

From the Cork Processing Wastewaters to the Leather Industry: Recovery and Reuse of Phenolic/Tannic Compounds

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Cork Processing

stripping



Wine stoppers

Floor and wall covering

Manufactured products

exposed to the open air for about 6 months



Wastewater:

**Phenolic compounds;
Sugars; Salts**

**Replaced after
2 to 4 days**

Boiling

Cork wastewater problematic

Three major problems:

- 1. Environmental problem due to the high organic load of this wastewater;**
- 2. High consumption of fresh water.**
- 3. Quality control of cork planks;**

Wastewater Characterization - PARAMETERS

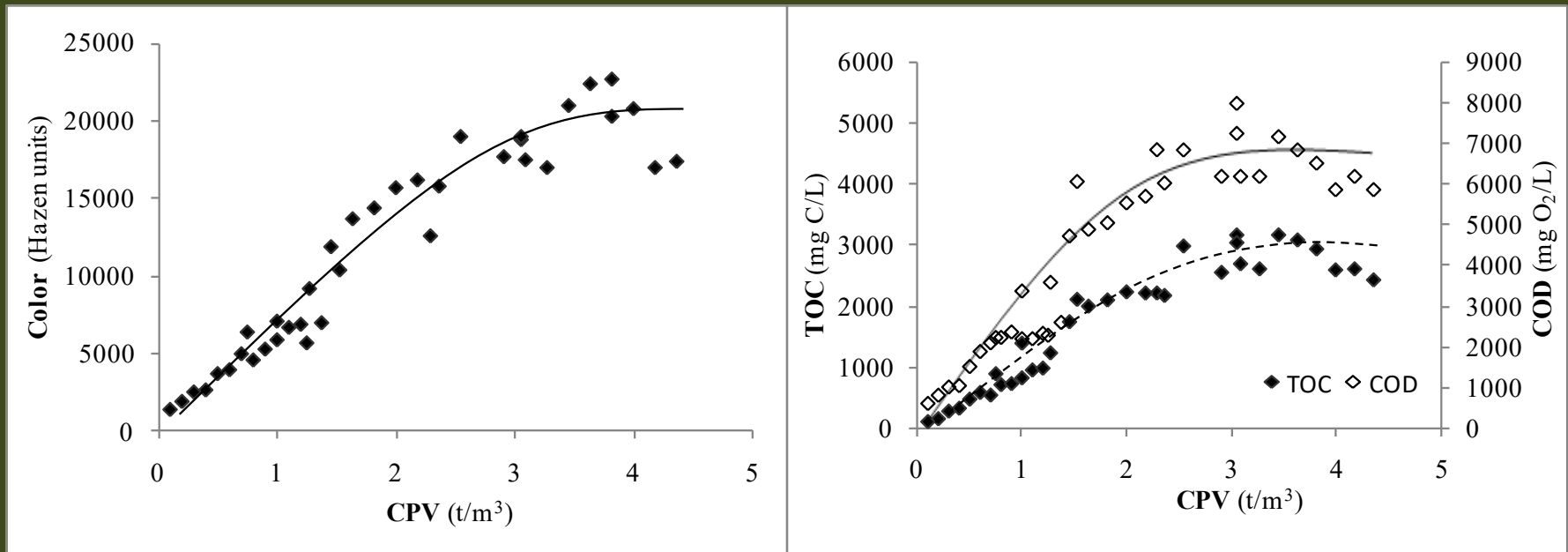
Physicochemical parameters:

- pH
- Colour
- Conductivity
- Total Organic Carbon (TOC) - 5310B - [1]
- Chemical Oxygen Demand (COD) - 5220 B [1]
- Total Suspended Solids (SST) - 2540D [1]
- Biochemical Oxygen Demand (BOD₅) - 5210 D [1]
- Total Phenolic content (TP) – Folin-Ciocalteu [2]
- Total Tannic content (TT)

