WINE CLARIFICATION: IMPROVEMENT OF CROSSFLOW MICROFILTRATION USING A HYBRID PROCESS

Dissertation presented

by

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INTRODUCTION

WINE STABILISATION & CLARIFICATION

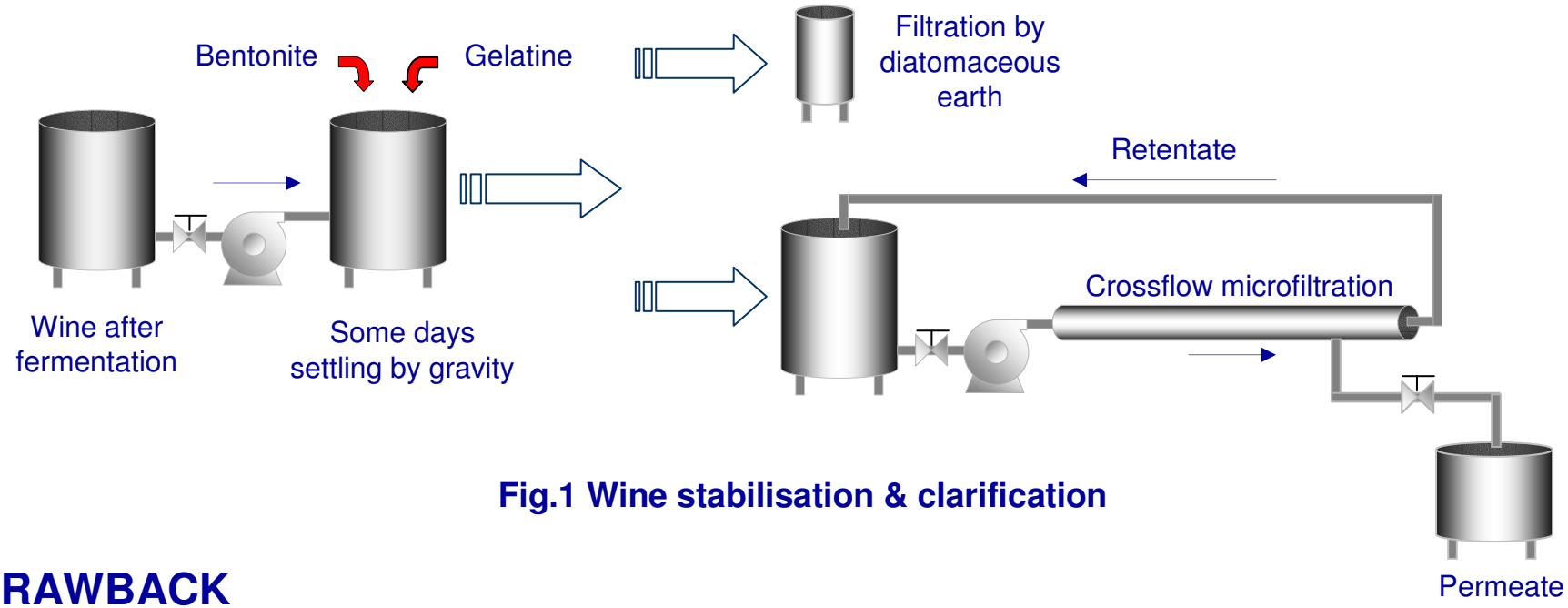


Fig.1 Wine stabilisation & clarification

DRAWBACK

- Low selectivity of adsorbent material (wine quality changes)
- Batch process
- High environmental impact
- **Flux decline during the crossflow microfiltration**

INTRODUCTION

HOW TO SOLVE THE PROBLEM?

