Adsorption of Phenolic Compounds from Wine on Mesoporous MCM-41 Molecular Sieve

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Mesoporous silica-MCM-41 molecular sieve was synthesized following a hydrothermal synthesis route using tetraethylorthosilicate as silica source, cethyltrimethylammonium bromide as surfactant (structure-directing agent) and ammonium hydroxide as mineralizing agent. This mesoporous material exhibits a type IV nitrogen adsorption-desorption isotherm, has a specific surface area of 1170 m^2/g, a total pore volume of 0.91 cm^3/g and cylindrical pores of an average diameter of 2.67 nm. The adsorption properties of the calcined mesoporous silica MCM-41 material, as a consequence of the presence of single and geminal silanol groups that are active sites for adsorption were evaluated in the clarification process of red wine. The total polyphenols content (reduction), the selectivity and stabilization for some compounds (phenolic acids, catechin, epicatechin, stilbenes) and the chromatic characteristics of wine (no modification) were investigated. The use of mesoporous silica MCM-41 molecular sieve in red wine treatment is feasible, softer and ecological.

Keywords: MCM-41, phenolic compounds, adsorption

Wine is a drink derived from the fermentation of grape juice. For many countries wine is a traditional product, made from ancient times, with important economic and social implications. It is known that the aroma of wine is due to over a thousand volatile compounds found in wine, with concentrations from a few ppms up to 10-15% mass concentration. There were identified several classes of compounds in wine aroma profile, the most important being alcohols, esters, acids, ketones, aldehydes, ethers, lactones, sulfur compounds, nitrogen, phenolic compounds. All these compounds play an important role in characterizing the aroma of wine [1].

Browning and lack of color, aroma and taste constitute the main enological problems during storage for wine producers. Browning of wines is a result of phenols oxidation to quinones (catalyzed by Fe^{2+}/Fe^{3+} or Cu^{2+} and oxidative enzymes) and of condensation reactions between phenolic compounds with the formation of stable colored polymers in the yellow-brown spectral region [2-7].

The reduction or recover of various phenolic compounds may be achieved by specific adsorbents: activated carbon S5X-Agrovin [8-10] polymeric adsorbents of biological origin – chitin and chitosan[11,12], synthetic polymeric adsorbents – hypercrosslinked polystiren Amberlite XAD-2, Amberlite XAD-4, Ambersorb XE340 [13], polyvinyl-polypyrrolidone, PVPP [14], modified natural polymers – microcrystalline cellulose [15], proteic adsorbents - albumin, gelatin, fish-glue (isinglass) [16-19], potassium caseinate, wheat gluten, yeast as sorbent [11, 20-21], zirconia [22], and siliceous adsorbents – bentonite [23-25] and zeolites [26,28].

Ordered mesoporous inorganic silica and aluminosilica of the M41S family, first synthesized in 1992 [29] have important technological applications as size selective adsorbents, sieves, supports or nanoscale chemical reactors [30].

Among the members of M41S family of materials, the so-called MCM-41 has been most widely studied, mainly because of its pseudo-crystalline and textural properties, such as the hexagonal arrangement of one-dimensional channels [29] with a sharp pore –size distribution and large specific surface area.

Mesoporous MCM-41 materials are characterized by narrow distribution of mesoporous size, with diameters ranging from 2 nm to 15 nm (most often between 2 nm and 4 nm), due to dimensions of surfactant used as a structure-directing template, very high BET specific surface area (between 700 to 1400 m^2/g), total pore volume between 0.2 and 2.0 cm^3/g, very large porosity (up to 80%) and a thermal stability up to 800^0C [31]. The uniform hexagonal pore structure of MCM-41 is reflected in a set of XRD peaks at low angles in the 2θ range from 1.5 to 7^0 (2θ = 2.25, 3.88, 4.43 and 5.840), corresponding to planes (100) (110) (200) and (210) [31].

Mesoporous silica MCM-41 is a non-acidic and biocompatible material; silica walls are inert to both acid and basic medium, with exception of hydrofluoric acid and concentrated basic solutions. The structure is resistant to abrasion and compression.

The objective of this study is to synthesize mesoporous silica MCM-41 and to examine the performance of this mesoporous adsorbent in the stabilization of wine.

Materials and methods

Chemicals

Tetraethylortosilicate (TEOS, 98% Merck) as silica source, cethyltrimethylammonium bromide (C_{16}TMAB) (Aldrich) as structure-directing agent (surfactant), NH_4OH 20% solution (Merck), methanol (Sigma) and deionized water were used, as received, in the synthesis of silica MCM-41.

