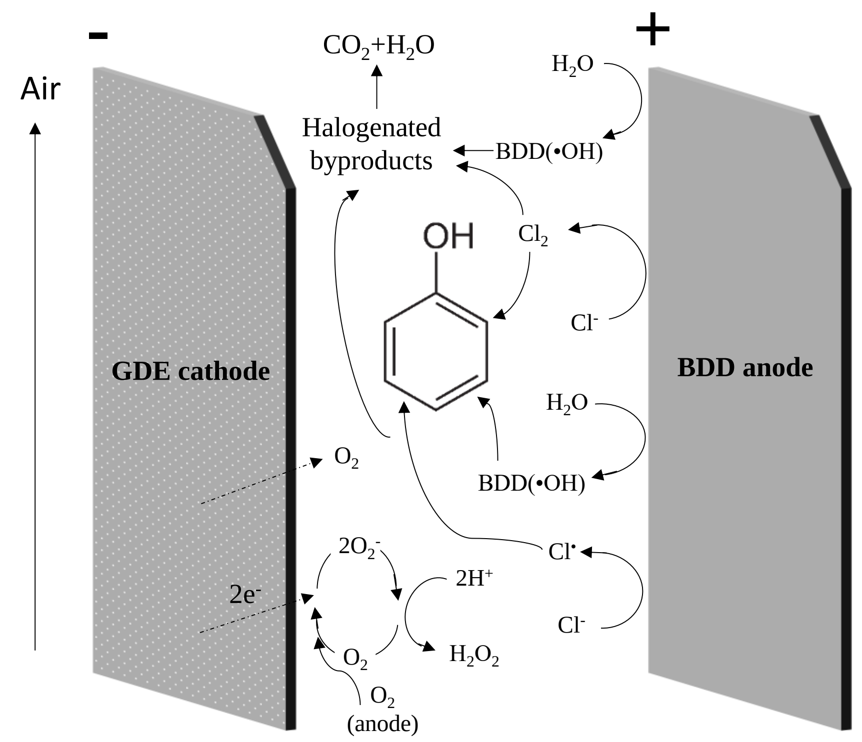
Effectively remove organic and inorganic pollutants with ***fast kinetics***, ***no use of chemicals*** and ***reduced energy consumption***

- ❖ Design and construction in-house of a novel ECF lab pilot unit
- ❖ Upgrade of an EO bench-scale unit for anodic oxidation (AO) studies
- ❖ Validation of the ECF and EO processes in laboratory environment (simulated SCWG saline wastewater) (TRL 4)
- ❖ Validation of the hybrid ECF / EO process in relevant environment (TRL 5) (real SCWG saline wastewater)

Principle of Electrocoagulation-Flotation (ECF)

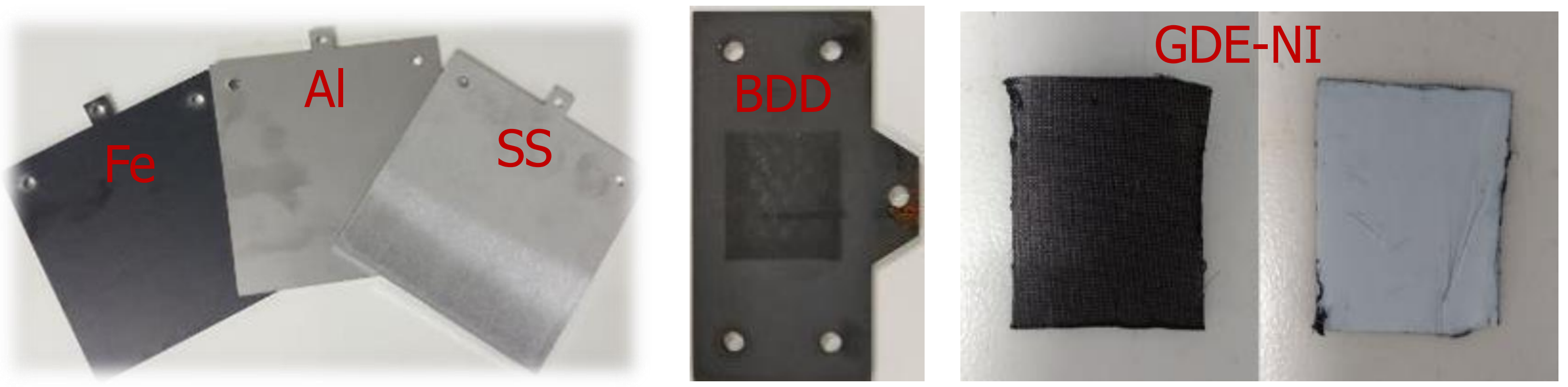


Principle of Electrochemical Oxidation (EO)

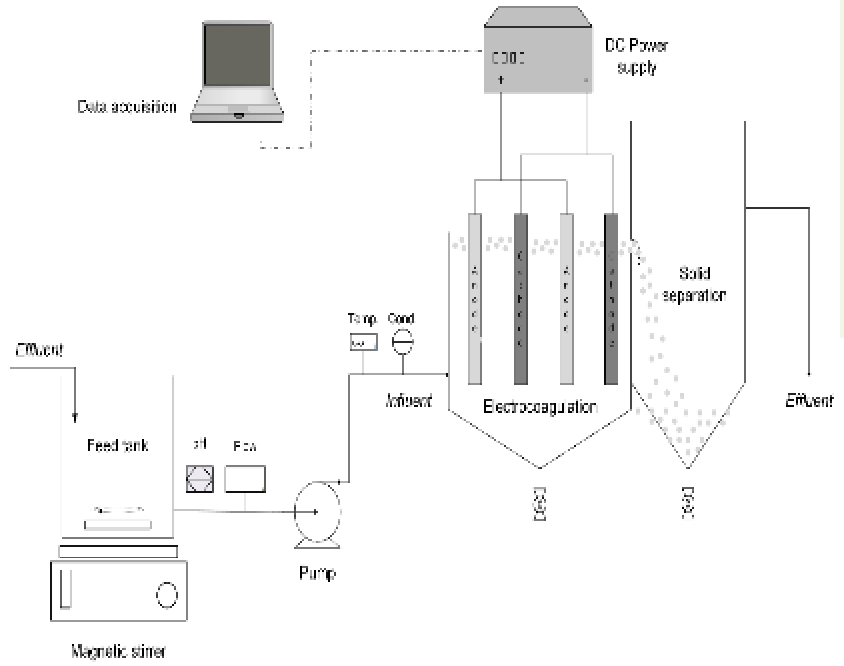


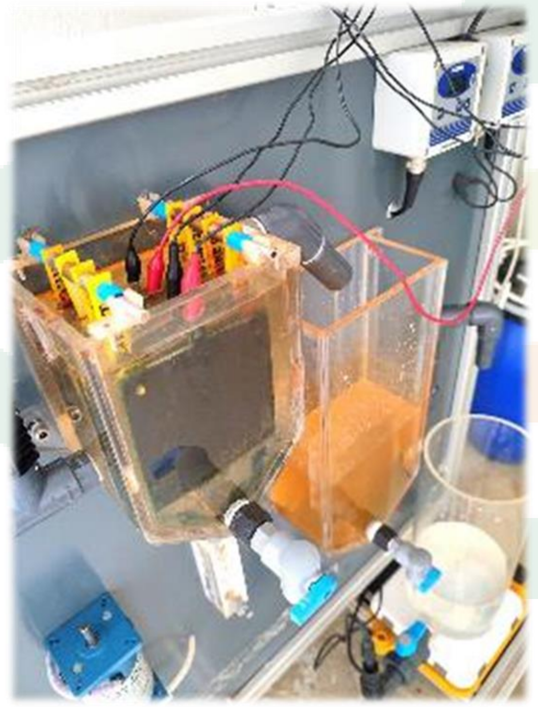
Electrochemical decontamination of SCWG saline wastewater

