

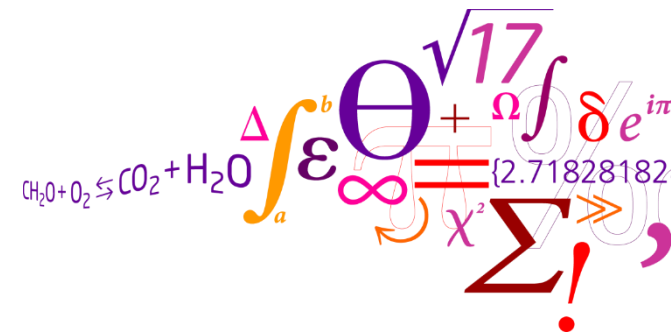
Towards the Recovery of valuable chemicals through Forward Osmosis (FO)

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16-05-2019



- 1. Ceit-IK4**
- 2. Introduction**
- 3. Objective**
- 4. Material and Methods**
- 5. Results and Discussion**
- 6. Conclusions**





- ▶ Ceit is an independent, private, non-profit¹ RTO (Research and Technology Organization)
 - Created in 1982 by the University of Navarra
 - Associated with the University
 - Supported by the Basque Government as part of the Basque network of Science, Technology and Innovation

- ▶ Ceit's mission is to serve society and industry by
 - developing research projects
 - training young researchers

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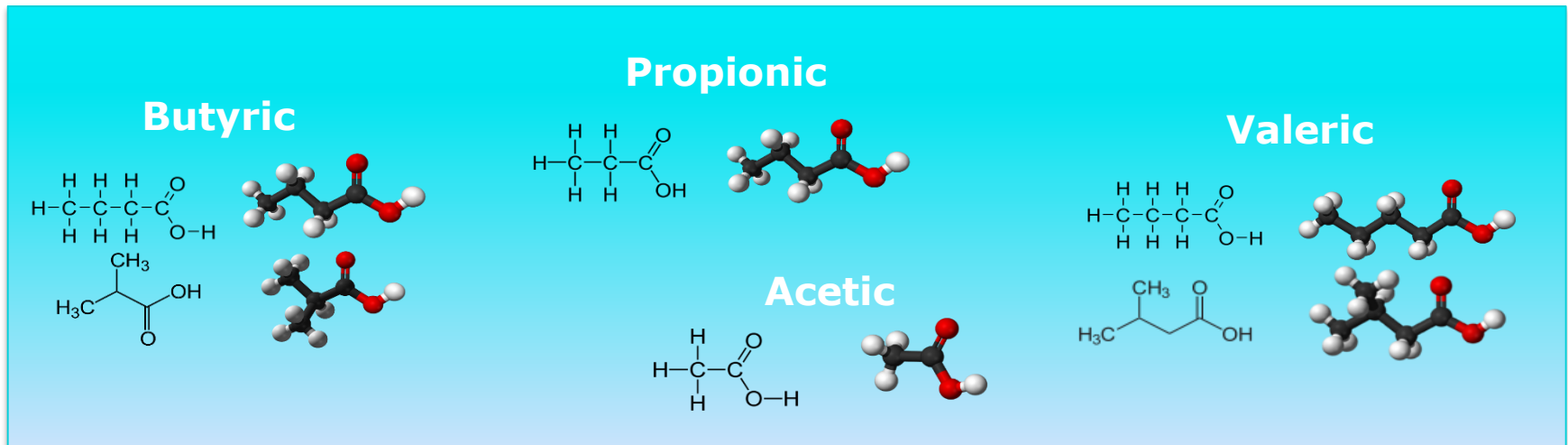
ANAEROBIC DIGESTION

- Mature technology
- Biogas market
- Legislation



BIOREFINERY

- VFA production
- Experimental phase
- Application
(Pure form & mixtures)



Introduction

VFA market

Carboxylic acids	Chemical formula	Market size (tonnes/year)	Price per tonne (USD, \$)
Formic	HCOOH	30,000	800–1,200
Acetic	CH ₃ COOH	3,500,000	400–800
Propionic	CH ₃ CH ₂ COOH	180,000	1,500–1,650
Butyric	CH ₃ (CH ₂) ₂ COOH	30,000	2,000–2,500
Caproic	CH ₃ (CH ₂) ₄ COOH	25,000	2,250–2,500

