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Chemically Modified Clay Adsorbents Used in the Retention of Protein and Polyphenolic Compounds from Sauvignon Blanc White Wine

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Abstract: During the manufacturing process of white wine, various physicochemical reactions can occur and can affect the quality of the finished product. For this reason, it is necessary to apply different treatments to minimize distinct factors such as protein instability and pinking phenomenon, which can affect the organoleptic properties of wines and their structure. In this work, a new method for the preparation of a sorbent-type material is presented through the fractional purification of native bentonite in three fractions (Na-BtF1, Na-BtF2, and Na-BtF3). Furthermore, the influence of the prepared sorbents on pH, conductivity, and amino nitrogen level was analyzed. The absorbents prepared and tested in wine solutions were characterized using the following physico-chemical methods: Brunauer–Emmett–Teller and Barrett–Joyner–Halenda (BET-BJH) method, X-ray diffraction (XRD) technique, and transform-coupled infrared spectroscopy Fourier with attenuated total reflection (FTIR-ATR). Following the analyses carried out on the retention of protein content and polyphenolic compounds, it was found that materials based on natural clay have suitable adsorption properties.

Keywords: bentonite; wine; proteins; polyphenols; tannins

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1. Introduction

The presence of tannins mixed with proteins in white wine can form a negative hydrophobic colloid that can flocculate in the presence of cations. The aggregation of the proteins present in white wine is usually associated with a change in the protein structure due to the elimination of water. Due to the possibility of the phenomenon of flocculation in the glass of white wines kept at an elevated temperature above 25 °C, degradation of the finished product occurs through the appearance of the protein aggregation process.

Most of the proteins responsible for the instability of white wines come from the raw material [1]. The haze phenomenon often takes place during the wine storage process. This phenomenon occurs because of the deformation of the proteins present in the raw material and in the final product (wine). The molecular weights of the proteins are low, up to 40 kDa [2], and are resistant to the pH of the wine and to the proteolysis process [3]. However, the molecular structure of wine, consisting of polyphenols, polysaccharides, and ethanol, usually produces a complex interaction and leads to the apparition of haze phenomenon in white wine [4–6].

The content of unstable proteins depends on many factors, such as grape variety (Sauvignon Blanc white wine variety is rich in thermo-unstable proteins), maturity, viticultural practices, pre-fermentation techniques, etc. [7–9]. In the oenology laboratories, various tests are carried out to assess the risk of protein disturbance under different conditions: at high temperatures or in the presence of different compounds (trichloroacetic and phosphomolybdic acids, ammonium sulfate, etc.) [10]. Bentonite is a mineral resulting from the decomposition of some volcanic rocks. It is a hydrated aluminum silicate with a phyllite structure like montmorillonite, with the property of swelling in a dispersed environment. Immersed in wine, bentonite forms a colloidal dispersion with negatively charged particles, which have the role of fixing the proteins in the wine at an optimal environmental pH (pH 3.0–3.3) [11,12]. Due to the high density of bentonite, it will settle to the bottom of the storage vessel, being easily recovered from the wine [13].

In practice, the use of sorbents of this type in the process of obtaining wines can affect their quality, such as reducing the aromatic potential of white wine [14]. Instead, the use of bentonite treatment of young white wines has a favorable effect from an organoleptic point of view, highlighting the properties of the finished product on the taste and smell of the wine. Bentonite also contributes to microbiological stabilization in winemaking by removing unwanted microorganisms. Another factor that affects the quality of white wines is the browning phenomenon [15]. The browning phenomenon of wines often occurs during the technological process due to non-compliance with the working conditions during the pre-fermentation process of the must [10].

According to Revi M. and Serra-Cayuela, A. [16,17], polyphenolic compounds manage the formation of oxidation reactions. Through the research carried out, it was determined that the main polyphenolic compounds of white wine that are prone to these reactions are flavonoids (yellow or colorless substances) and catechins (3-flavanols, main substances of tannins in grape seeds) [18,19]. A current technique for stabilizing white wines against oxidation of polyphenolic substances is hyper-oxygenation. The procedure presented by Romanini E. and Lingua, M.S. [20,21] is based on the controlled oxidation of polyphenols and must be performed immediately after the pressing and deburring stages.

The aim of this paper is to present the effects of chemically modified bentonite on the adsorption of protein and polyphenolic compounds from white wines. Due to its availability in nature and its suitable adsorption capacity in wine, native bentonite was chosen as the base material.

