# PRELIMINAR STUDY OF ADSORPTION OF UNSTABLE WHITE WINE PROTEINS USING ZIRCONIUM OXIDE SUPPORTED ON ACTIVATED ALUMINA BY ATOMIC LAYER DEPOSITION METHOD

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## Introduction

A common problem in wineries is haze formation after bottling, mainly caused by unstable proteins present in white wine. The most used material to eliminate these proteins is bentonite. This material effectively removes proteins, but it is very harmful to white wine since it removes all kinds of proteins and other **essential compounds** from wine. Zirconium oxide ($ZrO_2$) has been shown to remove the proteins responsible for haze selectively, but $ZrO_2$ must be modified to increase the active surface area that adsorbs the proteins. This work aims to use zirconium oxide properties to produce a porous material coated on the surface by a **new impregnation technology** such as atomic layer deposition (ALD), which is highly active and allows the **selective removal** of haze-causing proteins from white wine.

## Key words

Haze, unstable proteins, protein stabilisation, protein removal, zirconium oxide

## Methodology

Zirconium oxide was deposited on 6 mm activated alumina spheres by the ALD method*. Modified supports were analysed for SEM, XRD and BET techniques. As a result, two modified materials (M60 and M80) were obtained and were compared with pure zirconium discs of 3 mm (ZP). Batch and continuous experiments were carried out with untreated Gewurztraminer white wine, subsequently analysed for total protein content by Bradford and polysaccharide and protein content by HPLC. The regeneration of the material was carried out for 4 hours at 500°C.

## Atomic layer deposition method

*ALD is a sequential automated procedure that surface coats a material with a precursor (gaseous compound of interest). The deposition sequence, as shown in figure 1, consists of fed with the primary precursor (i), which is zirconium tetrachloride ($ZrCl_4$), deposited on the surface of the support. Then the procedure is purged with nitrogen (ii), removing the remaining $ZrCl_4$ that was not impregnated on the support. The secondary precursor (water) is added (iii) allowing the exchange of ligands for oxygens, generating the zirconium oxide layer on the surface. Finally, it is purged again (iv), ending the cycle. Each cycle generates a monoatomic layer, so the number of cycles defines the thickness of the layer.

## Preliminary results

SEM-EDX analysis detected small particles of $ZrO_2$ in different parts of the sphere of the modified materials (MM). However, XRD technique did not find the presence of $ZrO_2$; this occurs when the $ZrO_2$ content is less than 5%. In previous analyses of MM with fewer layers (cycles), SEM-EDX detected about ~1% $ZrO_2$ content in the sphere. BET technique detected a decrease in surface area of ~186 and 202 $m^2/g$ corresponding to 60 and 80 cycles (M60 and M80) less than the original alumina (~383 $m^2/g$ surface area), indicating a deposition. Preliminary results indicated that MM remove between 12-18% of total proteins from batch experiments processing 13 BV (expressed in mL of the wine per gram of adsorbent) (Figure 2.A) and 19-27% from continuous experiments processing 39 BV (Figure 2.B), where regeneration (M60_R1 and M80_R1) did not significantly affect the protein adsorption, although it slightly enhances it. Content of proteins <25 kDa processed with MM decreased (Figure 3), and higher molecular weight proteins were not affected, while polysaccharide content was slightly reduced. ZP removed more proteins and polysaccharides than MM. However, zirconium content in MM had a lower surface area than ZP that is 100% zirconium (quantity per unit is more), i.e. it has a upper active surface area.

