Development of an integrated extraction and purification process for the recovery of high-value compounds from onion peels

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5-CIAB. 5th Iberoamerican Congress on Biorefineries. Jaén (Spain), 2-4 October 2024

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Onion Peel Wastes

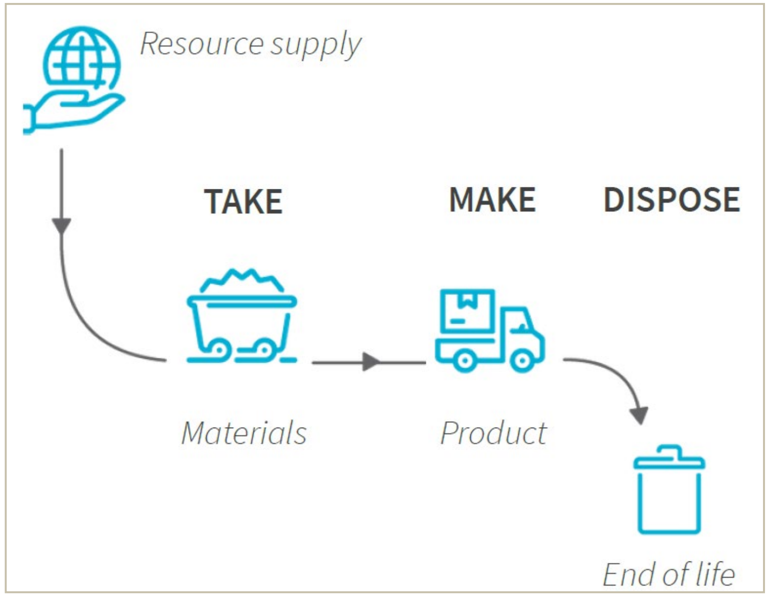
Valorization Strategy

- Flavonoids Recovery
- Subcritical Water Extraction
- Purification: membrane technology

Conclusions

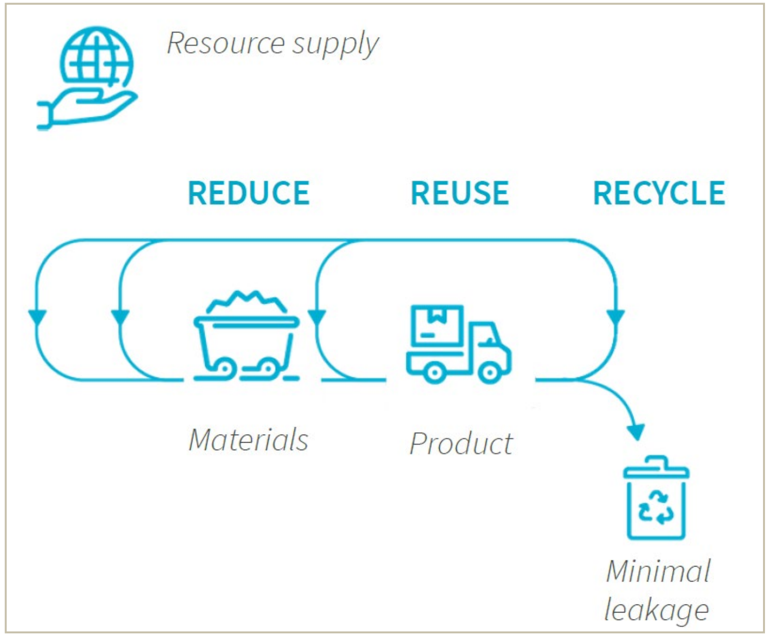
BACKGROUND

We are transitioning from a traditional linear economic model to an innovative framework based on the principles of the circular economy



Valorization of agroindustrial by-products:

- Rich in bioactive compounds and structural components (cellulose, pectin, lignin)
- Utilization as raw materials in innovative processes that transform by-products into valuable compounds
- Significant potential for the establishment of biorefineries to facilitate these transformations



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BACKGROUND: Onion

➢ ONION (*Allium cepa*)

2022: 6.2 Mt produced in the UE; 110.6 Mt worldwide

10% are wasted as peels

➢ "HORCAL" CULTIVAR

Highly appreciated for cooking

Key ingredient for blood sausage production

Production located in areas of Burgos and Palencia

- 130 Ha
- Productivity ~ 50 t/Ha
- 2023: 8000 t

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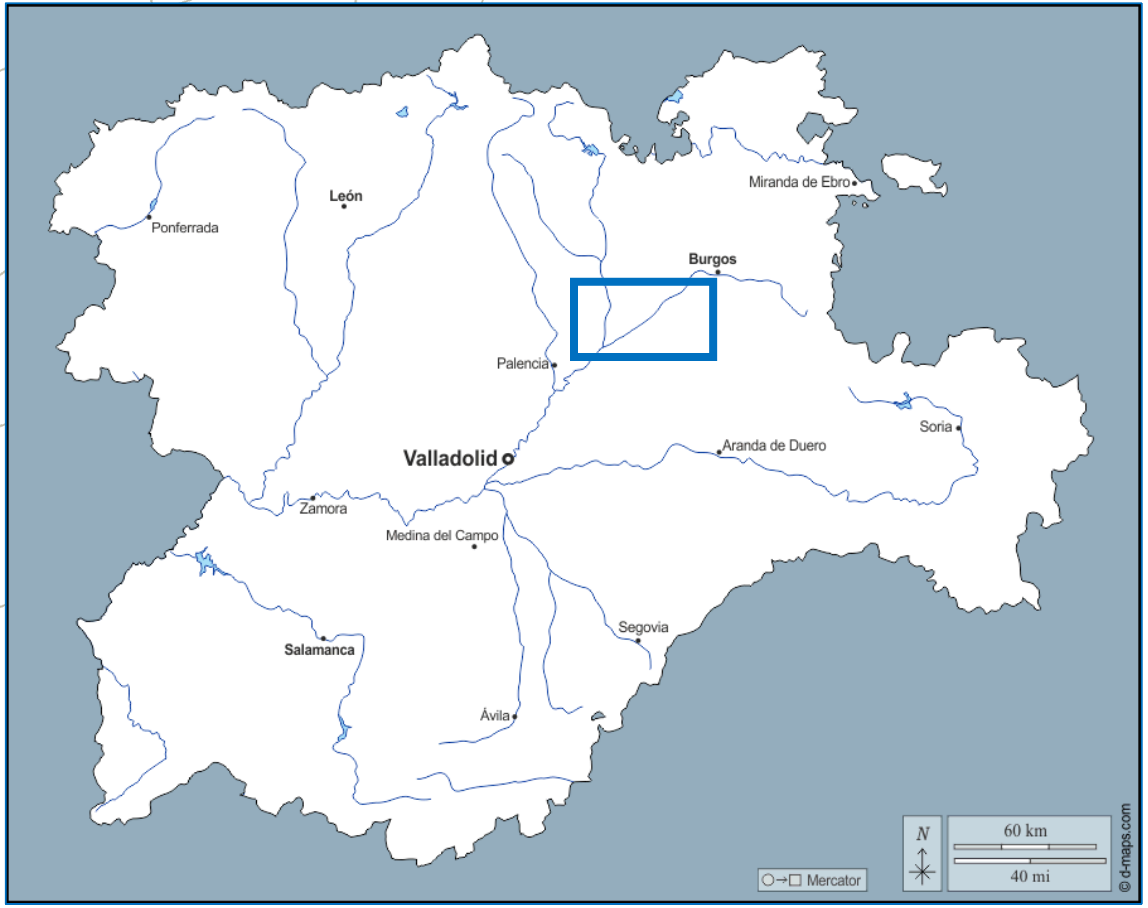

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Production located in areas of Burgos and Palencia

- 130 Ha
- Productivity ~ 50 t/Ha
- 2023: 8000 t

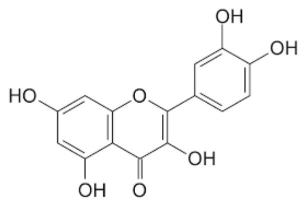
BACKGROUND: Onion peels

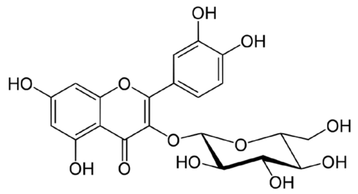
- **HORCAL CULTIVAR**

- Onion peels generated during harvesting and processing stages.
- A local blood sausage producer uses 350 t/y, generating 11 tons of external peels per year.
- These underutilized wastes cannot be repurposed as fertilizer or animal feed due to their high sulfur content.
- There is a pressing need for alternative strategies to valorize the onion peels produced.
- From a **local** problem to a **global** solution

BACKGROUND: Onion peels

➢ **RICH IN <u>BIOACTIVE COMPOUNDS</u>**





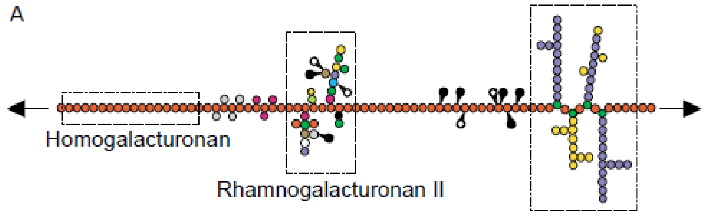
> 10% of extractives

Quercetin (QC) and derivatives (QC4’ or QC3,4’): antioxidant activity

➢ **HIGH CONTENT IN <u>PECTIN</u>**

26%

Increased demand by the industry for different applications as a function of the molecular weight and branching



