REDUCTION OF PHENOLIC COMPOUNDS LEVEL FROM RED WINE, FOLLOWING TREATMENT WITH MICRO- AND MESOPOROUS MATERIALS

REDUCEREA CONȚINUTULUI DE COMPUŞI FENOLICI DIN VINUL ROŞU LA TRATAREA CU MATERIALE MICRO- ŞI MEZOPOROASE

LUCHIAN Camelia[1], *COTEA V.V.*[1], *PATRAŞ Antoanela*[1], *NICULAUA M.*[2], *SEFTEL Elena*[3]
e-mail: kamelia_luchian@yahoo.com

Abstract. *Phenols represent a large and complex group of compounds, with great importance, determining the characteristics and quality of red wines in particular. In this paper we tested the action of micro- and mesoporous materials on the concentration of phenolic compounds in red wines. We performed such experiments, which have demonstrated that micro- and mesoporous materials retain phenolic compounds from wine. Taking into account the maximum rate of retained phenolic compounds on the three studied materials, SBA-15, MCM-41, KIT-6, the results show that all three retain phenolic compounds from wine, the material with the maximum efficiency being SBA-15, with a rate of 19.15% retained phenolic compounds for 8.04 g adsorbent/ L wine.*
Key words: wine, phenolic compounds, nanomaterials, adsorption

Rezumat. *Fenolii sunt un grup mare şi complex de compuşi de importanță deosebită care determină caracteristicile şi calitatea îndeosebi a vinurilor roşii. În această lucrare s-a testat acțiunea unor materiale microporoase şi mezoporoase asupra concentrației compuşilor fenolici din vinurile roşii. Am realizat astfel experimente care au demonstrat că materialele micro şi mezoporoase, datorită structurii lor, rețin compuşii fenolici din vin. Ținând cont de procentul maxim de compuşi fenolici reținut pe cele trei materiale studiate, SBA-15, MCM-41, KIT-6, rezultatele obținute dovedesc că toate trei rețin compuşii fenolici din vin, eficiență maximă având materialul SBA-15, cu un procent de 19.15 % compuşi fenolici reținuți, pentru 8.04 g adsorbent/L vin.*
Cuvinte cheie: vin, compuşi fenolici, nanomateriale, adsorbție

INTRODUCTION

Wine collect in its composition more than 1000 compounds, associated in a complex and inconstant way, some come from grapes, in an unchanged state, such as acids: tartaric, malic, citric; carbohydrates, minerals etc. Others are formed during alcoholic fermentation and in other fermentative processes such as alcohols, lactic and succinic acids, etc.; other part is formed by nonfermentative processes (Cotea et. al., 2009).

[1]University of Agricultural Sciences and Veterinary Medicine of Iasi, Romania
[2] Oenology Research Center – Iasi Branch of the Romanian Academy, Romania
[3] University of Antwerpen, Laboratory of Adsorption and Catalysis, Belgium

Changing the color, the flavor and the taste of wine are the main oenological problems facing the wine producers during its storage. The change of wine color is the result of phenolic compounds oxidation to quinones (catalyzed by Fe^{2+} / Fe^{3+}, Cu^{2+} and oxidative enzymes), and of condensation reactions between phenolic compounds, with formation of stable colored polymeric structures, from the yellow-brown spectral region (Fabios et. al., 2000;. Castro et al., 2001). Phenolic compounds, including phenolic acids (hydroxybenzoic acids and hydroxycinnamic acids), catechins, anthocyanins, procyanidins and flavonols are subject to oxidation processes (Margheri et. al., 1980).

Reducing the concentration of phenolic compounds in wine with adsorbent materials is a frequently used method in winemaking to control color and organoleptic changes (Spagna et. al., 1996; Spagna et. al., 2000).

In 1992, researchers at Mobil Corporation published the siliceous and aluminosiliceous mesoporous molecular sieves synthesis (ordered mesoporous materials) of M41S family (Beck et. al., 1992). Siliceous material MCM-41 is part of the M41S family, together with MCM-48 and MCM-50.

M41S mesoporous materials have pores with diameters between 2.0 nm and 10 nm; specific sizes of mesopores are from 2.0 to 50 nm (meso from Greek means between) (IUPAC, 1972).

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 (Corma et. al., 1995).

SBA-15 mesoporous silica is a material obtained by using the structure directing agent, Pluronic P123, tribloc copolymer. Structurally, SBA-15 has a 2-D arrangement of tubular channels (Zhao et. al., 1998).