Chemical



Biomaterials



Biofuels



WWTP



Animal Feed

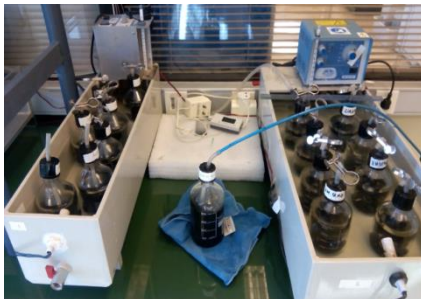


Methodology



Laboratory scale

- Acidogenic potential
- pH: acid & alkaline
- T: 35°C y 55°C

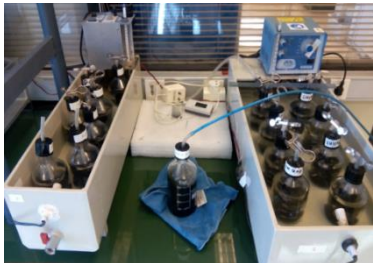


Pilot scale

- Batch and continuous
- Mono fermentación
- Co-fermentación



Motivation of the stay



Motivation of the stay

Anaerobic fermentation

Raw waste



Soluble fraction



Valuable bioproducts



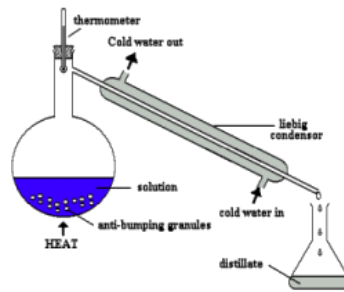
Motivation of the stay

Downstream options

Solvent extraction

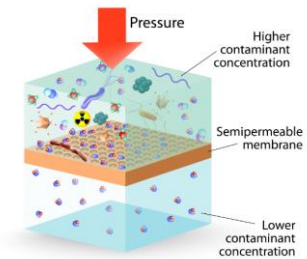


Distillation

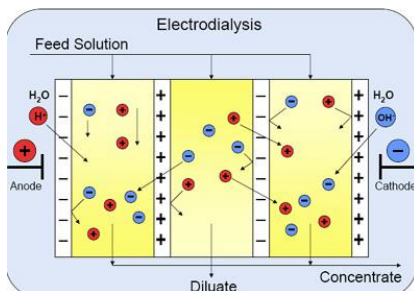


Membrane technologies

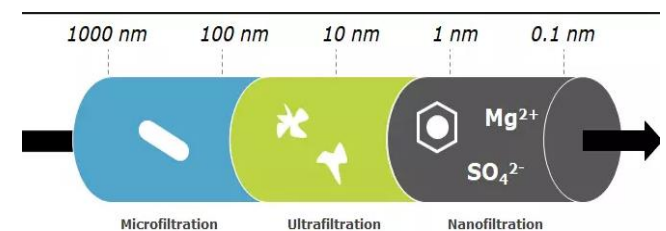
REVERSE OSMOSIS



Electrodialysis

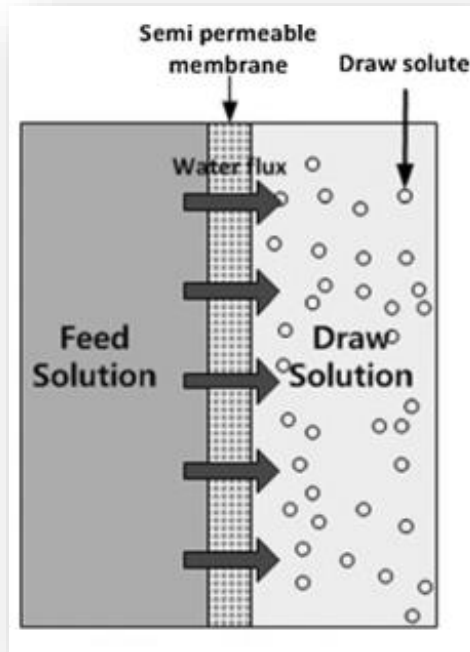


Nanofiltration



FORWARD OSMOSIS?

FORWARD OSMOSIS (FO)

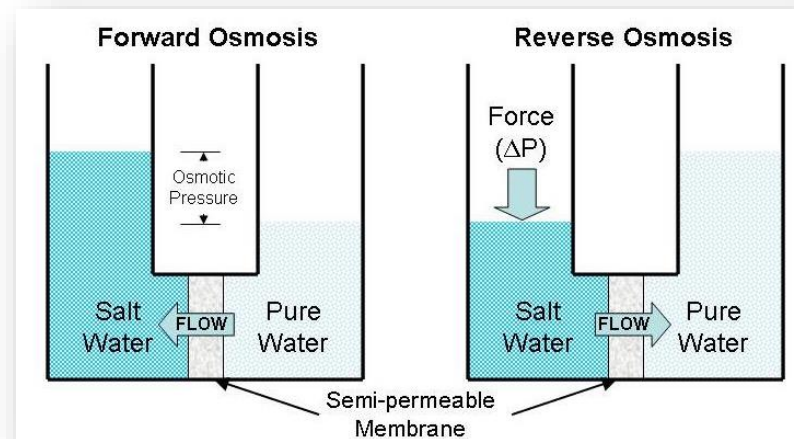


$$P_1 < P_2$$

Driving force = ΔP osmotic pressure

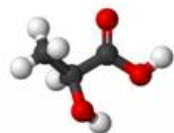
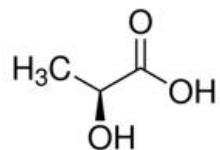
Advantages

- ✓ Low energy requirement
- ✓ Lower fouling propensity
- ✓ Higher water recovery

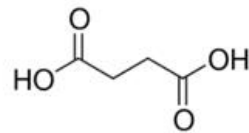


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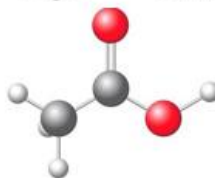
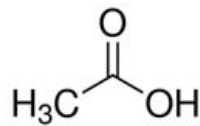
1. Application of FO technology with Synthetic mixtures



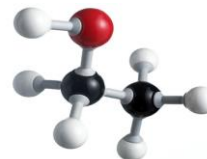
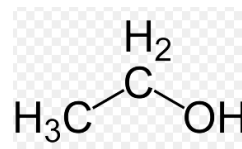
Lactic acid



Succinic acid



Acetic Acid



Ethanol



pH 3
pH 7



Flat sheet



Hollow fibre

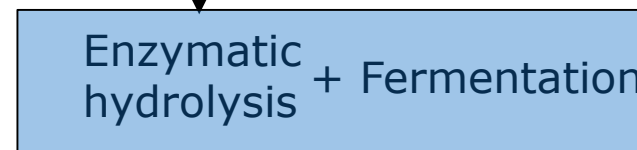
2. Application of FO with real fermentation broths

Macroalgae

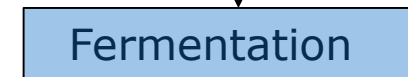


1. **Succinic Acid** broth

Biopulp



2. **Lactic acid** broth



3. **Ethanol** broth

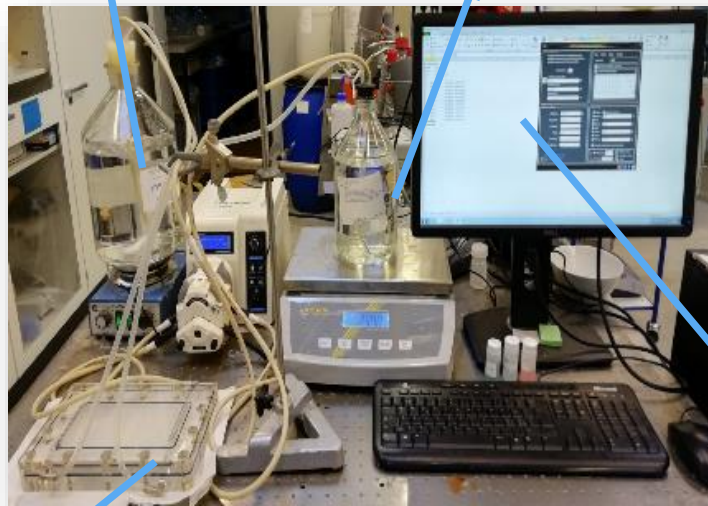
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Synthetic FO experiments

Membrane Characteristics		
	Flat sheet	Hollow fibre
Membrane area	0.014 m ²	0.3 m ²
Company	FTSH20	Aquaporin

