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Phenolic stabilization of wines using mesoporous silica SBA-15 molecular sieve

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Browning of wines is often the result of an auto-oxidation process due to presence of oxygen (the initiator of the process), polyphenols (the oxidable matter) and of certain metal ions (e. g. iron, copper, as activators of the process). The reduction of phenolic compounds by means of an adsorbent is the most frequently used method to avoid this defect. In this study, we investigate the possibilities of reducing phenolic compounds of red wine with the help of mesoporous silica molecular sieve (SBA-15) in comparison with the conventionally used activated carbon. Mesoporous silica SBA-15 is favorable for the adsorption of large molecules because of its large pore size (3 to 30 nm) and high specific surface area (500 to 1000 m^2/g). The initial total polyphenol index (index D_{280}) of the experimental wine was decreased from 1591,13 mg/l to 1286,99 mg/l after treatment with mesoporous SBA-15 molecular sieve (up to 8 g/l). HPLC analysis of the material adsorbed to the molecular sieve exhibited a strong retention of quercitin, cis- as well as trans-resveratrol and a weak retention of gentisic acid, gallic acid and catechin. The adsorption of polyphenols on activated carbon was higher than that on the mesoporous silica but it was not specific for some polyphenols.
Keywords: wine, mesoporous silica, molecular sieve, phenolic compounds, adsorption

Phenolstabilisierung von Weinen unter Verwendung eines mesoporösen Silica-Molekularsiebs (SBA-15).
Die Bräunung von Weinen ist ein Ergebnis der Auto-Oxidation auf Grund des Vorhandenseins von Sauerstoff (dem Initiator des Prozesses), Polyphenolen (den oxidierbaren Substanzen) und bestimmten Metallionen (z. B. Eisen und Kupfer als Aktivatoren des Prozesses). Die Reduktion von phenolischen Verbindungen mit Hilfe eines Adsorbens ist die am häufigsten angewandte Methode zur Vermeidung dieses Fehlers. In vorliegender Studie untersuchten wir die Möglichkeit, den Phenolgehalt von Rotwein mit einem mesoporösen, auf Silicium basierendem Molekularsieb (SBA-15) zu reduzieren. Für Vergleichszwecke wurde Aktivkohle verwendet. Das mesoporöse Molekularsieb SBA-15 ist für die Adsorption großer Moleküle auf Grund seiner großen Porengröße (3 bis 30 nm) und seiner hohen spezifischen Oberfläche (500 bis 1000 m^2/g) gut geeignet. Nach Behandlung eines Rotweines mit dem Molekularsieb SBA-15 nahm der gesamte Polyphenol-Index (Index-D_{280}) von 1591,13mg/l auf 1286 mg/l ab (bei einer Dosierung von 8 g/l). Die HPLC-Analyse der auf dem Molekularsieb adsorbierten Substanzen zeigte eine starke Retention von Quercitin, cis- und trans-Resveratrol und eine schwache Retention von Gentisinsäure, Gallussäure und Catechin. Auf Aktivkohle war die Adsorption von Polyphenolen zwar höher als auf dem Silica-Molekularsieb, aber es gab keine spezifische Bevorzugung einzelner Polyphenole.
Schlagwörter: Wein, mesoporöses Silicium, lekularsieb, Polyphenole, Adsorption

La stabilisation des vins au phénol à l'aide d'un tamis moléculaire mésoporeux au silicium (SBA-15). *Le brunissement des vins est un résultat de l'auto-oxydation due à la présence d'oxygène (l'initiateur du processus), de polyphénols (substances oxydables) et de certains ions métalliques (p. ex. fer et cuivre en tant qu'activateurs du processus). La réduction de composés phénoliques à l'aide d'un adsorbant est la méthode la plus fréquemment utilisée pour éviter cette altération. Dans la présente étude, nous avons examiné la possiblité de réduire la teneur du vin rouge en phénols à l'aide d'un tamis moléculaire mésoporeux à base de silicium (SBA-15). À des fins de comparaison, nous avons utilisé du charbon actif. Grâce à la grande taille de ses pores (de 3 à 30 nm) et à sa surface spécifique élevée, le tamis moléculaire mésoporeux SBA-15 convient bien à l'adsorption de grands molécules. Après le traitement d'un vin rouge au tamis moléculaire SBA-15, l'indice polyphénolique total (indice-D_{280}) a baissé de 1591mg/l à 1286mg/l (pour un dosage de 8 g/l). L'analyse par HPLC des substances adsorbées sur le tamis moléculaire a montré une forte rétention de quercétine, de resvératrol cis et trans, et une faible rétention d'acide gentisique, d'acide gallique et de catéchine. Il est vrai que l'adsorption des polyphénols était plus élevée sur le charbon actif que sur le tamis moléculaire au silicium, mais il n'y avait aucune préférence spécifique de polyphénols individuels.*
Mots clés : vin, silicium mésoporeux, tamis moléculaire, polyphénols, adsorption