**RECOVERABLE
PRODUCTS**

Wastewater Characterization - PARAMETERS

Parameter evolution along the boiling stage of the process

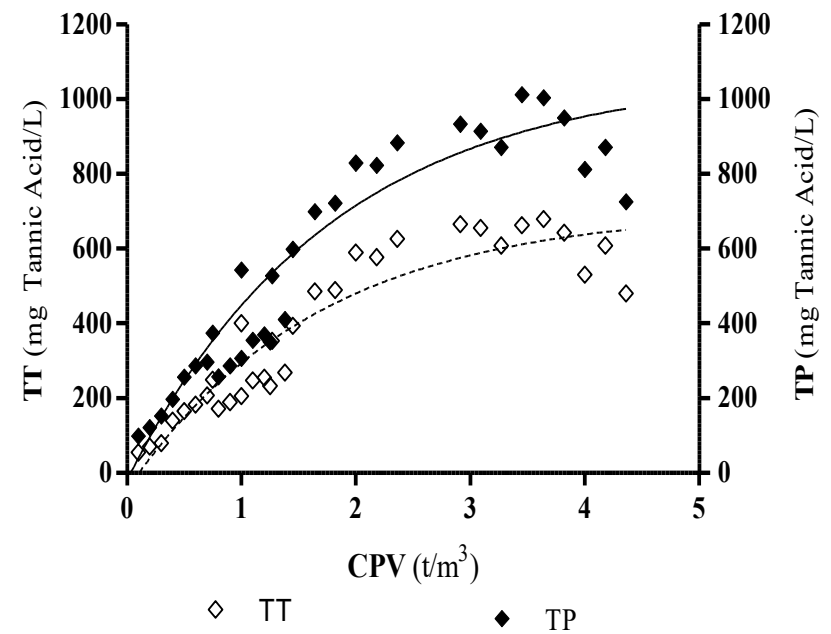
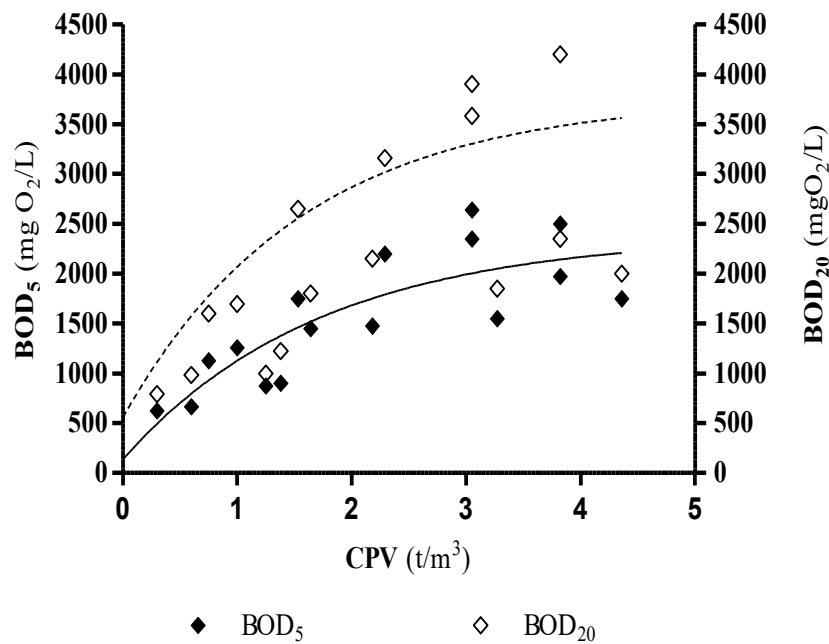


CPV – Cork processed per boiling tank volume (t/m³)

For low values of cork weight/volume, the parameters increase linearly with the increase of quantity of cork processed, being this increase less pronounced towards the higher quantities of cork processed