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ACTIONS

NEW RAW MATERIAL

Onion peel wastes, source of bioactives and pectin

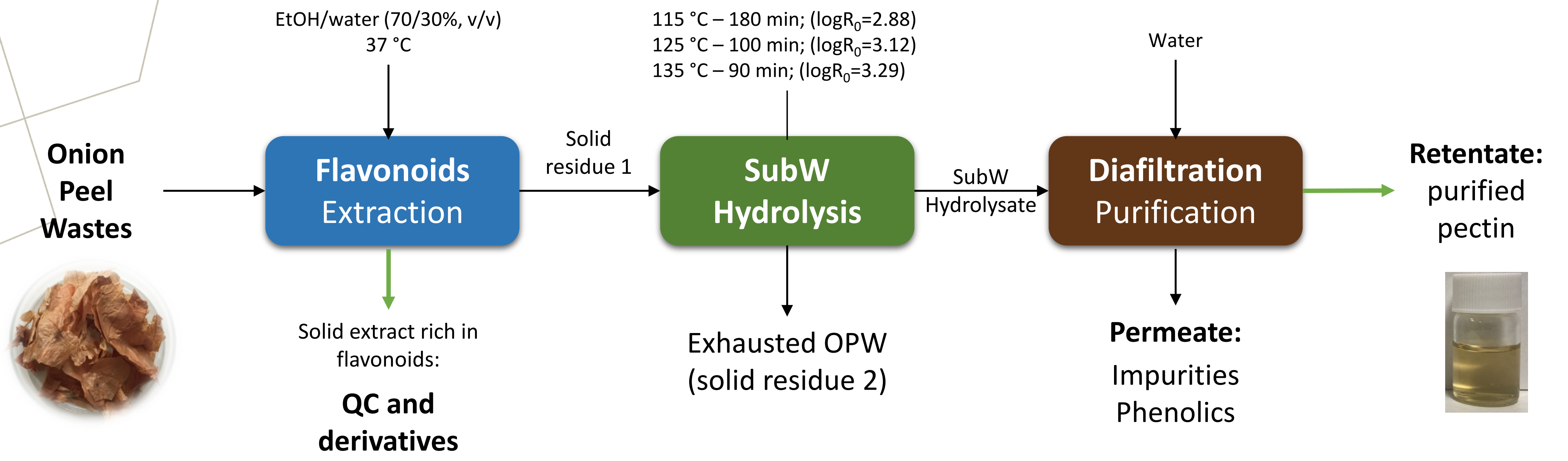
COMPLETE VALORIZATION STRATEGY

Development of extraction technologies based on green solvents

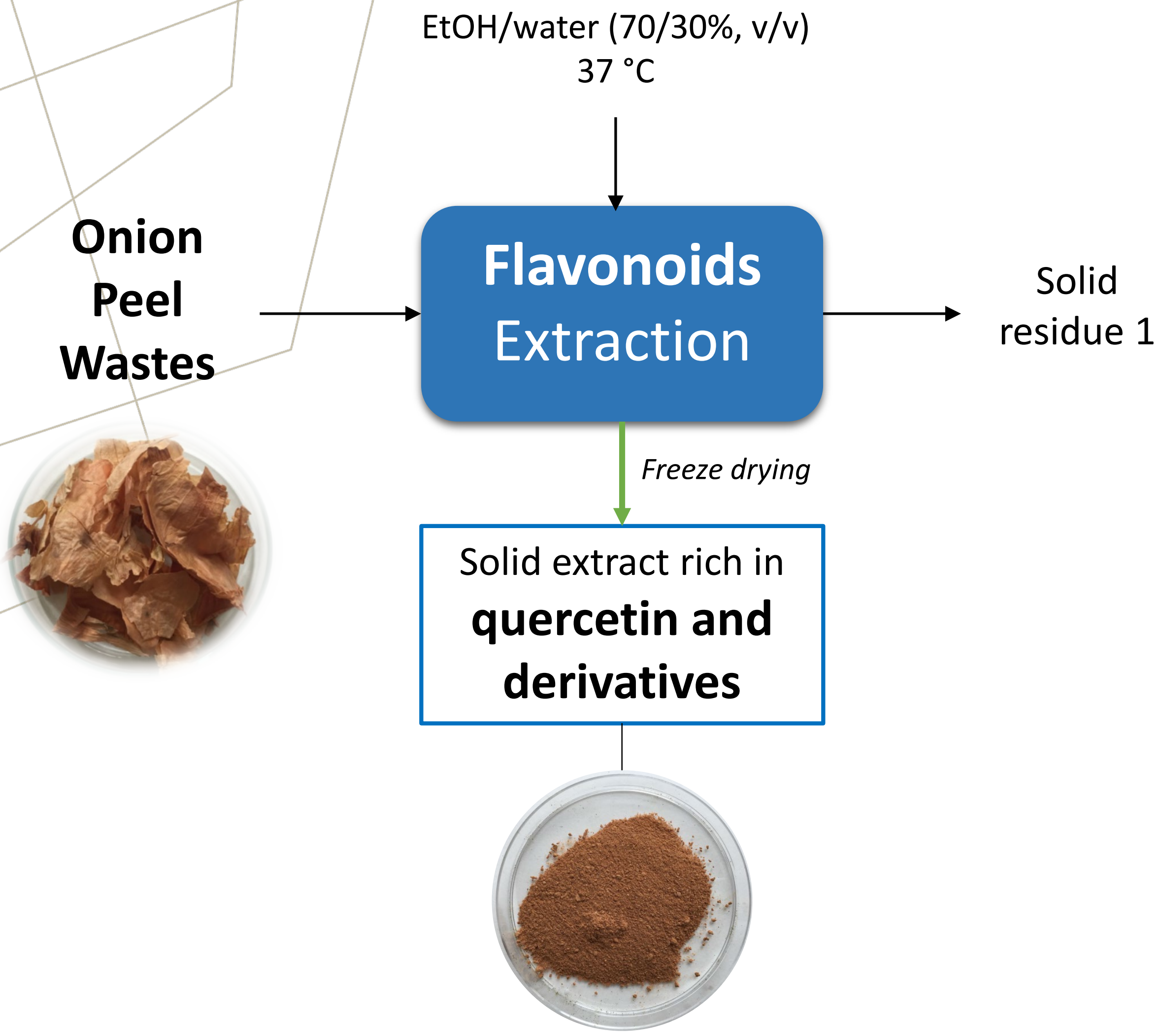
Dowstream processing: membrane technology

VALORIZATION STRATEGY

➢ SIMPLIFIED CASCADE PROCESS



1ST STAGE: Flavonoids recovery



FINAL PRODUCT: SOLID EXTRACT

10% yield

Composition:

- 18% flavonoids (50% QC4'; 33% QC)

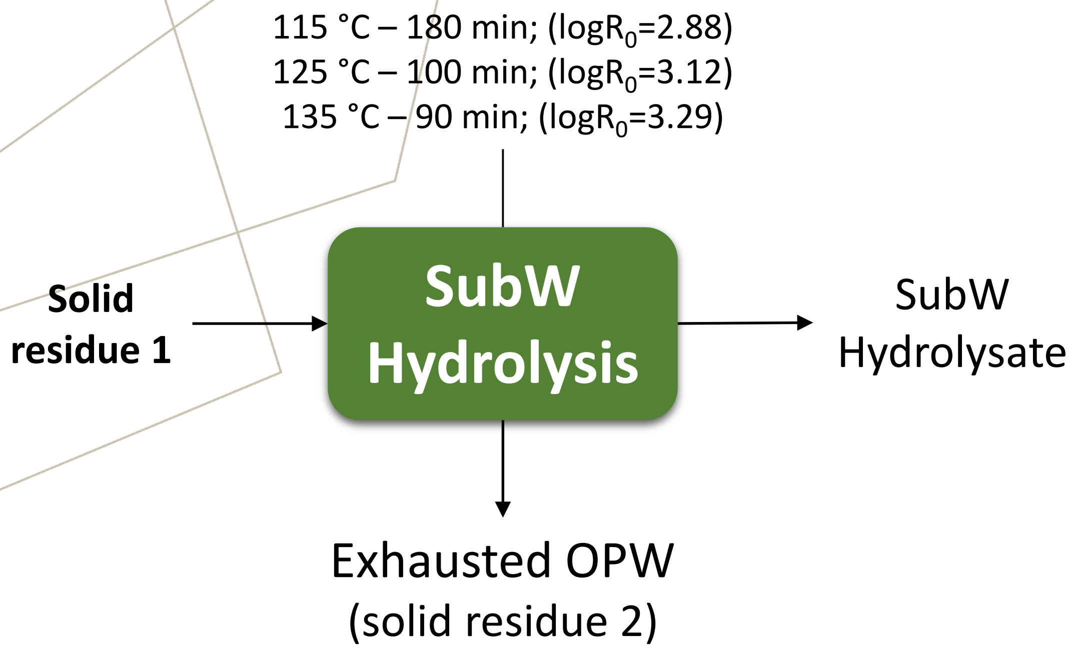
High antioxidant capacity

SOLID EXTRACT USE

Incorporation in meat preparations

Substitute artificial antioxidants

2ND STAGE: Subcritical Water Hydrolysis



SUBCRITICAL WATER (SubW)

Water at temperature ranging from 100 °C (boiling point) to 374 °C (critical point); remains in a liquid state due to the application of pressure

Change in physical properties (viscosity, surface tension, dielectric constant, ionic product…)