Browning and lack of color, aroma and taste constitute the main enological problems during storage of wine. Browning of wines is often a result of oxidation of phenols 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 (Sims and Morris, 1984; Metche, 1986; Singleton, 1987; Cheynier et al., 1990; Fabios at al., 2000; Castro and Barroso, 2001; Clark and Scollary, 2002 and 2003). Phenols are responsible for astringency (tannins, flavanoids), color, structure, mouthfeel and bitterness of wines (Fischer and Noble, 1994). The phenolic compounds including phenolic acids (hydroxybenzoic acids and hydroxycinnamic acids), catechins, anthocyanins, procyanidins and flavonols are subject of oxidation (Margheri et al., 1980).

The reduction of various phenolic compounds may be achieved by specific adsorbents: activated carbon (Corcho-Corral et al., 2005; Dabrowski et al., 2005; Sanborn et al., 2010), polymeric adsorbents of biological origin – chitin and chitosan (Cesarin and Pifferi, 1986; Spagna et al., 1996 and 2000), synthetic polymeric adsorbents – hypercrosslinked polystyren like Amberlite XAD-2, Amberlite XAD-4, Ambersorb XE340 (Oh et al., 2003), polyvinylpolypyrrolidone, PVPP (Sims et al., 1995), modified natural polymers – microcrystalline cellulose (Puig-Deu et al., 1999), protein adsorbents – albumin, gelatin, fish-glue (isinglass), potassium caseinate, wheat gluten (Gicomini, 1987; Manfredini, 1989a and b; Sims et al., 1995; Puig-Deu et al., 1999; Sanborn et al., 2010), yeast as adsorbents (Razmkhab et al., 2002; Lopez-Toledano et al., 2006; Chassagne et al., 2005), zirconia (Salazar et al., 2007), and siliceous adsorbents – bentonite (Acherandio et al., 2001; Oiv, 2003; Eisenhour and Brown, 2009; Lambri et al., 2010) and zeolites (Ciambelli et al., 1998; Mercurio et al., 2010).

The high adsorption capacities of activated carbons are usually related to their big surface area, pore volume and high porosity. Bentonite is the most used adsorbent in the wine industry (as far back as 1930), more especially to remove proteins that are a main source of haze in wines. However, also other molecules, like volatile compounds, higher alcohols, polyphenols and flavorings are slightly removed.

The major characteristic required for a material to be used as adsorbens is its nanoporosity. Nanoporous materials have the following features:

- high adsorption capacity due to their high specific surface area (m^2/g), pore volume (cm^3/g), the nanopore size distribution and the very ordered structure
- high selectivity, due to their narrow pore size distribution and to the specific interaction with pore walls
- favorable adsorption kinetics resulting from the regular pore structure, dimensionality and pore size dimensions
- stability and durability in use, assuring the reversibility of adsorption and desorption process
- good mechanical properties to abrasion and copression

If the pore widths are between 2 and 50 nm, the pores are called mesopores (Everett, 1972).