Wastewater Characterization - PARAMETERS

Parameter evolution along the boiling stage of the process



Wastewater Characterization - PARAMETERS

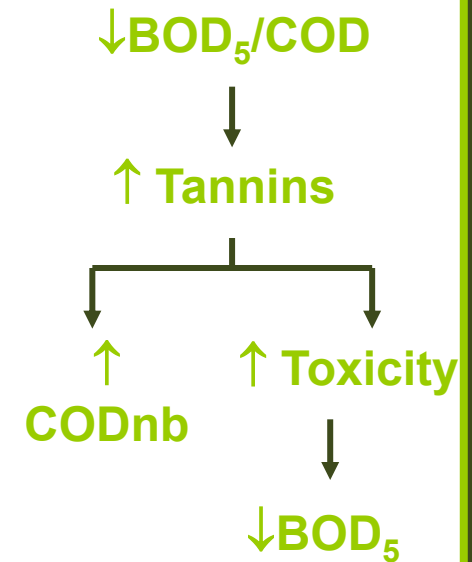
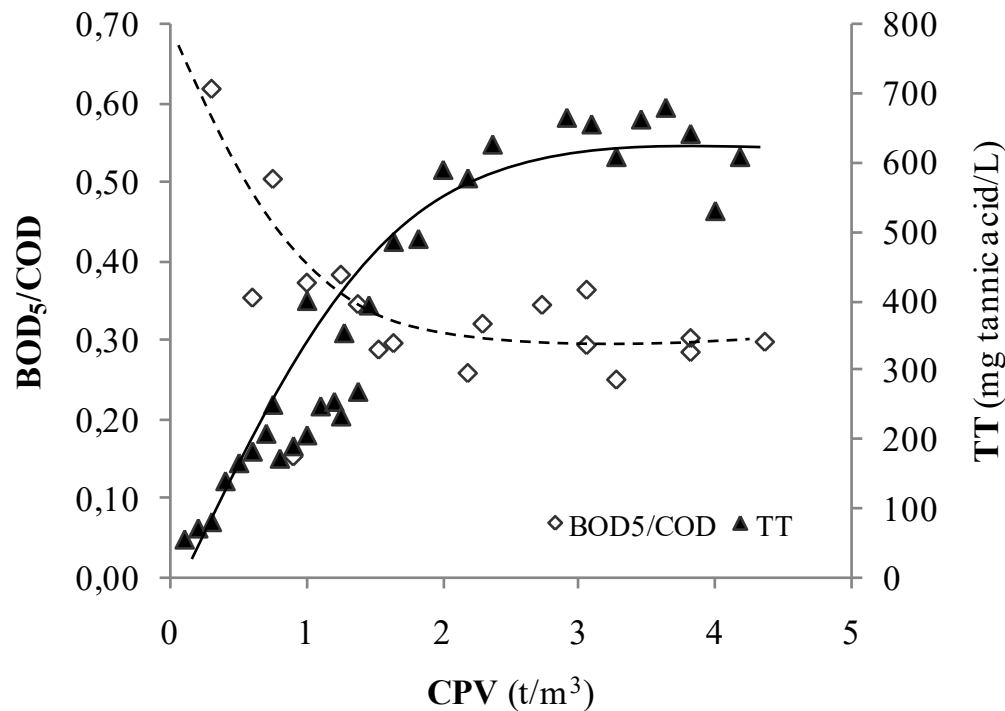
Discharged wastewater composition

PARAMETER	VALUE AFTER 2 OR 4 DAYS	LEV
pH	5.1 - 4.97	6.0 - 9.0
Conductivity (mS/m)	0.993 - 2.76	-
Colour (PtCo units)	6400 - 18800	Not visible
TOC (mg C/L)	894 - 3169	-
COD (mg O ₂ /L)	2230 - 7262	150
BOD ₅ (mg O ₂ /L)	1125 - 2642	40
TSS (mg/L)	2305 - 8160	-
TP (g tannic acid/L)	0.37 - 1.92	0.01
TT (g tannic acid/L)	0.25 - 1.53	-
BOD ₅ /COD	0.50 - 0.36	-