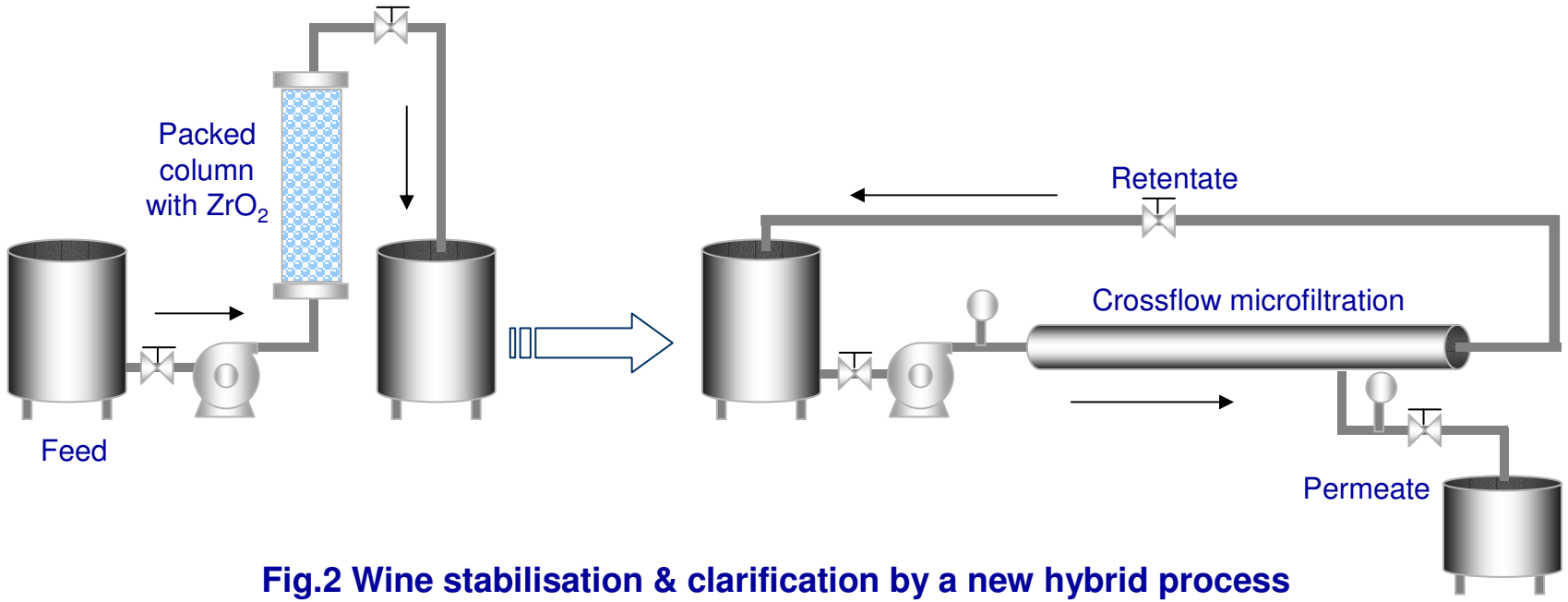


Fig.2 Wine stabilisation & clarification by a new hybrid process

ADVANTAGES

- Possibility of applying a continuous process
- Low environmental impact
- Possibility of regenerating the adsorbent material

INTRODUCTION

WHY USING ZIRCONIUM OXIDE?

- Insoluble in water and negligible solubility in other solvents
- Inert and innocuous, though the ZrO_2-powder or a bad manipulation could cause irritation
- High chemical, thermal and mechanical resistance
- Possibility to regenerate it

OBJECTIVES

The main goal of this work is to increase the yield of the wine crossflow microfiltration using a new hybrid process

- ✓ To evaluate the yield of the crossflow microfiltration
- ✓ To evaluate the effect of the proteins and polyphenols content on the permeate flux
- ✓ To evaluate the wine protein stabilisation
- ✓ To identify the molecular weight range of unstable proteins or causing of membrane fouling

MATERIALS & METHODS

WINE SAMPLES

- Pinot Noir wine monovarietal
- Harvests 2004
- These samples were obtained from Mas dels Frares Winery, Tarragona, Spain.