Opposed to MCM-41, SBA-15 can be prepared with mesopores up to 30 nm and is more thermally stable due to higher thickness of the cylindrical pores walls (2-3 nm compared to 0.9-1.1 nm) (Zhao et. al., 1998).

In literature it was reported 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 unique 3-D structures (Xiaoying et. al., 2002).

MATERIAL AND METHOD

1. SBA-15 synthesis

Materials: Tetraethylortosilicate (TEOS) 98% Merck as silica source, amphiphilic nonionic triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, molecular weight 5800) (Aldrich) as structure directing agent (SDA), hydrochloric acid (solution 37%, Merck) and deionized water were used as received in the synthesis of silica SBA-15. The molar ratio of the components was as follows: 1SiO_2: 0.017 P123: 5.87 HCl: 194 H_2O (Zhao et al., 1998). The synthesis was performed using ultrasounds to shorten the reaction time.

2. MCM-41 synthesis

Materials: 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. The molar ratio of the components was as follows: $1SiO_2$: $0.2C_{16}TMAB$: $5.7NH_3$: 113 H_2O (Corma et. al., 1995).

3. KIT-6 synthesis

Materials: P123 ($EO_{20}PO_{70}EO_{20}$, molecular weight 5800) (Aldrich), n-butanol (0,8 g/cm^3, Merck), (TEOS, solution 98% Merck) as silica source, hydrochloric acid (solution 37%, Merck) and deionized water were used as received.

Silica KIT-6 was synthesized using Pluronic P123 and n-butanol, a mixture as structure directing agent (Xiaoying et. al., 2002). The molar ratio of the components was as follows: 0.017 P123: 1.3 TEOS: 1.31 BuOH: 1.83 HCl: 195 H_2O

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.

4. Characterization of synthesized materials:

N_2 sorption. The textural properties were determined with a NOVA 2200 Quanta Chrome Inc.) sorption apparatus. The sample was degassed at 300^{0}C for 3 hours before the measurement was taken. The BET surface area was calculated based on the adsorption data in the relative partial pressure range of 0.05-0.25. Pore size distribution was determined based on the Barret-Joyner-Halenda (BJH) adsorption curve.

5. Total index of phenols from wine was determined spectrophotometrically using a Spectrophotometer Analytik Jena S 200 at 280 nm (D280 – OIV method).

6. Adsorption of phenolic compounds on nanoporous materials

Adsorption experiments were conducted at 5^{0}C for 24 hours adding increased amounts of SBA-15 powder into 50 mL wine. After filtration, the total content of phenols in the liquid phase was determined spectrophotometrically, at 280 nm using the OIV method.

RESULTS AND DISCUSSIONS

1. Physical adsorption, BET

Fig. 1, 2, 3 exhibits the N_2 adsorption – desorption isotherm at -196^{0}C for calcined materials: silica-SBA-15, KIT-6 and MCM-41. Typical isotherm is of Type IV with a hysteresis loop Type H1, a characteristic of mesoporous solids, according to the IUPAC classification. The structural parameters of calcined mesoporous materials are summarized in tab. 1.

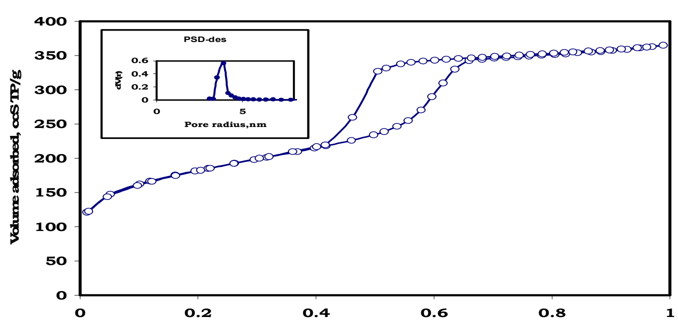

Fig. 1 - The N_2 adsorption – desorption isotherm at -196^{0}C of silica-SBA-15.
Inset: the pore size distribution (PSD)