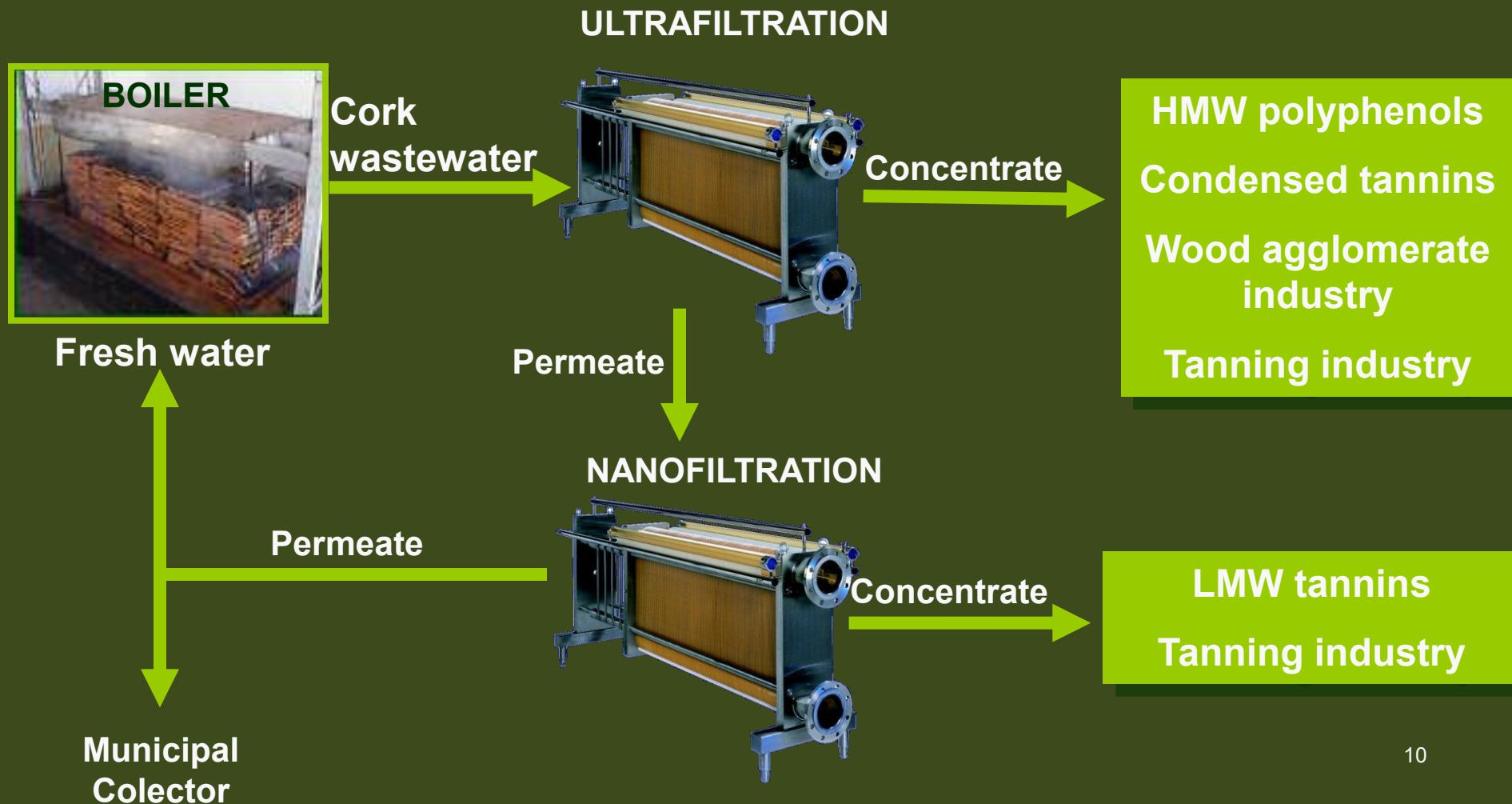
LEV – Limiting Emission Value

Assessment of treatability and sub-products recovery

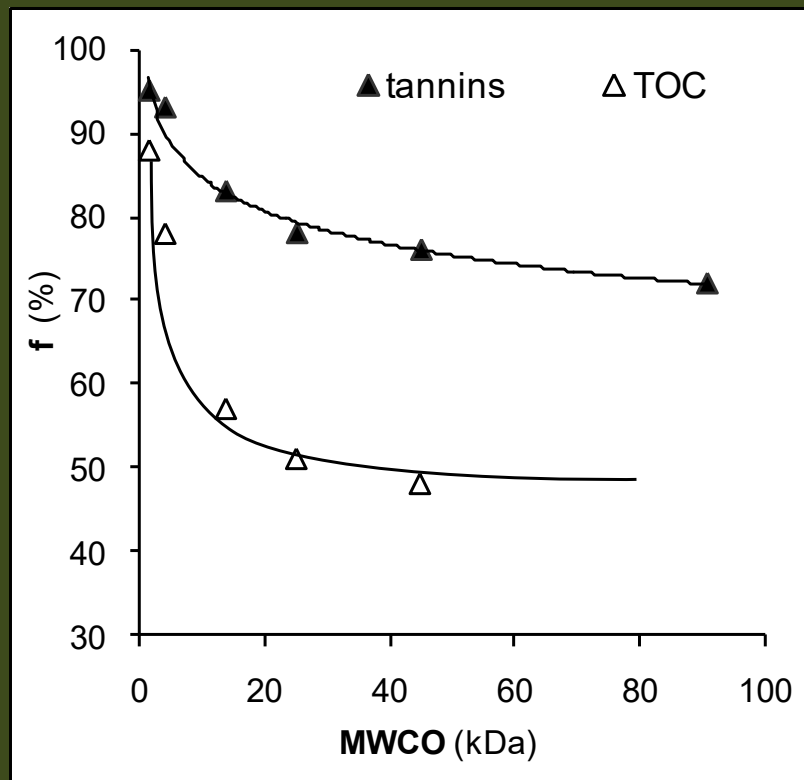
Discharged wastewater composition



Assessment of treatability and sub-products recovery