Draw solution

Feed: 20 g/L

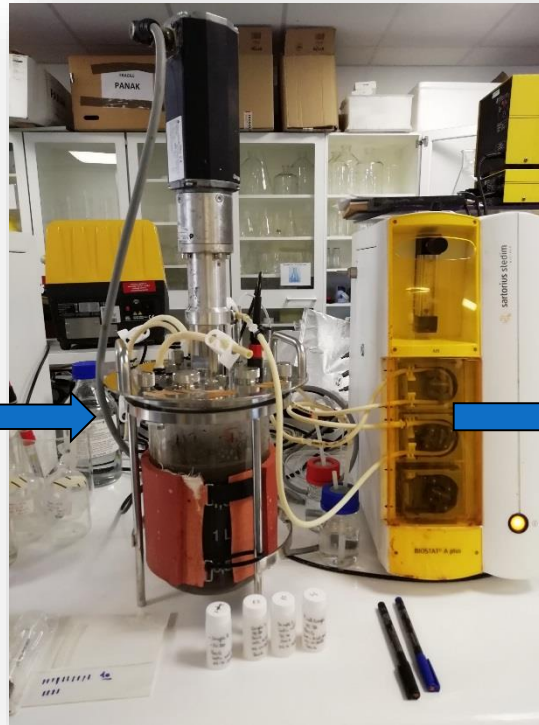


Mass transfer

Weight change measurement (Feed)

Fermentation tests

Inoculation of
Lactobacillus Delbrueckii



Number of tests: 3

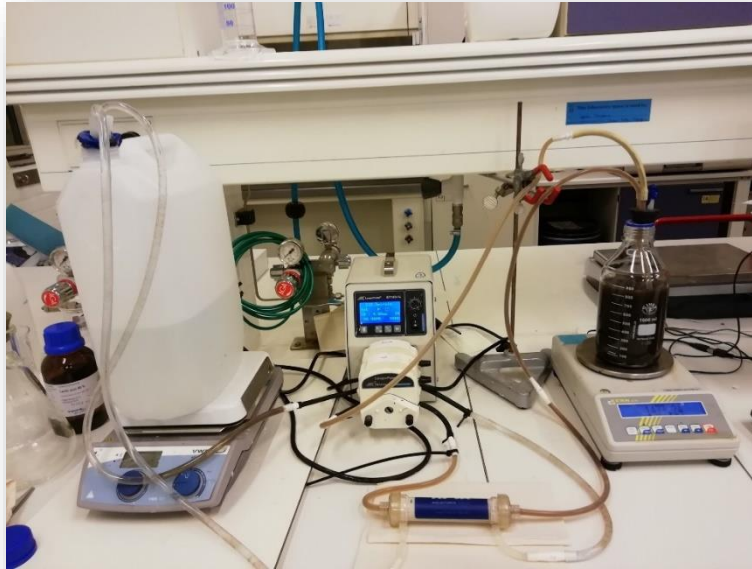
Substrates:

- Diluted biopulp 1:1 (ethanol production)
- Hydrolized biopulp (lactic acid prod.)



Soluble fraction for FO tests

Real broth FO tests



- Water flux $L/m^2 h$
- Conductivity change: mS/cm
- Osmotic Pressure change: $mOsmol/kg$
- Composition: HPLC, VFA (Feed, DS)

Feed solution (1L)

- Lactic Acid broth
- Succinic Acid broth
- Ethanol broth

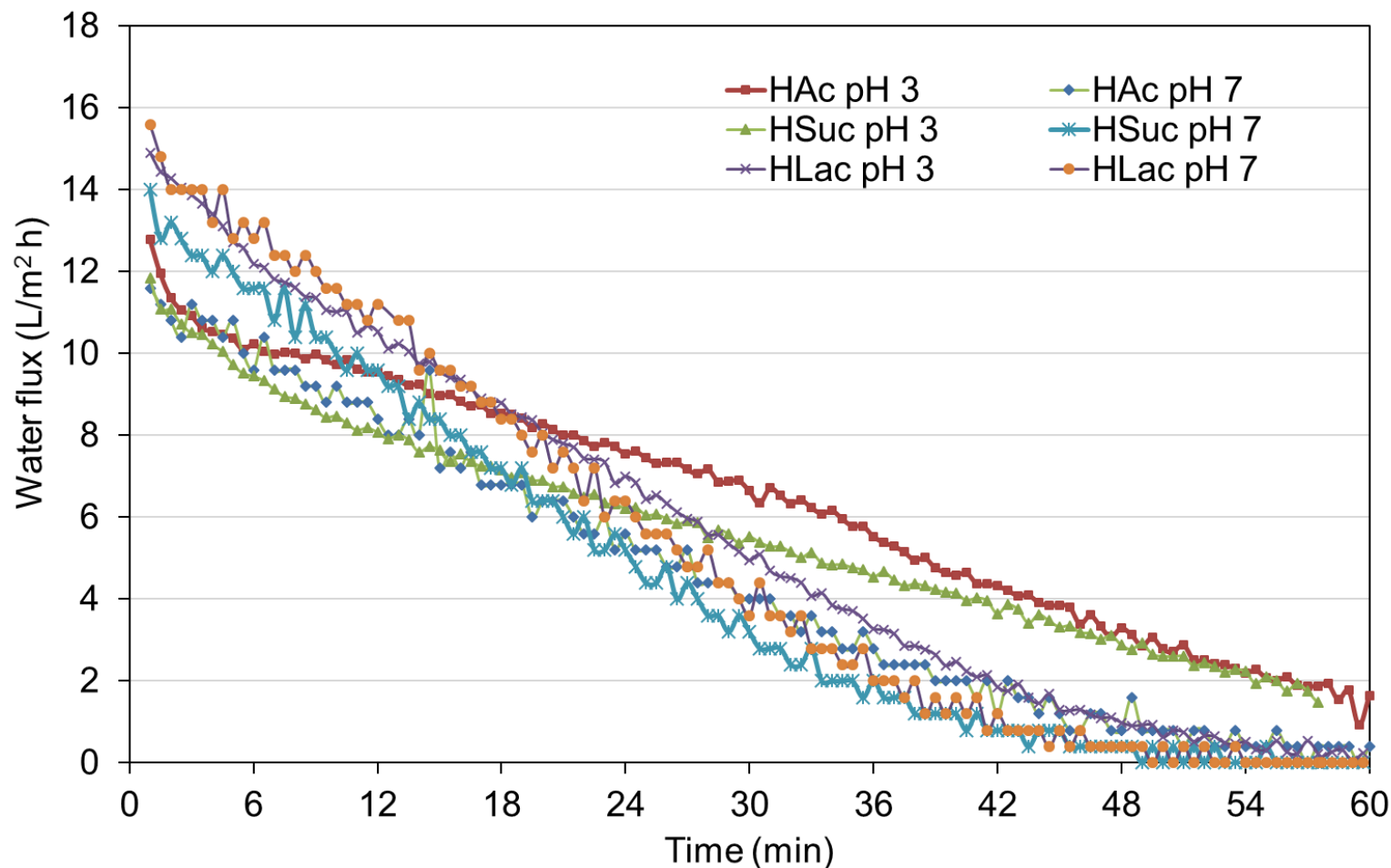
Process conditions

- Room T
- No pH adjustment
- Draw solution (4L):
 - NaCl 1.5 M
 - NaCl 5 M
- Duration: 1h