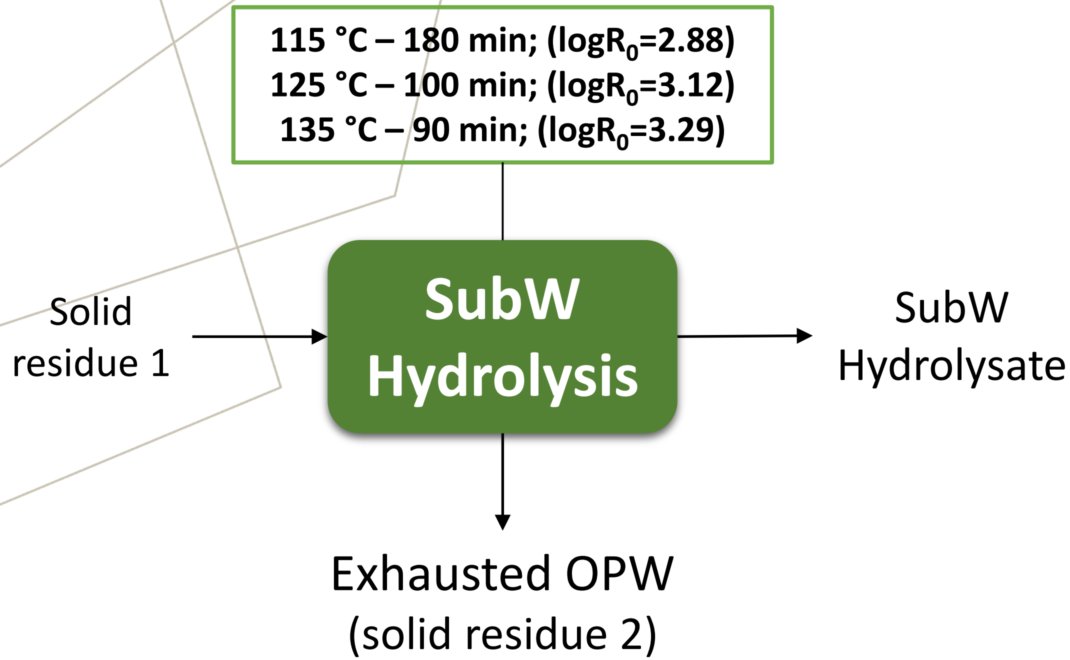
PROMOTION OF THE HYDROLYSIS REACTIONS

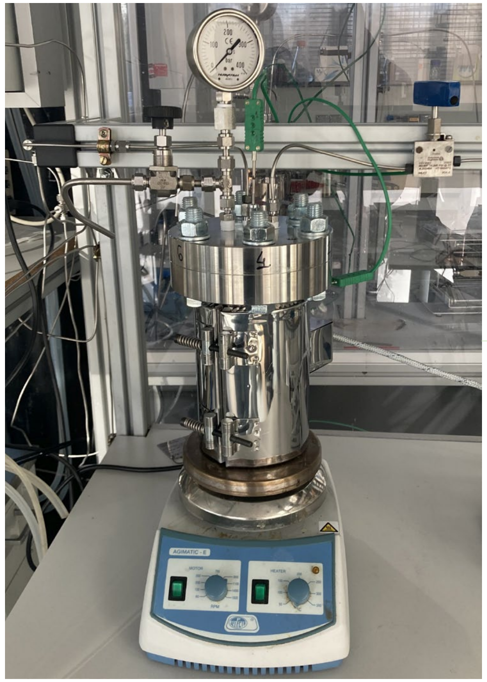
Enhances the release of pectin, as an alternative to the conventional processes based on acid hydrolysis

Drawbacks:

- Pectin molecular weight loss
- Formation of degradation products

2ND STAGE: Subcritical Water Hydrolysis





Batch extractor (0.5 L)

105-160 °C

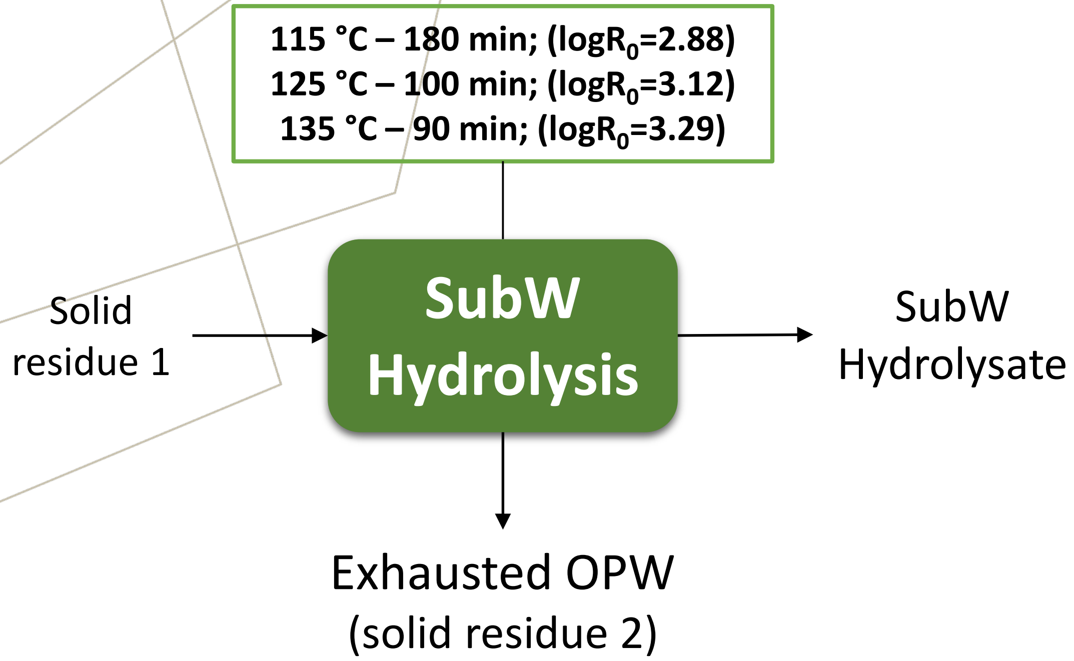
Up to 180 min

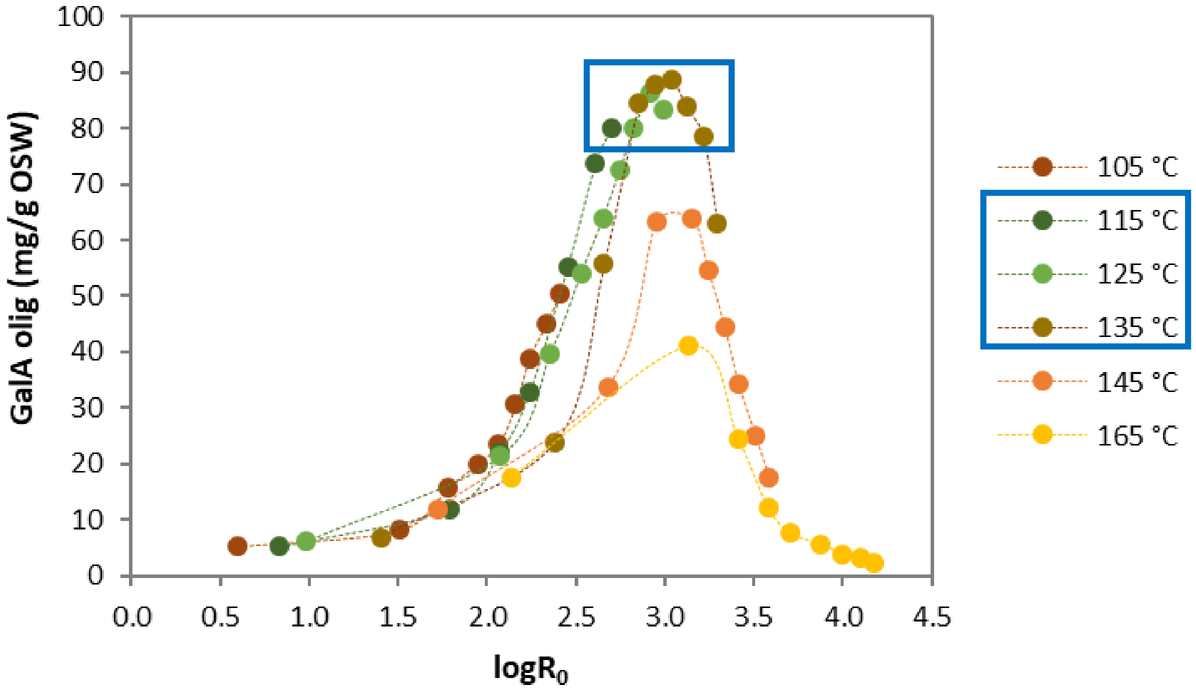
- Severity factor: heating + isothermal + cooling

$$logR_0 = log\left[\int_0^{t_H} exp\left(\frac{T(t)-100}{14.75}\right)\cdot dt + t\cdot exp\left(\frac{T(t)-100}{14.75}\right) + \int_0^{t_C} exp\left(\frac{T(t)-100}{14.75}\right)\cdot dt\right]$$

