THE EFFECT OF CARBON BASED MATERIALS TREATMENTS ON CABERNET SAUVIGNON WINE COMPOSITION

EFECTUL TRATAMENTELOR CU MATERIALE PE BAZĂ DE CARBON ASUPRA COMPOZIŢEI VINULUI CABERNET SAUVIGNON

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Abstract. *The aim of this paper is to investigate new possibilities of using carbon based materials in winemaking technology. In this study, Cabernet Sauvignon wine was treated with following materials: graphene (G), graphene oxide (GO) and carbon nanotubes (CNTs). The total polyphenols content expressed as mg of gallic acid showed that carbon based materials reduced the amount of phenols in wine from 5623,60 mg/L to 5053,89 mg/L. Major colour and hue differences for Cabernet Sauvignon wines are found in the samples treated with graphene and carbon nanotubes. HPLC determination of organic acid content revealed that carbon based materials treatments contributed at decreasing the amount of malic acid in wine.*

Key words: Cabernet sauvignon, carbon nanotubes, graphene, reduced graphene oxide

Rezumat. *Scopul acestei lucrări este de a investiga noi posibilităţi de utilizare a materialelor pe bază de carbon în tehnologia de vinificaţie. În acest studiu, vinul Cabernet Sauvignon a fost tratat cu următoarele materiale: grafen (G), oxid de grafen (GO) şi nanotuburi de carbon (CNT). Conţinutul în polifenoli, exprimat în mg de acid galic, a arătat că materialele pe bază de carbon au redus cantitatea de polifenoli în vin de la 5623,60 mg/L până la 5053,89 mg/L. Diferenţe de culoarea şi de ton faţă de proba martor se observă în vinurile Cabernet Sauvignon tratate cu grafen şi nanotuburi de carbon. În urma determinării conţinutului de acizi organici prin HPLC, s-a remarcat o diminuare a conţinutului de acid malic în urma aplicării tratamentelor cu nanomateriale.*

Cuvinte cheie: Cabernet Sauvignon, nanotuburi de carbon, grafen, oxidul de grafen redus

INTRODUCTION

In the wine making technology, use of nanomaterials is still in the research stage. Among carbon based materials, the following may have significant importance:

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carbon nanotubes (CNTs), graphene (G) and reduced graphene oxide (rGO). Carbon nanotubes are cylindrical nanostructures with exceptional thermal and electrical conductivity and high mechanical strength and rigidity.

Studies have shown that CNTs can be an attractive option as artificial flocculants; Mamvura *et al.* (2012) demonstrated that CNTs can improve beer yeast flocculation function of pH, temperature and concentration.

Used as filtering membranes, carbon nanotubes eliminate the multiple components of heavy hydrocarbons in oil, while, in water, they remove bacteria such as *Escherichia coli* and 25 nm nano-sized poliviruses (Srivastava *et al*., 2004; Upadhyayula *et al*., 2009; Sweetman, 2012).

Recently characterized as "the thinnest material of the universe" (Geim and Macdonald, 2007), graphen (G) is the two-dimensional version of graphite consisting of a two-dimensional arrangement of carbon atoms disposed in a hexagonal grid. Graphene is the best known conductor of electricity and heat.

Graphene and reduced graphene oxide (GO) which is graphene oxide that has been reductively processed by different methods to reduce its oxygen content, present a whole range of special properties, which gives them great potential for the practical production of new uses. It has been used in the manufacture of bio-systems consisting of nucleic acids, peptides, proteins and enzymes (Katz and Willner, 2004; Mohanty and Berry, 2008; Wang *et al*., 2011), active adsorbent materials that eliminate ions of heavy metals, pesticides and natural colorants from water (Bradder *et al*., 2011; Chandra and Kim, 2011; Gupta, 2012).

MATERIALS AND METHODS

The Cabernet Sauvignon grapes were processed in 25 L vats, with skin maceration until the alcoholic fermentation finished. After destemming and crushing, 30 g/hL Nutristart fermentation activators and 25 g/hL Laffort® Saccharomyces cerevisiae RX 60 yeast were added according to the protocols prescribed by the manufacturers. Manual punching down was done twice a day. After the alcoholic fermentation was complete, the wines were removed from the yeast deposit, and divided in equal parts and treated with carbon based materials in following doses:

G – 250 mg/L; **rGO** – 25 mg/L, **CNTs** – 1g/L.

After 3 weeks, the wines were filtered with 0.45 µm sterile membrane filters and were bottled in 0.75 L glass bottles, using Nomacork Select 100 Series TM closures. The maceration process and alcoholic fermentation were conducted at 10 °C in a room with controlled temperature. The wine was stored in a cellar at 12 °C. The control sample **(M)** for each trial was obtained without any addition of nanomaterials and the analyses were performed intriplicate, and a mean value was calculated.

Reagents. Nanomaterials were purchased from Graphene Laboratories Inc. (Calverton, New York).

Graphene Nanopowder (G): 1.6 nm flakes (dry black powder), carbon: 97%, hydrogen: 1%, oxygen: 2%, specific surface area: 510 m^2/g, solid content: 98%, average particle (lateral) size: ~10 microns.