MATERIALS & METHODS

HYBRID PROCESS

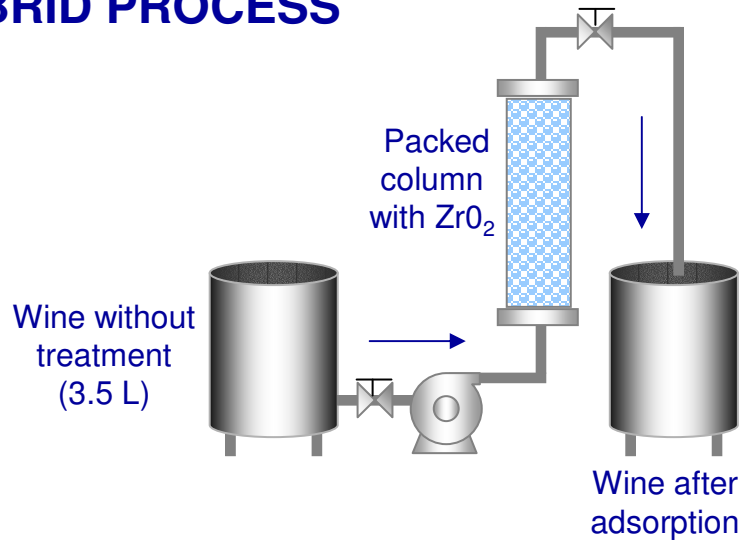


Fig.3 Adsorption Process

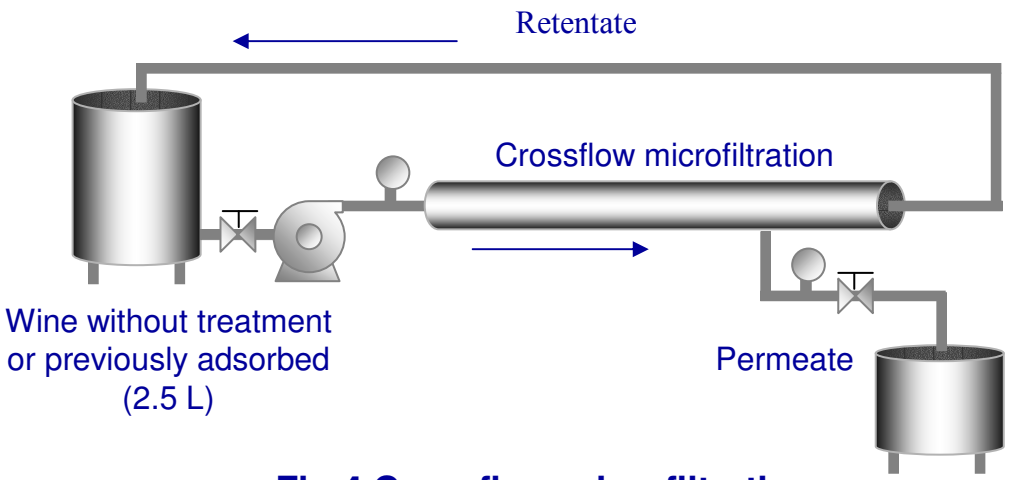


Fig.4 Crossflow microfiltration

Adsorption process

- Zirconium oxide pellet 3-6 mm
- The packed column is of 40x165 mm with 250 g of ZrO_2
- Flow rate of 4 mL/min (1 h residence time, 1 BV/h)
- Process time ≈ 14.5 h

Crossflow microfiltration

- Tubular module membrane: ceramic ZrO_2-TiO_2, length 25 cm, area 0.0094 m^2, pore size 0.2 µm
- Transmembrane pressure: 1.5 bar
- Crossflow velocity: 2 m/s
- Volumetric flow rate of retentate: 3.7 L/min
- Room temperature ≈20 ºC
- Process time 30 min

MATERIALS & METHODS

THERMAL REGENERATION AND CHARACTERIZATION OF ADSORBENT MATERIAL

Thermal regeneration:

- 500ºC for 24 hours

Characterization of adsorbent material (Brunauer-Emmet-Teller):

- Surface area
- Pore size
- Pore Volume
- Pore size distribution

MATERIALS & METHODS

PHYSICOCHEMICAL PROPERTIES OF WINE (*)

- pH
- Total acidity, g/L tartaric acid
- Volatile acidity, g/L acetic acid
- Fixed acidity, g/L tartaric acid
- Reducing Sugar, g/L
- Volumetric alcoholic degree, %vol
- Total dry extract, g/L
- Sulphates, g/L K_2SO_4
- Free Sulphurous, SO_2 (mg/L)
- Total Sulphurous, SO_2 (mg/L)
- Chromatics characteristics (absorbance at 420, 520 and 620nm)

(*) Official Newspaper of the European communities. Commission Regulation (EEC) No 2676/90 of 17 September 1990, Methods for the Analysis of Wines.

MATERIALS & METHODS

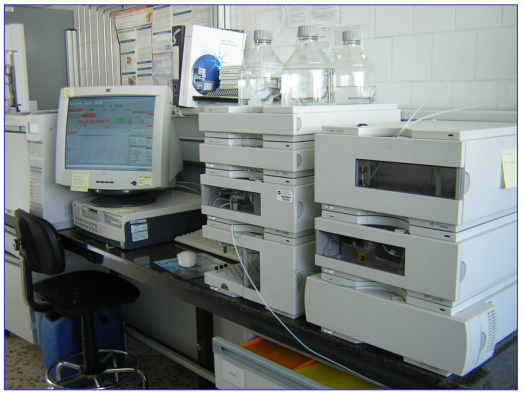
PROTEINS ANALYSIS

TOTAL PROTEINS

- Bradford's Method (BSA, Bovine serum albumin)