Experimental

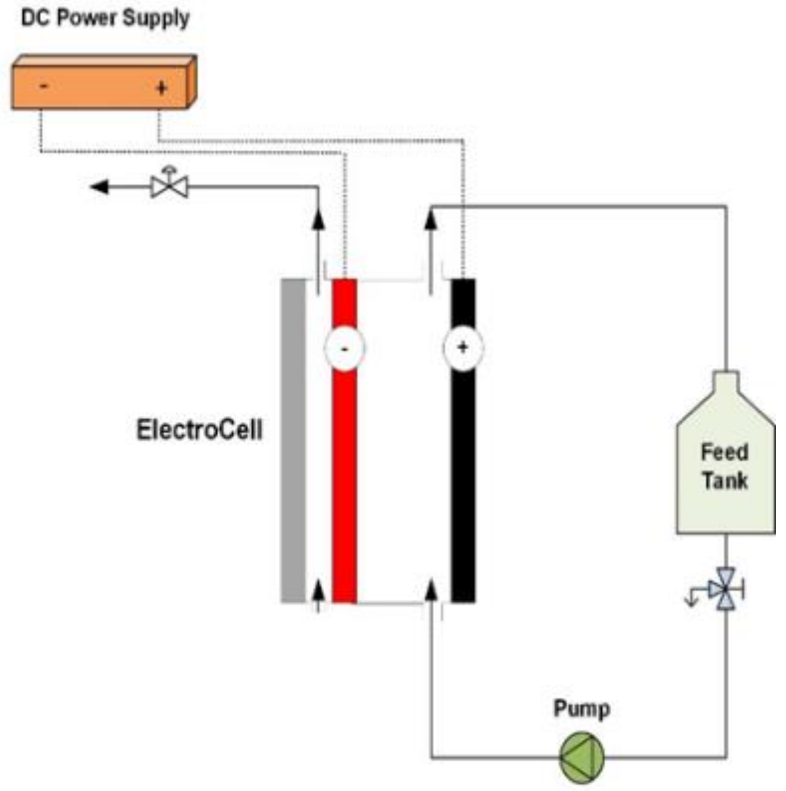


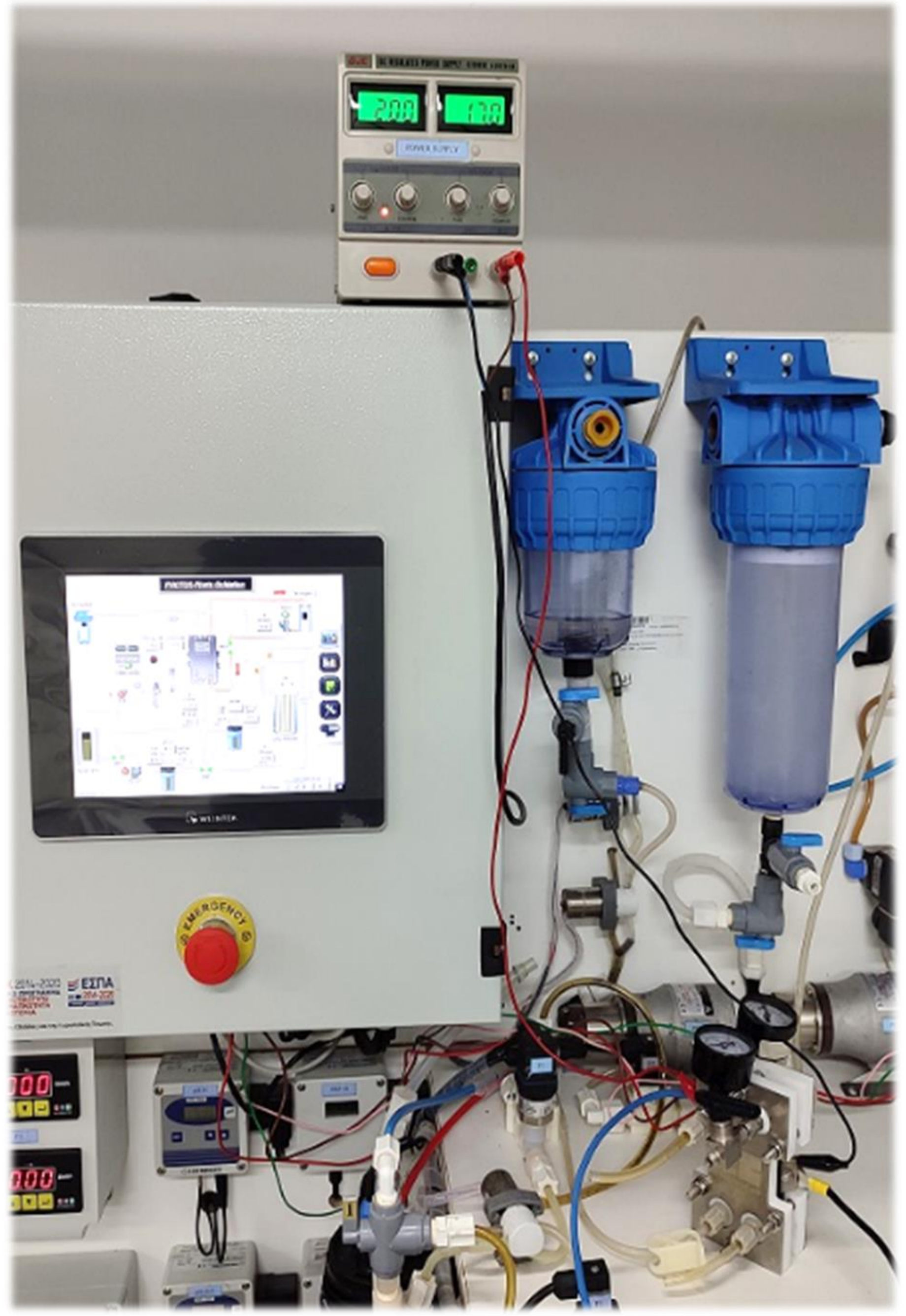
ECF laboratory pilot setup





EO bench-scale setup





Electrodes

- ECF: Fe, Al, SS
- EO: Anode (+): Boron-doped diamond (BDD) (Electro Cell) ; Cathode (-): GDE-Ni (Gaskatel) or SS

Feed solutions

- Synthetic ECF: $Pb(NO_3)_2$, K_2CO_3, KCl in DI water
- Synthetic EO: Phenol, K_2CO_3, KCl in DI water
- Real SCWG brine: Concentrated salt solution supplied by KIT [COD: 2775 mg/L, TSS: 79 mg/L, K: 863 mg/L, Cl: 28 mg/L, Phenol: 411 mg/L, eC: 3.32 mS/cm, pH: 8.6]

Electrochemical decontamination of SCWG saline wastewater

Results

ECF optimization – Removal of Pb^{2+} ions

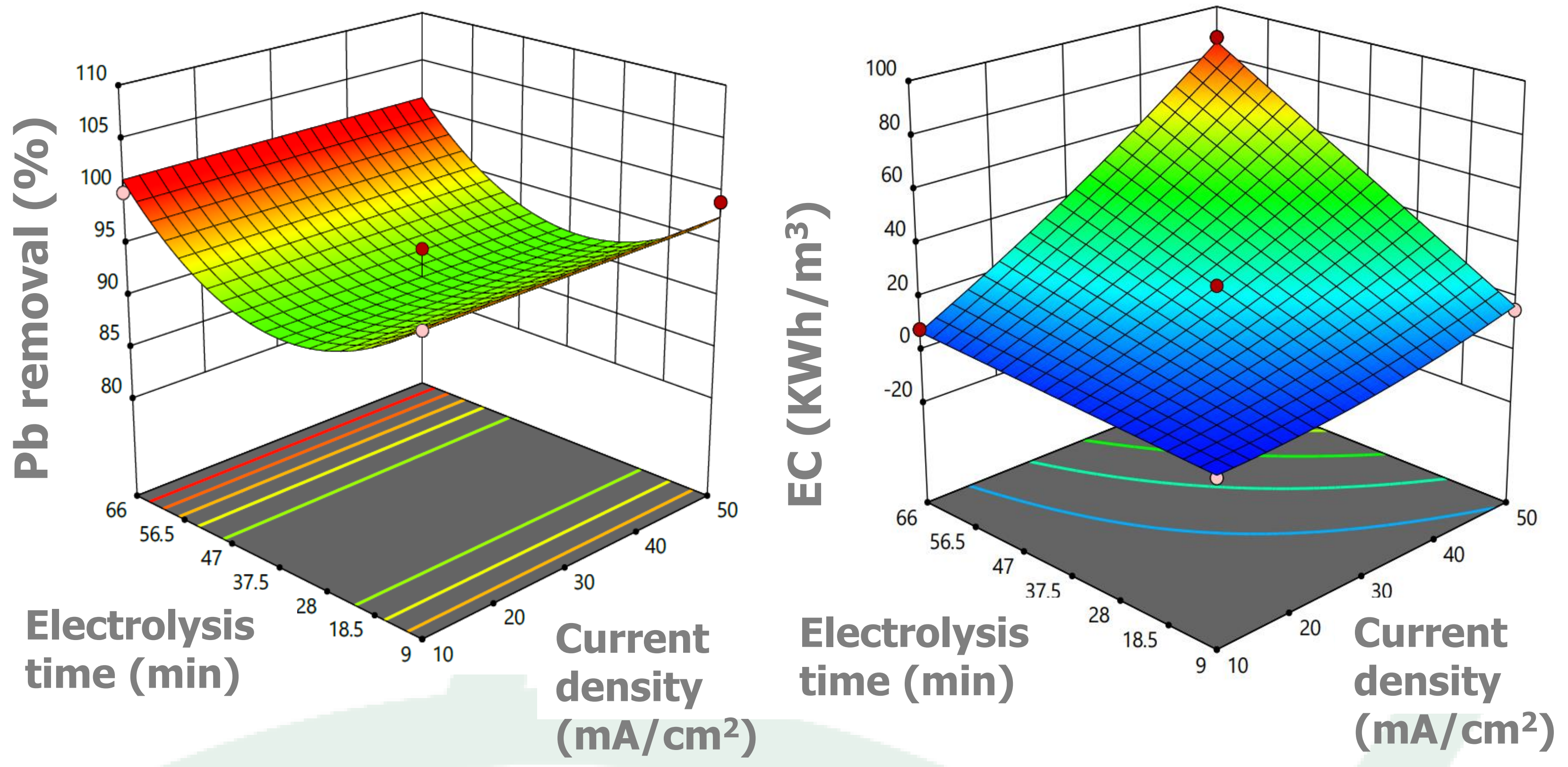


Figure: Pb removal and Energy Consumption (EC) versus current density (CD) and electrolysis time (ET)

EO optimization – Removal of phenol

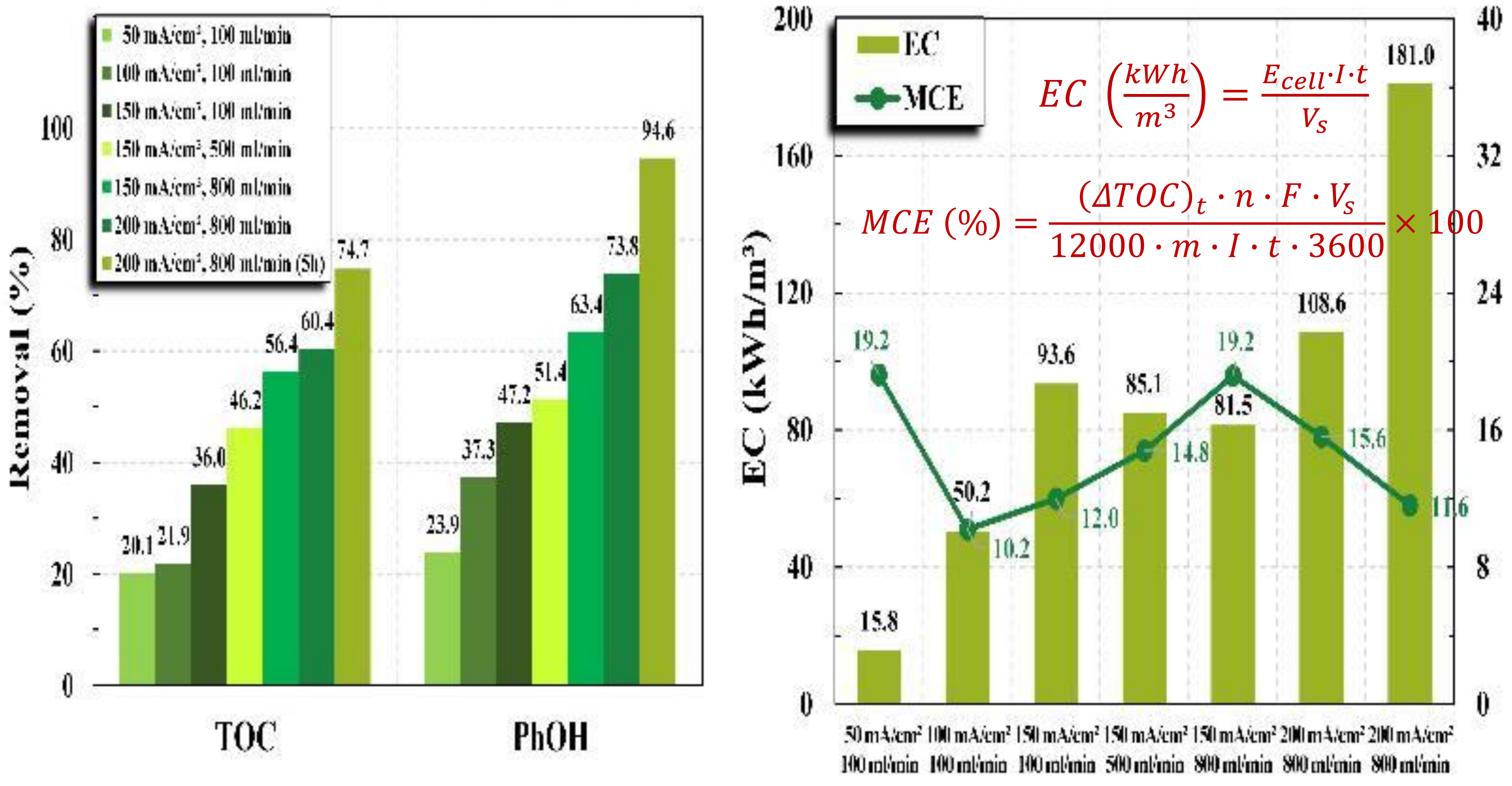


Figure: Percentage removal of TOC and PhOH concentration, energy consumption and mineralization current efficiency