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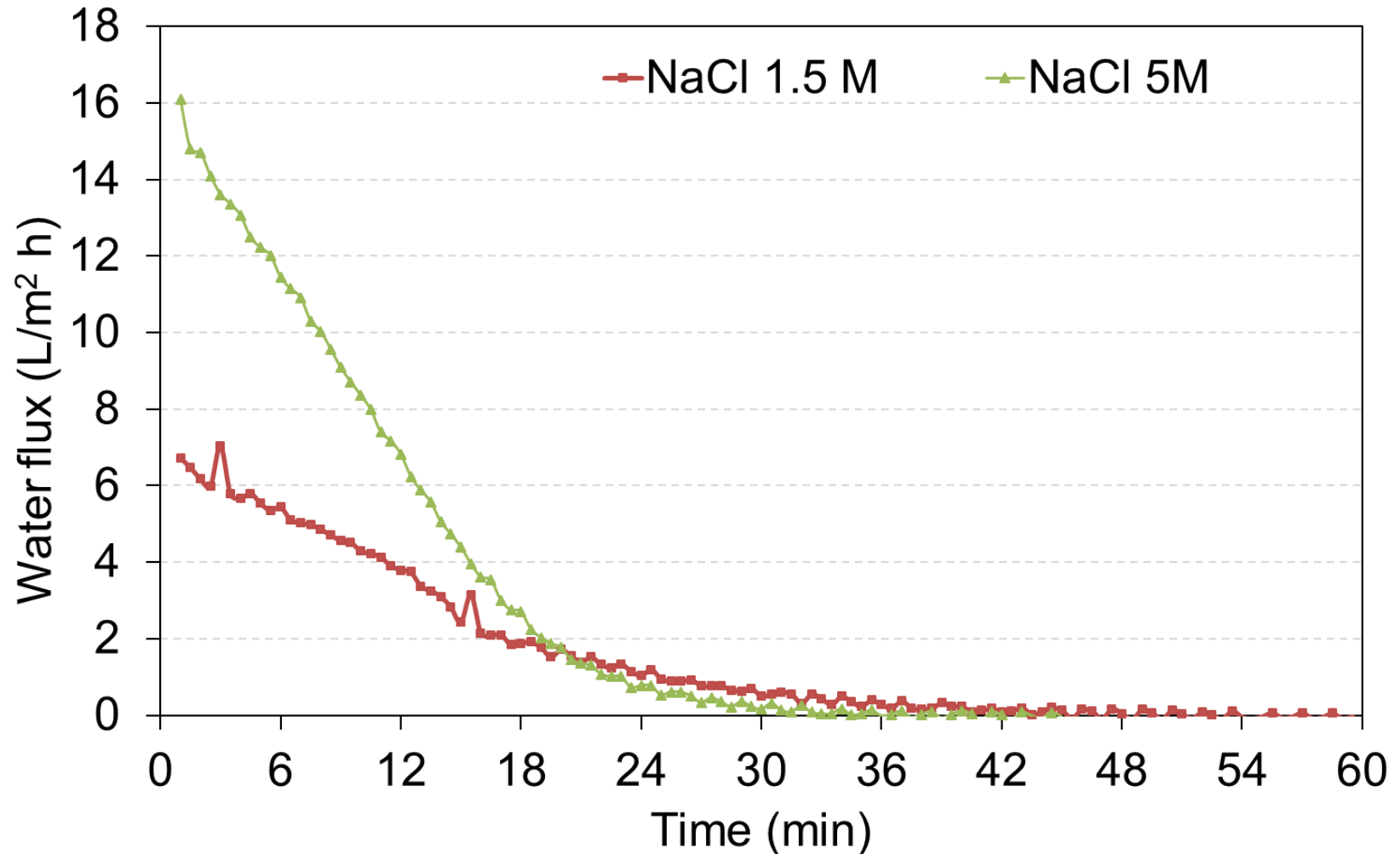
Results and Discussion

Example of decline in the water flux; Effect of pH and chemical



Results and Discussion

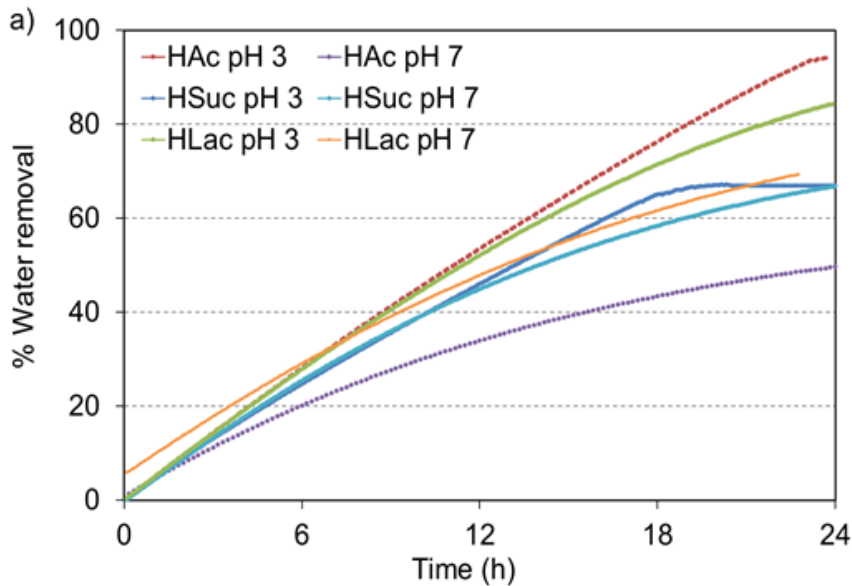
Example of the effect of DS concentration