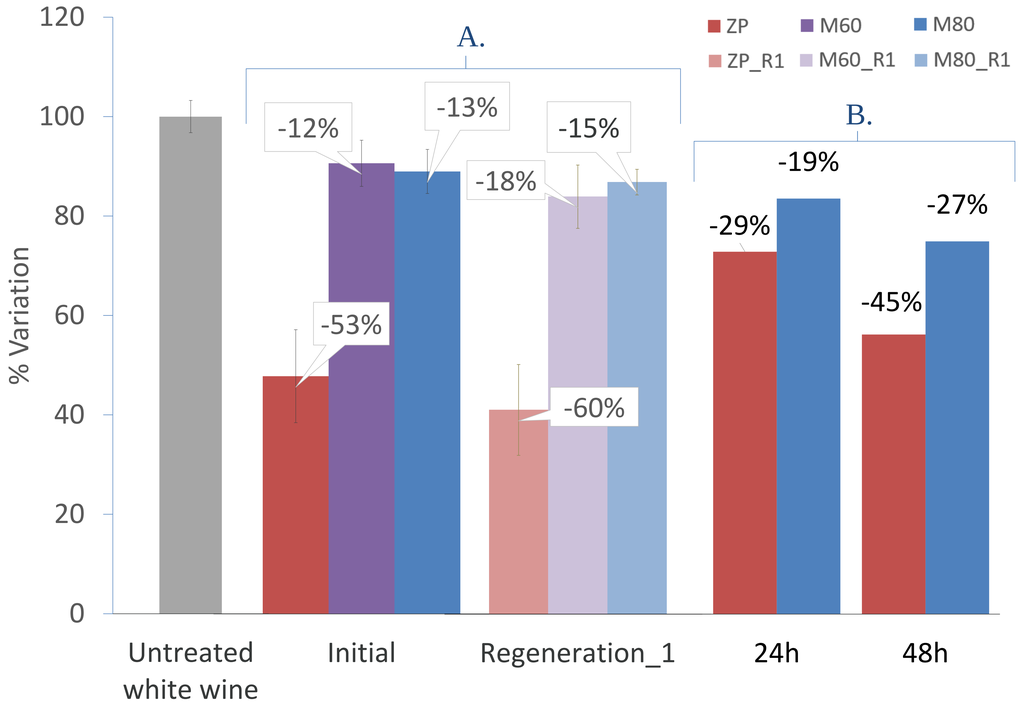


Figure 2. (A) Batch experiments with 1 regeneration (B) Continuous experiments to 24 and 48 hours

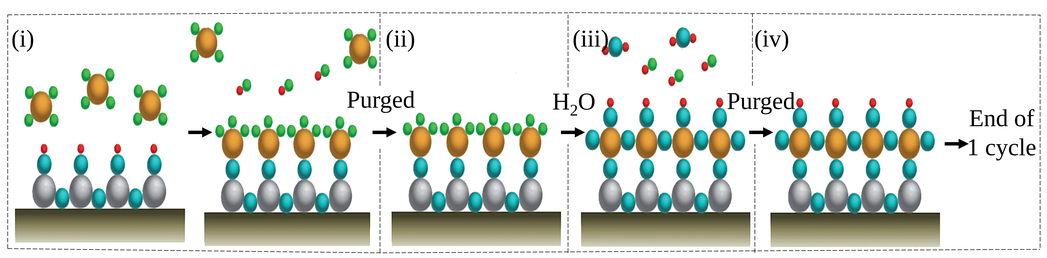


Figure 1. Sequence of zirconium oxide deposition on alumina surface by ALD

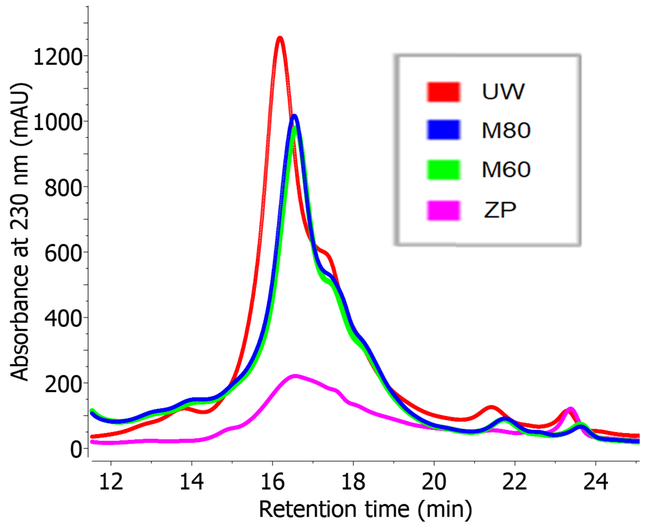


Figure 3. Protein profiles by HPLC of Gewurztraminer untreated white wine (UW), ZP, M60 and M80 materials

## Conclusions

Therefore, we can conclude that there was a selective reduction of proteins, but this was not enough; this may be due to two aspects: the surface area of pure zirconium was higher than the modified material, and the content was also lower. Therefore, to improve protein removal with the modified materials, it is necessary to increase the active surface area by reducing the size of the spheres from the original 6 mm to 2-4 mm. In order to improve the deposition of the material, an organic compound will be used, which is easier to handle as it works at lower temperatures.

## References

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