Silica mesoporous molecular sieve is the most versatile material and with the largest number of possible struc-

tures (Ozin et al., 2009). The ordered mesoporous silicates, designed as M41S-family, were discovered in 1992 by the Mobil Corporation, by using supramolecular aggregates of surfactant molecules (Beck et al.,1992; Kresge et al., 1992). From this family, the most studied member is MCM-41 which possesses a large specific surface area (1000 to 1200 m^2/g), a hexagonal array and uniform mesopore channels ranging from 2 to 10 nm in diameter.
In 1998 a new mesoporous silica molecular sieve with uniform hexagonal channels ranging from 3.5 to 30 nm in diameter, designed SBA-15, was first synthesized by the research group lead by the Stucky Group at University of California-Santa Barbara (Zhao et al., 1998), by using the amphiphilic triblock copolymer Pluronic P123 as template. SBA-15 is an ordered amorphous silica mesoporous material with microporous walls (Ryoo et al., 2000; Imperor-Clerk et al., 2000; Flodstrom et al., 2004) (Fig. 1).

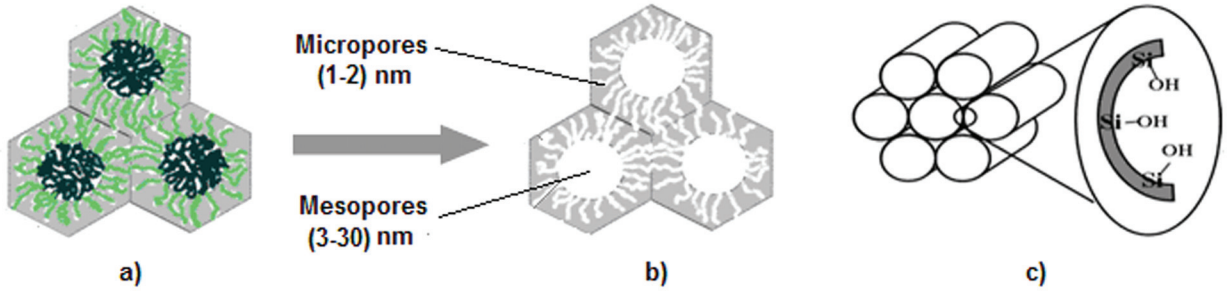

Fig. 1: The structural geometry of mesoporous-microporous silica SBA-15 as synthesized (a) and calcined (b) (You, 2007) and the internal silanol groups (c)

In SBA-15 structure, mesopores are formed by parallel long cylindrical channels packed one close to the other in a hexagonal pattern connected by micropores in the walls.
On the internal surface of pore walls the amorphous silica is terminating in silanol (Si-OH) groups and siloxane (Si-O-Si) bridge groups (Fig. 1c). The distribution of silanol groups is not homogeneous and the number is related to different condensation degrees during synthesis and calcination (Shenderovich et al., 2003; Zhao et al., 2004; Meynen et al., 2009).
The mesoporous silica SBA-15 has a silanol density of about 4.0 mmol/g and the distribution is estimated in a range of 2.5 to 3.7 SiOH per nm^2 (Shenderovich et al., 2003; Zhao et al., 2004). The presence of these free hydroxyl groups has an influence on the adsorption properties and the hydrophilic character of the surface. The isoelectric point of silica SBA-15 (pH_{iep}) is in the pH range between 1 to 3, and it is close to point of zero charge (pH_{PZC}). The surface is negatively charged at pH > pH_{PZC}.
It can be assumed, that mesoporous molecular sieves SBA-15 are ideal for size and shape exclusion separation of polyphenols, proteins and other biological molecules from wines due to their high surface area (500 to 1000 m^2/g) and tuneable uniform pore size of 3 to 30 nm.
Silica SBA-15 is a biocompatible material; the pore structure is stable at high temperatures (over 1000 °C) and silica walls are inert to both acid and basic media, with exception of hydrofluoric acid and concentrated basic solutions. The structure is resistant to abrasion and compression.
In this research, SBA-15 mesoporous silica synthesized from tetraethylortosilicate in presence of Pluronic P125 as template in hydrochloric acid media, was used as a new adsorbent for wine stabilization.

Materials and method

Chemicals

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 in the synthesis of silica SBA-15.
A red wine of the variety 'Cabernet Sauvignon', vintage 2009 from the Cozmesti area (Romania) was selected as a typical wine for the experiments.

Activated carbon carbon (Charcoal, activated, 50 to 200 Mesh, Fisher Chemicals) was used in the adsorption process for comparison purpose.