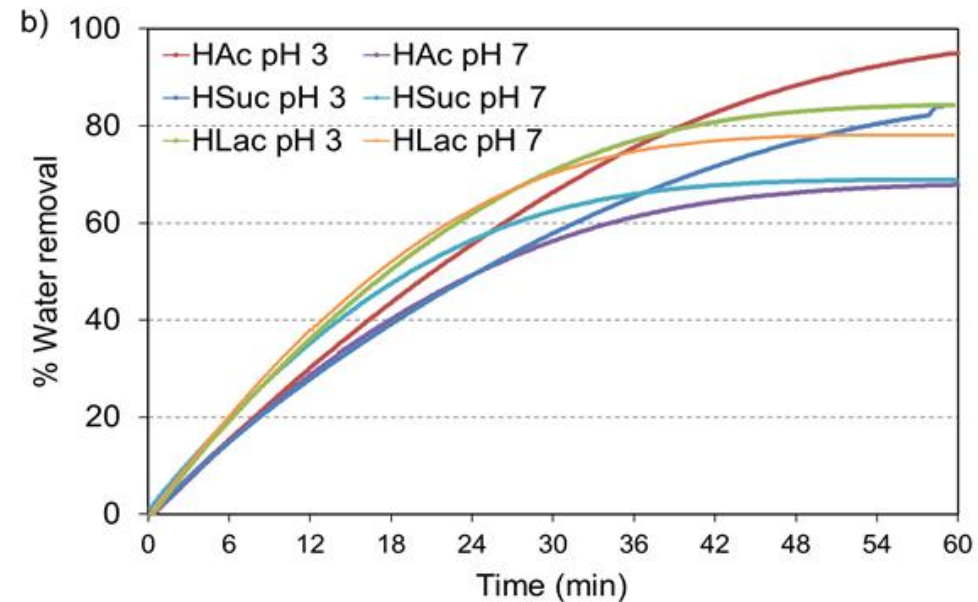
1. FO SYNTHETIC TESTS RESULTS

1. SYNTHETIC TESTS: Percentage of water removal from the Feed

Flat sheet results



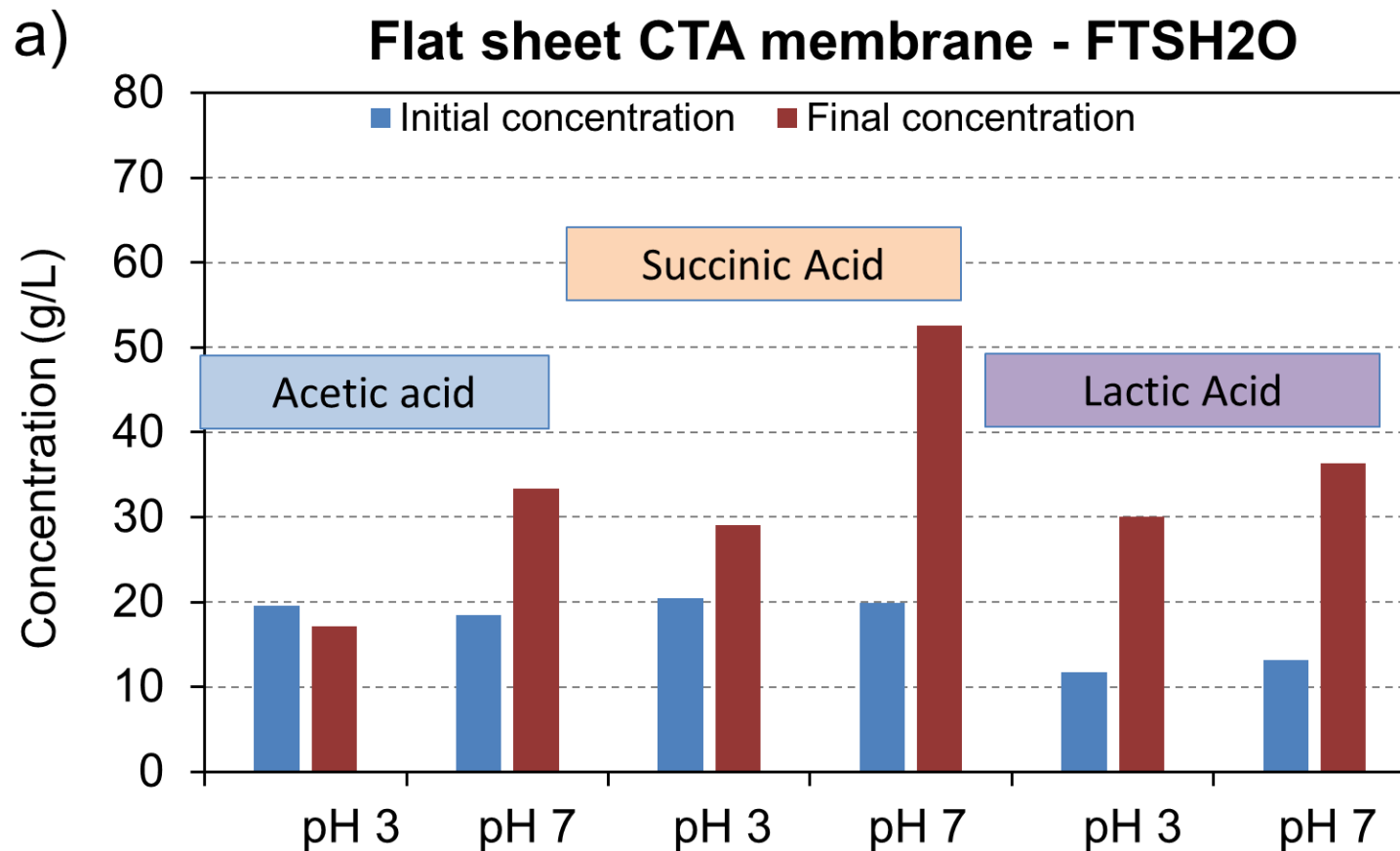
Hollow fibre results