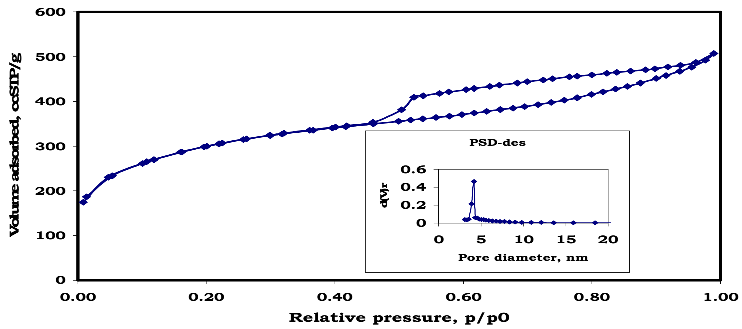

Fig. 2 - The N_2 adsorption – desorption isotherm at -196^{0}C of KIT-6.
Inset: the pore size distribution (PSD)

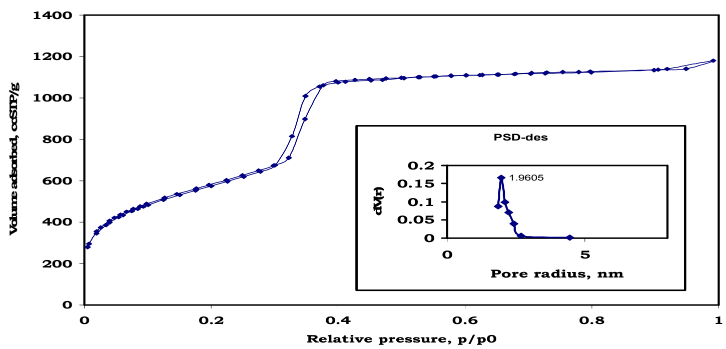

Fig. 3 -- The N_2 adsorption – desorption isotherm at -196^{0}C of MCM-41.
Inset: the pore size distribution (PSD)

Table 1

Structural parameters of the synthesized nanomaterials derived from nitrogen adsorption

Adsorbent	S_{BET} (m^2/g)	D_{BJH} (nm)	Total pore volume (cm^3/g)
SBA-15	508.6	7.6	0.565
KIT-6	644,5	4,17	0.761
MCM-41	2098	3,12	0,691

2. Adsorption of phenolic compounds on nanoporous materials

The total polyphenols content of the red wine was determined by measuring the absorbance at λ=280 nm (A_{280}) 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:

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

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 index total polyphenol content for red wine was found as being 1591.13mg/L (A_{280} = 54.025). The results of the adsorption experiments are summarized in tab. 2.

Table 2

Variation of total phenols content in red wine with the adsorbent dose

specification	Amount of adsorbent (g/L)	Absorbance (λ=280 nm)	Residual concentration of polyphenols in wine (mg/L)	Polyphenols removed (%)
wine	0	54.025	1591.13	0.00
SBA-15	0.5256	51.050	1503.67	5.51
	1.0216	49.785	1466.47	7.85
	1.5104	49.570	1460.15	8.25
	2.0510	48.950	1441.93	9.39
	2.5082	47.645	1403.56	11.81
	3.0994	47.050	1386.07	12.91
	4.0204	46.520	1370.48	13.89
	5.0200	45.875	1351.52	15.09
	6.1344	44.690	1316.68	17.28
	6.9974	44.370	1307.27	17.87
	8.0404	43.680	1286.99	19.15
MCM-41	0.518	50.66	1492.23	5.27
	1.035	50.65	1491.11	5.28
	1.5112	50.24	1479.25	6.06
	2.1744	49.12	1446.15	8.15
	2.513	48.69	1434.18	8.95
	3.0602	48.58	1431.26	9.15
	4.249	48.53	1429.46	9.25
KIT-6	0.606	33.02	973.21	2.6
	1.098	32.93	970.43	2,92
	2.138	31.53	929.31	7
	3.026	31.05	915.22	8.4
	4.1298	30.87	910.23	8.9
Activ carbon	0.2808	47.180	1389.89	12.67
	0.6594	43.940	1294.63	18.67
	1.0130	40.110	1182.03	25.76

CONCLUSIONS

1. Mesoporous materials synthesized and used during the experiments (SBA-15, MCM-41, KIT-6) have been characterized and are in agreement with literature reports.

2. For the synthesis of SBA-15 and KIT-6 materials, has been used an innovative method for synthesis, using ultrasounds.

3. SBA-15, MCM-41, KIT-6 were used for the first time in wine treatment.

4. Taking into account the maximum percentage of phenolic compounds retained on the three studied materials: SBA-15, MCM-41, KIT-6, the results demonstrate that all three retain phenolic compounds from wine, with maximum

efficiency for SBA-15 material with 19.15% retained phenolic compounds, for 8.0404 g adsorbent / L wine.

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