High Surface Area Reduced Graphene Oxide (rGO) - dry black powder, specific surface area: 833 m^2/g, solid content: 98%, carbon/oxygen ratio: 10.5, average flake thickness: 1 monolayer, average particle (lateral) size: ~3-5 microns.

Multi-Walled Carbon Nanotube Powder (CNTs) - diameter: 50-85 nm, length: 10-15 micrometers, nitrogen surface area: 60-90 m^2/g, volume resistivity: 2¡<<5x10^{-4} ohm-cm, carbon content: >94%.

Standard analysis

Each wine, after decarbonatation, was analysed for: volatile acidity OIV-MA-AS313-02, total acidity OIV-MA-AS313-01, alcoholic strength by frequency oscillator OIV-MA-AS312-01A, reducing substances OIV-MA-AS311-01A, pH OIV-MA-AS313-15, total dry matter and non-reducing substances OIV-MAAS2-03B were done according to present standards (OIV, 2013).

Total phenolic compounds (TPC) contained in the wines were oxidized by the Folin-Ciocâlteu reagent. The resulting blue coloration has a maximum absorption at approximately 750 nm that is proportional to the total quantity of phenolic compounds originally present. The absorbances of the wines were measured at 750 nm according to the Folin-Ciocâlteu method OIV-MA-AS2-10 using an Analytik Jena Specord S200 UV-VIS spectrophotometer with a 10 mm optical path length cuvette (Hellma® made of Quartz SUPRASIL®). TPC was expressed in mg of gallic acid per liter. Calibration curve equation was: $\boldsymbol{y} = 78.693\boldsymbol{x} - 179.09$. Correlation coefficient (r) for calibration curve was 0.9761. Color analyses: Analytik Jena S 200 spectrophotometer was used to determine the chromatic characteristics according to CIE Lab 76 (OIV, 2013).

Organic acid content: (OIV MA-E-AS313-04-ACIORG and OIV MA-E-AS313-17-ACSHIK). The samples were processed by using a Shimadzu HPLC composed of: autoinjector Shimadzu series Prominence SIL-20AC (used injection volume: 10 µL, samples temperature 20 °C), quaternary pump Shimadzu series Prominence LC-20AD with five channels, degassing device Shimadzu series Prominence DGU-20A5, column oven Shimadzu series Prominence CTO-20AC, Photo Diode Array Shimadzu series Prominence SPD-M20A (used scanning segment: 200-440 nm), controler of cromatographic system Shimadzu series Prominence CBM-20A and PC conectivity through LAN. Standard solutions and juice samples were filtered through a 0.45 mm millipore membrane filter (HAWP Millipore Co., Bedford).

RESULTS AND DISCUSSIONS

Standard chemical analyses of wine were performed according to the methods proposed by O.I.V. (tab. 1). Due the fact that wine was not sulfited, we did not determine free and total SO_2. The results obtained for standard chemical analyses of wine showed that carbon based materials didn't have a strong influence on wine composition, the results presenting similar values.

Total phenolic content suffered a decrease following the use of carbon based materials (fig. 1). It was observed that the phenolic content decreases after carbon based treatments treatments from 5623.6 mg/L in the untreated wine (M) to 5053.89 mg/L in the graphene (G) sample. Among nanomaterials, reduced graphene oxide (rGO) removed the smallest amount of phenolic compounds from wine, instead graphene (G) contributed to a visible reduction of polyphenols in Cabernet Sauvignon wines.

The chromatic parameters of the Cabernet Sauvignon wines were calculated according to the CIE Lab 76 methods and to the registered absorption spectrum of each wine sample. The values of the L-parameter show that the wines obtained by applying graphene and carbon nanotubes were the clearest (tab. 2), also these wines showed major hue and colorimetric differences compared to untreated sample (M).

Table 1

Mean values and standard deviation of standard chemical analyses of Cabernet Sauvignon wine

Sample	pH	Conductivity µS/cm	Volatile acidity (g acetic acid/L)	Total acidity (g tartaric acid/L)	Alcohol (% vol)	Relative density	Reductive substances (g/L)	Total dry extract (g/L)	Non reductive extract (g/L)
M	3.59±0.02	2050±0.03	0.2±0.01	6.12±0.12	14.09±0.17	0.9933±0.16	4.94±0.03	28.7±0.02	25.2±0.02
G	3.61±0.01	1987±0.03	0.2±0.01	5.88±0.17	13.85±0.16	0.9927±0.13	5.33±0.04	28.1±0.04	24.59±0.03
rGO	3.61±0.01	2060±0.02	0.23±0.02	6.12±0.11	14.02±0.19	0.9932±0.15	6.67±0.02	28.1±0.03	24.6±0.04
CNTs	3.61±0.01	1971±0.04	0.23±0.02	6.12±0.12	13.85±0.16	0.9931±0.18	5.62±0.02	28.1±0.03	24.6±0.05

Data are means of triplicate determinations ± standard deviation over the three replications in one wine sample. **M** – untreated sample; **G** – graphene nanopowder ,**rGO** - high surface area reduced graphene oxide; **CNTs** – multi-walled carbon nanotube powder.