A Cabernet Sauvignon bottled wine originated from Cozmesti area (Romania) and winified in 2009 was selected as a typical wine for the experiments.

Activated carbon (Fisher Chemicals) was used in adsorption process for comparison purpose.

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Synthesis of mesoporous silica MCM-41

Silica MCM-41 mesoporous material was synthesized using tetraethylorthosilicate (TEOS) as silica source, cethyltrimethylammonium bromide (C_{16}TMAB) as structure-directing agent (surfactant), concentrated ammonia solution as mineralizing agent and deionized water as solvent. The pure silica MCM-41 was prepared according to the procedure given in the literature [29]. The molar composition of the gel was:

$$1SiO_2: 0.2C_{16}TMAB: 5.7NH_3: 113\ H_2O$$

A solution of surfactant was prepared by dissolving C_{16}TMAB in deionized water, under magnetic stirring for a half hour at room temperature until the solution becomes clear. To this surfactant solution the concentrated ammonia solution was added under stirring for half an hour. Then, to the alkaline solution, the silica source (TEOS) was added drop wise under stirring and the resulted gel was aged for 3 h at room temperature. The gel was heated at 80°C for 4 days. The synthesis product was recovered by filtration, washed with deionized water, dried at 80°C in air and calcined in air at 550°C for 7 h (heating rate of 1°C/min) in a programmable furnace [29] to remove the organics.

Characterization

X-ray diffraction. The small-angle XRPD pattern of the calcined material was performed using a PANalytical X'Pert PRO MPD diffractometer using Ni filtered CuKα radiation (λ= 0.15406 nm). The data were collected with 2θ varying from 0.5 to 7° at room temperature.

N_2 sorption. The nitrogen adsorption isotherm at -196°C was determined on a NOVA 2200 Quantachrome sorption apparatus. Prior to the adsorption measurement the sample was outgassed for 3 h at 300°C. The BET surface area was calculated based on the adsorption data in the relative pressure range of 0.05-0.25. The pore size distribution was calculated from the nitrogen adsorption isotherm using the Barret-Joyner-Halenda (BJH) method [32].

Scanning Electron Microscopy (SEM) and elemental analysis of sample (EDX) were carried out on a SEM VEGA II LSH (TESCAN) with EDX detector tip Quantax QX2 (Bruker/ Roentex).

FTIR spectra were performed in the range of the wave numbers 600 - 4000 cm^{-1}, using a unit TENSOR 27, Brucker FTIR.

Total index of phenols from wine was determined spectrophotometrically using a Spectrophotometer Analytik Jena S 200 at 280 nm (OIV method).

Wine phenolic compound analysis. The wine phenolic compounds were carried out with high-performance liquid chromatograph (HPLC) Shimadzu equipped with two chromatographic columns Merck Chromolith Performance RP-18.

Evaluation of chromatic characteristics of wine. Wine colour was evaluated by simple CIELab76 methods reflecting the colour visual appreciation. This method has been proposed as an OIV method for colour determination.

Adsorption of phenolic compounds on silica MCM-41

Batch adsorption experiments were carried out by shaking the increased amounts of MCM-41 powder with 50 mL of wine for 24 h at 5°C. After filtration, the total content of phenols in the liquid phase was analyzed spectrophotometrically, at 280 nm using the OIV methods. Identification of phenolic compounds retained on silica MCM-41 was carried out using high performance liquid chromatography (HPLC method)

Results and discussions

X-ray Powder Diffraction Analysis (XRPD)

Figure.1 shows the small-angle XRPD pattern of the calcined silica MCM-41. The diffractogram presents three well-resolved peaks in the lower 2θ angle range of 0.5-7°, that can be indexed as (100), (110) and (200) crystal planes confirming the hexagonal mesophase of the material. The fourth peak less intense, according to the plan (210), can sometimes be absent. These peaks are characteristic of 2-D hexagonally ordered structure with p6mm symmetry for the reflection planes (hk0). The very strong peak corresponding to d_{100} spacing (2θ=2.2°) is characteristic to sample that possesses periodic structure.

According to Bragg's law ($n\lambda=2d_{(100)} \times \sin\theta$) and based on hexagonal symmetry ($a=2d_{(100)}/\sqrt{3}$) the parameter $d_{(100)}$ and the lattice constant a_0 were calculated.