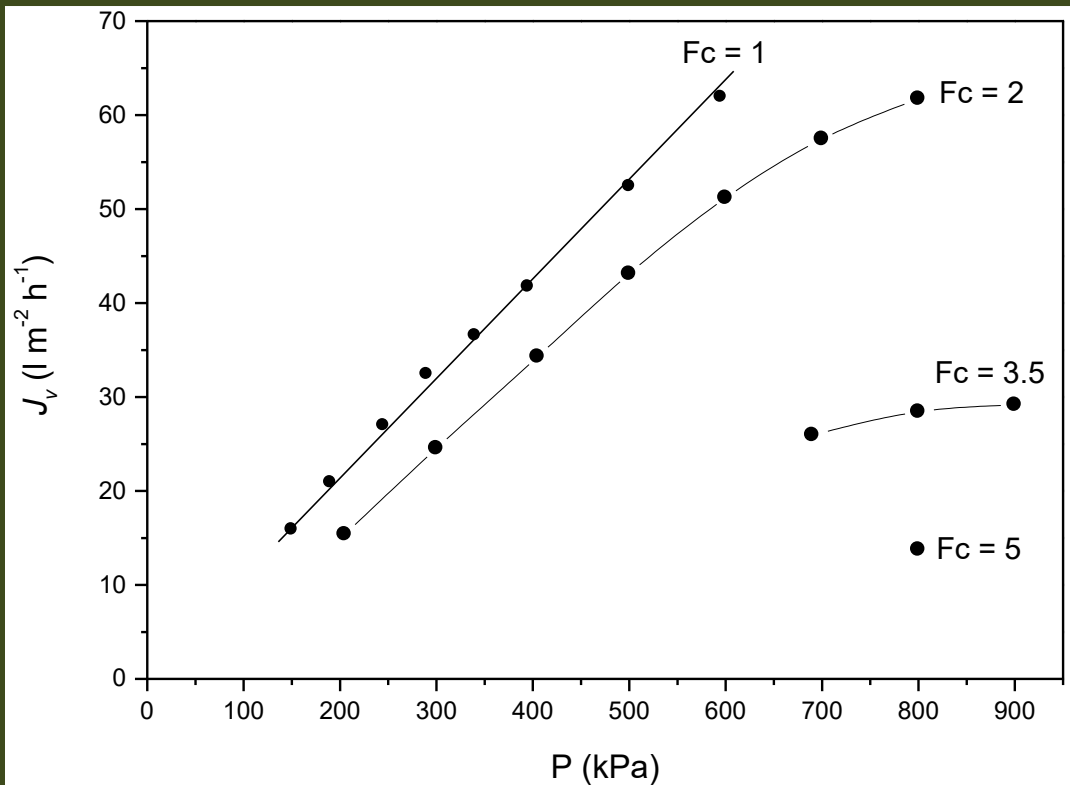
Permeation Experiments: Ultrafiltration



Cellulose Acetate
MWCO: 1,2 - 91 kDa

Recirculation mode
Pressure: 3 bar
Feed flowrate: 200 L/h
Flat sheet cell
Surface area: 0,294 m²