Synthesis of mesoporous silica SBA-15

The mesoporous silica SBA-15 was prepared using the nonionic triblock copolymer Pluronic P123 as template following the procedures of literature (Zhao et al., 1998) with some modifications. The molar ratio of the components was as follows:

SiO2:P123:HCl:H2O = 1: 0.017:5.87:194

The formation of the mesostructure is based on the hydrogen bonding $(S^0H^+)(X^-I^+)$ templating route using following abbreviations: S^0 = nonionic block copolymer, I^+ = inorganic silica; H^+X^- = acidic conditioner (HCl).

The process to obtain solid powder SBA-15 involves dissolving of P123 (4 g) in acidic solution (HCl, 2 M, 150 ml) under stirring to form unidirectional, cylindrical micelles in hexagonal arrays, adding drop-wise TEOS – as silica source (9.6 ml) which polymerizes around the organic micelles forming the pore walls. The mixed solution was aged at 45 °C for 8 hours and finally the sol-gel suspension was heated up to 80 °C for 5 hours in a conventional oven. The white solid was filtered off, washed several times with deionized water, dried at room temperature and finally calcined at 550 °C for 6 hours (heating rate of 1 °C/min) in air in a programmable furnace.

Characterization of mesoporous silica SBA-15

X-ray diffraction

The small-angle XRPD pattern was collected by 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 5^0 at room temperature.

N_2-sorption

The textural properties were determined with a NOVA 2200 (Quantachrome Inc., Florida, USA) sorption apparatus. The sample was degassed at 300 °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 to 0.25. Pore size distribution was determined based on the Barret-Joyner-Halenda (BJH) adsorption curve.

Scanning Electron Microscopy (SEM) and elemental analysis of sample (EDX)

SEM and EDX were carried out on a SEM VEGA II LSH TESCAN with EDX detector tip QX2 (Bruker/Roentex).

Total index of phenols

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

Wine phenolic compounds analysis

The wine phenolic compounds analyses were carried out with high-performance liquid chromatograph (HPLC) Shimadzu equipped with two chromatographic columns Merck Chromolith Performance RP-18 (Castellari et al., 2002).

Adsorption of phenolic compounds on SBA-15

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

Results and discussion

X-ray Powder Diffraction Analysis (XRPD)

Figure 2 shows the small-angle XRPD pattern of the calcined silica SBA-15. The diffractogram presents three well-resolved peaks in the lower 2θ angle range of 0.5 to 2°, that can be indexed as (100), (110) and

(200) crystal planes with the corresponding d spacing of 9.00, 5.19 and 4.55 nm, respectively. These peaks are characteristic of a 2-D hexagonally ordered structure with p6mm symmetry. The very strong peak corresponding to d_{100} spacing is characteristic to samples that possess periodic structure.

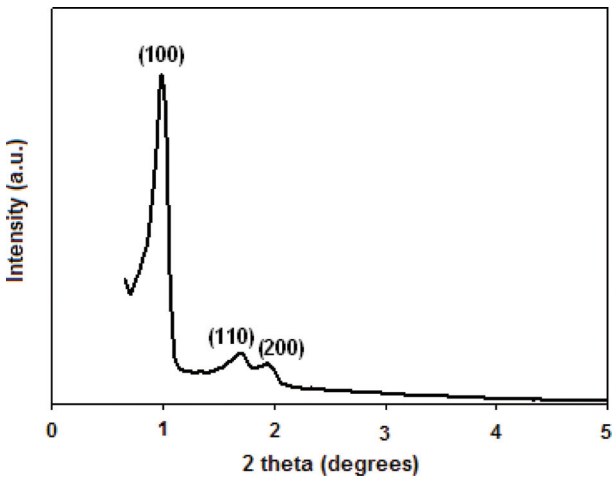

Fig. 2: Small-angle XRPD pattern of Si-SBA-15

The first intense peak having a d_{100} of 9.00 nm, calculated with Bragg law, is used to obtain the cell parameter a_o of 10.4 nm ($a = 2d_{100}/\sqrt{3}$). The thickness of the mesopore wall (t) is calculated by the difference between a_o-parameter value and the mesopore diameter D_{BJH} ($t = a_o - D$), 3.78 nm, respectively.