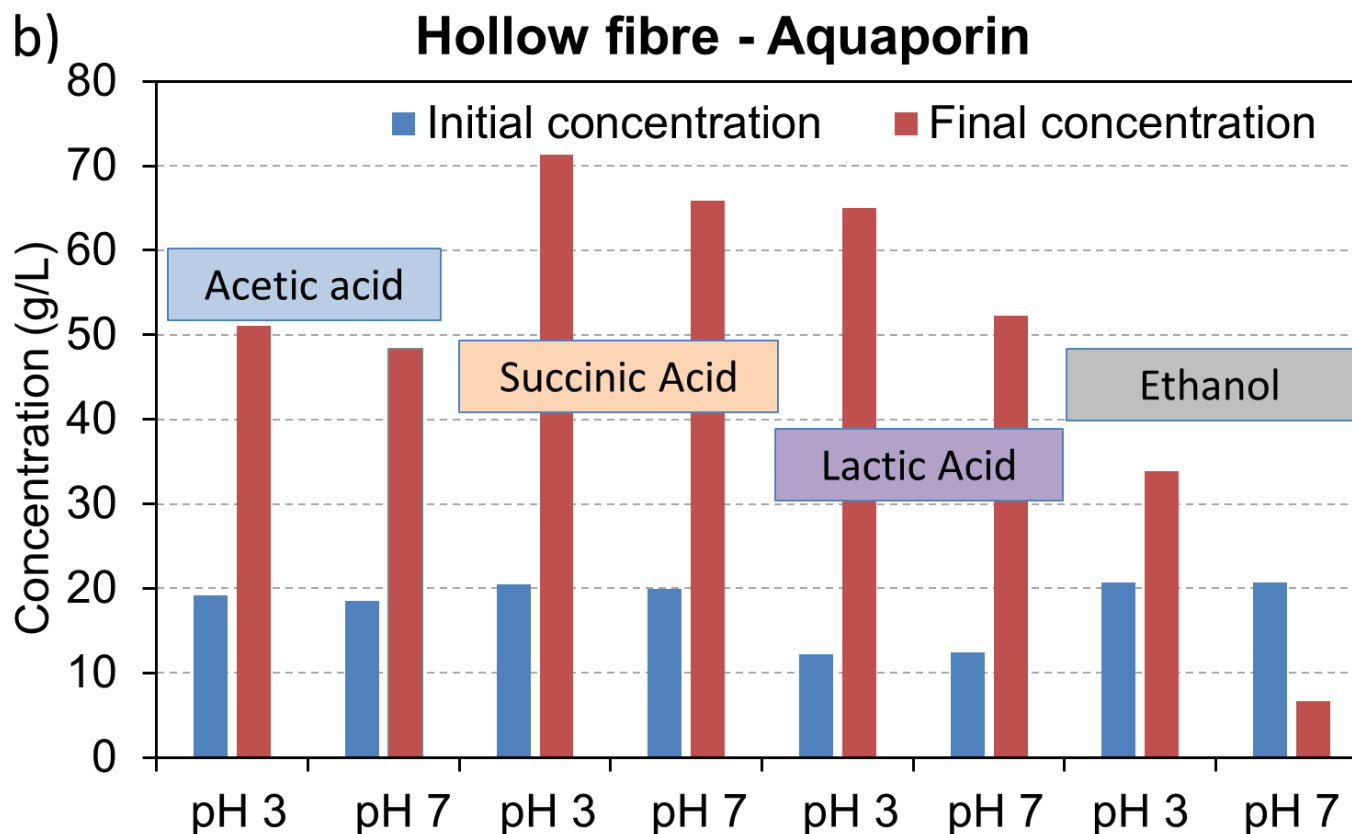
Observation

- Higher water removal with hollow fibre > 65%
- Higher water removal at pH 3
- Hac > HLac > HSuc

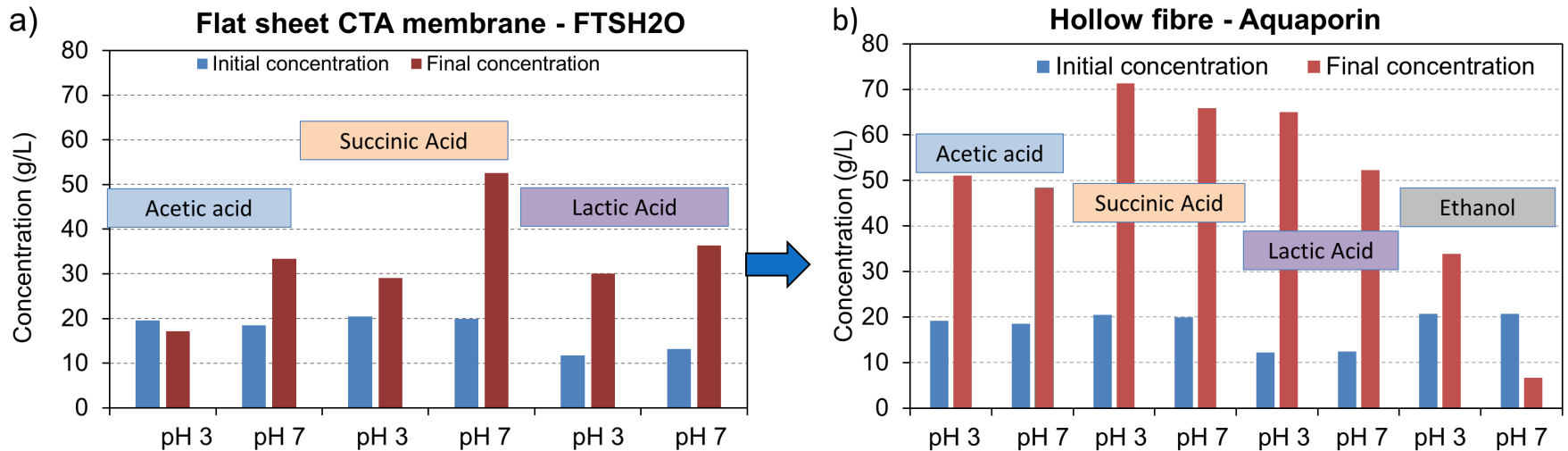
1. SYNTHETIC TESTS: Flat sheet membrane up-concentration