Benito Román et al. Food Hydrocolloids, 2024, 153, 109957

2^{ND} STAGE: Subcritical Water Hydrolysis





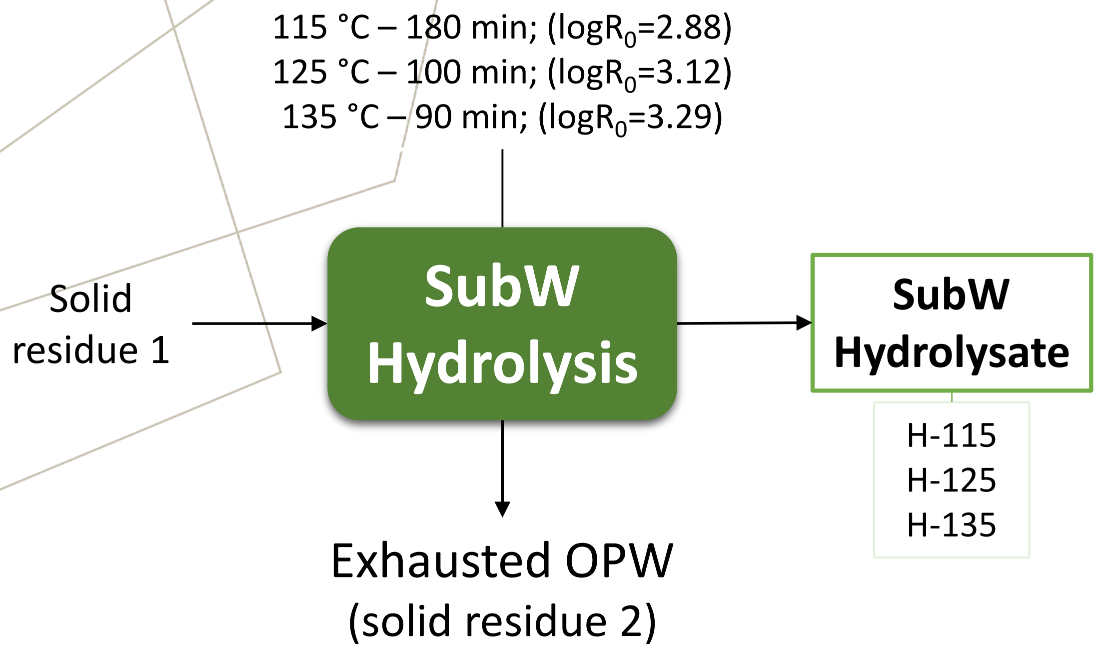
- **<u>Maximum</u>**

  Log R_0 2.9-3.3
  Narrow window

- Sharp decrease when increasing severity factor

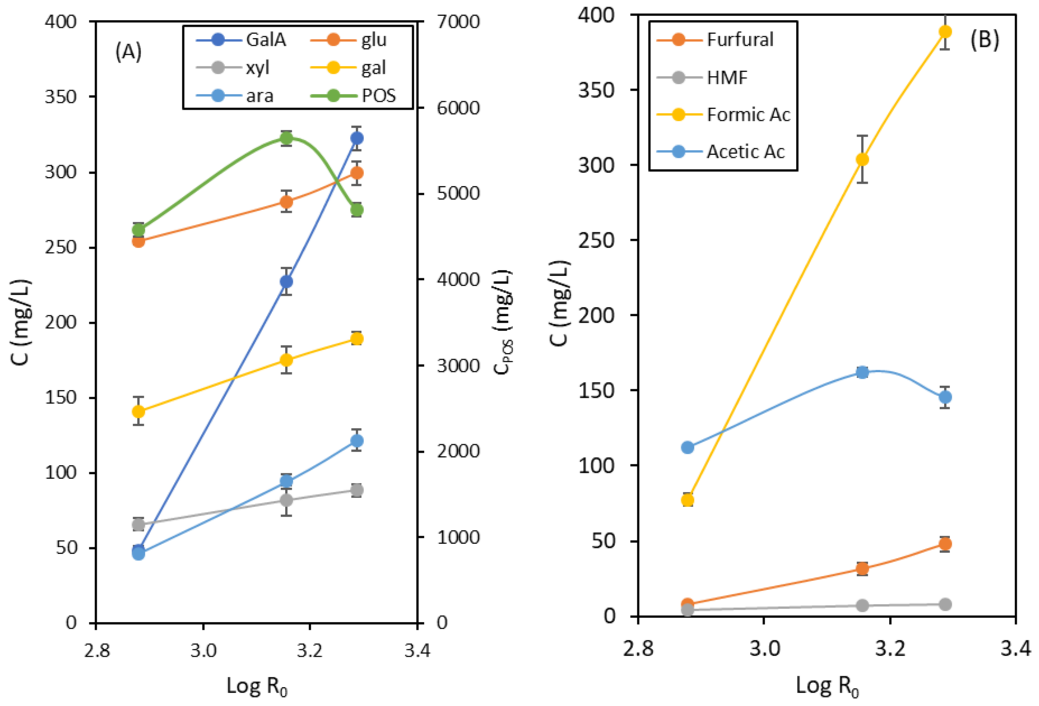
Benito Román et al. Food Hydrocolloids, 2024, 153, 109957

2ND STAGE: Subcritical Water Hydrolysis



Complex composition:

- Mixture of pectin, free monosaccharides, organic acids (formic and acetic) and sugar degradation products (furfural, HMF)
- Intensity increases degradation



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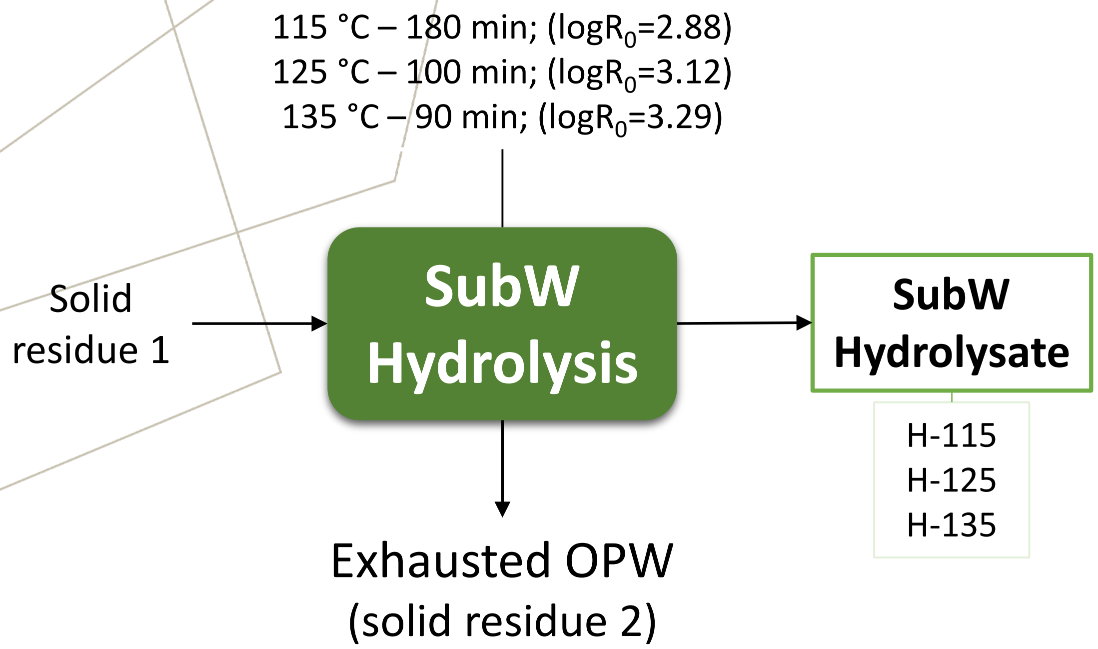


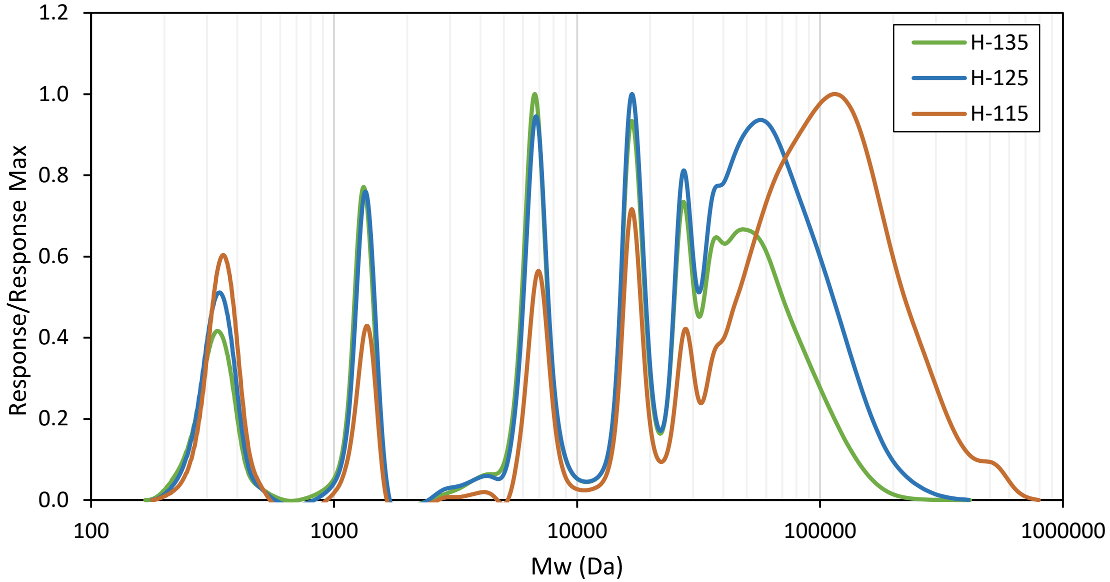
Complex molecular weight distribution:

- Several families
- Most abundant:

H-115: 126 kDa; average 96 kDa

H-125: 78 kDa; average 45 kDa

H-135: 70 kDa; average 36 kDa



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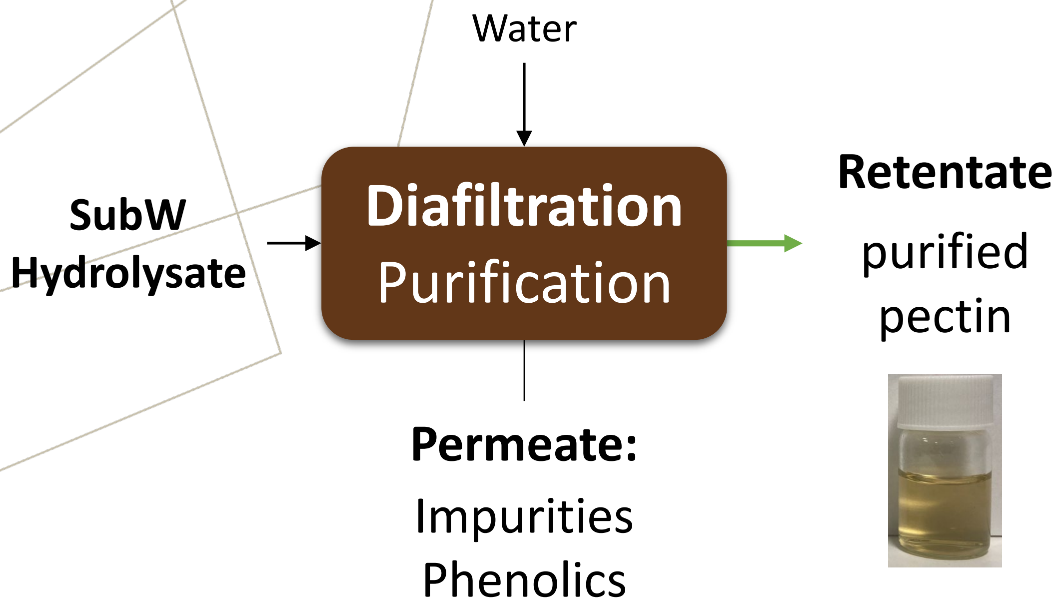
3RD STAGE: Purification