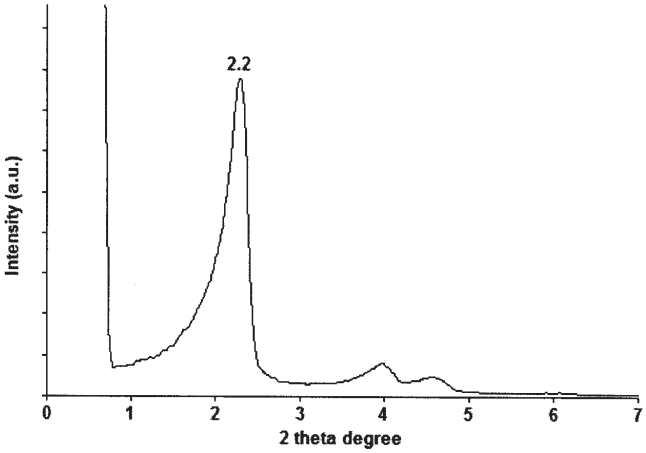

Fig. 1. Small-angle XRPD pattern of calcined MCM-41

This XRPD pattern coincide well with the data already reported in literature for mesoporous silica MCM-41[29, 31]

N_2 physical adsorption-desorption

Figure 2 exhibits the typical nitrogen adsorption – desorption isotherm at -196°C for calcined silica-MCM-41. It corresponds to a reversible type IV isotherm with a hysteresis loop Type H1 what is characteristic for mesporous materials with cylindrical pores and a high degree of pore size uniformity, according to the IUPAC classification [33].

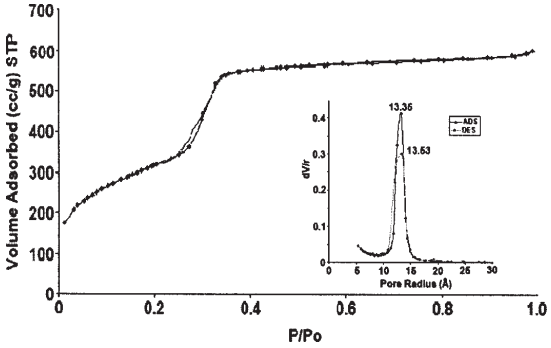

Fig. 2. N_2 adsorption – desorption isotherm at -196°C of silica MCM-41 The inset shows the pore size distribution curve (PSD)

A sharp increase in the adsorption amount of nitrogen at the relative pressure of about 0.3 can be seen which is due to capillary condensation.

Specific surface area was calculated by using the multiple point BET method and BET equation, the pore size distribution curve was computed based on the BJH model and the mean pore size estimated from the peak position

Table1
STRUCTURAL AND TEXTURAL PARAMETERS OF CALCINED SILICA MCM-41 DERIVED FROM XRPD DATA AND NITROGEN PHYSISORPTION

Sample	Basal lattice spacing, d_{100} (nm)	a_0 (nm)	S_{BET} (m^2/g)	Pore diameter D_{BJH} (nm)	Pore volume (cm^3/g)	Wall thickness (nm)
MCM-41 (calcined)	4.01	4.63	1170	2.67	0.910	1.96

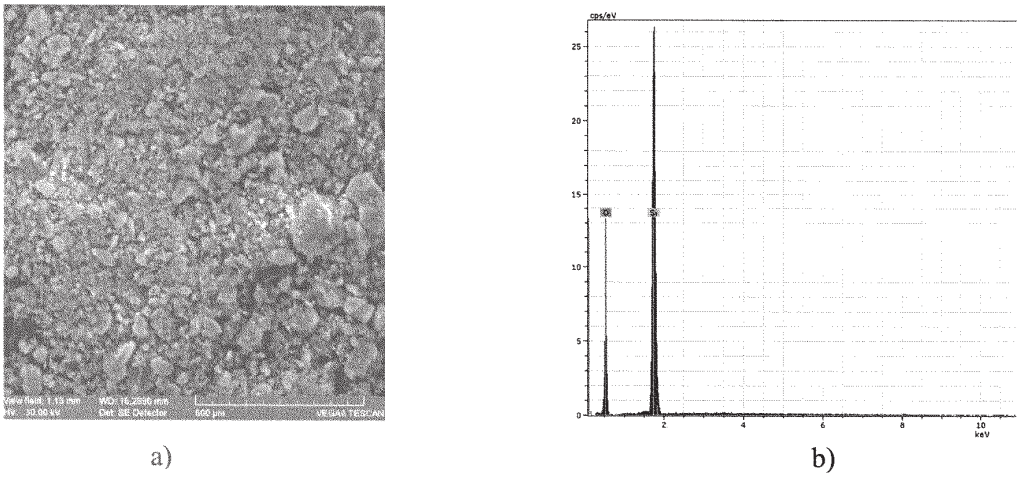

Fig. 3. SEM micrograph (a) and EDX spectra (b) of silica –MCM-41

in BJH curve. The total pore volume was obtained from the volume of N_2 adsorbed at a relative pressure $p/p_0 = 0.94$. Table 1 summarizes the structural and textural parameters of calcined mesoporous silica MCM-41 used in the experiments.

