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PERSPECTIVES OF UTILIZATION OF NANODISPERSIVE MATERIALS BASED ON SIO_2, TIO_2 AND SIO_2–TIO_2 FOR WINE FINING

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Abstract: *The present paper analyzes the efficiency of various mineral fining agents (nano dispersion composites SiO_2, TiO_2, TiO_2-SiO_2, bentonite and saponite) in the process of white and red wines fining. The influence of both the mass of the adsorbent and the time of the storage in wine on the optical density of wine was investigated.The best results were obtained with TiO_2, AMD-2 and SiO_2 for white wines, and bentonite and AMD-2 – for red ones. It was shown that the optimal time of contact for wine with the fining agent is: four days - for white wines and two days for red ones.*

Keywords: *fining agent, adsorbent, wine, TiO_2, SiO_2, bentonite.*

1. Introduction

Stable transparency of beverages and wines is an indispensable feature of their quality. At the end of fermentation, young wine materials self-illuminate, that is, they become transparent. To accelerate the process of juices and wine materials' clarification, special techniques are used: fining, filtering and combining of them. The substances used to fine wines must meet a number of requirements, among which: to have a developed surface, to cause coagulation of organic suspensions (proteins, polysaccharides), do notexhibit the toxic effects, easily stand out from wines, do not change the organoleptic properties, etc. In addition to the above, their utilization should be economically feasible.

There are a lot of substances that might be used as wine fining materials. Among them: minerals, proteins, woodcharcoal, synthetic polymers, enzymes and many others. In the wine industry coal [1] and natural mineral sorbents, in particular "bentonites" and "saponites" [2], are quite popular because of their ability to bind tannins and other organic substances [3].

Recently, the effectiveness of the wine fining with casein, potassium caseinate products, isinglass and egg albumin was confirmed [4]. Other works describe the development of conditions for utilization of chitin and chitosan [2], as well as the use of mineral adsorbents in a mixture with proteins or other organic substances [5]. However, it has been established that the applying of organic fining agents, especially proteins, may cause appearance of food allergies to consumers [6].

Hence, the search for new effective, health-safe, economically viable wine fining materials and the establishment of the mechanism and conditions of their applying remain current. The action of bentonites, carbon, ferrocyanides and other mineral agents has been studied in detail. Much less attention is paid to the use of silicon and titanium oxides [7]. For example, previously it was believed that the applying of silicon dioxide is ineffective, but its combination with gelatin gives a better result [8]. Although the utilization of nanodispersed oxide materials is not very widely covered in the literature, they can be successfully applied as fining agents. Therefore, our aim was to consider the posibility of using nanosized SiO_2, TiO_2, and TiO_2-SiO_2 compositions for white and red wines' fining. The conclusion about the possibility of oxide materials utilization as fining agents was based on the efficiency of clarification of wines. The content of dry substances and the ethanol content of the beverage were monitored before and after the fining procedure.

2. Materials and Methods

As fining agents, the following materials were selected: bentonite $Al_2[AlSi_3O_9\times(OH)](OH)_2\times nH_2O$; saponite $(Ca,Na)_{0.3}(Mg,Fe^{2+})_3(Si,Al)_4O_{10}(OH)_2\times 4H_2O$. Nanodispersed SiO_2 – product which was obtained by flaming hydrolysis of $SiCl_4$ vapors in an air-aqueous mixture at a temperature of 700 to 1100 °C. The size of the particles is of 10-20 nm, the specific surface area S_{BET} = 300 m^2/g. AMD-2 – high-disperse silicon dioxide modified by depolymerizate D-4, specific surface area S_{BET} = 280 m^2/g.TiO_2 – nanosized titanium dioxide. TiO_2-SiO_2 –a composite containing 6.0% wt of SiO_2.

The fining agents were placed in wine in the powder form, without any pre-treatment. Some of them (especially AMD-2) exhibit hydrophobic properties and the preparation of aqueous suspensions is not possible. For standardization of start conditions of this research, it was decided to put powders in wine without additional previous preparation. Powders stayed in wine from one to nine days. For each sample of the fining agent, three parallel experiments were performed. The final values presented in the work - the result of averaging the values obtained for each sample. At the end of the fining process, the powder-wine mixtures were filtered. The content of dry substances in white wine before fining was 8%, in red – 17% (at 20° C).The ethanol content did not change after fining: in white wine it was 13%, in red – 15%.

