INFLUENCE OF NEW MATERIALS ON THE CHEMICAL COMPOSITION OF MUSCAT OTTONEL WINES

INFLUENȚA MATERIALELOR NOI ASUPRA COMPOZIȚIEI CHIMICE A VINULUI MUSCAT OTTONEL

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Abstract. *Nanotechnology is a rapidly evolving field of research with many potentially applications, such as advanced chemistry, medicine, energy production, as well as the food and wine making industry. The aim of this paper is to study the influence of mesoporous materials (MCM-41, SBA-15 and KIT-6) on the white wines physical-chemical parameters, turbidity, phenolic content and color. The used experimental wine was Muscat Ottonel from Bucium vineyard, harvested in 2014. Phenolic compounds were characterized by measuring the absorbance at 280 nm and browning index at 420 nm. The color parameters was analyzed spectrophotometrically with CIE Lch space method. The analyses showed that nanomaterials reduce the nephelometric turbidity units (NTU), which are related with protein content. Also, the results indicate that the total polyphenol index (TPI) of treated wine samples decreased.*
Key words: *nanomaterials, Muscat Ottonel, phenolic compounds, color, turbidity.*

Rezumat. *Nanotehnologia este un domeniu de cercetare cu o evoluție rapidă cu multe aplicații potențiale, cum ar fi în chimia avansată, medicina, producția de energie, precum și în industria alimentară și a vinului. Scopul acestei lucrări este de a studia influența materialelor mezoporoase (MCM-41, SBA-15 și KIT-6) asupra parametrilor fizico-chimici, turbidității, conținutului fenolic și culorii vinurilor albe. Probele de vin utilizate au fost Muscat Ottonel din arealul viticol Bucium, iar anul de vinificație 2014. Compușii fenolici au fost caracterizați prin măsurarea absorbanței la 280 nm și a indicelui de oxidare la 420 nm. Parametrii de culoare au fost analizați spectrofotometric prin metoda CIE Lch. Analizele au arătat că nanomaterialele reduc tubiditatea vinului exprimată prin unități nefelometrice de turbiditate (NTU), care sunt corelate cu conținutul proteic. De asemenea, rezultatele indică faptul că indicele total de polifenoli (TPI) din probele de vin tratate a scăzut.*
Cuvinte cheie*: nanomateriale, Muscat Ottonel, compuși fenolici, culoare, turbiditate.*

INTRODUCTION

During the last two decades, nanostructured materials offer exciting opportunities for a large number of applications (Geszke-Moritz and Moritz, 2013; Ren *et*

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al., 2011). Among these nanomaterials, mesostructured materials have been intensively investigated. Mesoporous materials are defined by IUPAC as the materials with pore sizes between 2 and 50 nm. Mesoporous structures are presented by a wide class of substances including silica, metal oxides, metal hydroxides, metal salts, carbon structures, hybrid materials, organic structures and many others. Mesoporous materials are highly attractive for a wide variety of applications in technical sciences such as catalysis (Perego and Millini, 2013), electronics (Rauda *et al.,* 2013), photocatalytic hydrogen production (Onsuratoom *et al.,* 2011), solar cells (Zhu *et al.*, 2012) and others.

A family of ordered mesoporous silica molecular sieves known as M41S assures a bright future due to their properties: a well-defined pore size between 2-20 nm, an extraordinary high specific surface up to 1000 m^2/g and distinct adsorption properties due to their pore volume around 0.9 cm^3/g (Kresge *et al.,* 1992).

SBA-15 is by far the largest pore-size mesoporous material. It has highly ordered hexagonally arranged mesochannels, with thick walls, adjustable pore size from 3 to 30 nm, high hydrothermal and thermal stability. Also, they are ideal for size and shape exclusion separation of polyphenols, proteins and other small biological molecules (Zhao *et al.,* 1998).

In literature, it was reported that the synthesis of other mesoporous materials with larger pores, KIT-6, with Ia3d cubic type structure and a network of interconnected channels. Siliceous material KIT-6, has numerous applications in adsorption and catalysis, thanks to an unique 3-D structures (Xiaoying *et al.,* 2002).

Wine proteins may become insoluble and precipitate which is an important problem in wine stability. This fact is known as protein haze and it generally occurs when the wine is stored at a high temperature or when it is enriched with tannins from cork or wood. Higher protein levels are typical in overripe grapes, grapes sourced from warmer regions and grapes harvest mechanically. Skin contact will typically increase protein concentration. Protein haze is not common in red wines because the proteins flocculate with tannins during alcoholic fermentation. In white wines the protein are eliminated with a bentonite treatment (Sarmentoa *et al.,* 2000).

