THE USE OF ZIRCONIUM DIOXIDE ENCLOSED IN A METALLIC CAGE FOR THE STABILISATION OF CHARDONNAY WHITE WINE•

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Key words**:** Zirconium dioxide, protein stability, haze.

1. INTRODUCTION

Winemakers constantly need to deal with the possible appearance of turbidity during the storage of white wines after bottling. This occurrence can be caused by the insolubilisation of the grape proteins which remain in wine after the fermentation process (Bayly, Berg, 1967). Therefore the heat unstable proteins are commonly removed through adsorption by bentonite. Bentonite is still extensively used because of its established efficacy as well as its low cost. However bentonite is not an efficient wine processing step; alternative absorbents are thus sought. One promising solution is represented by the adsorption of unstable proteins on the surface of zirconium oxide (Pachova *et al*., 2002). The aim of this work was to assess the viability of zirconia treatments to stabilize white wines, with particular attention on process development.

2. MATERIALS AND METHODS

2.1. Materials

An unfined 2009 Chardonnay wine was used. The zirconia used was in pellet form and was donated by Prof Francisco López, Universitat Rovira y Virgili, Spain.

2.2. Protein content

Protein content was determined by EZQ® protein quantitation kit following the manufacturer's instructions.

2.3. Heat test

Wines were heated at 80 °C for 2 h and cooled in ice for 2 h. After equilibration at ambient temperature the haze was measured by calculating the difference in NTU by means of a nephelometer (Pocock, Rankine, 1973) between the heated and unheated samples.

• QUAD. ViTIC. ENOL. UNIV. TORINO, 31, 2009-2010

2.4. Metal analysis

Metal contents were determined by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES).

2.5. Regeneration procedure

After each application zirconia pellets were washed twice with 3 M NaOH (at 50 °C for 2 h) and then with 5 % citric acid (at room temperature for 30 minutes).

3. RESULTS AND DISCUSSION

Zirconia pellets were applied to the wine after being enclosed in a metallic cage. Preliminary experiments showed that to achieve protein removal stirring was essential. In order to treat the wine on a small scale in the laboratory a device was built (fig. 1).

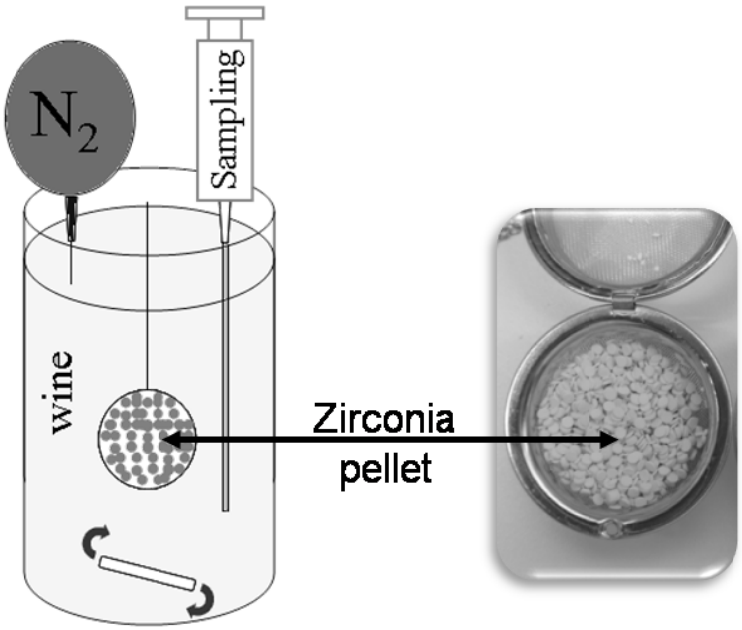

Fig. 1 - Scheme of the device used in the experiment (left) and details of the cage containing the zirconia pellets (right).

The wine was treated for 72 h and the residual protein content at intermediate time points was measured (tab. 1).

Proteins were removed in a time and dosage dependent manner. After 72 h, the treatment with 25 g L^{-1} of zirconia removed almost all proteins, and this was reflected in the wine becoming protein stable (tab. 2).