The thickness of the mesopores walls (t), calculated by the difference between a_o – unit cell parameter and the mesopore diameter D_{BJH} ($t = a_0 - D$) is cca 1.96 nm comparable to the largest reported wall thickness in silica MCM-41 [35].

SEM micrograph and EDX pattern

Figure 3 presents the SEM micrograph of calcined MCM-41 sample (a) and the elemental composition by EDX spectra (b).

The mesoporous silica MCM-41 is seen to result in a solid consisting of small agglomerates. The EDX spectra show only silicon and oxygen, so the sample is chemically pure.

FT-IR spectra of silica-MCM-41

As shown in figure 4, the calcined MCM-41 sample exhibited a band at 3740 cm^{-1} ascribed to the fundamental stretching vibrations of the terminal Si-OH group [35, 36] and adsorption broad band around 3412 cm^{-1} sorption which may be attributed to the adsorbed water molecules, while deformational vibrations of adsorbed water molecules cause the absorption bands at 1626 cm^{-1}. The absorption bands at 1212 and 1328 cm^{-1} are due to internal and external asymmetric Si-O-Si stretching modes. The symmetric stretching band at 831 cm^{-1} and too asymmetric stretching bands at 968 and 1053 cm^{-1} could be assigned to the tetrahedral SiO_4 structure units. These results confirm that the surface of silica MCM-41 molecular sieve possesses silanol groups, a required adsorption property.

Standard chemical analysis of wine

Ethanol, *p*H, total acidity, volatile acidity, total and free SO_2, sugars and total dry mater (TDM) of the used wine

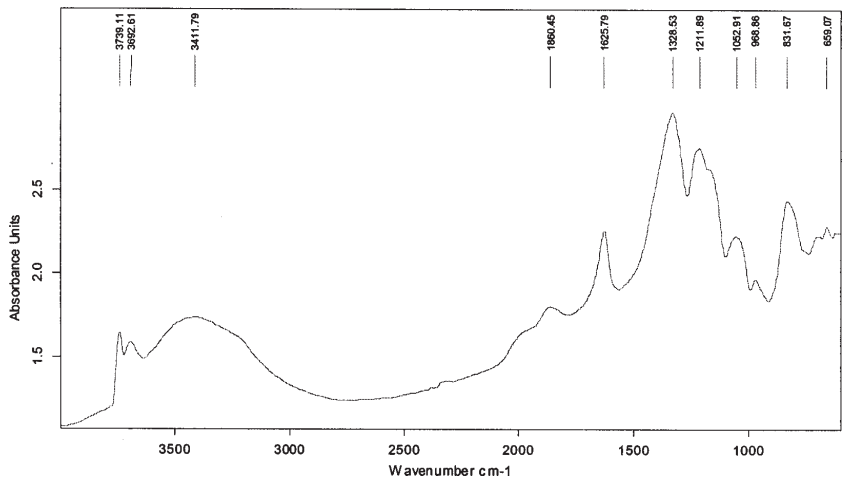

Fig. 4. FTIR spectra of calcined MCM-41

Table 2
STANDARD ANALYSIS OF CABERNET SAUVIGNON WINE

Parameter	Value
Ethanol	13.07 % v/v
pH	3.5
Total acidity	6.18 g/L (as tartaric acid)
Volatile acidity	0.52 g/L (as acetic acid)
Free SO_2	33.62 mg/L
Total SO_2	170.42 mg/L
Sugars	2.3 g/L
TDM	22.45 g/L

were analyzed according to the methods proposed by O.I.V. (2006) [37] (table 2).

$$y = 0.294x + 0.028 \quad (1)$$

where x is the absorbance value A_{280} afforded by spectrophotometer and y is the equivalent content of polyphenolic compounds expressed as mg of gallic acid equivalents per L (GAE/L).

The total index polyphenol content was found as 15.91 mg/L (A_{280} = 54.025). The results of the adsorption experiments are summarized in table 3.

As it is indicated in table 3 by increasing the adsorbent concentration from 0 to 4.249g MCM-41/ L, the total index of phenols in wine decreases from 15.91 mg/L to 14.29 mg/L and the polyphenols removal efficiency increases up to a value of 9.25%. Comparatively, using an activated carbon dose of 1.013 g/L wine, the polyphenols removal efficiency is 25.76 %. A dose of 1.035 g of MCM-41 for 1L of wine decreases the phenolic compounds concentration with only 5.28 %. The adsorption on activated carbon is nonspecific and has influence to quality and color of wine.