We researched samples of red and white wine made from Isabella and Flamingo grapes, respectively, in laboratory conditions using the traditional technology.These varieties of grapes are grown in the territory of Western Ukraine. They are actively used by locals for the production of home-made wines. Although, it should be noticed that these grape varieties are not used in industrial winemaking.The efficiency of fining was calculated based on the results of the optical density measurement (Eq. 1):

$$Fining\ efficency = \frac{A_0 - A}{A_0} \cdot 10,\ \% \qquad (1)$$

where A_0 is the optical density of wine sample before fining (0.555 for white, 1.957 for red), A is the optical density of the wine sample after fining procedure.

The optical density was measured with Agilent Cary 60 spectrophotometr. White wine was studied at the wavelength λ = 340 nm, absorbing layer thickness 5.075. The red wine was studied at the wavelength λ=540 nm, and the thickness of the absorbing layer was of 3.070. The comparing solution was water. The content of dry substances was evaluated refractometrically (Atago PAL-1 BLT Digital Brix Refractometer).

3. Results and Discussion

It is thought [8] that fining agents can act in two mechanisms: electrostatic interaction and adsorption. In the case of electrostatic interaction, the particles of the fining powder bind to the oppositely charged particles contained in wine. The result: large particles' formation and their deposition. For adsorption interactions – the process takes place on the surface of the adsorbents and in such a way that it is accompanied by the resulting composites separation from wine. In general, the effectiveness of the fining agent depends on many factors, such as: the nature of the substances, the method of its manufacturing and addition, concentration, external conditions, preliminary preparation of wine materials, and others.

It is known from the literature that the optimal concentrations of bentonite range from 0.2–1.5 g/l [9, 10] or 10–13 g/l of wine [11]. Therefore, for our studies we have chosen a row of concentrations 1–3–10 g/l of wine (or 0.05–0.15–0.5 g/ 50 ml).

This work consisted of two blocks. The first one is to evaluate the fining efficiency within 7 days after mixing the adsorbent with wine. The second is to observe the changes in the optical density of wines over time in order to determine the optimal time of wine – fining agent contact.

White wine. The research results show that all of the test substances show good efficiency as white wine clarifiers. Fig. 1 is a diagram illustrating the fining efficiency of wine with the studied agents at their various contents per 50 ml of wine.

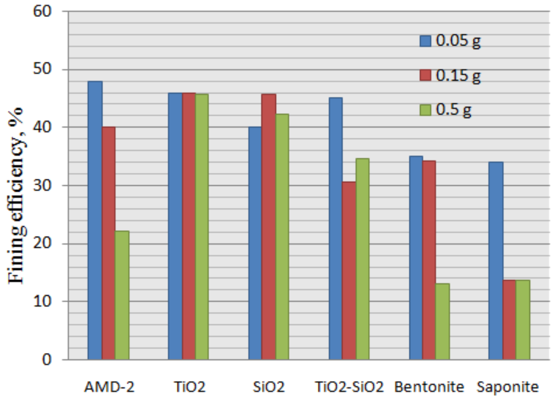


Fig 1. Efficiency of fining with different agents for a white wine for varies mass on 50 ml of wine

From the obtained results we concluded that the most effective is nano-dispersed TiO_2, regardless of its content. AMD-2 and SiO_2 are demonstrating really good results. Their effectiveness significantly decreases with the increase of their content in wine. It should be noticed that the highest fining efficiency and clarity were achieved with the use of 0.05 g AMD-2on 50 ml of wine (Fig. 2). This is an important observation, because the applying of minimum quantities of fining agents influences minimally the taste and physical and chemical properties of wine. This result is somewhat unexpected. On the one hand, AMD-2 has a large specific surface area. On the other hand, it is a highly hydrophobic powder. Unlike other substances, it formed a film on the wine-air surface and did not fall into the volume of the liquid.

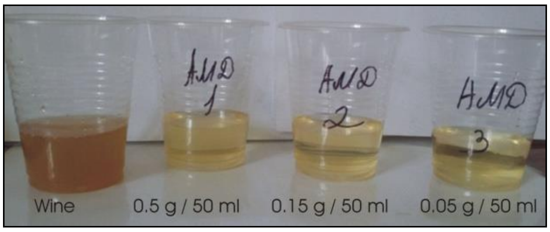


Fig. 2. The result of AMD-2 fining of white wine

Bentonite and saponite are the worst of the studied fining agents for white wines, which may be due to the fact that we did not pre-prepare the suspension, and all the substances were used as powders. The preliminary preparation is a factor that has a significant effect on the final result of fining. On the other hand, it is known that bentonite possesses a low ability to color reduction and weakly binds wine tannins [8]. From the obtained results, it can be argued that the fining efficiency decreases with the weight increase for all powders except SiO_2.