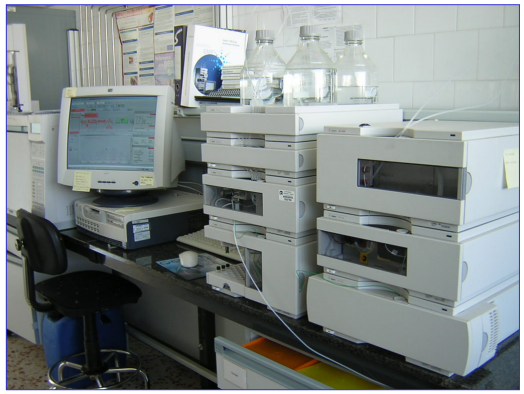
PROTEIN FRACTIONS (Czekaj et al., 2001)

- HPLC
- Molecular Weight (MW)
- Standard protein (100 mg/L):
  - Bovine serum albumin (BSA) (67 kDa)
  - Ovalbumin (OVA) (45 kDa)
  - Lysozyme (LY) (14.5 kDa)



MATERIALS & METHODS

POLYPHENOLS ANALYSIS



TOTAL POLYPHENOLS

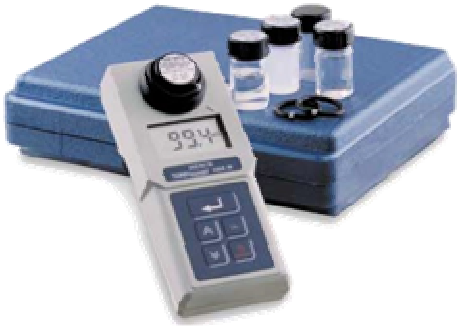
- Folin's Method (TPI)

POLYPHENOLIC PROFILE (Betés-Saura et al., 1996)

- HPLC
- Standard polyphenols:
  - Gallic acid, Benzoic acid, Furfural acid, etc.

MATERIALS & METHODS

PROTEIN HEAT STABILITY TEST (Moine-Ledoux et al., 1999)

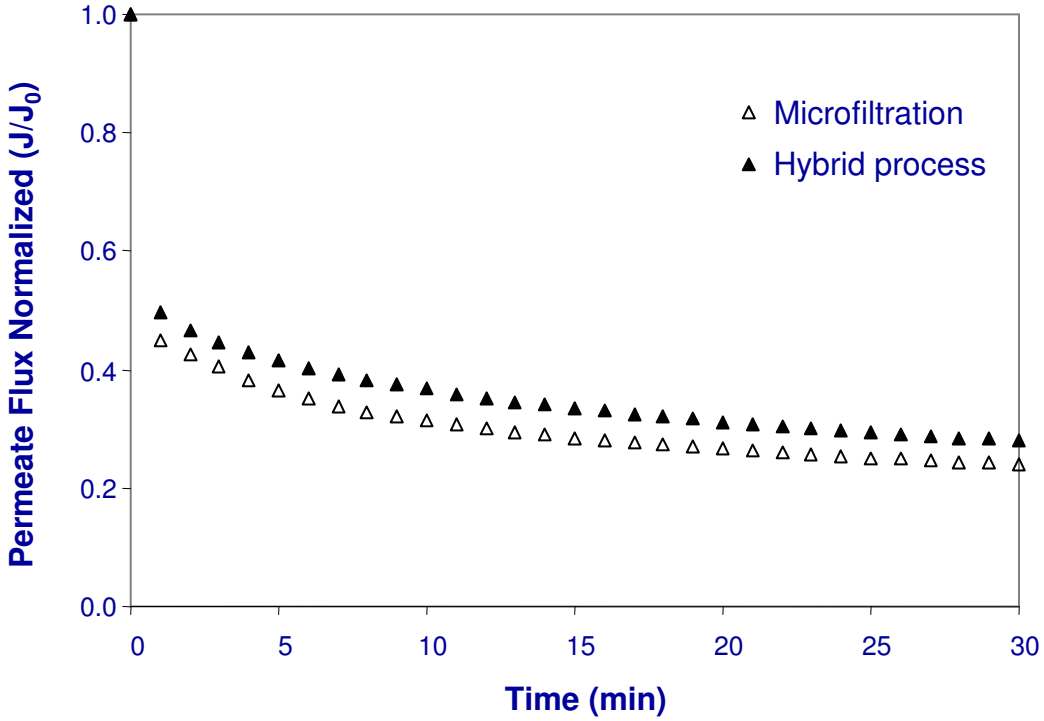


- 2 h at 80ºC and then 2 h at 4ºC
- Nephelometric turbidity units (NTU)
- Wine protein stable if turbidity < 2 NTU
- Also the precipitated proteins are removed by centrifugation and the supernatants of wine analysed by HPLC.

EFFECT OF PROTEINS AND POLYPHENOLS ON THE PERMEATE FLUX

- Bentonite (2g/L)
- Activated carbon (10 mL/L)
- Bentonite + activated carbon (2g/L+10 mL/L)

THE PERMEATE FLUX



- The permeate flux increased between 15 to 20% using the hybrid process.