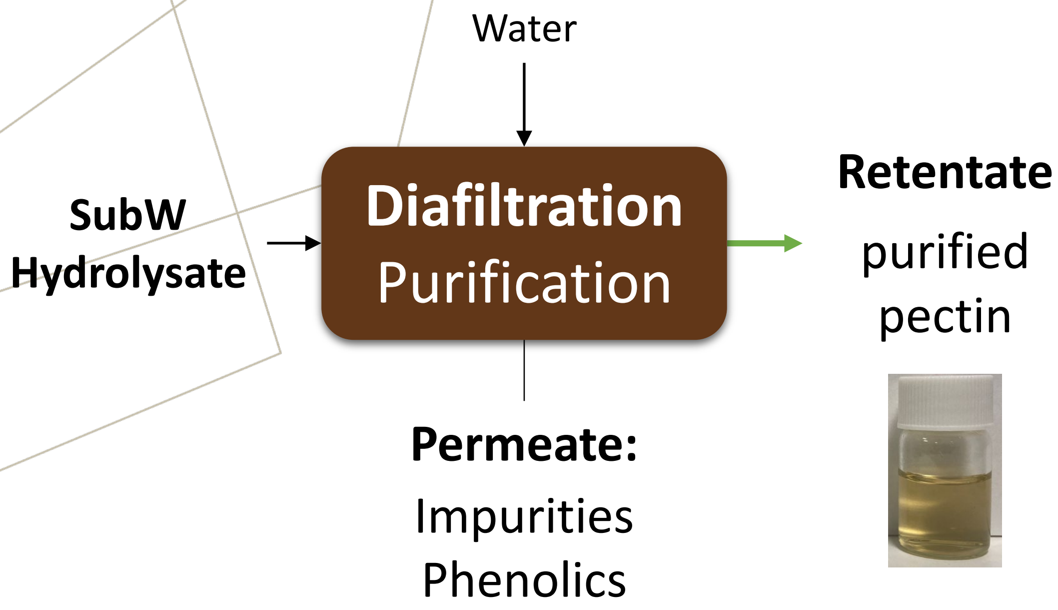


MEMBRANE TECHNOLOGY

- Ceramic membrane: Filtanium™, active layer of TiO_2 supported on titania (TAMI industries)
- MWCO: 50 kDa
- 7 inner channels; 25 cm; effective filtration area of 0.0132 m^2
- Operated in diafiltration mode

Ruiz et al. Journal of Membrane Science, 2024, 708, 123054

3RD STAGE: Purification



MEMBRANE TECHNOLOGY

Study of fouling mechanism: Hermia's equation

$$\frac{dJ}{dt} = -k \cdot (J - J^{*}) \cdot J^{2-n}$$

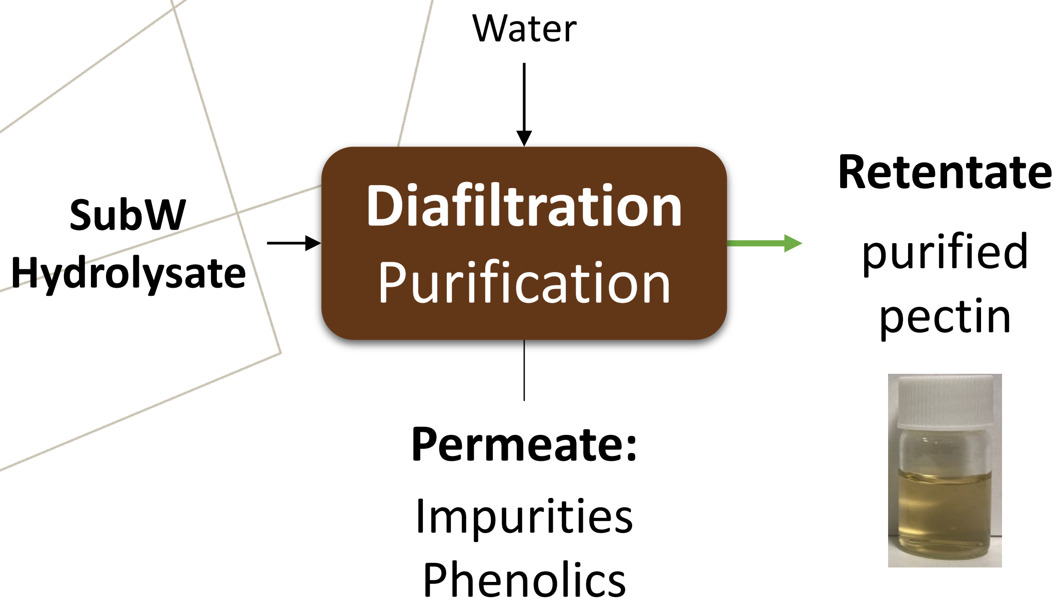
Where:

n=2, complete blocking model

n=1.5, standard blocking model

n=0, cake layer model

3RD STAGE: Purification

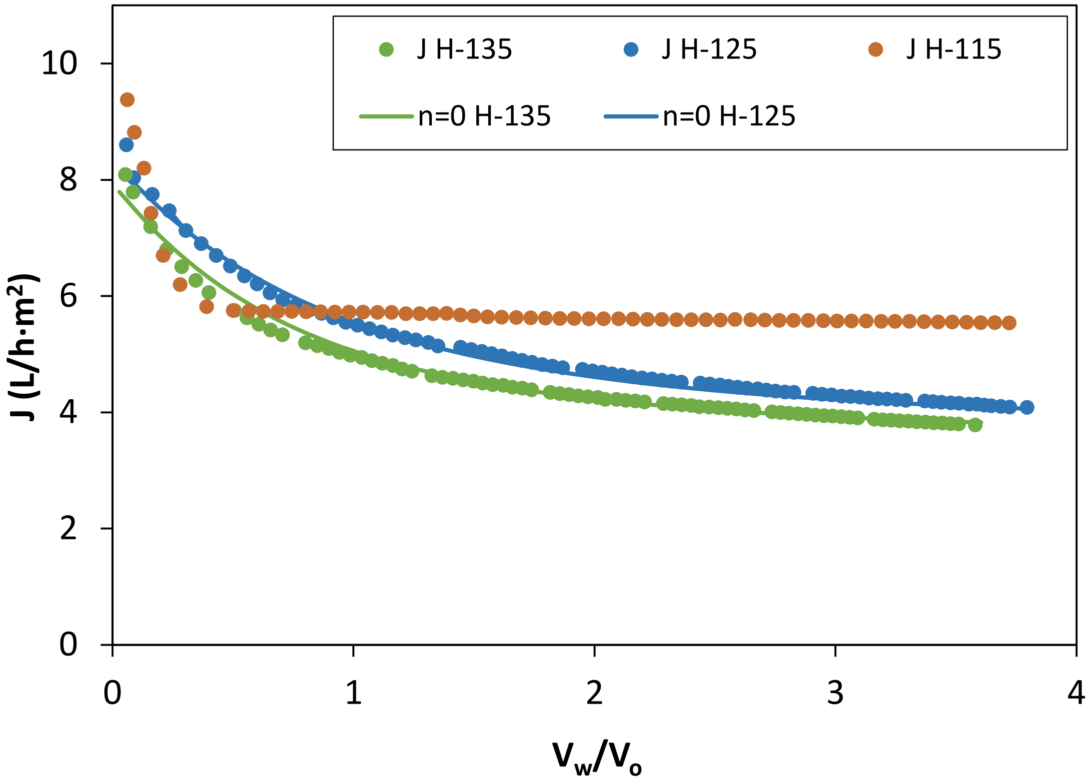


PERMEATE FLUX

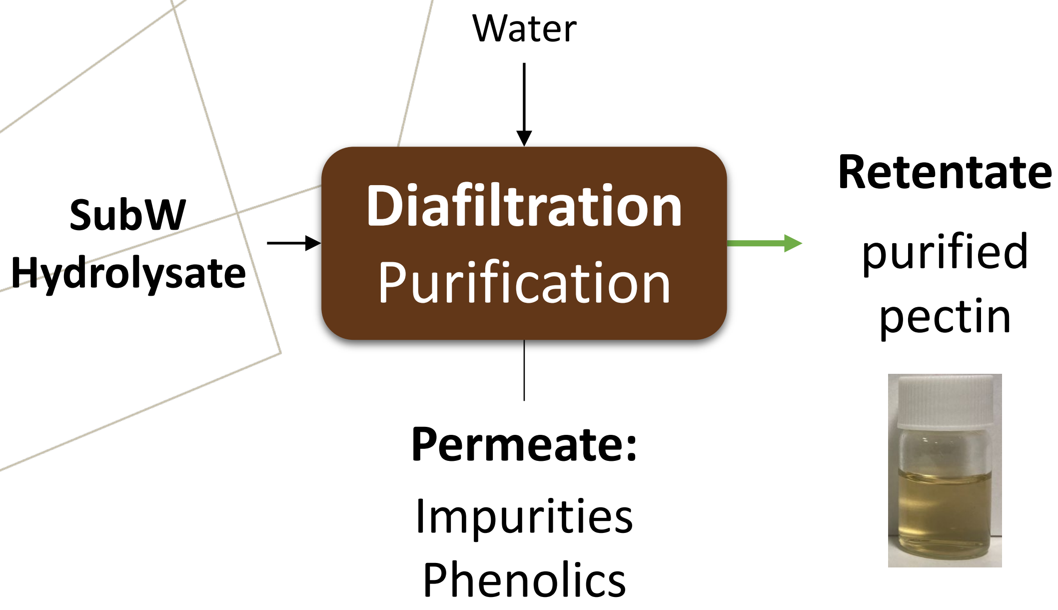
Pure water: 83 L/h·m^2

Dramatic reduction when filtering the SubW hydrolysates

Cake layer formation (n=0) is the dominant fouling mechanism.