The aim of this paper is to study the influence of mesoporous materials (MCM-41, SBA-15 and KIT-6) on the white wines physical-chemical parameters, turbidity, phenolic content and color.

MATERIAL AND METHOD

Muscat Ottonel grape variety (V. vinifera) harvested in 2014 from the Bucium vineyard (Iași, Romania) was crushed and the must obtained was fermented up to 14.2 alcohol degree.

2 g/L of three types of nanomaterials (Fig. 1) were added at three samples of wine. The solutions were stirred 30 minutes in hermetic glass flask. Also, a control was carried out without nanomaterials. The resulting samples were centrifuged at 5000 rpm and 4 ºC for 10 minutes.

Turbidity was measured with a nephelometer (HANNA instruments, HI 93703 C), browning index was determined by measuring the absorbance at 420. Wine color was defined by the CIE Lch space in which there are three axes: h* (hue), L* (lightness) and c* (chroma or saturation). Total phenolic content was determined by measuring the absorbance at 280 nm.

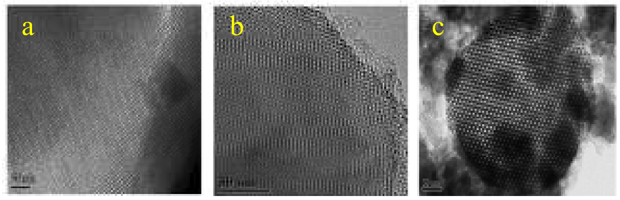

Fig. 1 - Transmission electron microscopy images of nanomaterials: KIT-6(a), MCM-41(b) and SBA-15(c)

All analyses were made for triplicate and a homogeneous group's analysis was made by means of the statistical package Statgraphics Centurion XVI from StatPoint Technologies, Inc. (Warrenton, VI, USA) to study if there were significant differences among the samples in the determined parameters.

RESULTS AND DISCUSSIONS

Protein instability in white wines causes clarity problems known as protein casse. The white wine is considered to be stable if the resulting turbidity, or haze, is less than 1.1 nephelometric turbidity units (NTU) (Moreno and Peinado, 2012). Results showed that all nanomaterials increased the limpidity of wines although only the treated wines with SBA-15 and MCM-41 shown an admissible NTU value (Fig. 2).

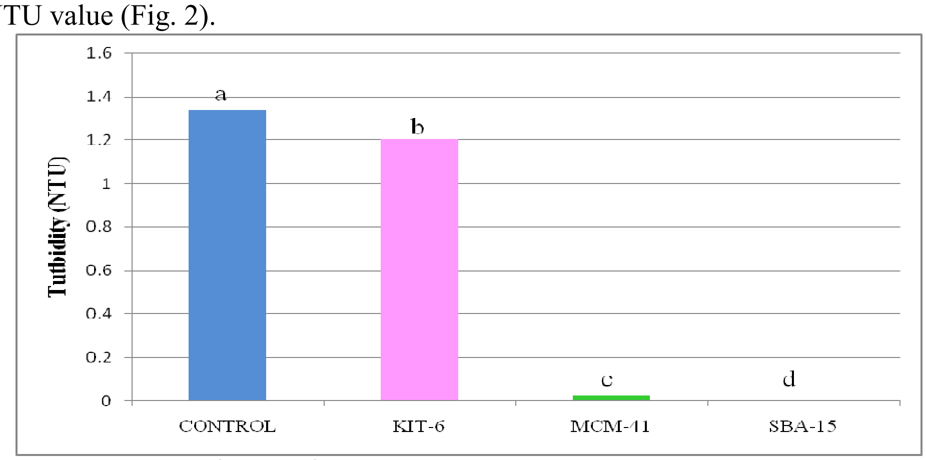

Fig. 2 - Turbidity of wines after treatment, expressed as nephelometric turbidity units (NTU). Different letters indicate significant differences at 95% of confidence level

The analytical parameters of control wine were habitual of white wines (Table 2). Enological parameters of treated wines showed slight decreases respect to control wine. This may be due to the interaction of nanomaterials with the components of wine or to the displacement of the chemical balances by the change of pH. Anyway, nanomaterials contribute to reduce both the volatile acidity and the browning index, parameters which are related to analytical quality of wine.