Treatment	Permeate Flux (L/h·m^2)
Microfiltration	130 ± 2.1
Hybrid Process	153 ± 6.4

Initial permeate flux 530 ± 9 L/h·m^2

Fig.5 Pinot Noir wine microfiltration with and without adsorption process

EFFECT OF PROTEINS AND POLYPHENOLS AND PROTEIN STABILITY

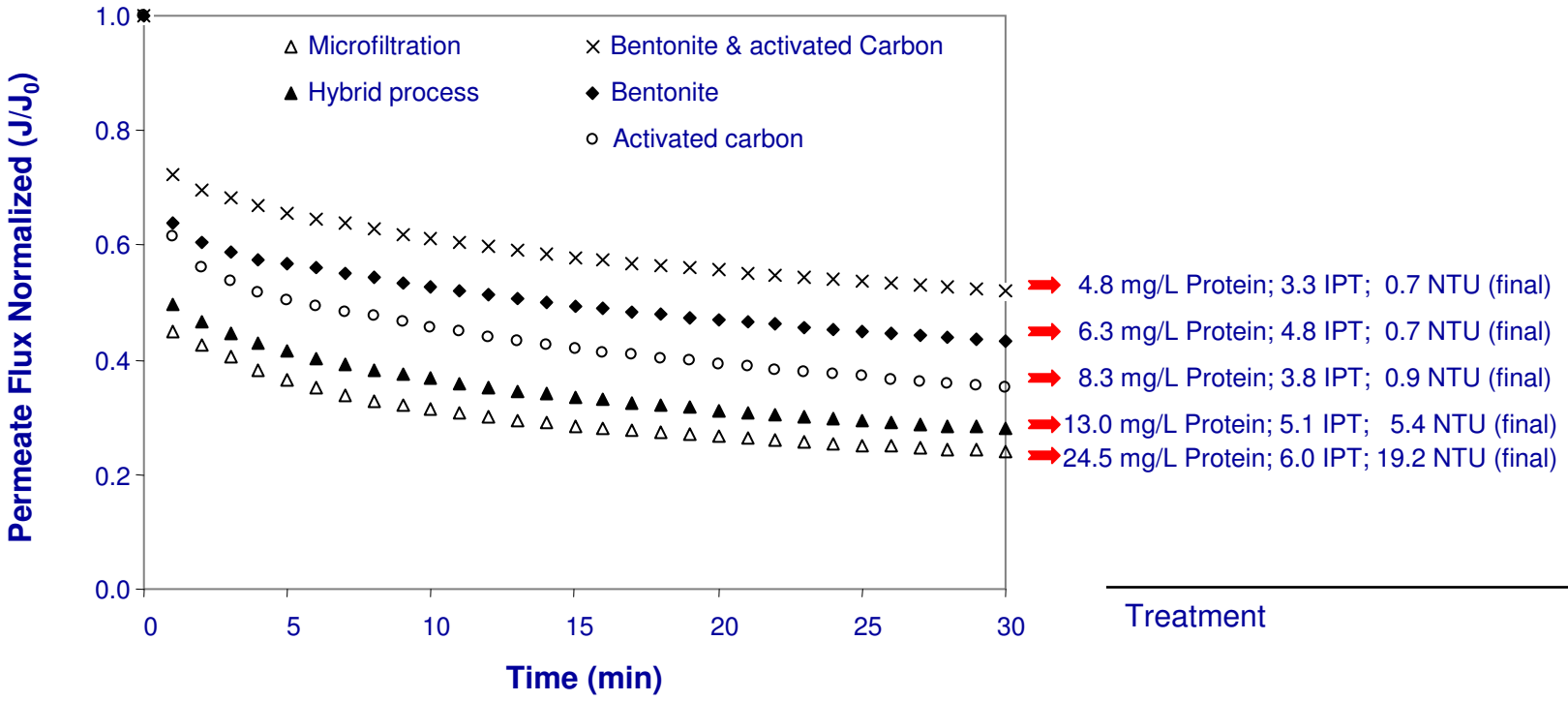


Fig.6 Permeate flux of Pinot Noir wine during the microfiltration process considering different treatments

Treatment	Permeate Flux (L/h·m^2) at 30 min
Microfiltration	130
Hybrid Process	153
Activated carbon	285
Bentonite	296
Bentonite + activated carbon	347

❑ Non-parametric statistical (Spearman and Kendall's tau coefficients) significance level of 1% (α=0.01) using WinSTAT® Software.