Tab. 1 - The effect of zirconia dose and contact time on the wine protein concentration (in mg L^{-1}). Wines were held at 18 ºC and stirred at 140 rpm during the experiment.

	Dose of zirconia (g L^{-1})			
Contact time (h)	**0**	**5**	**10**	**25**
0	100.6 ± 4.1	100.6 ± 4.1	100.6 ± 4.1	100.6 ± 4.1
2	108.1 ± 0.5	101.9 ± 4.9	103.2 ± 1.1	90.6 ± 4.2
6	99.8 ± 7.0	102.1 ± 9.2	116.1 ± 6.7	77.1 ± 5.4
24	98.6 ± 5.6	92.6 ± 3.5	101.6 ± 8.6	60.8 ± 10.1
48	84.5 ± 16.7	82.8 ± 8.5	69.8 ± 5.7	34.9 ± 4.0
72	87.2 ± 4.7	79.8 ± 13.9	48.4 ± 2.8	13.6 ± 8.4

Tab. 2 - The effect of zirconia dose on the haze potential of Chardonnay wine at the end of the 72 h of incubation.

Dose of zirconia (g L^{-1})	**Haze (NTU)**
0	53.4 ± 0.9
5	33.2 ± 1.5
10	20.5 ± 2.0
25	2.1 ± 0.4

Zirconia treatment caused some modification to the wine composition (tab. 3). In particular some metal ions, such as Fe and Cu, were removed and acidity was reduced, especially for the 25 g L^{-1} treatments.

Tab. 3 - The effect of zirconia dose on some physicochemical parameters of the wine.

	Dose of zirconia (g L^{-1})			
Parameter	0	5	10	25
pH	3.24	3.26	3.27	3.33
Titratable acidity (g L^{-1})	6.40	6.20	6.00	5.40
Fe (mg L^{-1})	0.58	0.58	0.08	0.03
Mn (mg L^{-1})	0.73	0.73	0.64	0.55
B (mg L^{-1})	6.00	5.97	5.89	5.40
Cu (mg L^{-1})	0.11	0.11	0.07	0.03
Zn (mg L^{-1})	0.51	0.51	0.48	0.42
P (mg L^{-1})	114.00	113.65	69.71	32.00

Other wine parameters as alcohol, volatile acidity, free and total SO_2 content and colour were unaffected (data not shown).

An informal sensory assessment of the wines was done by comparing untreated wine with wine stabilized with either bentonite or with 25 g L^{-1} zirconia for 72 h. Tasters were not able to clearly discriminate among wines, although some commented that the zirconia treated wine had slightly lower fruit aroma and flavour intensity.

One particularly interesting characteristic of zirconia as an adsorbent is its ability to be regenerated. We assessed the ability of cleaning products, such as citric acid and NaOH, to regenerate the material, and demonstrated that after 11 cycles of regeneration the ability of zirconia in removing proteins was maintained, as confirmed by measuring the heat stability of wines after treatment (data not shown).

4. CONCLUSIONS

Zirconia was confirmed to be a good candidate for protein adsorption from wines. We demonstrated that enclosing the pellets in a metallic cage makes addition to and removal from wine easy.

This study also demonstrated that regeneration of the material can be relatively simple. However there are some issues that need to be resolved, such as the necessity of stirring and the high dosages required.

Future work will be focussed on studying the possible application of zirconia during fermentation (to exploit the natural agitation), and in optimising zirconia physical properties in order to reduce the dosages required.

Abstract

White wines are commonly stabilised by removing the heat unstable proteins through adsorption by bentonite, an effective but inefficient wine processing step. Alternative absorbents are thus sought and zirconium dioxide (zirconia) is recognised as a promising candidate. The aim of this work was to assess the viability of zirconia treatments to stabilize white wines, with particular attention on process development. Effective protein removal was achieved by enclosing zirconia pellets into a metallic cage submerged in the wine. With this method the wine could be treated with the adsorbent for the time required for protein stabilisation, and then removed without further manipulation. Zirconia treatment of an unstable Chardonnay wine stabilised it without detectable modification of its physicochemical parameters and colour, apart from the removal of some metals (Cu, Fe) and acids. A simple, inexpensive and effective zirconia regeneration method was developed. Main drawbacks are the high dosages required and the necessity of stirring.

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