3^{RD} STAGE: Purification

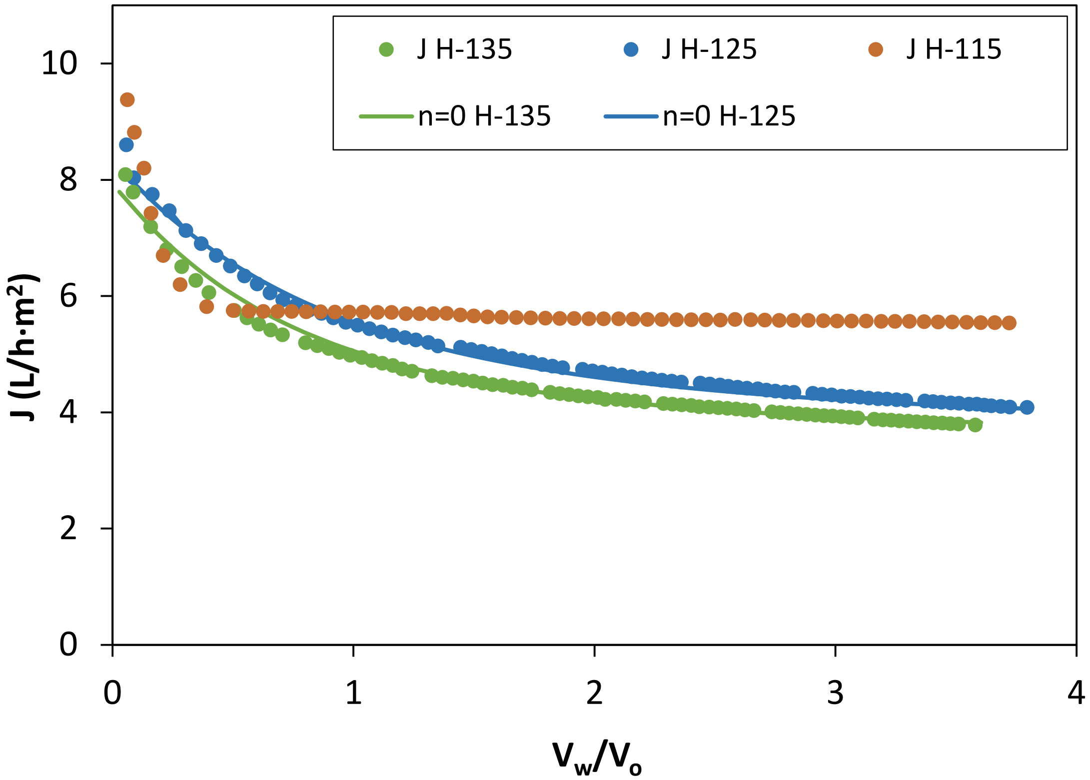


PERMEATE FLUX

Pure water: 83 L/h·m^2

Dramatic reduction when filtering the SubW hydrolysates

Cake layer formation (n=0) is the dominant fouling mechanism. **Strategy to mitigate fouling?**



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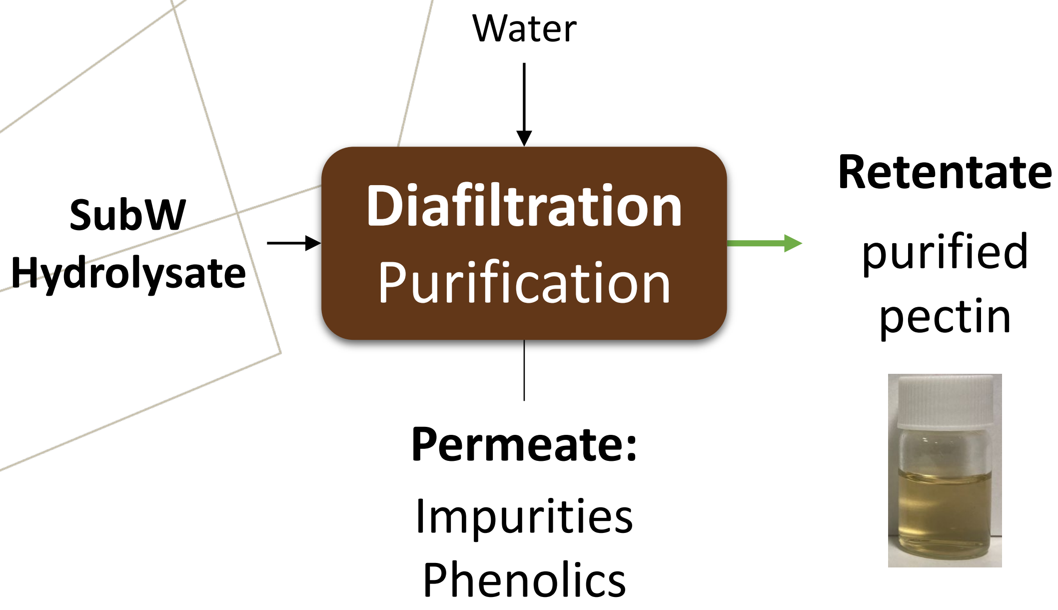
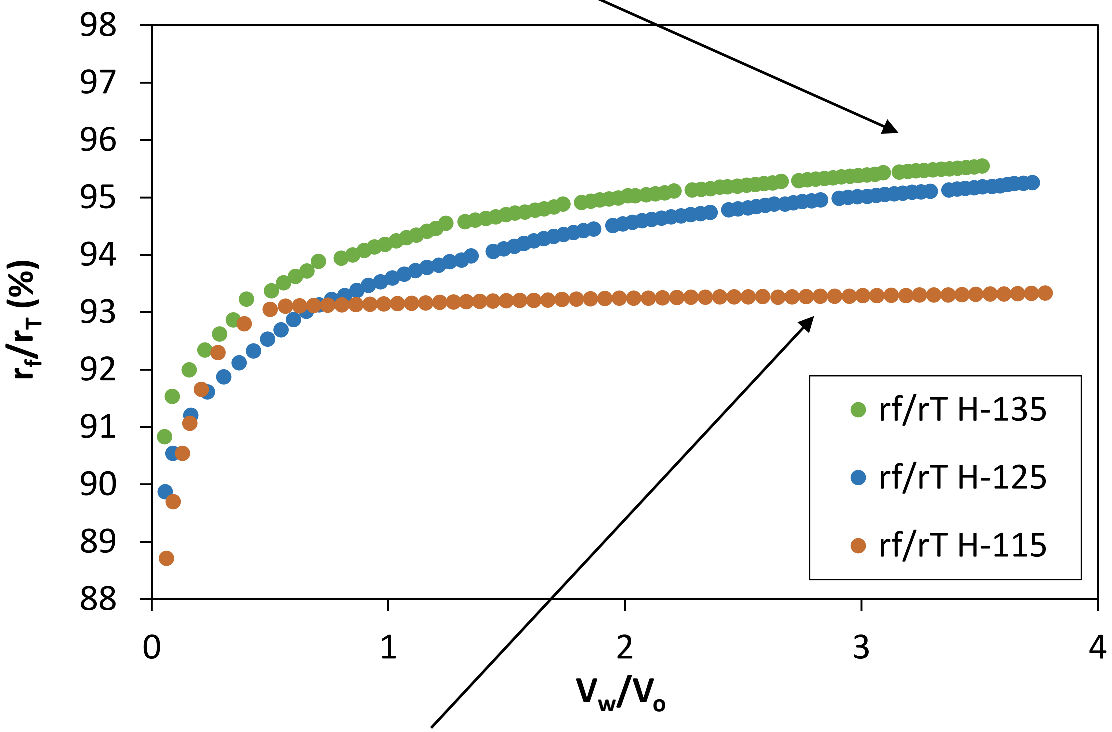


PERMEATE FLUX: Filtration resistance

H-135 and H-125 hydrolysates, increases throughout the diafiltration (DF) process



H-115 hydrolysate exhibited a different fouling behavior, with the r_f/r_T ratio stabilizing after a rapid increase at a diafiltration volume of just 0.5

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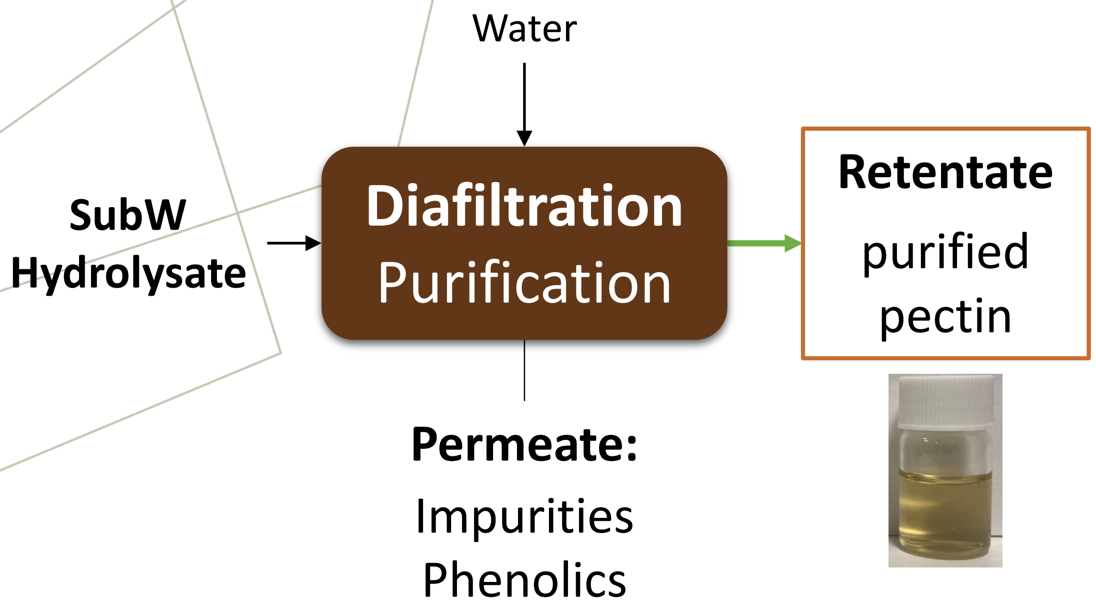
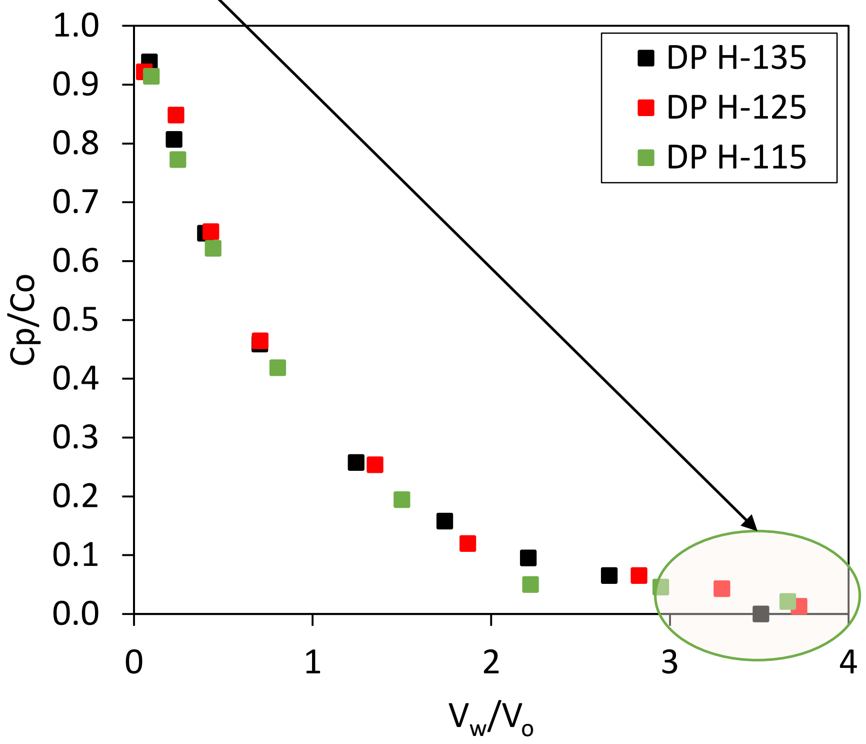
3RD STAGE: Purification