ECF/EO optimization – Real SCWG brine

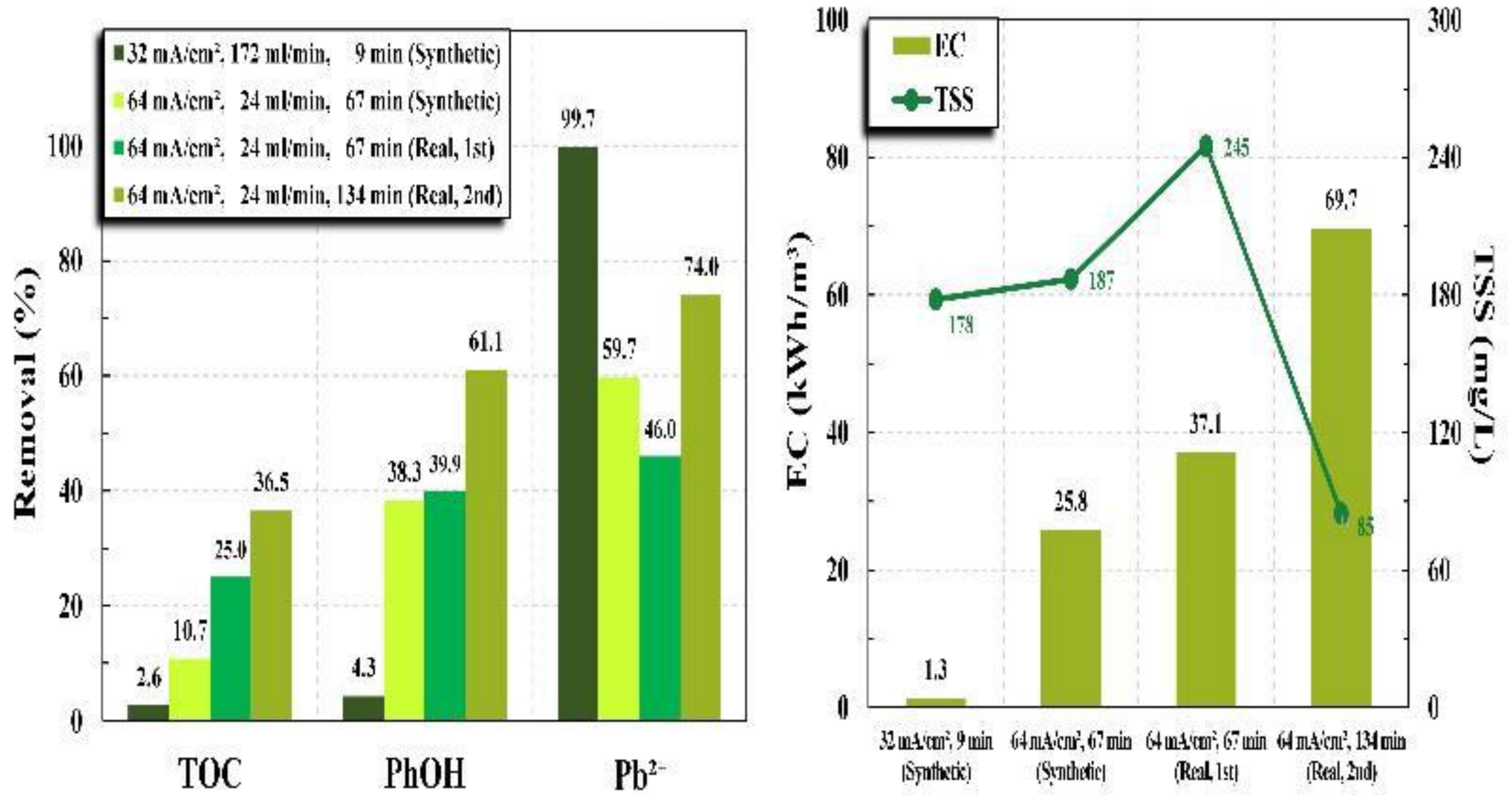


Figure: Percentage removal of TOC, PhOH and Pb concentration, energy consumption and TSS concentration

Correlation models

Pb%= 90.681 – 0.63*ET + 1.19*pH + 0.0092*ET^2

EC= 22.64 + 22.30*CD + 18.59*ET + 1.86*pH + 15.91*CD*ET + 1.23*CD*pH + 3.48*CD^2

First order kinetic constants

Phenol: k_1= 79.7x10^{-4} min^{-1} ; R^2=0.932

TOC: k_1= 49.2x10^{-4} min^{-1} ; R^2=0.983

First order kinetic constants

Phenol (synthetic): k_1= 24.5x10^{-4} min^{-1} ; R^2=0.944

Phenol (real): k_1= 43.1x10^{-4} min^{-1} ; R^2=0.921

Electrochemical decontamination of SCWG saline wastewater

Main conclusions

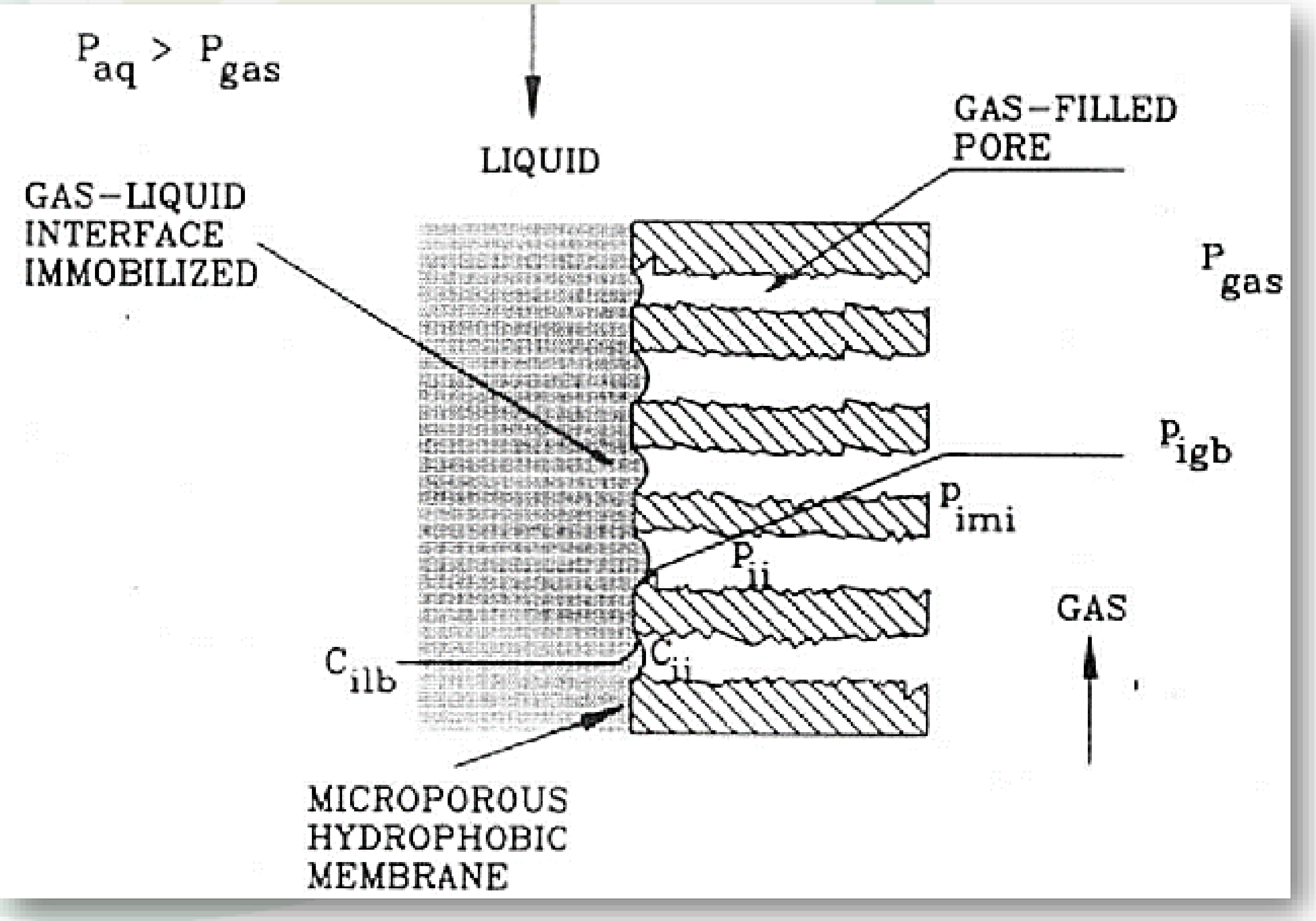
- ❖ Pb ions can be effectively removed by ECF, using Fe sacrificed electrodes, at low current densities (10 mA/cm^2) and electrolysis times (9 min), at basic pH (10), with a rather minimum energy consumption

- ❖ 75% TOC and almost complete (~ 95%) phenol removal are achieved by the BDD anodic oxidation of simulated SCWG brines, under near-optimal experimental conditions, i.e. a current density of 200 mA/cm^2, recirculation flow rate of 800 mL/min and treatment time of 5 hours

- ❖ The combination of ECF and EO processes in a single setup with 2 pairs of metal electrodes (BDD/SS and Fe/Fe) proved to be very efficient for the combined removal of phenol (37%), TOC (61%), Pb and Ni ions (approx. 75%) under optimum operating conditions