The treatment and purification of montmorillonite have been researched for years. Different methods of enrichment, activation, and application in wine have already been tested [22,23]. Different Na-activated bentonite labels have also been studied in wine fining [24]. Table 1 presents some of the used materials known as stabilizing agents.

Table 1. Materials used as stabilizing agents known up to now.

Test Type SP		Used Materials	Dosage in Wine	Purpose/Working Principle	References
Thermal stability	*Cold*	Sodium bentonite changed with Boltron dendrimers	10–50 mL sorbent/L white wine	- Induction of protein and polyphenolic complex precipitation in white wine; - Retention of polluting compounds in wine (e.g., phthalates);	[25–29]
	Hot	-	-	- Denaturation of wine proteins; - Induces precipitation of the wine; - Simulates the formation of protein turbidity;	[30,31]

Table 1. *Cont.*

Test Type SP		Used Materials	Dosage in Wine	Purpose/Working Principle	References
Thermal stability (hot/cold) with inorganic organic materials		Egg albumin, blood albumin	50–250 mg/L red wine;	- Removal of unwanted substances (phenolic compounds) to prevent colloidal precipitation and reduce wine astringency;	[32–35]
		Milk casein	150–300 mg/L white wine, 7–10.5 mg/L	- For adjusting the wine's flavor due to the ability of selective adsorption on tannin;	[36]
		Carrageenan	1.5–2% solution, 2 g in 200 mL wine	- Removing the proteins from the wine;	[7,37]
		Sodium bentonite (BS)	200–400 mg/L red + white wine	- Deproteinization of wine; - Clarification of white, red, rosé wines; - Stabilization against colloidal and protein disturbances; - Ultrasound (US) effects on white wine protein stability;	[30,38]
		Calcium bentonite (BC)	700–2000 mg/L white/red wine		
		BS + BC	700–1500 mg/L white/red wine		
		Active coal	100–500 mg/L wine	- Retention of phenolic compounds in wine; - For the correction of oxidized white wines; - Removing some defects in the wine (taste, smell);	[38]
		Kaolin	5000–6000 mg/L wine	- Clarification of the wine and removal of excess proteins;	[38]
		Sodium alginate	40–80 mg/L wine	- Formation of electronegatively charged alginic acid colloidal particles; - They mutually flocculate with the proteins in the wine, electron positively charged; - Alginic acid flocculates and clears wines that are in excess of stabilization;	[38]
Trichloroacetic (TCA)		TCA solution	1 mL TCA solution concentration 55% in 10 mL wine	- Precipitation of the total proteins present in the wine;	[2,39,40]
With tannin	-	Oenological, ethereal alcoholic	5 mg/10 mL wine	- Protein precipitation during wine storage by binding to phenolic compounds; - Data on the amount of protein compounds in wine precipitated by tannins;	[5,26,40]
	Hot	Condensed tannin (TC)	0.5 mL tannin solution (TC/TH) in water with 10% ethanol		[30]
		Hydrolyzed tannin (TH)			
	Cold	Condensed tannin (TC) Hydrolyzed tannin (TH)	5% TC/TH solution in water with 10% ethanol		
Bentotest		Phosphomolybdic acid (FA)	100 mL FA reagent in 10 mL wine	- Protein precipitation by neutralizing the protein charge; - Aggregation of proteins with the molybdenum ion;	[2,40]

Table 1. *Cont.*

Test Type SP	Used Materials	Dosage in Wine	Purpose/Working Principle	References
Protochek (PC)	Reagent PC	It is added to wine in a ratio of 1:2	- The ability of proteins to interact quickly with a negatively charged polymer;	[30]
Prostab (PS)	Reagent PS	0.05–0.1 mL PS/L white wine	- Specific reaction to proteins that cause turbidity; - The intensity of the turbidity is directly proportional to the protein instability of the wine;	[30]
With inorganic solvents	Ethanol	3% solution in white wine	- Reduction in protein solubility; - Precipitation of less soluble protein fractions at the pH of the wine;	[2,26]
With mannoproteins	-	-	- Reducing the degree of turbidity of the wine; - Gives a concrete answer about the presence of proteins in wine after treatment with tannin and PC;	[30,39]
With inorganic salts	Ammonium sulfate	0.5–2 g/L white wine	- Precipitation of wine proteins.	[41]

The novelty of this article is the use of autochthonous bentonite collected fractionally and used in winemaking as improved materials that keep white wine bio-polymers prone to flocculation and premature oxidation. The aim of this work was to study the retention degree of proteins and polyphenolic compounds in clay materials. In this work, thermal stability tests, oxidizability tests, and spectrophotometric and potentiometric analyses were applied.

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