IMPURITIES REMOVAL

Impurity Transport Profile Across the Membrane

Complete removal of the impurities after a diafiltration volume of 3.5



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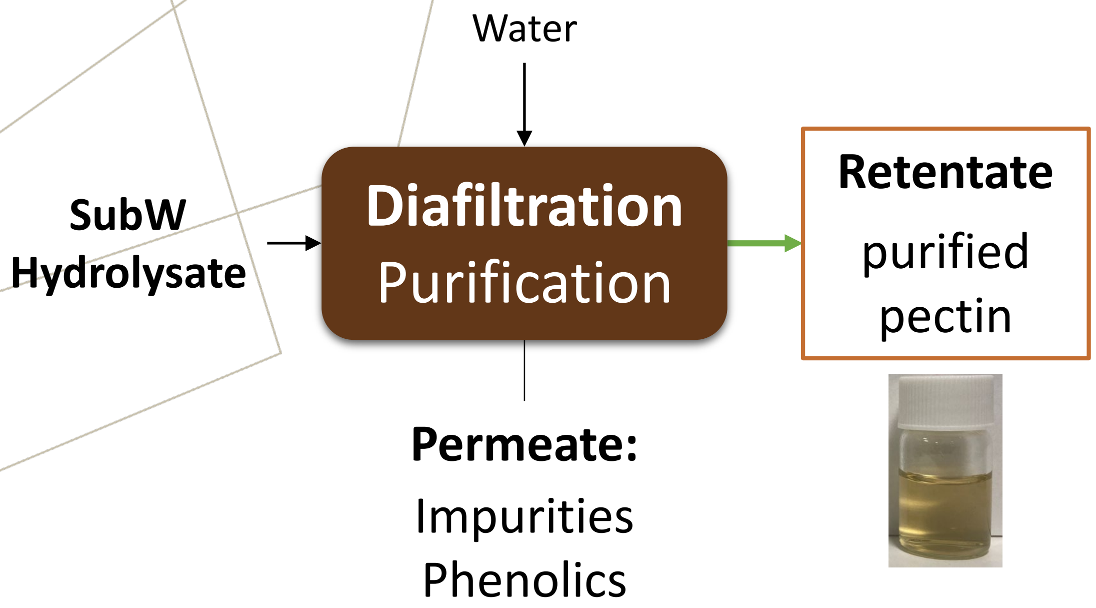
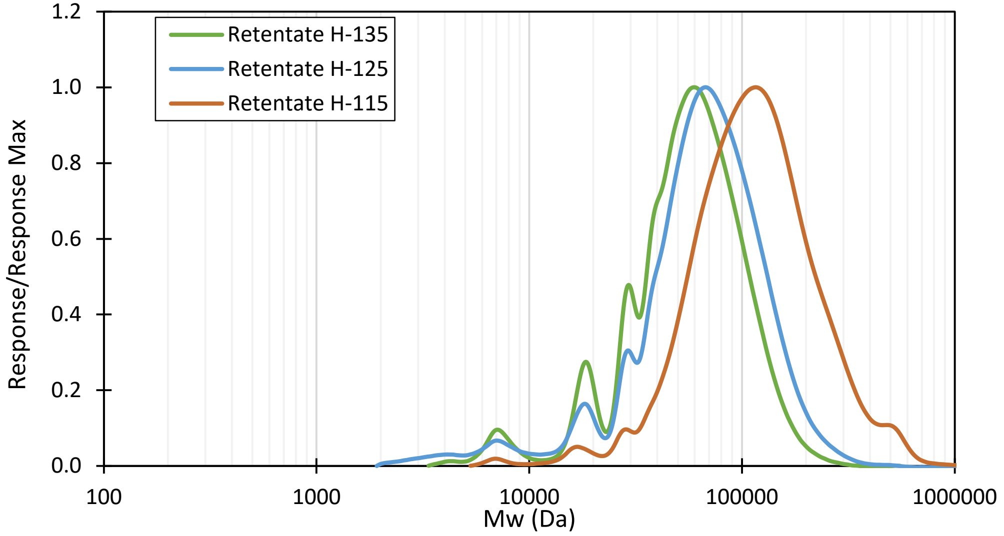


MOLECULAR WEIGHT PROFILE OF THE RETENTATE



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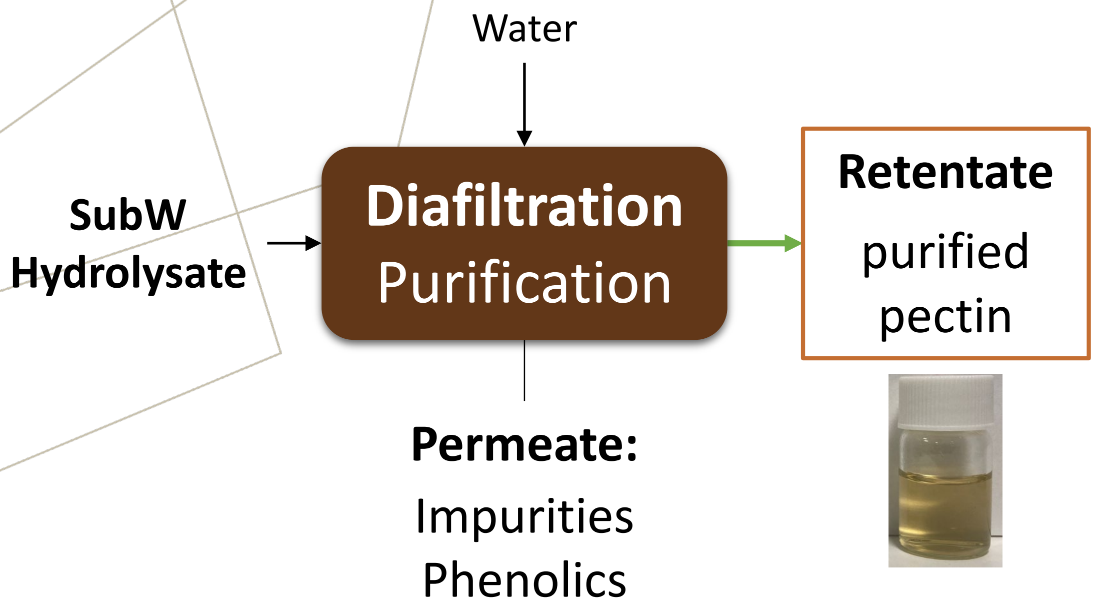

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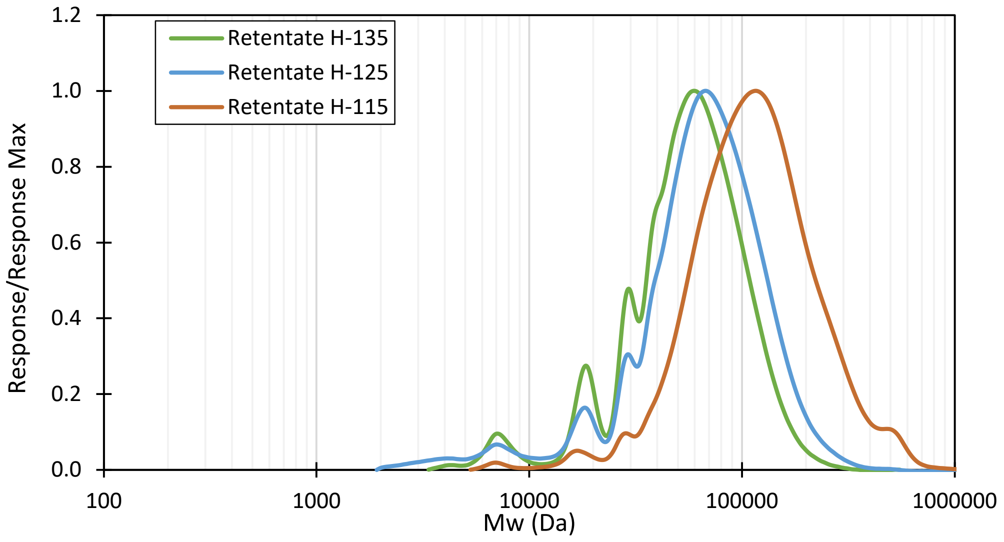
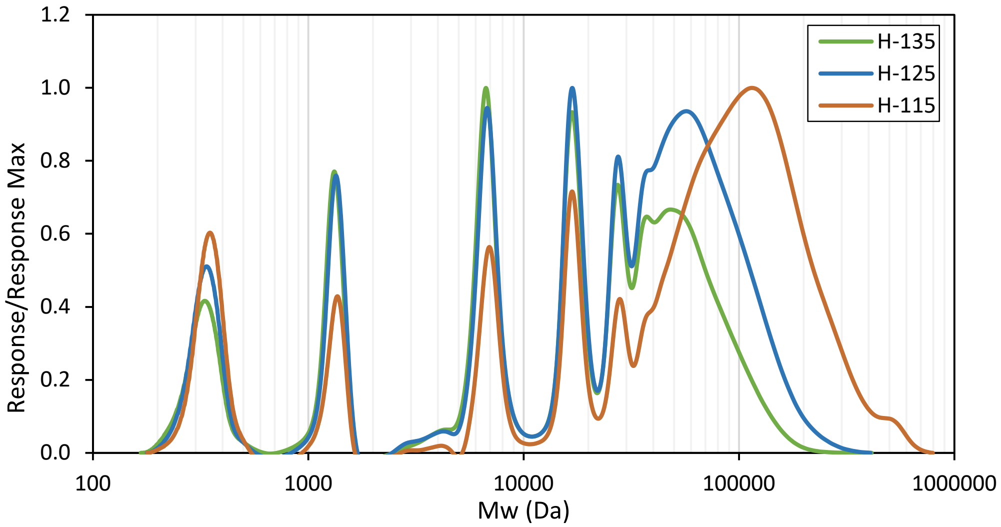
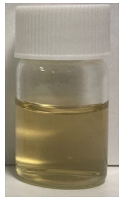