Development of MGA process for SCWG gaseous product upgrade

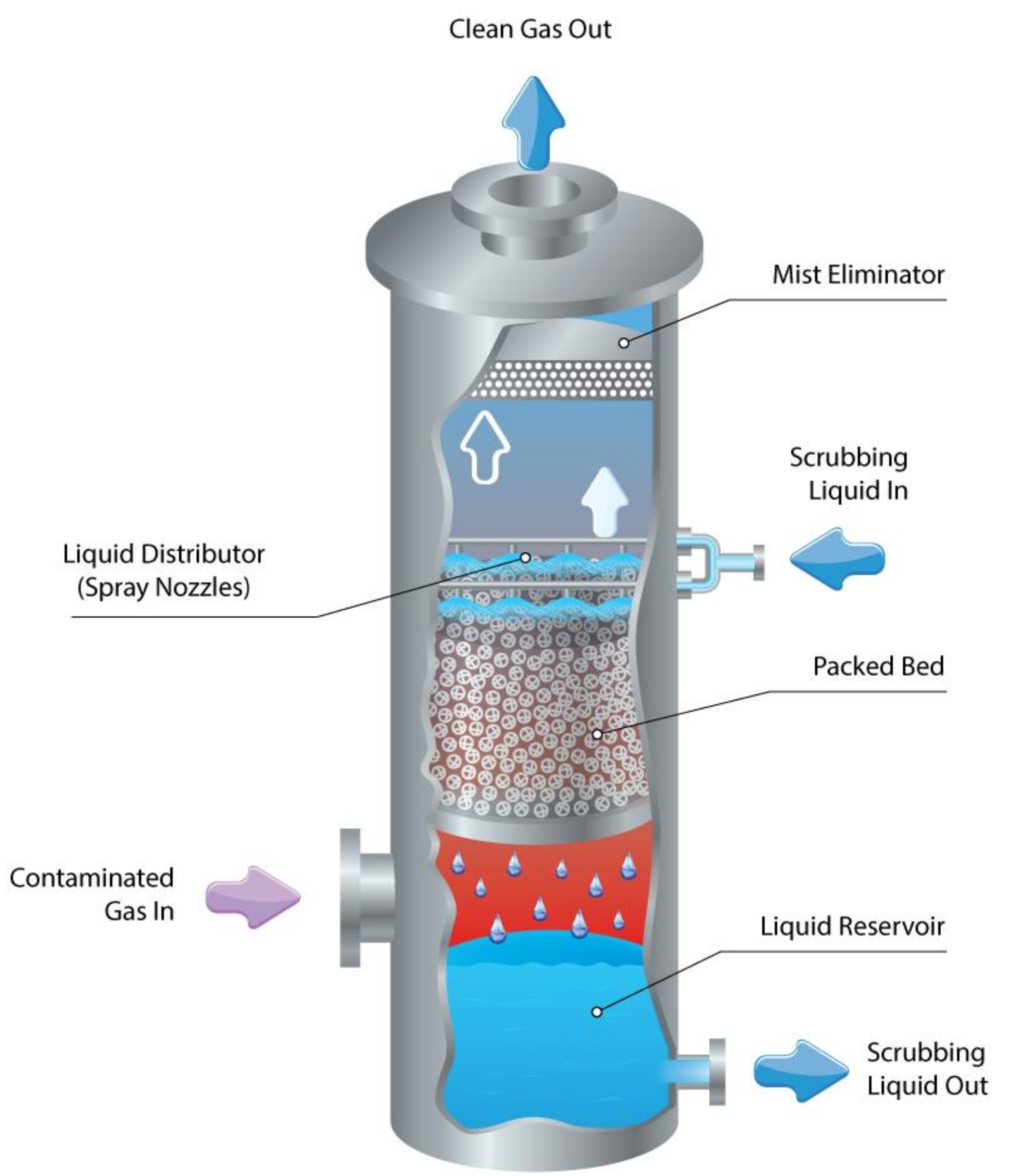
Membrane Gas Absorption (MGA) is a hybrid method that combines the advantages of membrane technology with that of conventional absorption processes by using microporous membranes instead of packing materials to provide the gas-liquid contact area.



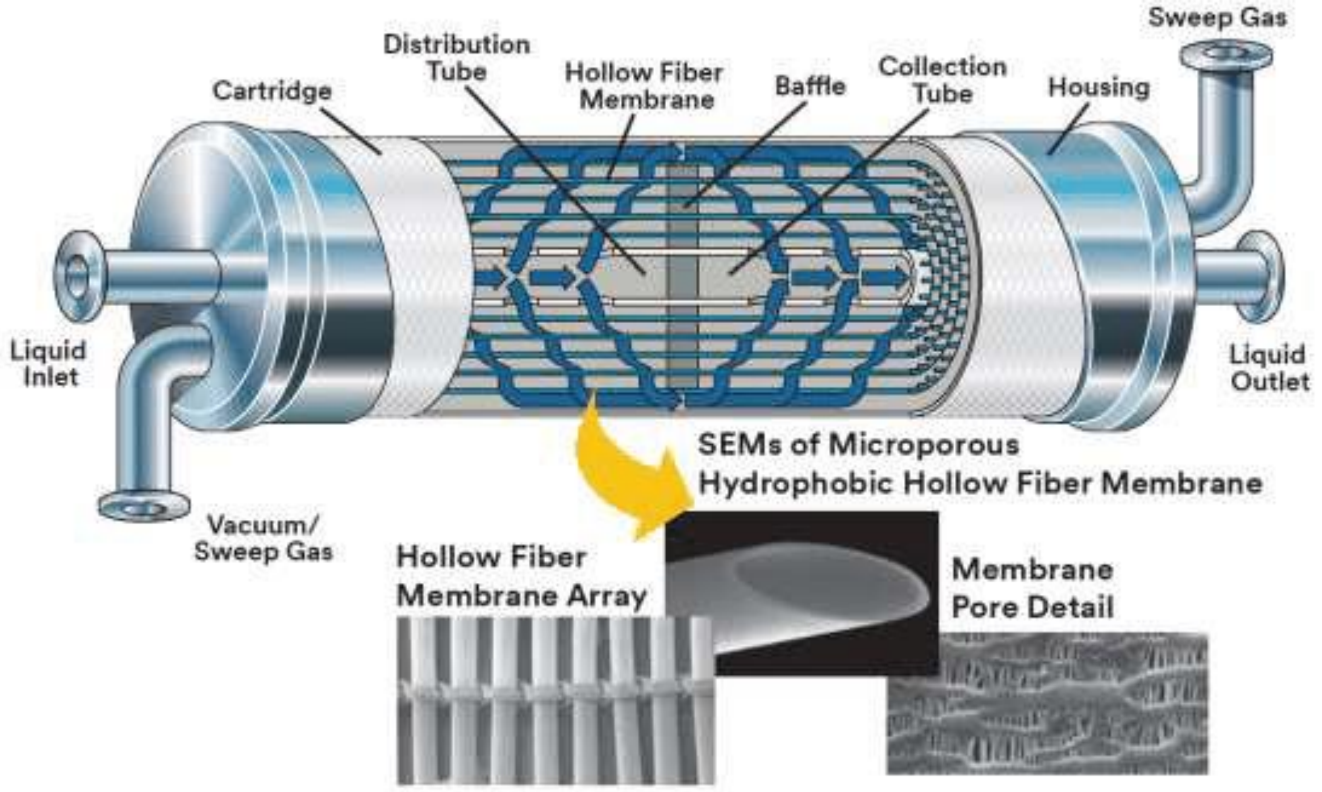
- Flows at the two sides of the membrane
- Hydrophobic membrane – Gas filled pores
- No dispersion of one phase in the other
- An immobilized gas-liquid interface is created at the pores mouth where reaction and/or absorption takes place
- Very high and well-defined surface areas can be obtained

Development of MGA process for SCWG gaseous product upgrade

Packed columns vs Membrane Contactors

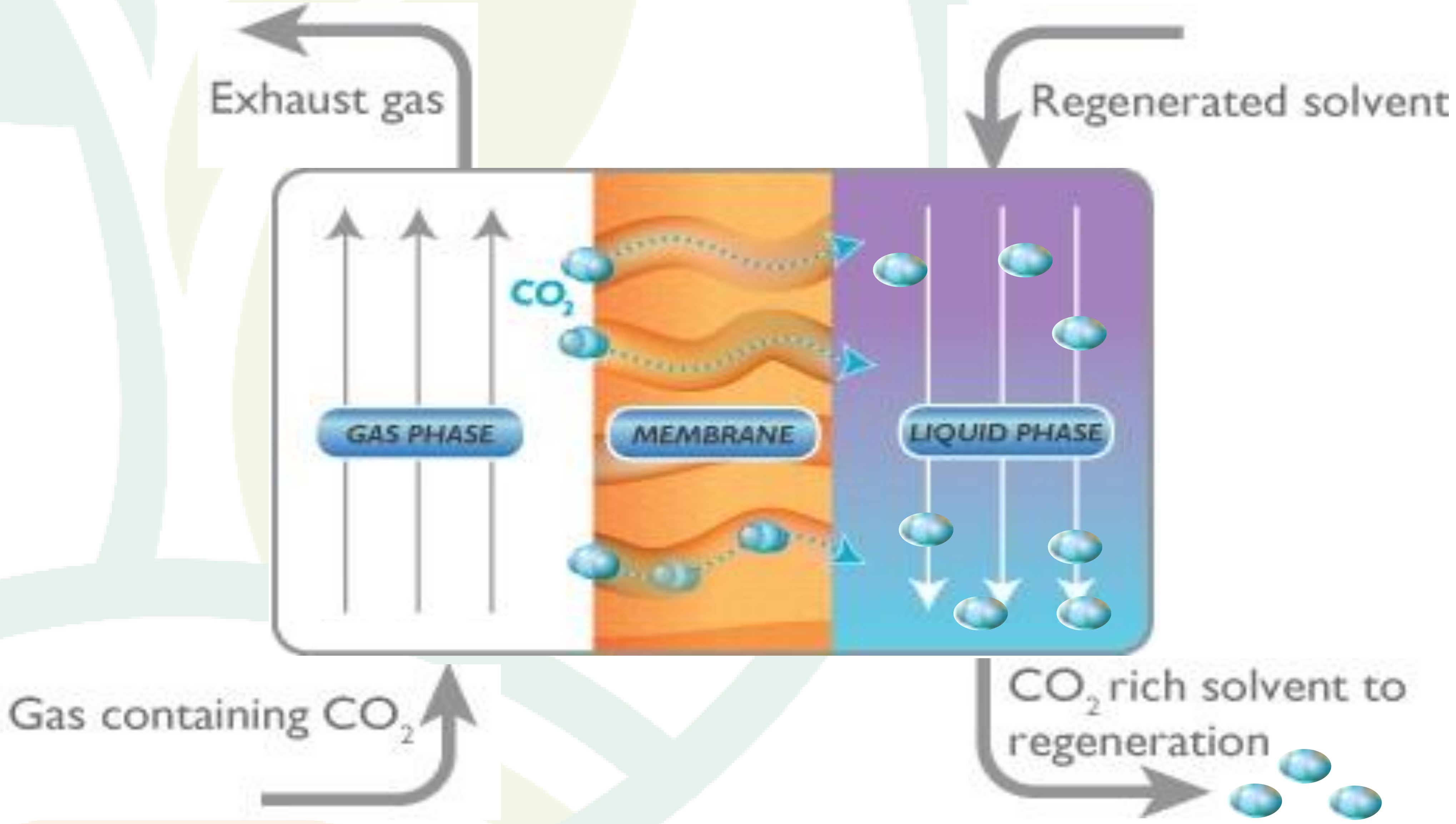


Packed columns		Membrane contactors	
Pros	**Cons**	**Pros**	**Cons**
Established process	Solvent foaming	High specific contact area	Membrane wetting
Different solvents can be used depending on the purification targets	Column flooding	Compact and modular design	Membrane stability
	Voluminous equipment	No foaming & flooding	
	Solvent losses, mainly during regeneration	Simple operation	
		Modular scale-up	