1. SYNTHETIC TESTS: Hollow fibre membrane up-concentration



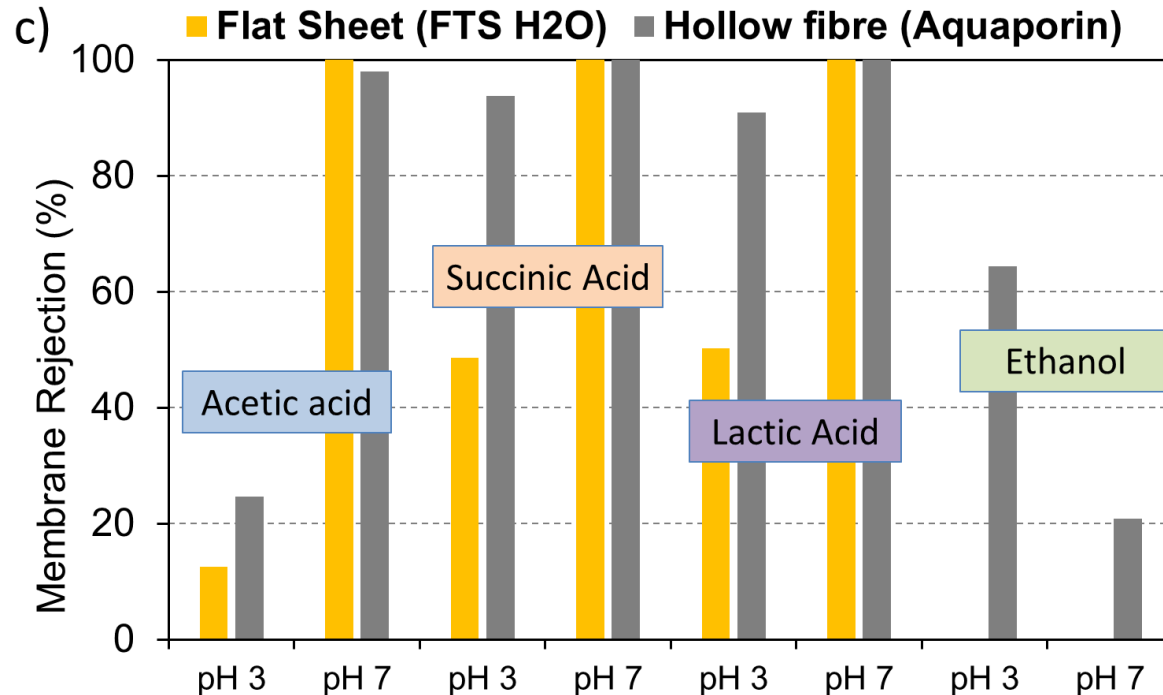
1. SYNTHETIC TESTS: Comparison of flat sheet and hollow fibre



Hollow fibre membranes

- A higher water flux
- Higher up-concentration potential (between 1.6 – 5.3 times)
- HSuc > HLac > HAc > Ethanol

1. SYNTHETIC TESTS: % rejection of solute



- 100% rejection rate of the solute at pH 7 (except ethanol)
- Better performance of Hollow fibre at pH 3 than flat sheet
- Poor rejection of HAc at pH 3

Results and Discussion

1. SYNTHETIC TESTS: best result for Succinic Acid



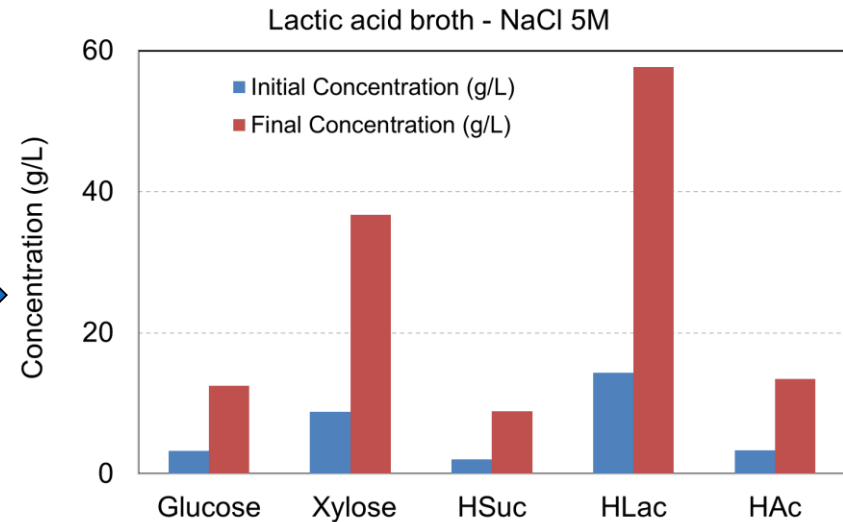
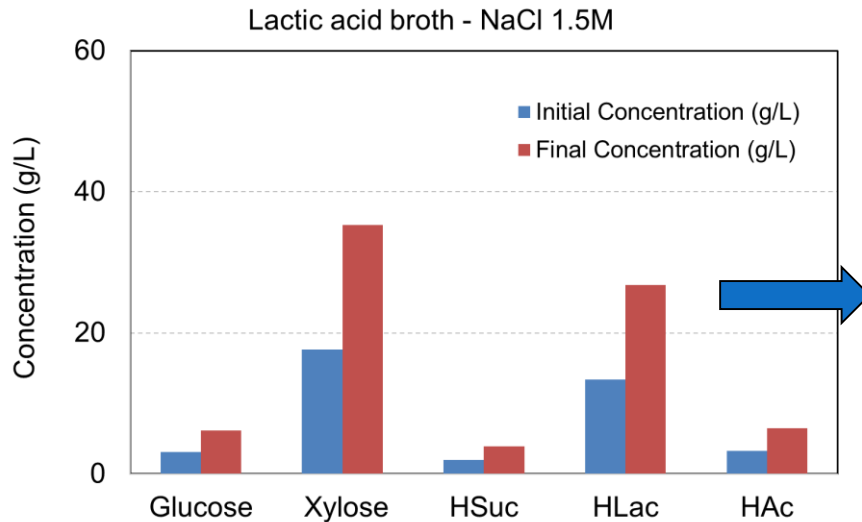
320 mL of a saturated solution of Succinic Acid

2. FO test results with real fermentation broths



Results and Discussion

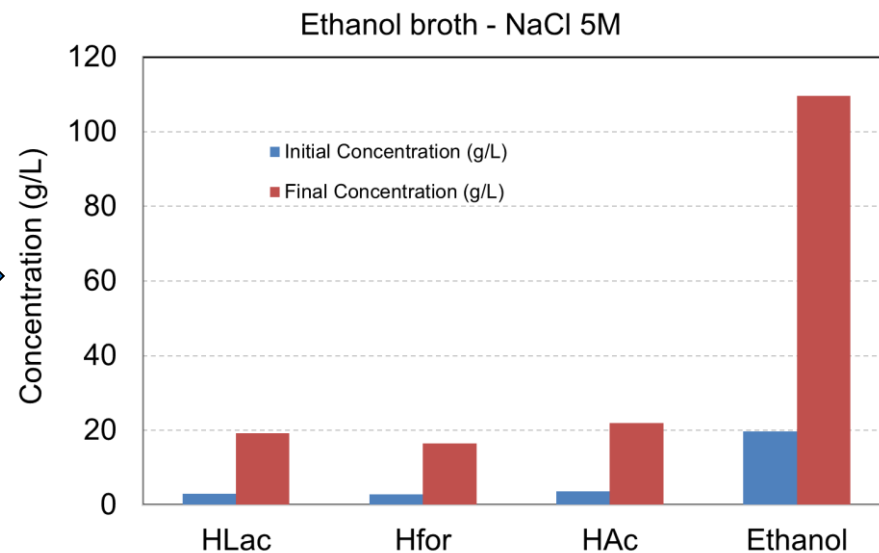
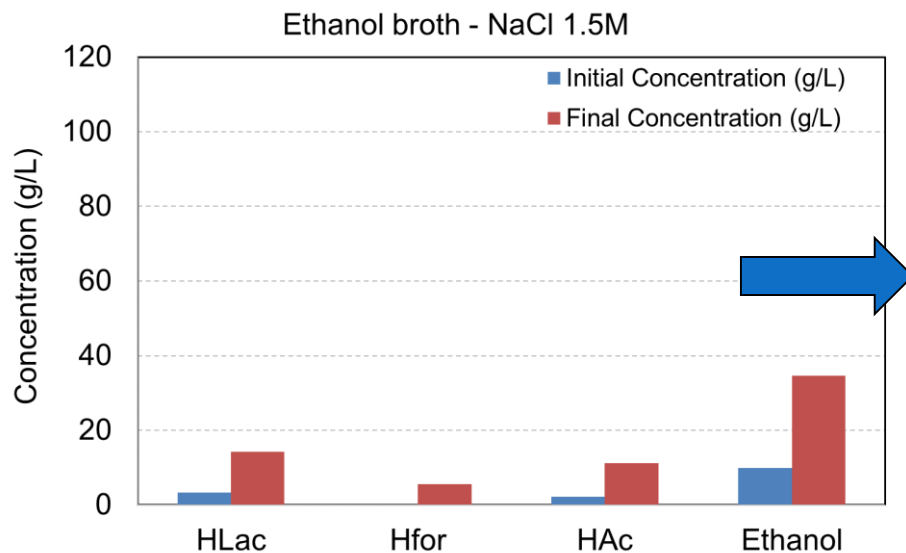
2. Real Fermentation broths: a) Lactic acid broth, pH = 5.90