Physical adsorption, BET

Figure 3 exhibits the N_2 adsorption-desorption isotherm at -196 °C for calcined silica SBA-15. Typical silica SBA-15 isotherm is of Type IV with a hysteresis loop Type H1, a characteristic of mesoporous solids, according to the IUPAC classification (Kruk et al., 2000; Kruk and Jaroniec, 2001).

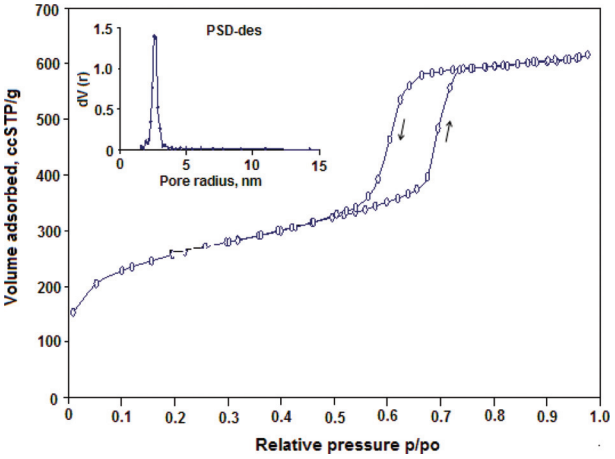

Fig. 3: The N_2 adsorption-desorption isotherm at -196 °C of silica SBA-15.
Inset: the pore size distribution (PSD)

The adsorption and desorption branches of the isotherm present a sharp inflection at $p/p_0 = 0.55 – 0.75$, which means a typical capillary condensation within mesopores of two-dimensional hexagonal structure (Kruk et al., 2000; Kruk and Jaroniec, 2001).
The specific surface area was calculated by using the multiple point BET method and BET equation in the relative pressure range of $p/p_0 = 0.05 – 0.25$. The pore size distribution curve (Fig. 3) was computed based on the BJH model and the pore size estimated from the peak position in the BJH curve. The total pore volume was obtained from the volume of N_2 adsorbed at a relative pressure $p/p_0 = 0.955$. The structural parameters of calcined mesoporous silica SBA-15 are summarized in Table 1.

SEM and EDX patterns

The particle morphology of the calcined silica SBA-15 sample shows that the small particles have a sand-like form, due to the fast hydrolysis rate of TEOS in presence of concentrated hydrochloric acid. The EDX

Table 1: Structural parameters derived from XRPD data and nitrogen physisorption

Sample	d_{100} spacing (nm)	a_0 (nm)	S_{BET} (m^2/g)	D_{BJH} (nm)	Total pore volume (cm^3/g)	Wall thickness (nm)
Si-SBA-15 (calcined)	9.007	10.40	774	6.62	0.942	3.78

spectra show only silicon and oxygen, so the sample is chemically pure.
Figure 4 shows the SEM images of the calcined SBA-15 sample (a) and the elemental composition by EDX spectra (b).