Development of MGA process for SCWG gaseous product upgrade

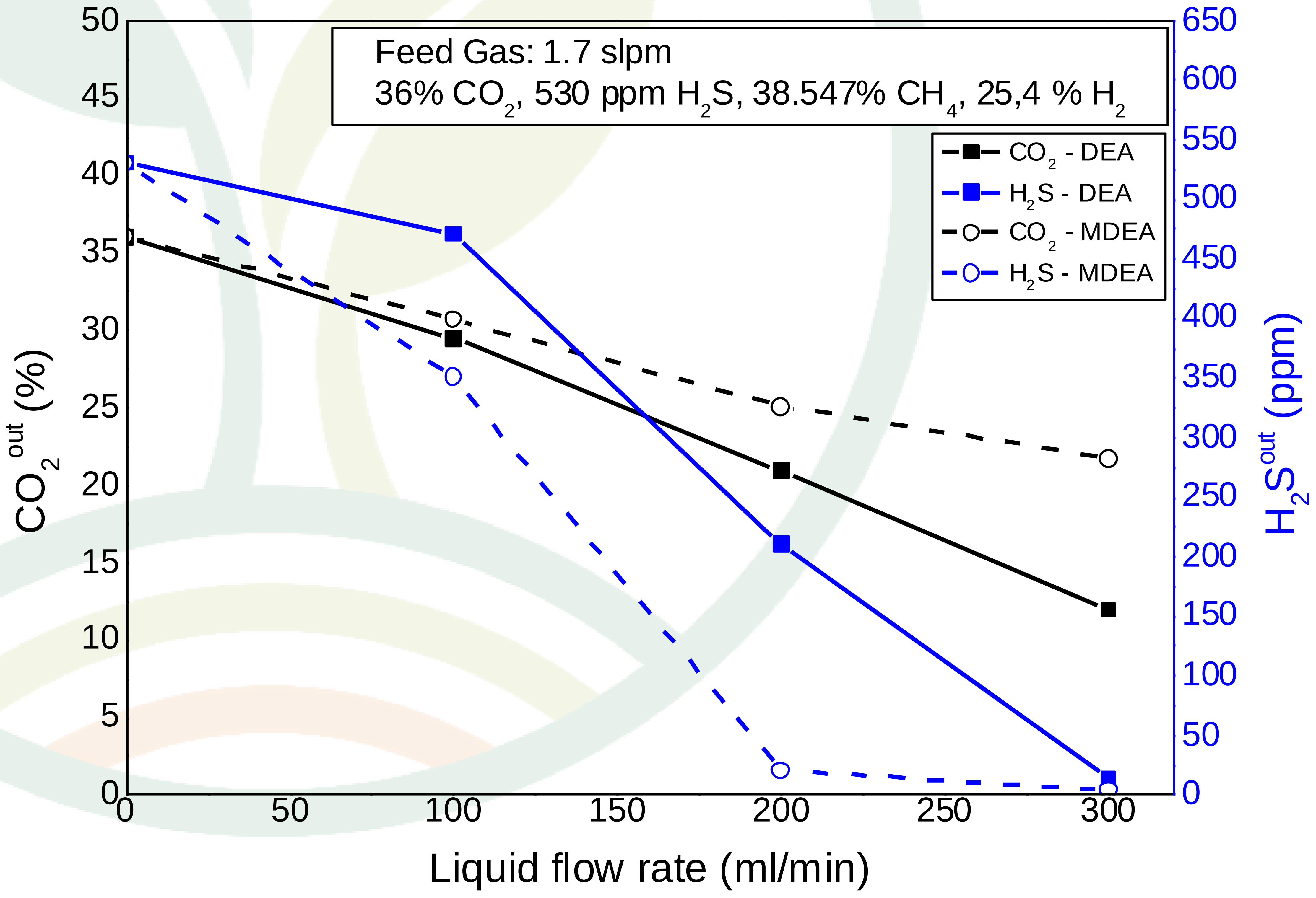
MAIN OPERATING PARAMETERS

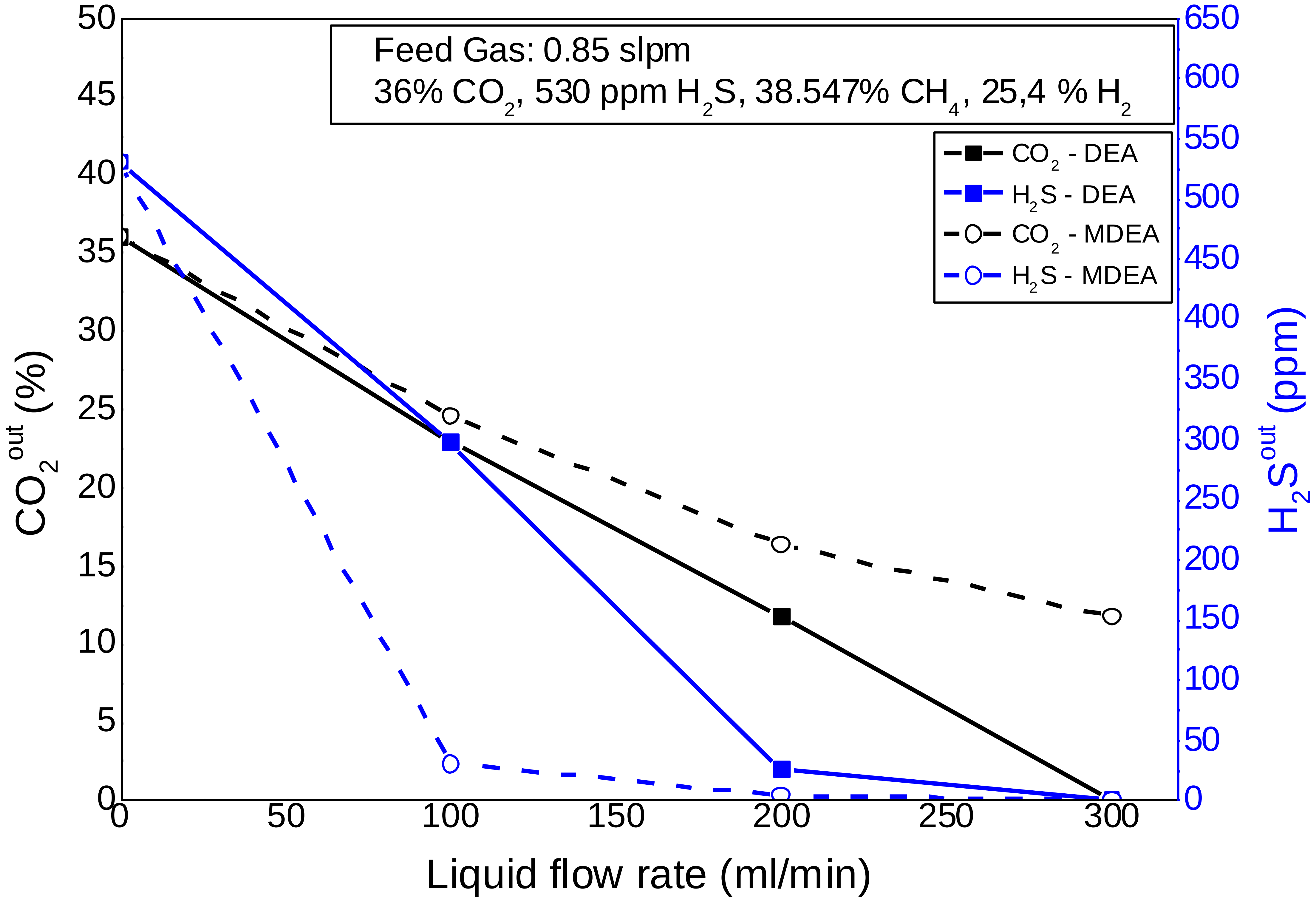


- Feed gas flow per membrane area
- G/L ratio
- Solvent type and concentration
- Operation mode