TABLE 4. PHYSICOCHEMICAL PROPERTIES OF WINE

Analytical Parameter	Wine without Treatment	Microfiltration	Adsorption	Hybrid Process
pH	3.04	3.02	3.05	3.08
Total Acidity, Tartaric acid (g/L)	6.53	6.47	5.89[a]	5.31[a]
Volatile Acidity, Acetic acid (g/L)	0.48	0.43	0.38[a]	0.36[a]
Fixed Acidity, Tartaric acid (g/L)	6.33	6.38	5.73[a]	5.19[a]
Volumetric Alcohol Degree (% v/v)	9.8	9.7	9.6	9.7
Reducing Sugar (g/L)	2.0	1.80	1.90	1.78
Total Dry Extract (g/L)	20.6	---	---	---
Sulphates, K_2SO_4	<0.7	<0.7	<0.7	<0.7
Free Sulphurous, SO_2 (mg/L)	21	---	---	---
Total Sulphurous, SO_2 (mg/L)	83	---	---	---

[a] There was significative differences due to treatment, according to analysis of variance (One –factor ANOVA) to $p \leq 0.05$

TABLE 5. CHROMATIC CHARACTERISTICS

Treatment	Chromatics Characteristics				
	420 nm	520 nm	620 nm	Colour Intensity[b] (IC)	Tonality[c] (N)
Wine without treatment	0.086	0.092	0.011	0.188	0.934
Microfiltration	0.075	0.087	0.007	0.168[a]	0.861
Adsorption	0.079	0.093	0.013	0.185	0.849
Hybrid Process	0.067	0.082	0.007	0.155[a]	0.822

[a] There was significative differences due to treatment, according to analysis of variance (One –factor ANOVA) to $p \leq 0.05$

[b] A420+A520+A620

[c] Corresponding to relation between 420 and 520 nm

PROTEIN FRACTIONS

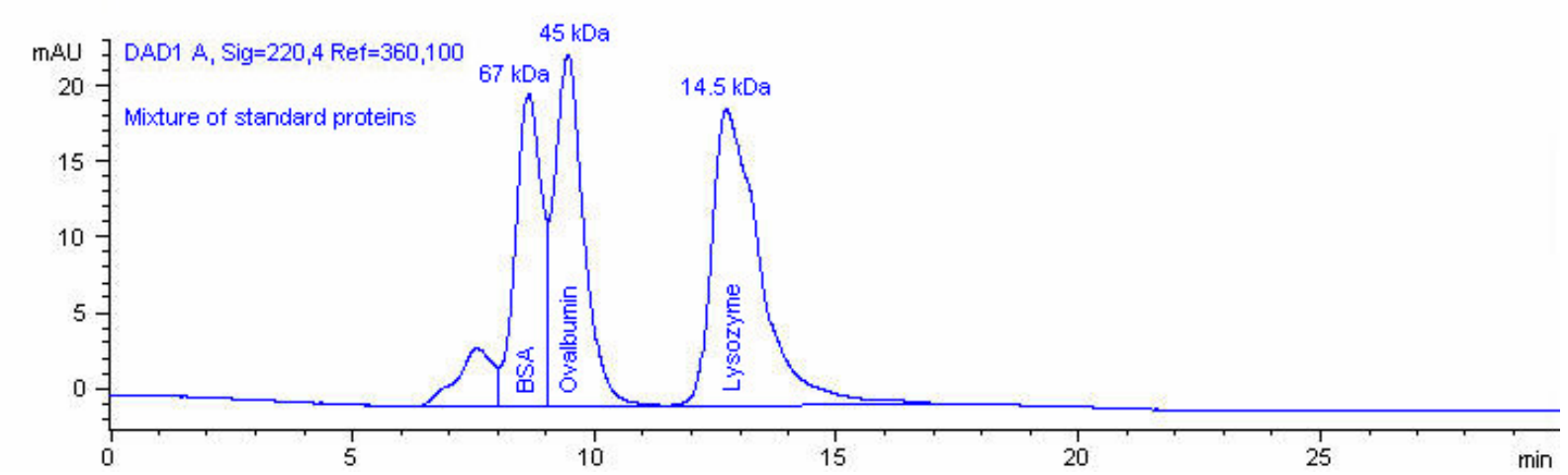


Fig.7 Retention time of mixture standard proteins (100 mg/L BSA; 100mg/L OVA; 100 mg/L LY)