Refractometric studies conducted after removing of adsorbents showed that the content of dry matter in the wine practically did not change as compared with the original wine. Based on the results of previous investigations on the effect of luminaries, several samples were selected for detailed re-studies to determine the optimal time for the wrapping of wines on the illuminator.

Red wine. Similar studies have been conducted for red wines. However, in the case of red wines, the substances showed a significantly worse fining ability. Fig. 3 shows the results of the study on the fining efficiency for red wine samples. In general, bentonite has shown the best action as fining agent. It should be noticed that the most effective at low content (0.05 g / 50 ml of wine) were TiO_2 and AMD-2. In the case of TiO_2, the fining effect varied insignificantly with an increase in powder weight. A similar situation was observed in the case of white wines. For SiO_2, the fining effectiveness became negative with an increase of its weight (0.5 g / 50 ml of wine), which means that the optical density of wine after clarification became larger than before.

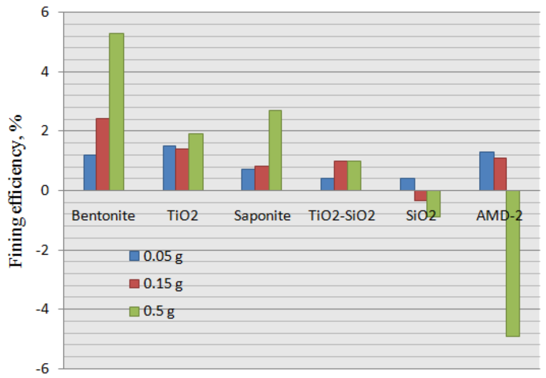
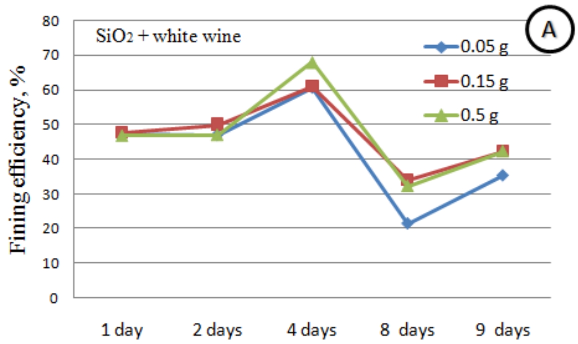


Fig 3. Efficiency of fining with different agents for a red wine for varies mass on 50 ml of wine

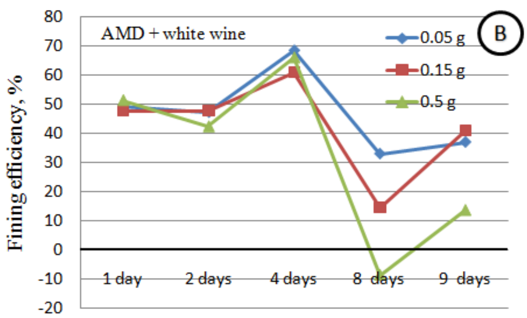
It has been shown that for bentonite and saponite there takes place a significant improvement in the fining effect with an increase of powders' weight. At the same time SiO_2 has proved to be ineffective for the treatment of red wines. A comparison of silica gel and bentonite showed that bentonite is not the most effective fining agent [12]. Silica gel used to provide a better binding of proteins contained in the wine and had less effect on the product's organoleptic properties.

Selection of optimal fining time. Based on the results of previous investigations, several samples were selected for detailed re-studies. The subject matter of re-studies was the determination of the optimal time for the delaying of the wines with powder. The information described in the literature is somewhat controversial. For example for bentonite, on the one hand, it is recommended to provide fining "in flow" in order to minimize the contact time of the mineral with wine. It is believed that when the "bentonite-wine" mixture is standing, some of the adsorbed proteins may return to the solution [9]. On the other hand [8, 11], it is best to delay the wine with the fining agent for 2 days.

White wine. Of all the previously selected fining agents, the best for the white wine were: AMD-2, SiO_2, TiO_2. To establish the time dependence "optical density – delay time", the wine was kept in contact with the powders from one to nine days (Fig. 4).



a).



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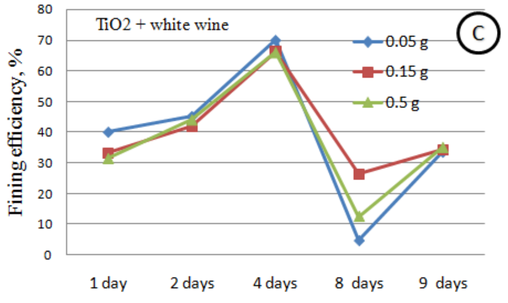


c).