Table 1

Enological parameters of wines after treatment. TA: titratable acidity (g tartaric acid/L), VA: volatile acidity (g acetic acid/L), BI: browning index, HGA: homogenous groups analysis, different letters indicate significant differences at 95% of confidence level

	pH	TA	VA	BI
Control	3.38±0.01	4.05±0.02	0.5±0.0	0.091±0.003
KIT-6	3.37±0.00	4.00±0.09	0.4±0.0	0.071±0.005
MCM-41	3.37±0.01	4.05±0.04	0.4±0.0	0.079±0.007
SBA-15	3.37±0.01	4.05±0.01	0.4±0.0	0.074±0.006
HGA	a b b b	a b a a	a b b b	a d b c

Figure 3 shows the color properties h* (hue), c* (chroma) and L* (lightness) for the wine samples. All wines had a yellowish hue –the hue values can range from 0º (red), through 90º (yellow), 180º (green), 270º (blue) and back to 360º or 0º– but the treated KIT-6 and MCM-41 wines showed a more orange-yellow hue that treated wines with SBA-15 and Control.

The property chroma or saturation is related with purity color (bandwidth) and it can range from 0, which is completely unsaturated (very broad set of wavelengths), to 100 for pure color (very limited set of wavelengths). All wine samples showed very little saturated colors, being the treated wines those with the lowest values.

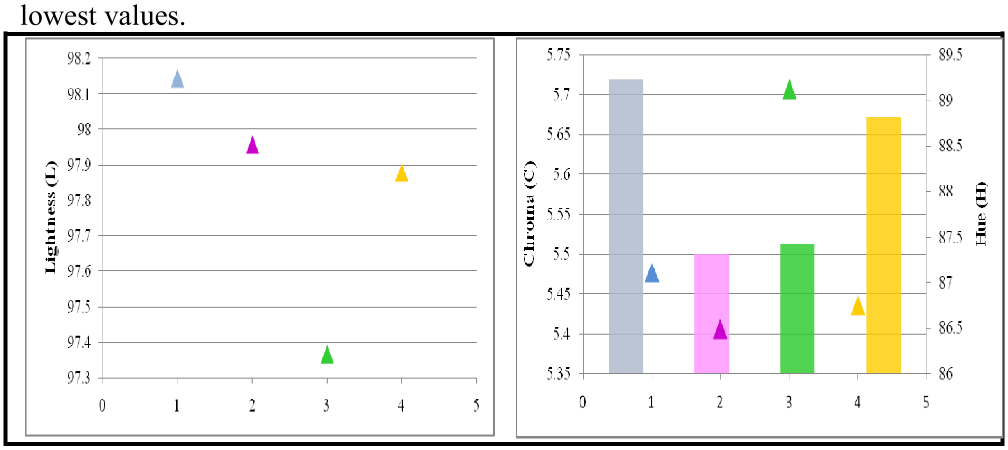

Fig. 3 - Color properties lighteness, chroma (triangle) and hue (full bars) of control wine (blue) and wines treated with KIT-6 (pink), MCM-41 (green) and SBA-15 (yelow)

Finally, the property lightness shows clarity or darkness color (pigment concentration). It can range from 0, which has no lightness (pigment concentration very high, i.e. absolute black), to 100, which is maximum lightness (pigment concentration very low, i.e. absolute white). All wine samples had colors very lightness, their L values were above 97. Moreover, the treated wines showed lower pigment concentration that control wine, which may be due to the interaction of nanomaterials with the pigments of wine.

Relative to total polyphenols index (Fig. 4), the nanomaterials modify significantly the phenolic content respect to control wine. It can be observed that between three types of nanomaterials, MCM-41 retained the highest amount of phenols.