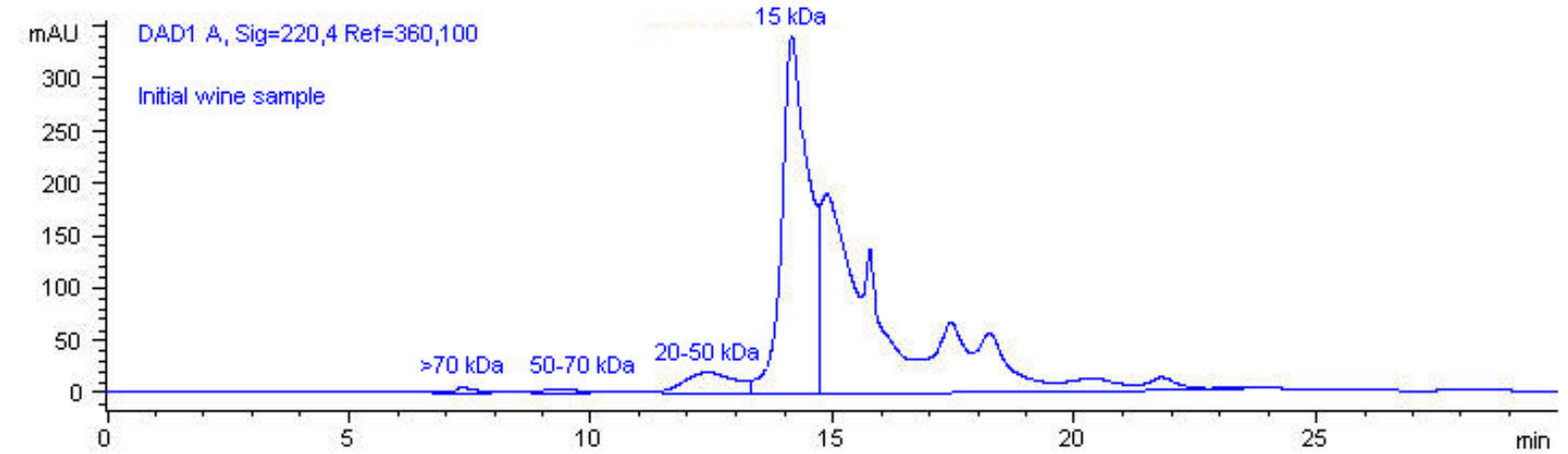


Fig.8 Protein molecular weight ranges of initial wine sample

RESULTS & DISCUSIONS

PROTEIN FRACTIONS REMOVED

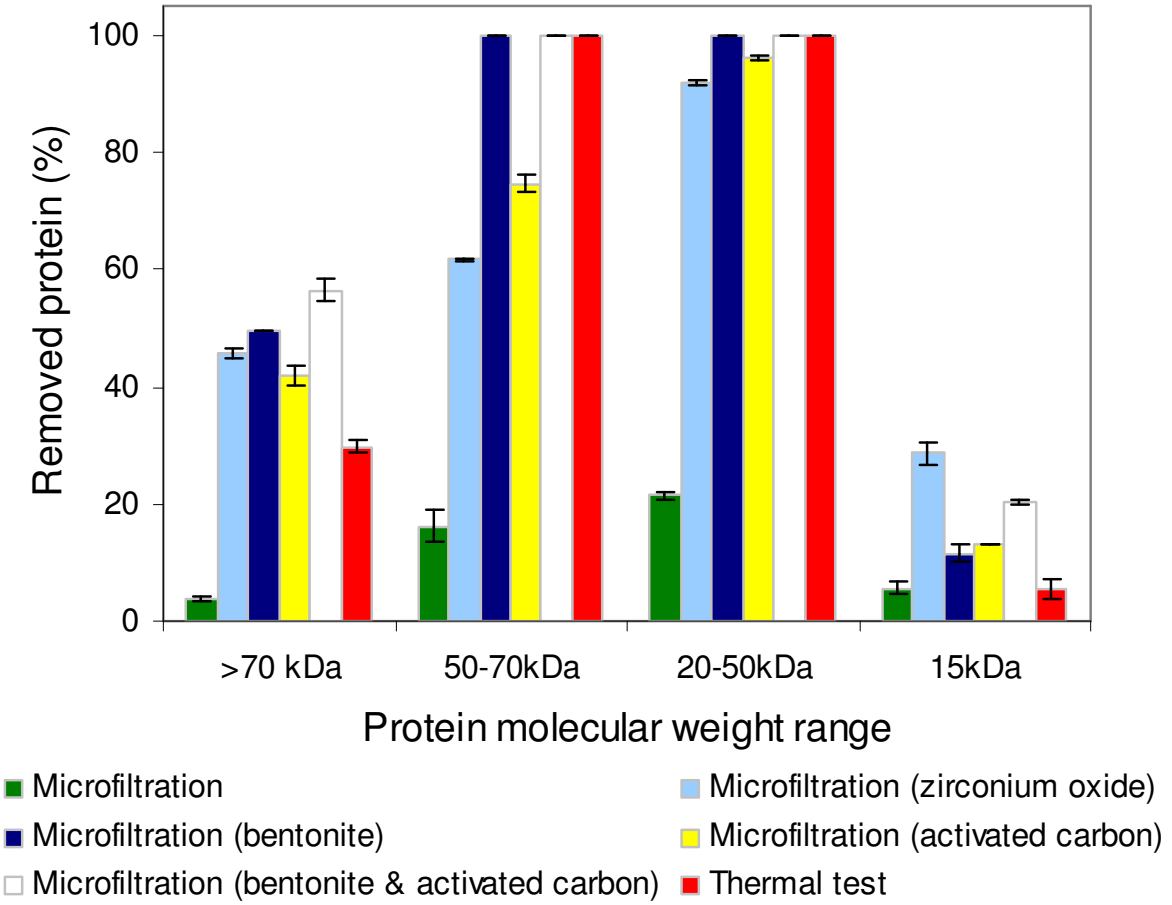


Fig.9 Percentage of protein removed from wine after each microfiltration and thermal test

PHENOLIC PROFILE

Table 6. Identification of phenolic compounds in the initial wine and after each treatment

Compound	Concentration (mg/L)				
	Initial wine	Zirconium oxide	Microfiltration	Microfiltration (zirconium oxide)	Thermal Test
Gallic acid	7.43 ±0.76	6.52 ±0.01	7.65 ±0.06	7.03 ±0.03	11.55 ±0.28
Tyrosol	12.27 ±0.05	10.96 ±0.14	12.18 ±0.71	11.32 ±0.03	17.02 ±0.29
Vanillic acid	0.98 ±0.02	0.59 ±0.02	1.06 ±0.19	0.94 ±0.01	2.09 ±0.08
Syringic acid	1.18 ±0.10	0.99 ±0.17	1.22 ±0.17	0.86 ±0.01	1.64 ±0.04
(-) -Epicatechin	2.25 ±0.03	2.64 ±0.12	2.50 ±0.52	1.99 ±0.00	2.98 ±0.11
Chlorogenic acid	1.48 ±0.01	1.50 ±0.18	1.38 ±0.01	1.32 ±0.00	1.45 ±0.01
Caffeic acid	19.86 ±0.13	17.82 ±0.26	18.39 ±0.17	16.75 ±0.08	20.59 ±0.23
P-Coumaric acid	0.32 ±0.00	0.32 ±0.00	0.31 ±0.01	0.26 ±0.00	0.40 ±0.01
Ferulic acid	0.18 ±0.00	0.13 ±0.00	0.18 ±0.01	0.15 ±0.02	0.17 ±0.00

PHYSICAL PROPERTIES OF ADSORBENT MATERIAL

TABLE 7. PHYSICAL PROPERTIES OF ADSORBENT MATERIAL