Table 3
VARIATION OF TOTAL PHENOLS CONTENT IN RED WINE WITH THE ADSORBENT DOSE

	Amount of adsorbent (g/L)	**Absorbance (λ=280 nm)**	**Residual concentration of polyphenols in wine (mg/L)**	**Polyphenols removed (%)**
Red wine	0	54.025	15.91	0.00
MCM-41	0.518	50.66	14.92	5.27
	1.035	50.65	14.91	5.28
	1.511	50.24	14.79	6.06
	2.174	49.12	14.46	8.15
	2.513	48.69	14.34	8.95
	3.060	48.58	14.31	9.15
	4.249	48.53	14.29	9.25
Activated carbon	0.280	47.180	13.89	12.67
	0.659	43.940	12.94	18.67
	1.013	40.110	11.82	25.76

Adsorption of polyphenols

The most important functionality of the MCM-41 material is the surface silanol goups. The density of Si-OH groups over a calcined MCM-41 sample is about 2.5-3.0 per nm^2. Three types of silanol groups generally are distinguished: single (free), geminal and hydrogen-bonded (fig. 5) [36].

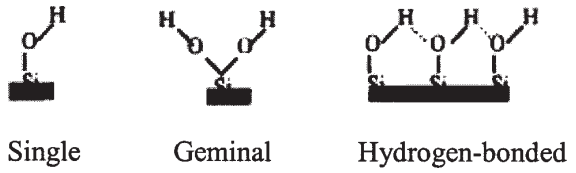

Fig. 5. Representation of the three types of SiOH groups in the siliceous MCM-41[36]

The silanol groups are not acidic; only the single and geminal silanols are active sites and highly accessible to the adsorption. They also act as ligands and can be employed to immobilize metal complexes.

The total polyphenols content of the red wine was determined by measuring the absorbance at λ =280 (A_{280}) nm in quartz cuvettes of 1 cm optical path, compared with deionized water. The calibration curve, using gallic acid solutions of concentration 0; 0,2; 0,4; 0,6; 0,8 mg/L is described by the following equation:

The polyphenols content removed by different doses mesoporous silica MCM-41 is shown in figure 6.

Up to a dose of 3.0602 g MCM-41/L from wine are adsorbed specific polyphenols, but after that the adsorption remain approximately constant.

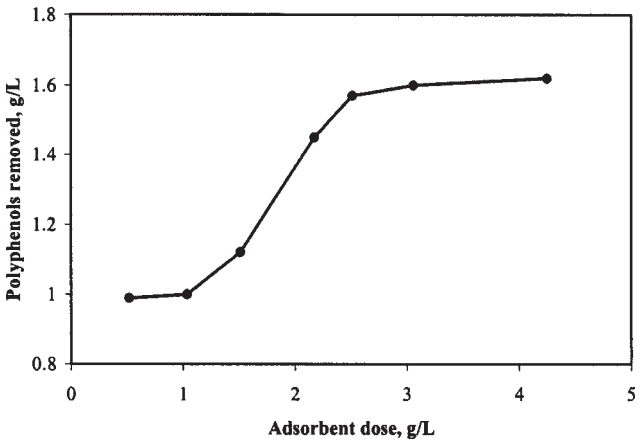

Fig. 6.Variation of polyphenols removed on microporous silica MCM-41 as a function of adsorbent dose

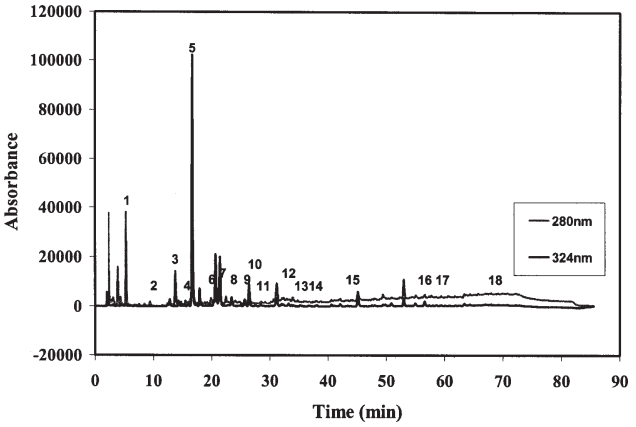

Fig. 7.Characteristic HPLC traces of the red wine analyzed illustring the constituents:1-gallic acid; 2-protocatechic acid; 3-*para*-hydroxybenzoic acid; 4-catechin; 5-gentisic acid; 6-vanillic acid; 7-siringic acid; 8-caffeic acid; 9-clorogenic acid; 10-epicatechin; 11-*meta*-hydroxybenzoic acid; 12-*para*-coumaric acid; 13-salicylic acid; 14-ferulic acid; 15-sinapic acid; 16-*trans*-resveratrol; 17-rutin trihydrate; 18-quercitin