Development of MGA process for SCWG gaseous product upgrade

RESULTS – PROCESS PARAMETRIZATION

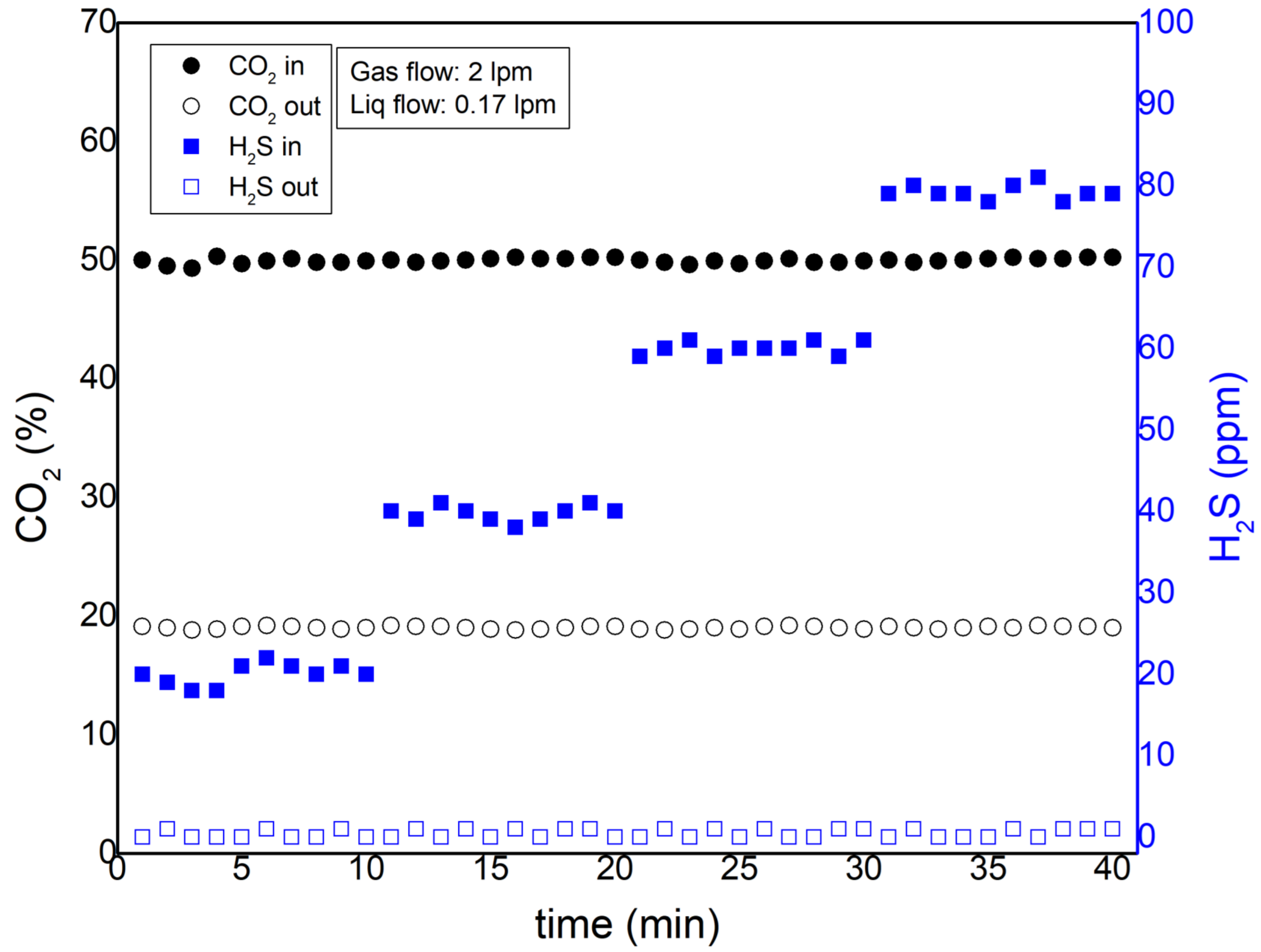


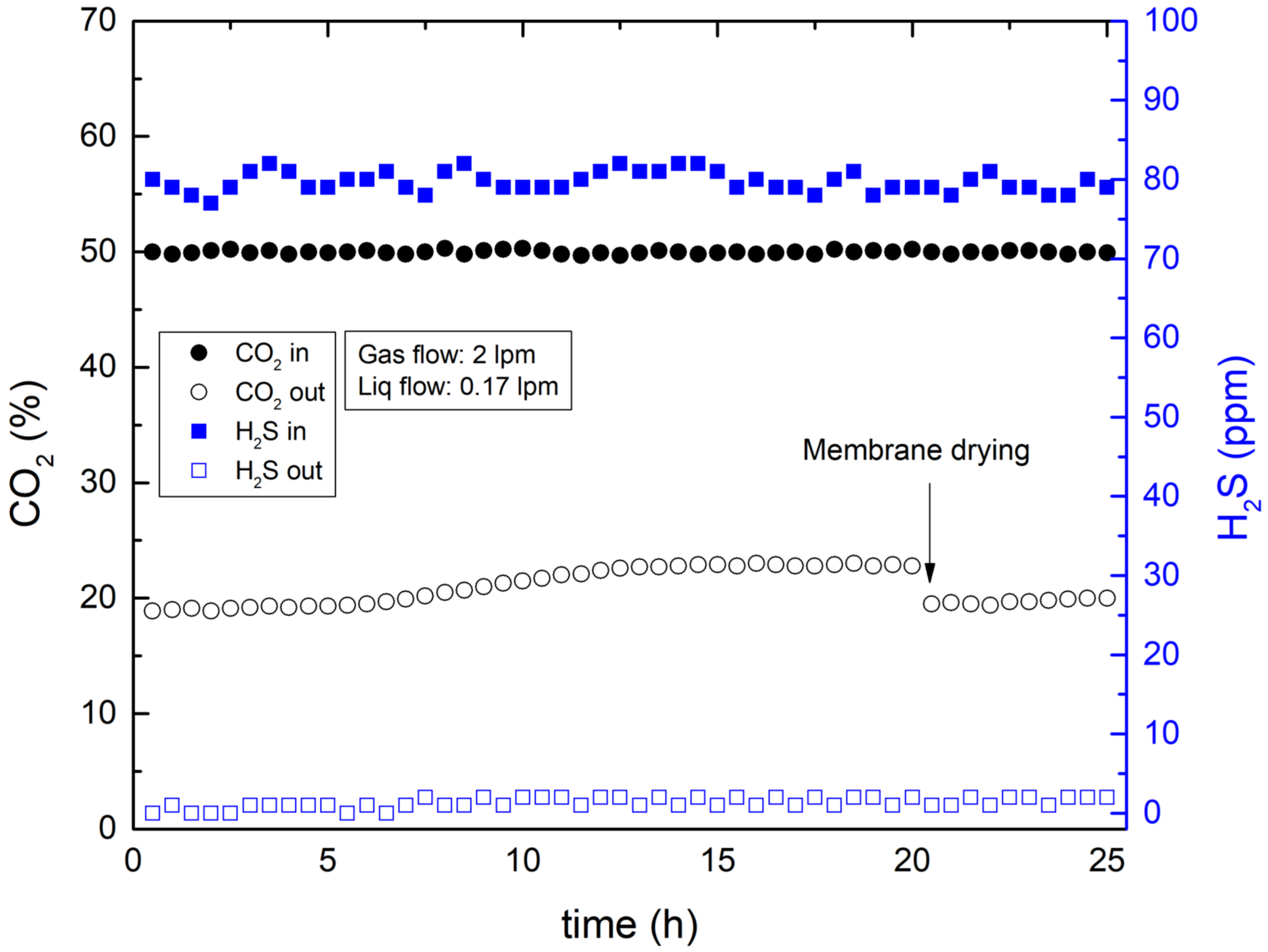


Development of MGA process for SCWG gaseous product upgrade

RESULTS – TESTS AT APPLICATION RELEVANT ENVIRONMENT

CO_2: 50%, CH_4: 20%, H_2S: 20-80 ppm, H_2: Balance (~30%)





Development of MGA process for SCWG gaseous product upgrade

Main conclusions

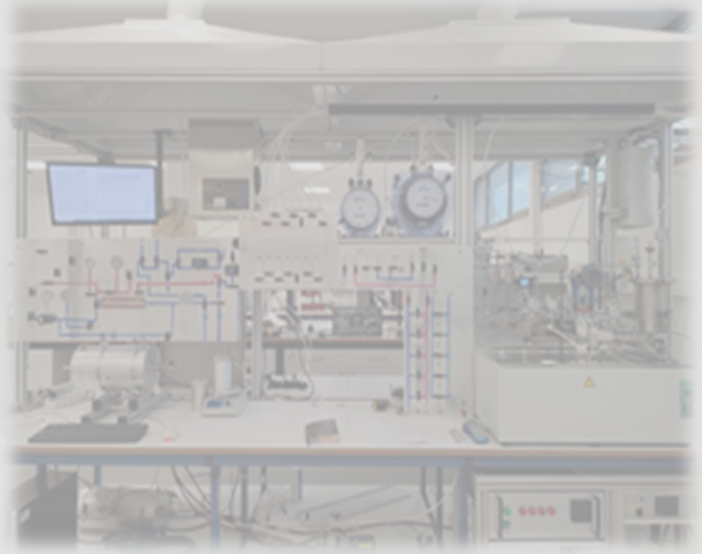
❖ A highly efficient and flexible process was designed and developed.

❖ MDEA and high gas flow rates favor selective H_2S removal, while DEA and lower gas flow rates favor combined H_2S and CO_2 removal.

❖ Process conditions for deep H_2S and moderate CO_2 removal were identified and demonstrated at application relevant environment.

❖ In any case almost 100% of CH_4 and H_2 recovery was achieved in treated gas.

SCWG process



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Feedstock | Liquids | Solids | Gases

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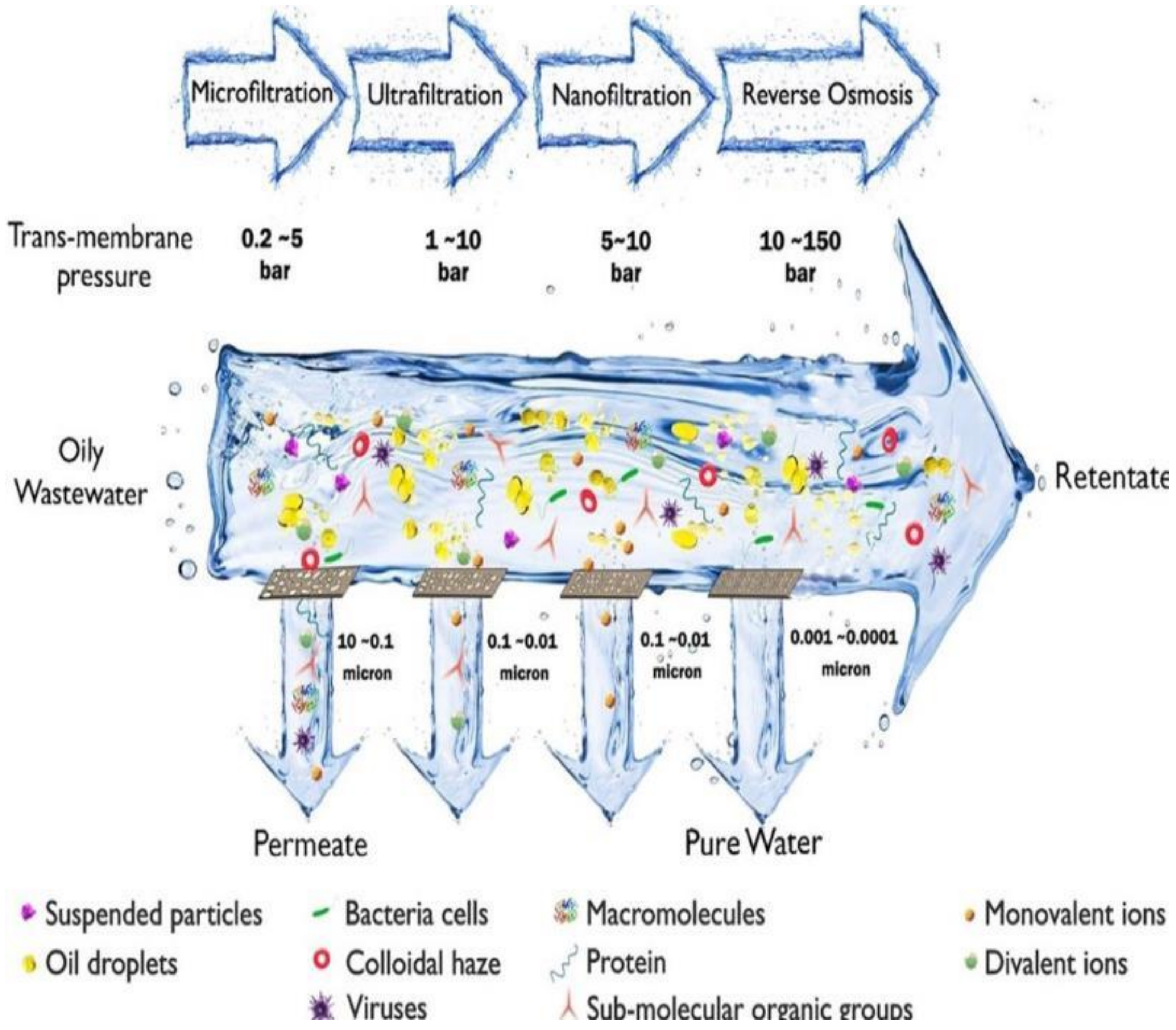
Microfiltration of Fast Pyrolysis Bio-oil