Permeation Experiments: Nanofiltration



NF200 Filmtec

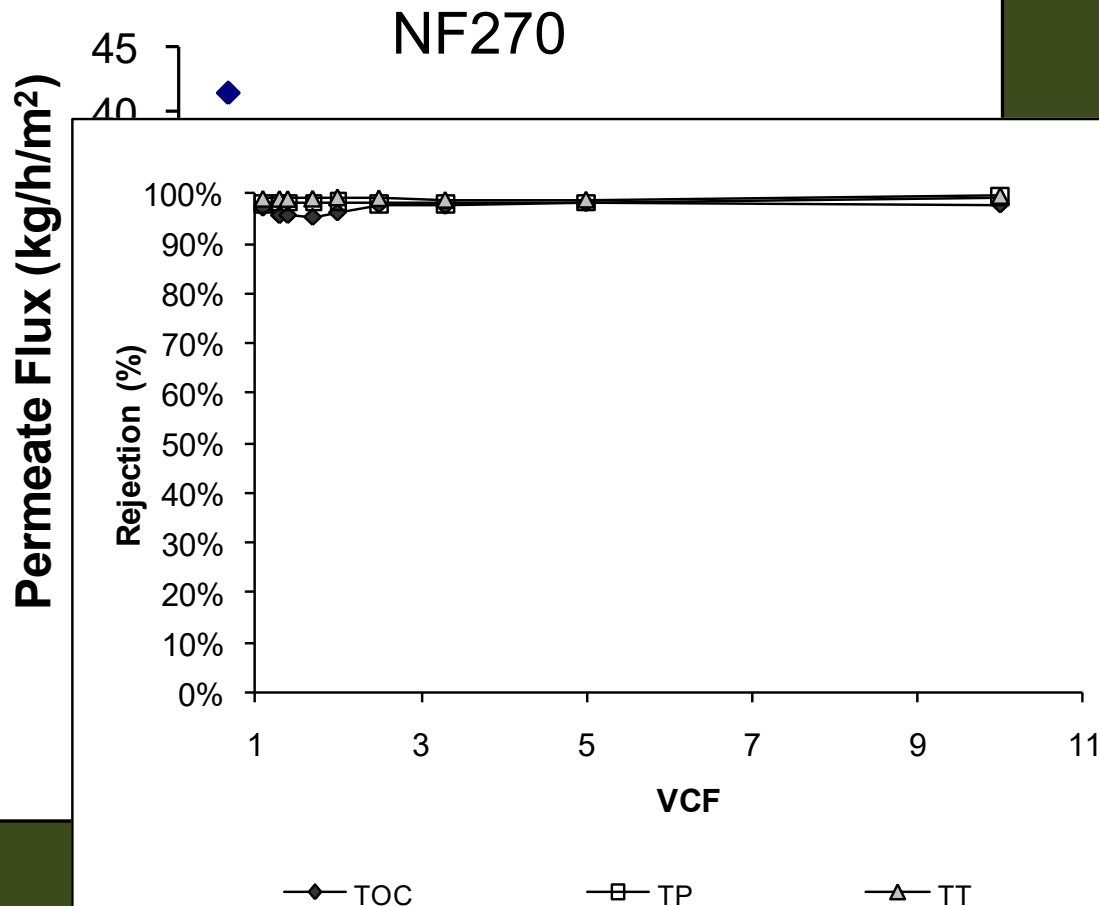
MWCO: ~200 Da

Spiral wound module

Memb. Area: 2.6 m^2

$T=25^\circ\text{C}$, $P=150\text{-}900 \text{ kPa}$

Permeation Experiments: Nanofiltration



NF270 Filmtec

MWCO: ~300 Da

Spiral wound module

Memb. Area: 2 m²

T=25°C, P=12,5 bar; 300 L/h

Permeate

TOC = 74 mg C/L

BOD₅ = 100 mg/L

BOD₅/COD = 0,72

Concentrate
(VCF=10)

TP = 6,9 g/L

TT = 5,9 g/L

Tanning Experiments

thickness (mm)		Filling coefficient	Shrinkage temp. (°C)	
Skin	Leather		Skin	Leather
1.1	1.79	62.7 %	38	71

based on the tanning of 4 samples of pelts (15×15 cm²) using concentrated cork processing wastewaters

Cork wastewater tannin converted the skins to leathers that have a shrinking temperature of 71 °C, well above the shrinking temperature of the skins (38 °C). The shrinking temperature of produced leather is in the range typical of commercial leathers produced with several types of vegetable tannins, from 70 to 85 °C

The results show that the tannins present in the boiling water of cork planks when subjected to concentration by NF membranes have the technical feasibility for application in the Tannin industry

[CONCLUSIONS]

- **Cork processing wastewater presents a very high content in organic matter, namely in tannins**
- **The biodegradability of these wastewaters is low**
- **NF permeate can be either re-used in the process or discharged in municipal collectors**
- **Membrane processes can generate permeates that have higher biodegradability indices**
- **UF and NF can concentrate tannins in the concentrate stream that can be used in the Tanning Industry together with the usual tanning agents (mimosa extracts)**

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Thank you for your attention