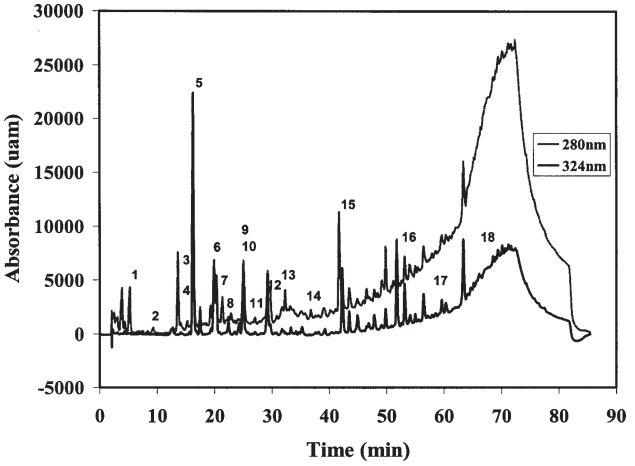

Fig. 8. The chromatogram of polyphenols adsorbed onto MCM-41: 1-gallic acid; 2-protocatechic acid; 3-*para*-hydroxybenzoic acid; 4-catechin; 5-gentisic acid; 6-vanillic acid; 7-siringic acid; 8-caffeic acid; 9-clorogenic acid; 10-epicatechin; 11-*meta*-hydroxybenzoic acid; 12-*para*-coumaric acid; 13-salicylic acid; 14-ferulic acid; 15-sinapic acid; 16-*trans*-resveratrol; 17-rutin trihydrate; 18-quercitin

Table 4
EVALUATION OF CHROMATIC CHARACTERISTICS OF RED WINE AFTER TREATMENT WITH MCM-41 AND ACTIVATED CARBON

	Clarity L 0- 100	Colourimetric coordinates		Tint	Δ E	Δ H
		a	b			
wine	21	51.48	34.05	0.68	-	-
1.013 g/L A.c.	30.6	53.64	30.82	0.75	22.8353	13.57831
0.518 g/L MCM-41	21	51.02	33.3	0.67	16.5334	3.932493
1.035 g/L MCM-41	20	50.46	32.48	0.67	15.1871	2.484452
1.5112 g/L MCM-41	20	50.4	32.43	0.67	15.1195	2.618225
2.1744 g/L MCM-41	20	50.81	32.94	0.68	15.7023	1.459315
2.513 g/L MCM-41	20	50.81	32.94	0.68	15.7023	1.459315
3.0602 g/L MCM-41	20	51.035	33.27	0.67	16.0602	0.213307
4.249 g/L MCM-41	21	51.36	33.8	0.68	17.0641	3.441003

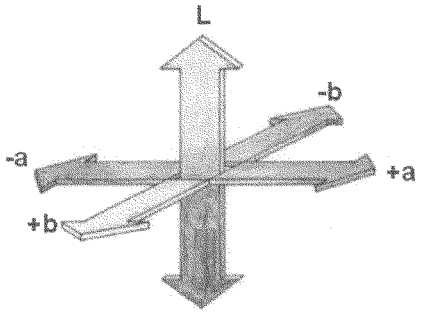

Fig. 9. Diagram of colourimetric coordinates according to *Commission Internationale de l'Eclairage* (CIE, 1976) [41].

Identification of the phenolic compounds from wine adsorbed on MCM-41 was carried out using HPLC method [38- 40]. In this case, 500 mL of red wine were mixed with 4.0273 g of MCM-41 for 30 min and kept for 24 h at a temperature of 5°C. The solid adsorbent was filtered, dried at the room temperature and then was treated with 50 mL of methanol; the methanolic extract was used for the qualitative analysis of phenolic removed compounds. The chromatograms of the native red wine and of methanolic extract of phenols removed from SBA-15 are shows in figures 7 and 8.

In the wine chromatogram it was observed that the characteristic pick for many phenolic compounds are very low: clorogenic acid, epicatechin, sinapic acid, *trans*-resveratrol para-hydroxybenzoic acid, vanillic acid, while in the chromatogram of extract these peaks are much better represented. This demonstrates that using the mesoporous silica MCM-41 it is possible to concentrate some phenolic compounds from wine. This material retains a large amount of gentisic acid and other unidentified compounds.