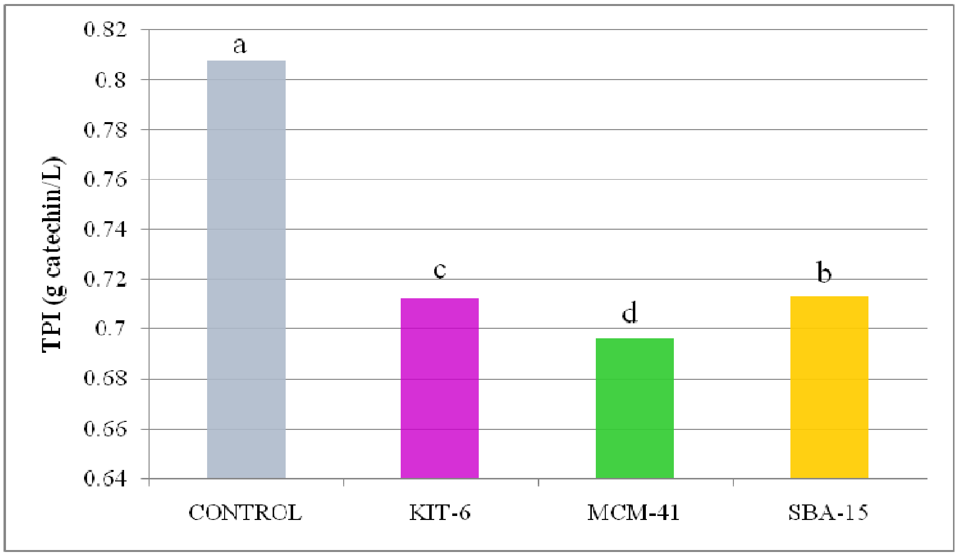

Fig. 4 - Total polyphenols index (TPI), expressed as grams of catechin per liter (full bars) of wines after treatment. Different small letters indicate significant differences at 95% of confidence level in TPI values.

CONCLUSIONS

1. Results had showed that nanomaterials reduce the NTU value, which are related with protein concentration, without adversely modifying the parameters measured.

2. Enological parameters of treated wines showed slight decreases respect to control wine. Anyway, nanomaterials contribute to reduce both the volatile acidity and the browning index, parameters which are related to analytical quality of wine.

3. The nanomaterials modify significantly the phenolic content respect to control wine. The results indicate that the total polyphenol index (TPI) of treated wine samples decreased.

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REFERENCES

1. **Geszke-Moritz M., Moritz M., 2013 -** *Quantum dots as versatile probes in medical sciences: synthesis, modification and properties***.** Mater. Sci. Eng. C, 33: 1008–1021.
2. **Kresge C. T., Leonowicz M. E., Roth W. J., Vartuli J. C., Beck. J. S., 1992 -** *Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism.* Nature, 359: 710–712.
3. **Moreno J., Peinado R., 2012 -** *Enological Chemistry*. Academic Press. Elsevier.
4. **Onsuratoom S., Chavadej S., Sreethawong T., 2011 -** *Hydrogen production from water splitting under UV light irradiation over Ag-loaded mesoporous-assembled TiO_2–ZrO_2 mixed oxide nanocrystal photocatalysts*. Int. J. Hydrogen Energy, 36: 5246–5261.
5. **Perego C., Millini R., 2013 -** *Porous materials in catalysis: challenges for mesoporous materials*. Chem. Soc. Rev., 42: 3956–3976.
6. **Rauda I. E., Saldarriaga-Lopez L. C., Helms B. A., Schelhas L. T., Membreno D., Milliron D. J., Tolbert S. H., 2013 -** *Nanoporous semiconductors synthesized through polymer templating of ligand-stripped CdSenanocrystals*, Adv. Mater., 25: 1315–1322.
7. **Ren X., Chen C., Nagatsu M., Wang, X., 2011 -** *Carbon nanotubes as adsorbents in environmental pollution management: a review.* Chem. Eng. J., 170: 395–410.
8. **Xiaoying, L., Bozhi, T., Chengzhong, Y., Feng, G., Songhai, X., Bo, T., Renchao, C., Lian-Miao, P., Dongyuan, Z., 2002 -** *Room-Temperature Synthesis in Acidic Media of Large-Pore Three-Dimensional BicontinuousMesoporous Silica with Ia3d Symmetry*. Angew. Chem., 114: 4032-4034.
9. **Zhao D. Y., Feng J. L., Huo Q. S., Melosh N., Fredrikson G. H., Chmelka Stucky B. F., 1998-***Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores.* Science, 279: 548-552.
10. **Zhu P., Reddy M. V., Wu Y., Peng S., Yang S., Nair A. S., Loh K .P., Chowdari B. V. R., Ramakrishna S., 2012-***Mesoporous SnO2 agglomerates with hierarchical structures as an efficient dual-functional material for dye-sensitized solar cells*. Chem. Commun., 48: 10865–10867.