Treatment	BET surface area (m^2/g)	Micropore area (m^2/g)	Mesopore external surface (m^2/g)	Average pore diameter (nm)	Pore size distribution Microporo (%)	Mesoporo (%)
ZrO_2-1	74.2 ±2.0	5.3 ±0.9	69.0 ±1.1	12.0 ±0.7	7.1 ±1.0	92.9 ±1.0
ZrO_2-2	64.2 ±1.4	5.9 ±0.9	58.4 ±0.1	13.7 ±0.0	9.2 ±1.1	90.8 ±2.2
ZrO_2-3	67.5 ±3.3	5.8 ±0.1	61.8 ±2.4	12.8 ±0.7	8.5 ±0.2	91.5 ±2.7

ZrO_2-1 Zirconium oxide without thermal treatment

ZrO_2-2 Zirconium oxide regenerated after the first adsorption process

ZrO_2-3 Zirconium oxide regenerated after the second adsorption process

Adsorbed protein

✓13.1 % First adsorption process

✓12.9% Second adsorption process

CONCLUSIONS

✓By hybrid process was possible to increase 15-20% the permeate flux during the crossflow microfiltration.

✓Proteins and polyphenols are responsible of the permeate flux decline

✓The wine protein stabilisation by hybrid process can be considered acceptable considering their lower effect on the physicochemical properties and phenolic compounds of wine.

✓The protein molecular weight range of 20-70 kDa could be related with unstable proteins or causing of membrane fouling.

Thanks for your attention!!

Any questions?

Oral communication presented at the 5th Ibero American Congress on Membrane Science and Technology (CITEM2005), Valencia, Spain July 6 - 8, 2005