Evaluation of chromatic characteristics of wine

Evaluation of chromatic characteristics of wine was made with the method CIELab76 [41]. This CIELab76 colour or space system is based on a sequential or continuous Cartesian representation of 3 orthogonal axes: *L, a* and *b* (fig.). L is clarity, *a* is component of green / red colour and *b* is component of blue / yellow colour.

The chromatic characteristics were calculated by equations:

$$L=116(Y/Yn)^{1/3}-16 \quad (2)$$
$$b=200-[(Y/Yn)^{1/3}-(Z/Zn)^{1/3} \quad (3)$$
$$a=500[(X/Xn)-(Y/Yn)] \quad (4)$$
$$C=(a^2+b^2)^{1/2} \quad (5)$$
$$H=tg^{-1}(b/a) \quad (6)$$
$$\Delta H=[(\Delta E)^2-(\Delta L)^2-(\Delta C)^2]^{1/2} \quad (7)$$
$$\Delta E=[(\ddot{A}\Delta L)^2+(\Delta a)^2+(\Delta b)^2]^{1/2} \quad (8)$$
$$\Delta E=[(\Delta L)^2+(\Delta C)^2+(\Delta H)^2]^{1/2} \quad (9)$$

The results of chromatic analysis are summarized in Table 4.

As it is indicated in table 4 the mesoporous MCM-41 material does not change the color of red wine. The clarity L values of wine sample treated with increasing amounts MCM-41 remain almost equal to that of initial wine. The clarity L value of red wine treated with activated carbon is modified .

Conclusions

The mesoporous silica MCM-41 molecular sieve showed ability in light decreasing of the total polyphenol content in red wine without a modification of chromatic characteristics.

The treatment of red wine had a positive effect on the several of the most important compounds such as hydroxybenzoic and hydroxycinnamic acids, anthocyanins, flavonols, flavan-3-ol, tannins and proteins. The use of mesoporous silica MCM-41 molecular sieve as specific adsorbent for the anti-oxidants compounds from red wine can be a possibility to get some pharmaceutical drugs.

Further studies are necessary in order to evaluate effect the of the mesoporous silica on the aroma, flavor, bitterness and astringency of red wine.

References

1.COTEA, V.D, ZANOAGA, C.V, COTEA, V.V, "Tratat de oenochimie", vol I şi II, Ed. Academiei Române, Bucureşti, 2009

2.SIMS, C., MORRIS, J., Am. J. Enol. Vitic., **35**, 1984, p.35

3.METCHE, M., Bull. Liason Groupe Polyphenols, **13**, 1986, p.292-298

4.SINGLETON, V., Am. J. Enol. Vitic., **38**, 1987, p.69-77

5.CHEYNIER, V., RIGAUD, J., SOUQUET, J.M., DUPRAT, F., MOUTOUNET, M., Am. J. Enol. Vitic., **41**, 1990, p.346

6. FABIOS, M., LOPEZ-TOLEDANO, A., MAYE, N.M., MERIDA, J. , MEDINA, M., J. Agric. Food Chem., **48** (3), 2000, p.2155

7. CASTRO, R., BARROSO, C.G., Vitis, **40**(1), 2001, p. 39

8. CORCHO-CORRAL, B., OLIVARES-MARIN, M., VALDES-SANCHEZ, E., FERNANDEZ-GONZALES, C., MARCIAS-GARCIA, A., GOMEZ-SERRANO, V., J. Agric. Food Chem., **53** (3), 2005, p.644

9. DABROWSKI, A., PODKOSCIELNY P., HUBICKI, Z., BARCZAK, M., Chemosphere, **58**, 2005, p.1049

10. DI STEFANO, R., CRAVERO, M.C., GENTILINI, N., L'Enotecnico, **5**, 1989, p.83

11. SANBORN, M., EDWARDS, Ch.G., ROSS, C.F., Am. J. Enol. Vitic., **61**(1), 2010, p.31

12. CESARIN, E.R., PIFFERI, P.G., Metodo di trattamento di liquidi alimentari di origine vegetale per stabilizzare gli stessi particolarmente nel loro colore. Italian Patent no. 3224, 1986

13. SPAGNA, G., PIFFERI, P.G., RANGONI, C., MATTIVI, F., NICOLINI, G., PALMONARI, R., Food Research International, **29**(3-4), 1996, p.241