Table 2

Mean values and standard deviation of chromatic characteristics of Cabernet Sauvignon wines

Sample	Clarity L	Chromaticity		Chrome C	Tonality H	Intensity	Hue	ΔE	ΔH
		a	b						
M	8.55±0.15	39.83±0.15	14.55±0.12	42.40±0.10	20.07±0.09	10.52±0.11	0.84±0.0001	-	-
G	12.36±0.17	44.99±0.19	21.13±0.13	49.71±0.13	25.16±0.12	9.63±0.13	0.84±0.0001	9.19±0.02	4.06±0.03
rGO	8.87±0.14	40.24±0.18	15.10±0.14	42.98±0.11	20.57±0.12	10.32±0.11	0.84±0.0001	0.76±0.03	0.37±0.02
CNTs	12.60±0.12	45.29±0.13	21.55±0.14	50.25±0.11	25.39±0.10	9.62±0.18	0.84±0.0001	9.76±0.02	4.15±0.03

Data are means of triplicate determinations ± standard deviation over the three replications in one wine sample.

M – untreated sample; **G** – graphene nanopowder; **rGO** – high surface area reduced graphene oxide; **CNTs** – multi-walled carbon nanotube powder.

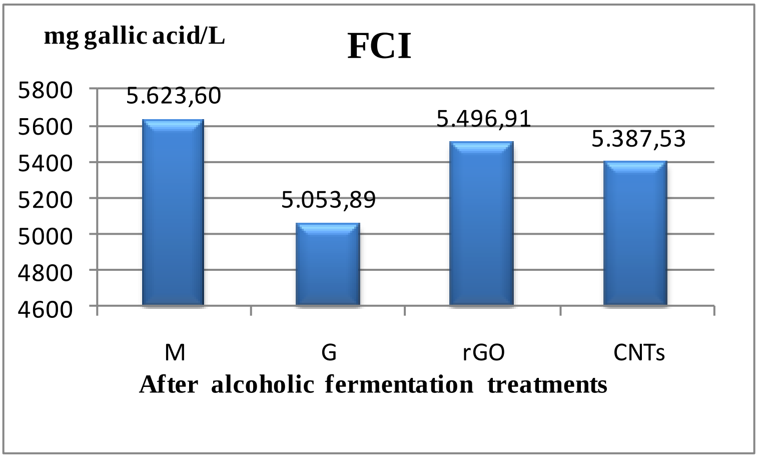

Fig. 1 Phenolic compounds of wines (Folin-Ciocâlteu method)

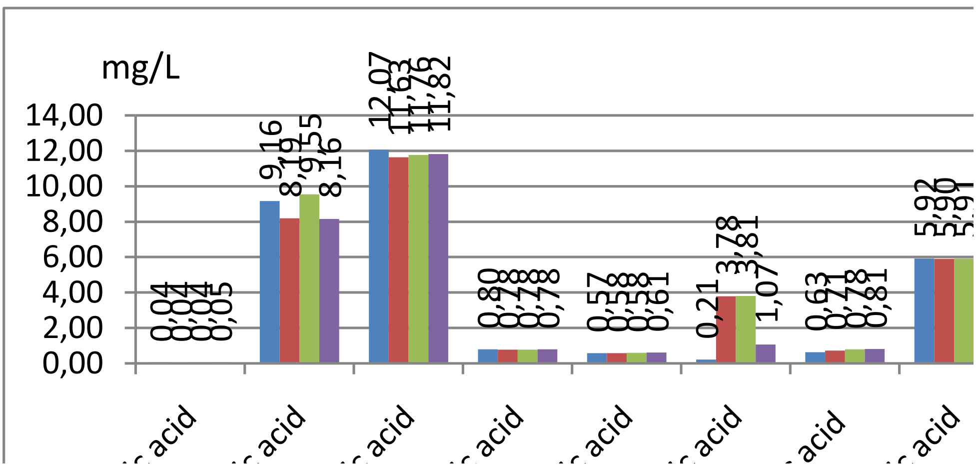

Fig. 2 Organic acids' content of wine

A small increase of oxalic acid content was observed in the samples treated with carbon nanotubes (CNTs). The results obtained showed that graphene (G), carbon nanotubes (CNTs) have reduced the level of tartaric acid in wine; instead, the wine elaborated with graphene oxide (rGO) presented the highest value for this acid (fig. 2). The contents of malic acid, shikimic acid and succinic acid decreased after addition of carbon based materials in the stage that follows alcoholic fermentation; but for lactic, acetic and citric acids contents, these treatments caused an increasing of these quantities.

CONCLUSION

1. Graphene (G) contributed to a visible reduction of polyphenols in Cabernet Sauvignon wines.
2. The wines treated with graphene and carbon nanotubes were the clearest ones.
3. The contents of malic acid reduced after addition of nanomaterials.

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