3RD STAGE: Purification

Water

SubW Hydrolysate → **Diafiltration** Purification → **Retentate purified pectin**



Permeate:

Impurities

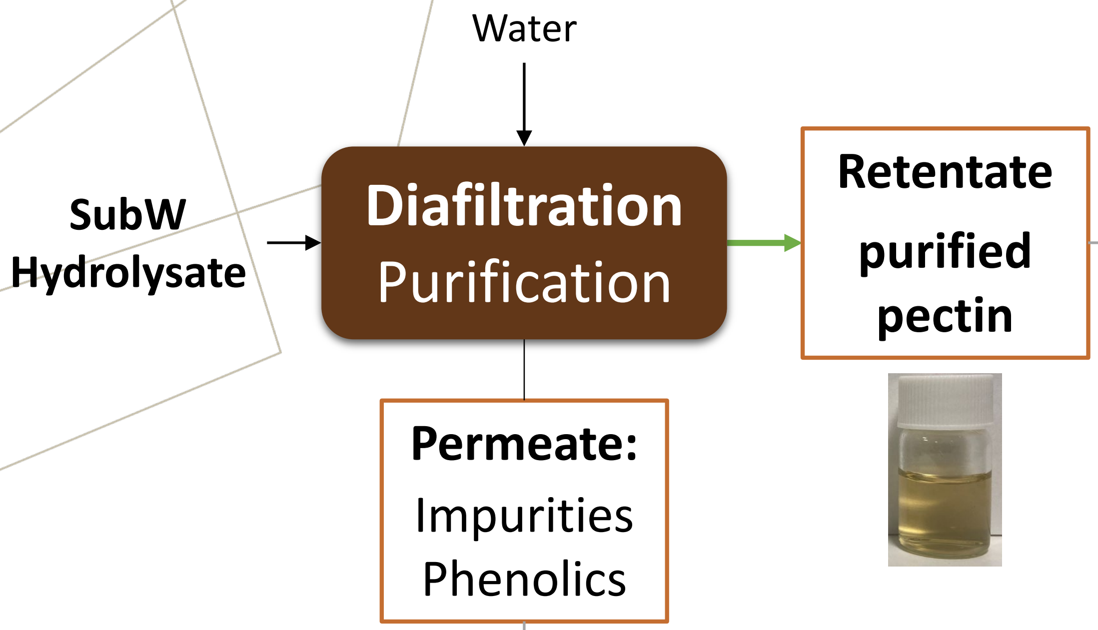
Phenolics

PURITY AND MW OF THE RETENTATES

Sample	Purity (%)	Mw (kDa)
H-135	64.1	74
H-125	68.3	84
H-115	74.6	135

$$\text{Purity (wt.\%)} = \frac{C_{\text{Pectin}}}{C_{\text{Total Solids}}} \cdot 100$$

3RD STAGE: Purification



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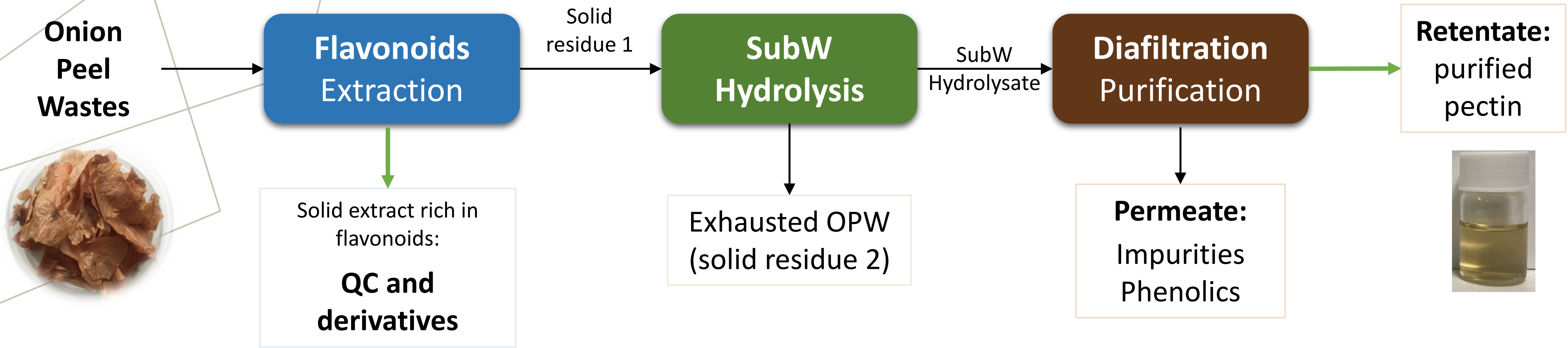
$$\text{Purity (wt. \%)} = \frac{C_{\text{Pectin}}}{C_{\text{Total Solids}}} \cdot 100$$

Further valorization by recovering phenolics and other low molecular weight compounds

VALORIZATION STRATEGY

➢ **Completing the cascade**

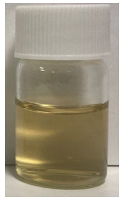


VALORIZATION STRATEGY

➢ **Completing the cascade**

Onion Peel Wastes

Flavonoids Extraction → Solid residue 1 → **SubW Hydrolysis** → SubW Hydrolysate → **Diafiltration** Purification → **Retentate:** purified pectin



Flavonoids Extraction → Solid extract rich in flavonoids: **QC and derivatives**

SubW Hydrolysis → Exhausted OPW (solid residue 2)

Composition

HHV

Cellulose or other compounds

Diafiltration Purification → **Permeate:** Impurities Phenolics

VALORIZATION STRATEGY

➢ **Completing the cascade**

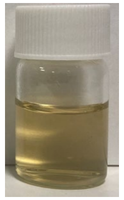
Onion Peel Wastes

→ **Flavonoids** Extraction → Solid extract rich in flavonoids: **QC and derivatives**

→ Solid residue 1 → **SubW Hydrolysis** → Exhausted OPW (solid residue 2) → **Composition**: HHV; Cellulose or other compounds

→ SubW Hydrolysate → **Diafiltration** Purification

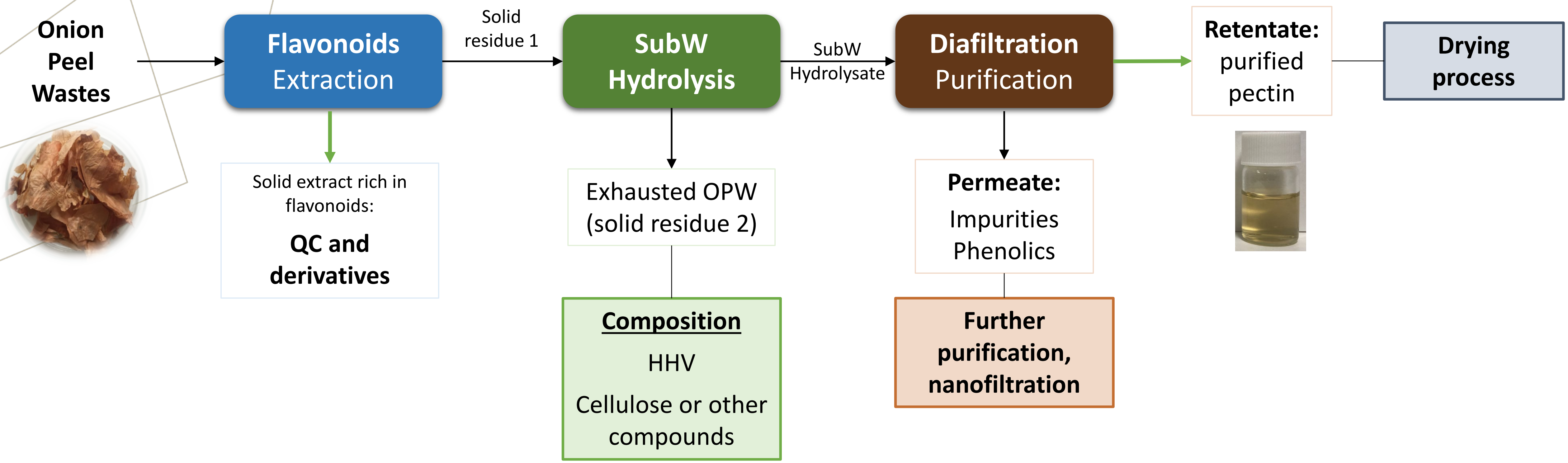
→ **Retentate:** purified pectin



→ **Permeate:** Impurities, Phenolics → **Further purification, nanofiltration**

VALORIZATION STRATEGY

➢ **Completing the cascade**



CONCLUSIONS

ONION PEEL WASTES

Rich in bioactive compounds

Local problem, global solution

MULTISTAGE CASCADE

Water-based technologies for extraction and purification:

1st product: extract rich in flavonoids with high antioxidant capacity

2nd product: purified pectin of controlled molecular weight

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CONCLUSIONS

FUTURE WORK

Develop and strategy to mitigate fouling during filtration

Complete the actual cascade: new stages to add more value to the onion peel wastes

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ACKNOWLEDGEMENTS

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