14. OH, C.-G., AHN, J.-H, IHM, S.-K., Reactive Funct. Polym., **57**, 2003, p.103

15. SIMS, C.A., EASTRIDGE, J.S., BATES, R.P., Am. J. Enol. Vitic., **46**(2), 1995, p.155

16. PUIG-DEU, M., LOPEZ-TAMAMES, E., BUXADERAS, S., TORRE-BORONAT, M.C., Food Chemistry, **66** (1), 1999, p.35

17. GIACOMINI, P., Vini d'Italia, **4**, 1987, p.41

18. MANFREDINI, M., Vignevini, **4**, 1989, p.43

19. ACHAERANDIO, I., PACHOVA, V., GUELL, C., LOPEZ, F., Am. J. Enol. Vitic., **52**(2), 2001, p.122

20. RAZMKHAB, S., LOPEZ-TOLEDANO, A., ORTEGA, J.M., MAYEN, M., MERIDA, J., MEDINA, M., J. Agric. Food Chem., **50**, 2002, p.7432

21. LOPEZ-TOLEDANO, A., MAYEN, M., MERIDA, J. and MEDINA, M., Food Chem., **97**(3), 2005, p.498

22. CHASSAGNE, D., GUILLOUX-BENATIER, M., ALEXANDER, H., VOLLEY, A., Food Chem., **91**(1), 2005, p.39

23. SALAZAR, F.N., de BRUIJN, J.P.F., SEMINARIO, L., GUELL, C., LOPEZ, F., J. Food Eng., 79, 2007, p.1329

24. *** OIV - Bentonites. Resolution OENO II/2003. Office International de la Vigne et du vin, 2003

25. EISENHOUR, D.D., BROWN, R.K., Elements, **5** (2), 2009, p.83

26. LAMBRI, M., DORDONI, R., SILVA, A., MARCO De FAVERI, D., Am. J. Enol. Vitic., **61**(2), 2010, p. 225

27. CIAMBELLI, P., Di MATTEO, M., NOTA, G., ROMANO, R., SPAGNA MUSSO, S., Industrie delle Bevande, **154**, 1998, p.120

28. MERCURIO, M., MERCURIO, V., De'GENNARO, B., De'GENNARO, M., GRIFA, C., LANGELLA, A., MORRA, V., Per. Mineral., **79**(1), 2010, p. 95

29. BECK, J. S., VARTULI, J. C., ROTH, W. J., LEONOWICZ, M. E., KRESGE, C. T., SCHMITT, K. D., CHU, C. T. W., OLSON, D. H., SHEPPARD, E. W., McCULLEN S. B., HIGGIENS, J. B., SCHLENKER, J. L., *J. Am. Chem. Soc*., **114**(27), (1992), p.10834

30. HO, K.Y., McKAY, G., YOUNG, K.L., Langmuir, **19**(7), (2003), p.3019-

31. KRESGE, C.T., LEONOWICZ, M.E., ROTH, W.J., VARTULI, J.C., BECK, J.S., *Nature*, **359**, (1992), p.710-

32. BARRETT, E.P., JOYNER, L.G., HALENDA, P.P, J. Am. Chem. Soc., **73**, 1951, p. 373

33. ROUQUEROL, F., ROUQUEROL, J., SING, K., "Adsorption by powders and porous solids", Academic Press: San Diego, USA, 1999

34. COUSTEL, N., RENZO, F.D., FAJULA, F., J. Chem. Soc., Chem. Commun., 1994, p.967

35. SELVARAJ, M., PANDURANGAN, A., SEMSHADRI, K.S., SINHA, P.K., LAL, K.B., Appl. Catal., A: General, **242**, 2003, p.347

36. ZHAO, X.S., LU, G.Q., WHITTAKER A.K., MILLAR, G.J., ZHU, H.Y., J. Phys. Chem. B, **101**, 1997, p. 6525

37. *** OIV, Recueil des methodes internationales d'analyse des vins et des mouts. Office International de la Vigne et du Vin, Editura O.I.V., Edition Officielle, Paris, 2006

38. CASTELLARI, M., SARTINI, E., FABIANI, A., ARFELLI, G., AMATI, A.,J. Chromatography, A, **973**, 2002, p. 221

39. DIACU, E., ENE, C.P., Rev. Chim., **61**(12), 2010, p.1177

40. POP, M., LUPEA, A X., GLEVITZSK,Y.M., ARDELEAN A., Rev. Chim.(Bucharest), **59**, no. 8, 2008, p.829

41.*** Commission Internationale de l'Eclairage (CIE). Colorimetry (2nd ed.). Publication of the CIE: Vol. 15.2. Vienna: CIE, 1986

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