Effectively ***remove undesirable heavy metal-laden char particles*** (less than 1 micron in size) from bio-oils by ceramic MF

CHALLENGE

Understand, quantify and reduce membrane fouling when dealing with highly viscous liquid streams – water/oil emulsions



- ❖ Design and construct in-house a ceramic membrane MF lab pilot unit
- ❖ Water permeability tests with different commercial ceramic modules at different crossflow velocities and trans-membrane pressure (TMP)
- ❖ Preliminary experiments with synthetic mixtures of glycerol/water/PAC emulating the relevant bio-oil properties
- ❖ Tests with real bio-oil produced by STEMS-CNR, Italy

Microfiltration of Fast Pyrolysis Bio-oil

Experimental

MF laboratory pilot setup

Membranes

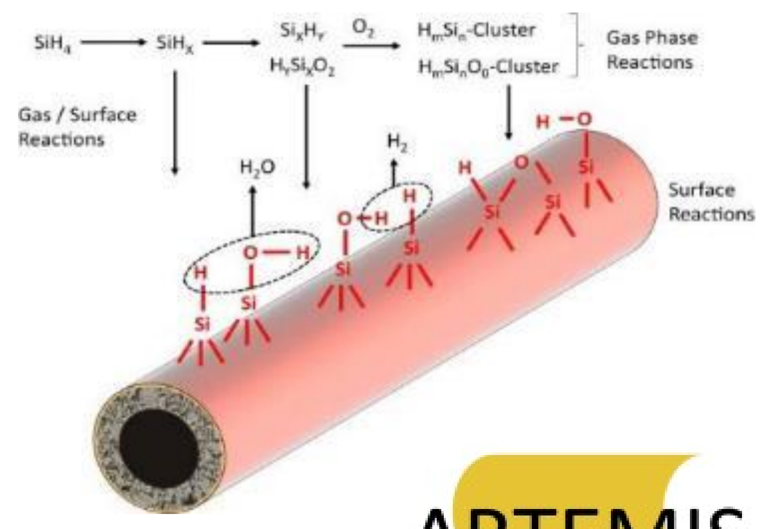
atech innovations gmbh

国初科技 GUOCHU TECHNOLOGY

Eight (8) ceramic modules
- ❖ Al_2O_3 support
- ❖ Active layer: Al_2O_3, TiO_2, or ZrO_2)
- ❖ Number of channels: 1, 7, & 19
- ❖ Filtration pore size: 0.01, 0.02, 0.05, 0.2 & 0.8 μm

Hydrophobic modification

In collaboration with ARTEMIS lab, CPERI / CERTH



ARTEMIS

Chemical Vapour Deposition (CVD) technique based on grafting using $C_9H_{22}O_3Si$ (stabilized by 1% ethanol)

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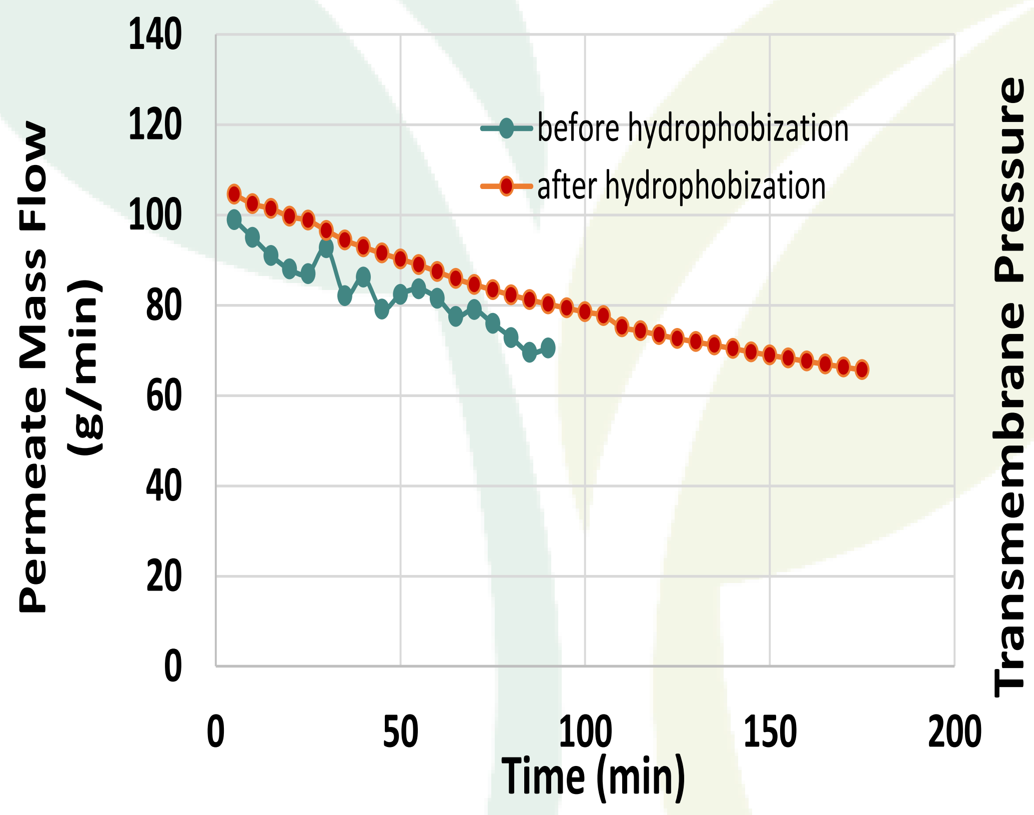
Microfiltration of Fast Pyrolysis Bio-oil

Results

Simulation experiments



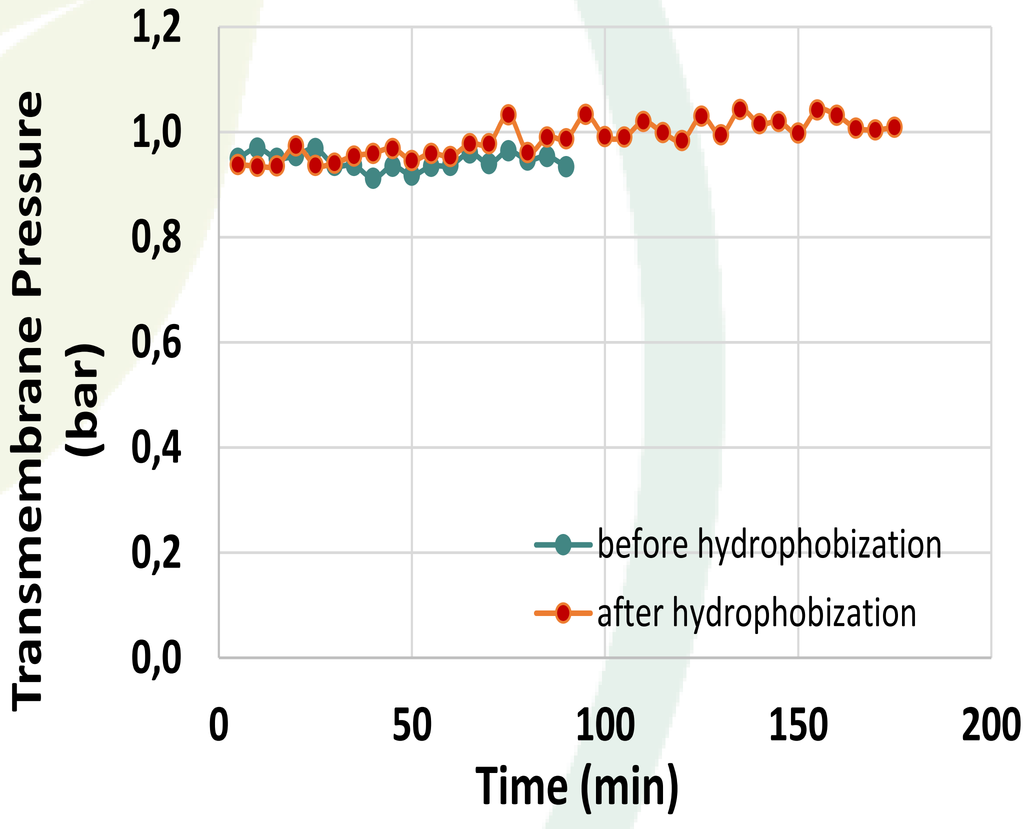


Figure: Glycerol/water solutions (75/25 % w/w); 40 °C, Q_{feed}=30 L/min, P_{feed}=1 bar, Al_2O_3/TiO_2 atech membranes, 19/3.3, 0.8 µm