Fig. 4. Dependence of the fining efficiency of white wine in time: A – SiO_2, B – AMD-2, C – TiO_2 (0.05-0.15-0.5 g / 50 ml of wine)

From the submitted data it is possible to draw the following conclusion: the maximum fining efficiency is reached after 4 days. Further exposure of wine with the powders is unreasonable and worsens its properties. However, our results contradict the described data [8, 11]: in the case of white wines, the contact for two days is insufficient.

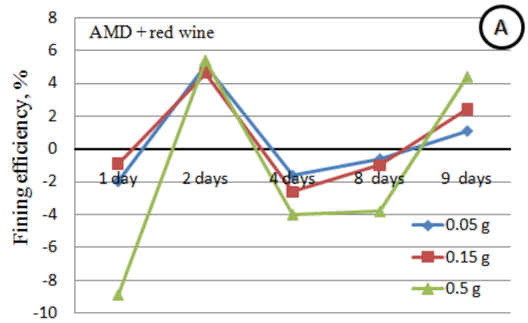
These three fining agents can be placed in a row in a descending order of efficiency: TiO_2> AMD-2 > SiO_2.

The highest effective for white wines was TiO_2. Moreover, the lowest values of the optical density were obtained using the least amounts of both SiO_2 and TiO_2 (0.05 g per 50 ml of wine). The minimization of the quantities of agents that are introduced in wine to improve its characteristics is important for wine industry.

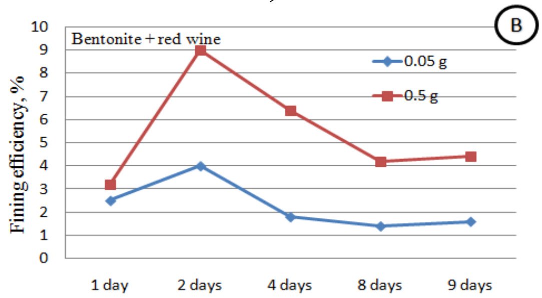
The refractometric studies before and after fining showed that the content of dry matter in the investigated wine practically did not change and was of 7.5-7.8%.

Red wine. Bentonite and AMD-2 were selected for studying the optimal contact time fining agents with red wine. Bentonite was chosen for comparison, since it is one of the most studied fining agents. And AMD-2 was chosen because it showed the highest efficiency with contents of 0.05 g per 50 ml of wine. The obtained dependences are presented in Fig. 5.

The analysis of Fig. 5 A shows that the maximum AMD-2 fining efficiency was achieved on the second day, therefore the further exposure of suspension was unwarranted. All the studied powders have a highly developed surface that is why with the increase of contact time, adsorption-readsorption of the components in wine on the surface of adsorbents could take place. Such processes may affect adversely wine quality.



a).



b).

Fig. 5. Dependence of the fining efficiency of red wine in time: A – AMD-2, B – bentonite (0.05-0.15-0.5 g/50 ml of wine)

Similar to AMD-2, bentonite exhibits the best fining result on the second day (Fig. 5 B). This result is fully consistent with the regularities described in the literature [8, 11, 13-14]. An interesting fact is that at low concentrations (0.05 g / 50 ml of wine), bentonite exhibited lower efficacy than AMD-2. This makes AMD-2 a promising agent for fining procedures.

It is well known that bentonite affects significantly the red wines' color due to its ability to bind positively charged anthocyanin monomers [8]. As a result of this binding, the intensity of red color decreases. So, since in our studies we observed a change in the color intensity, it is natural that bentonite showed the best result. At the same time, bentonites can be successfully used for fining wines' particles of which are positively charged. The mechanism of removing protein particles from wine under bentonite influence was induced by the interaction of negatively charged colloidal particles of bentonite with positively charged particles of protein substances, as well as their adsorption and subsequent sedimentation [15].

Refractometric control of dry matter in the samples of red wine before and after fining did not show significant changes. The content of dry matter in the samples of red wine ranged from 16.5 to 16.9%.

4. Conclusions

On the basis of the obtained results it can be argued that bentonite, nano-dispersed oxides of silicon, titanium and their composition can be proposed as an alternative to classical mineral adsorbents. In particular, for white wines, these are samples: TiO_2 > AMD-2 > SiO_2 (in order of efficiency decrease). A significant advantage of these substances is the high fining efficiency at small contents (0.05 g / 50 ml of wine). The utilization of AMD-2 can be recommended for red wine. Similar to previous studies it exhibits high efficiency (comparable with bentonite) at low content (0.05 g per 50 ml of wine). The optimal contact time of the wine with fining agents is of 4 days for white wine, and 2 days – for red wine, respectively.

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