57.7 g/L of Lactic Acid
Membrane rejection = 100%

Results and Discussion

2. Real Fermentation broths: b) Ethanol broth, pH = 7.10

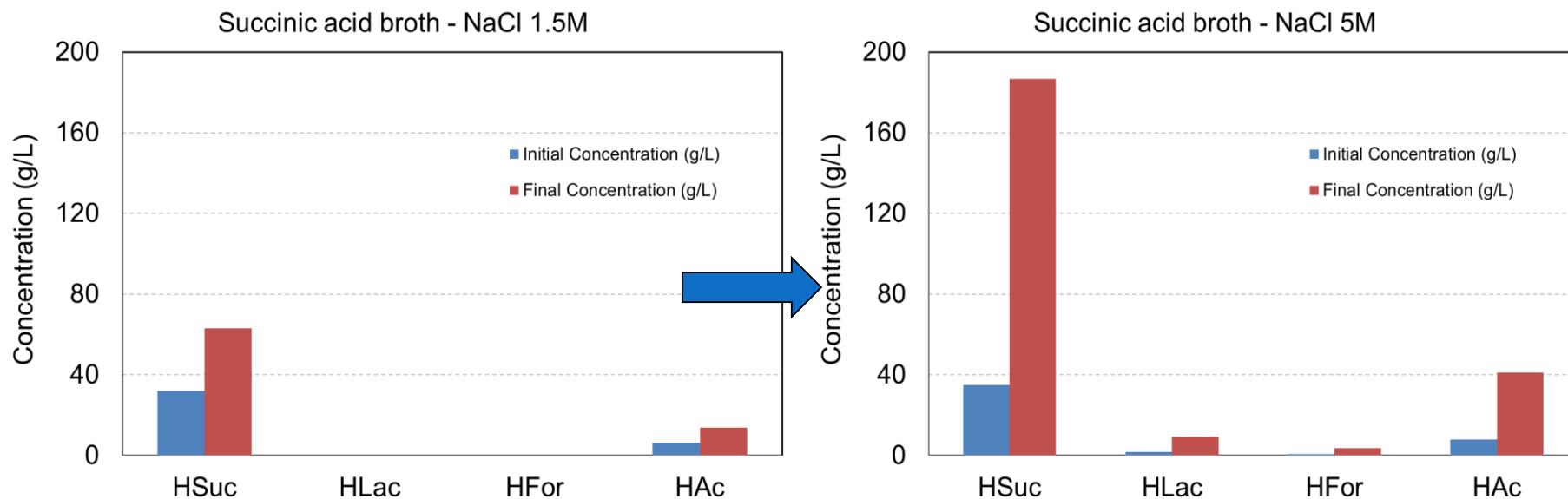


109.6 g/L of Ethanol

Membrane rejection = 100%

Results and Discussion

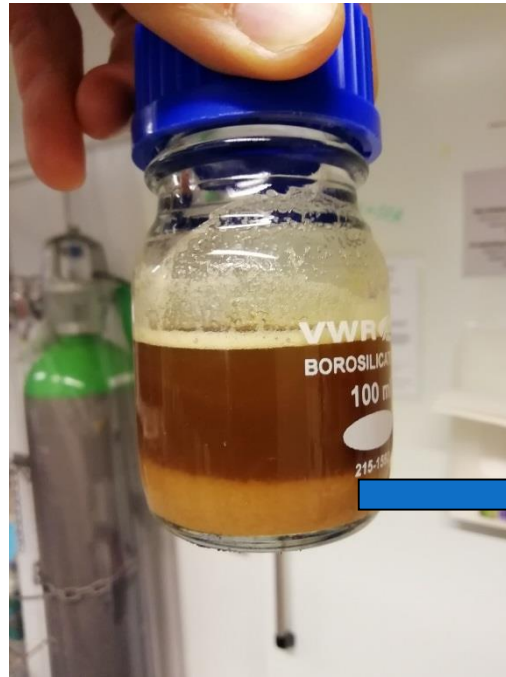
2. Real Fermentation broths: c) Succinic acid broth, pH = 7.50



186.8 g/L of Succinic Acid
Membrane rejection = 100%

2. Real Fermentation broths: a) Succinic acid cristallization

- pH: 3 (+ HCL)
- Time: 12 h
- 4 °C



Succinate salt
precipitation

Purity of the product?

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- FO technology was succesful for the scope of the study.
- The target chemicals: HSuc, HLac and HAc can be up-concentrated with 100% rejection at pH 7, during synthetic FO tests.
- Hollow fibre membranes showed benefits in terms of water flux, water removal and solute rejection rate.
- The application of hollow fibre membranes with real fermentation broths was succesful.
- The results with real broths were enhanced with 5M NaCl.
- 58 g/L of Hlac, 110 g/L ethanol and 186.8 g/L of succinic acid could be obtained.
- Cristallization could be the following step for HSuc recovery.
- FO could be a potential base technology in future downstream processes at local biorefineries.

Thank you!!!

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