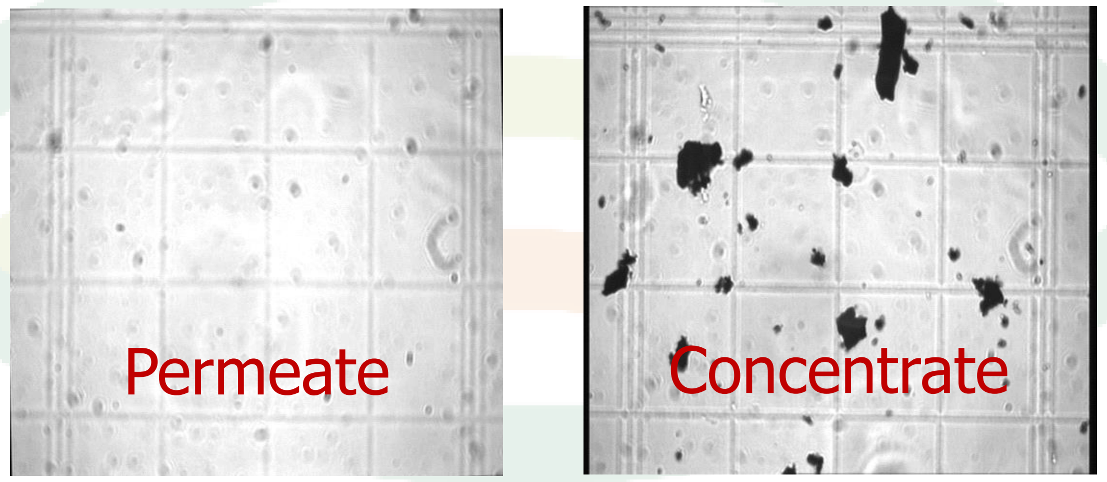
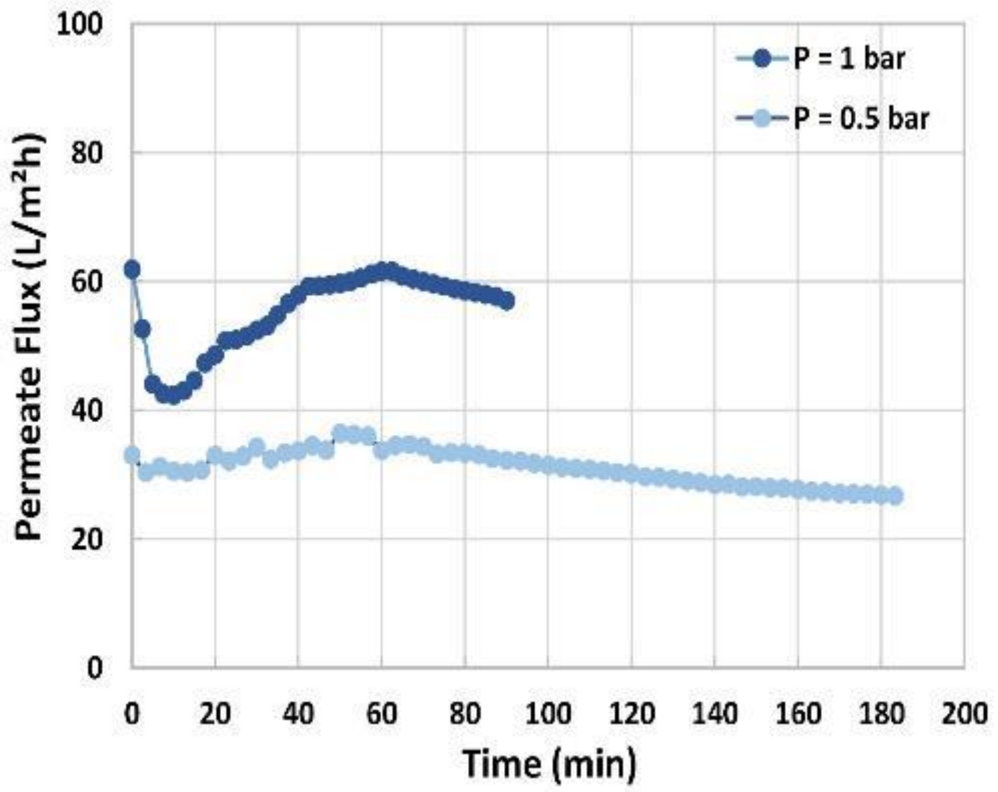


Figure: Microscopic analysis; glycerol/water (75/25 % w/w), 0.5% w/w powdered activated carbon (PAC), 40 °C, Q_{feed}=30 L/min, P_{feed}=1 bar, atech Al_2O_3/TiO_2, 19/3.3, 0.01 µm

Real bio-oil experiments



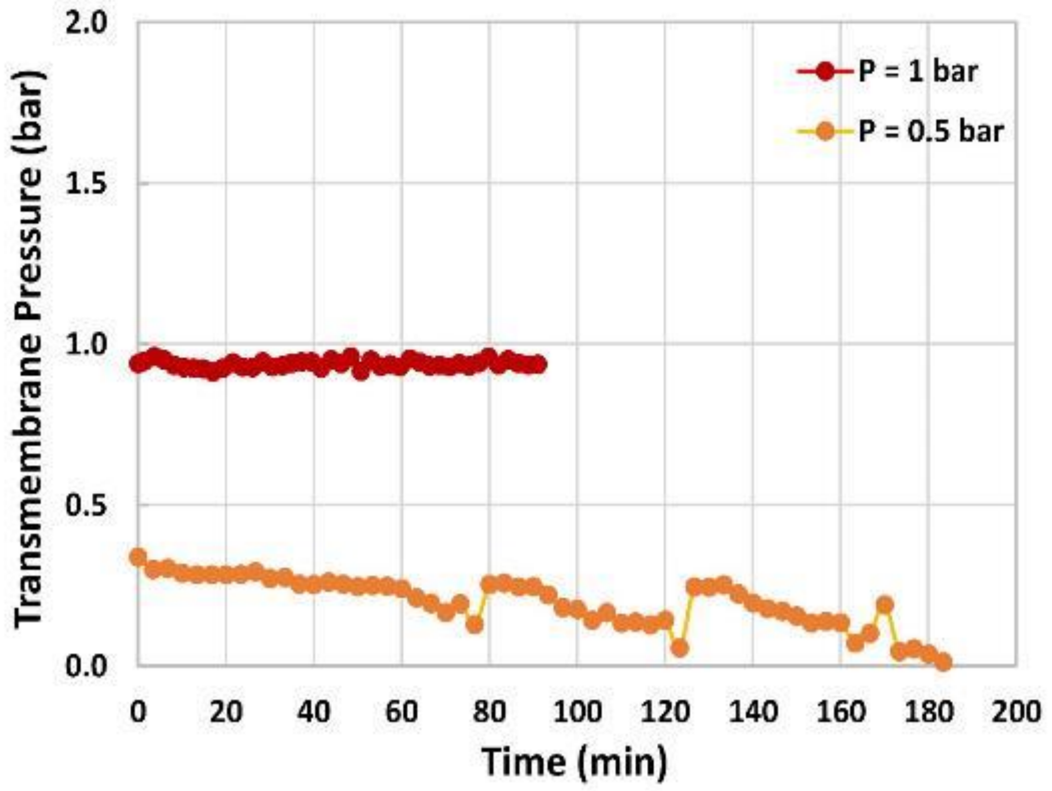


Figure: Experiments with FP bio-oil; 36 °C, Q_{feed}=30 L/min, P_{feed}=1 bar, hydrophobic atech Al_2O_3/TiO_2, 19/3.3, 0.8 µm

Figure: Microscopic analysis; 36 °C, Q_{feed}=30 L/min, P_{feed}=1 bar, hydrophobic atech Al_2O_3/TiO_2, 19/3.3, 0.8 µm

Atech membranes before and after cleaning with NaOH

Microfiltration of Fast Pyrolysis Bio-oil

Main conclusions

- ❖The membrane hydrophobization resulted in a significant decrease of water permeability (👍), with no effect in transmembrane pressure (👍)
- ❖Hydrophobic modification induced a slight improvement of mass flow and decreased water content in permeate and concentrate samples (10-15 wt%)
- ❖No fouling is indicated by the TMP profile during the MF of the FP bio-oil. In any case fouling was reversible!
- ❖Total retention of carbon particles in both simulated (PAC with particle size <149 nm) and real bio-oil samples

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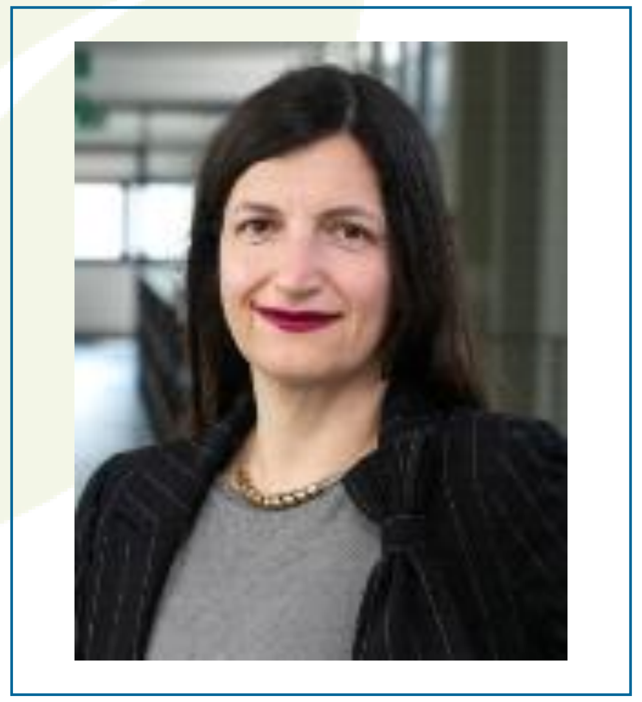

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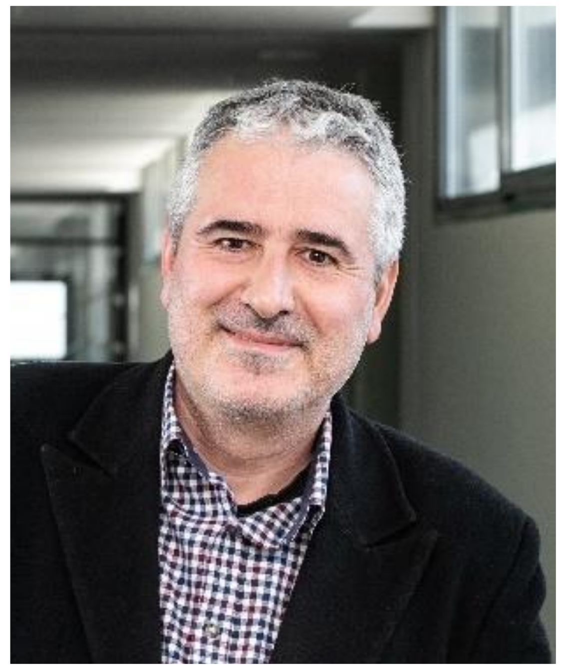

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