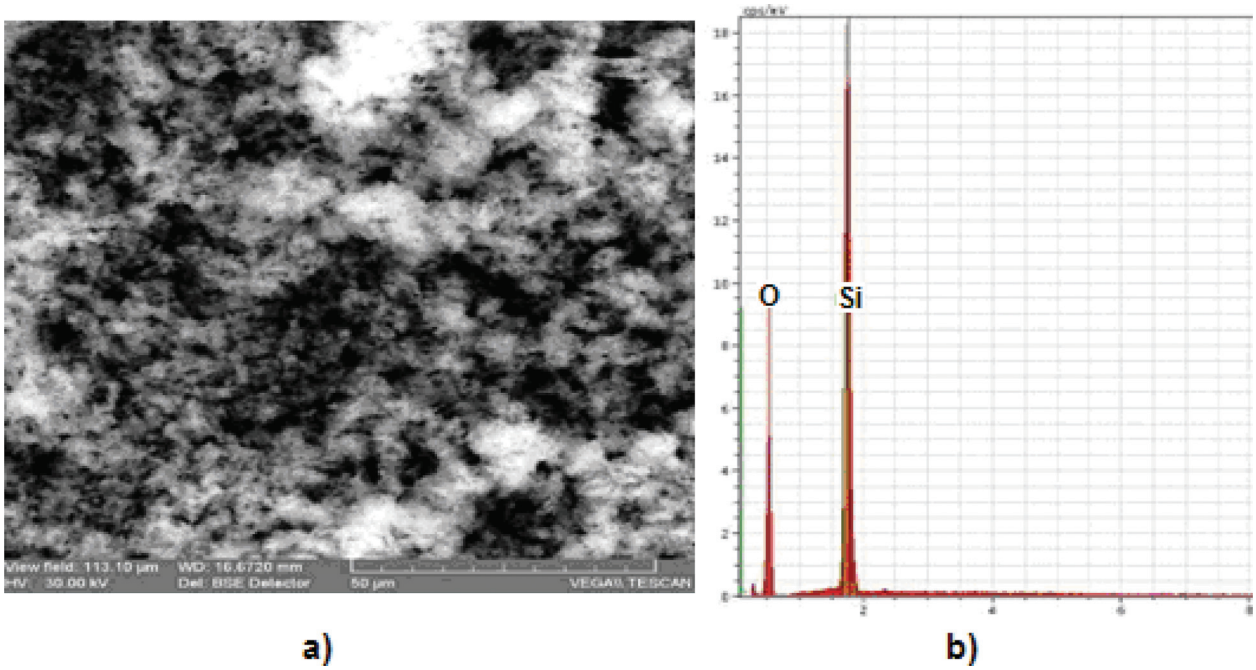

Fig. 4: SEM micrograph (a) and EDX spectra (b) of silica SBA-15

Standard chemical analysis of wine

Total acidity, ethanol, pH-value, volatile acidity, total and free sulphur dioxide, sugars and total dry extract (TDE) of the used wine were analyzed according to the methods proposed by OIV (2006) (Table 2).

Table 2: Traditional analysis of 'Cabernet Sauvignon' wine

Parameter	Value
pH-value	3.5
Total acidity	6.18 g/l (as tartaric acid)
Volatile acidity	0.5 g/l (as acetic acid)
Free SO_2	33.6 mg/l
Total SO_2	170.4 mg/l
Sugars	2.3 g/l
TDM	22.45 g/l

The total polyphenol content of the red wine was determined by measuring the absorbance at λ = 280 nm in quartz cuvettes of 1 cm optical path, compared with deionized water. The calibration curve, marked 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 + 0.0028 where x is the absorbance value A_{280} read from the device and y is the equivalent content of polyphenolic compounds expressed as mg of gallic acid equivalents (GAE/l).
The total index polyphenol content was found to be 1591,13 mg/l (A_{280} = 54.025).

Adsorption of polyphenols

Adsorption experiments of polyphenols from red wine on mesoporous silica SBA-15 were carried out in comparison with activated carbon as adsorbent. In Table 3 results concerning the effect of the adsorbent dose on the removal of polyphenols are quantified as residual concentration of wine polyphenols (mg/l) and as percent removal of polyphenolic compounds (%).
It was observed that by increasing the SBA-15 adsorbent concentration from 0 to 8 g/l, the total index of phenols in wine decreased from 1591,13 mg/l to 1286,99 mg/l; at the same time, the polyphenols removal efficiency increased up to a value of 19.15 %. However, using an activated carbon dose of 1.013 g/l

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	1591	0.00
SBA-15	0.5256	51.050	1503	5.51
	1.0216	49.785	1466	7.85
	1.5104	49.570	1460	8.25
	2.0510	48.950	1438	9.39
	2.5082	47.645	1403	11.81
	3.0994	47.050	1386	12.91
	4.0204	46.520	1370	13.89
	5.0200	45.875	1351	15.09
	6.1344	44.690	1316	17.28
	6.9974	44.370	1307	17.87
	8.0404	43.680	1286	19.15
Activated carbon	0.2808	47.180	1389	12.67
	0.6594	43.940	1294	18.67
	1.0130	40.110	1182	25.76

wine, the retained phenolic compounds represented 25.76 % of the initial quantity of polyphenols, whereas a dose of 1.0126 g of SBA-15 for 1 liter of wine reduced the phenolic compounds concentration by only 7.85 %.

The variation of the amount of adsorbed phenolic compounds with SBA-15 adsorbent dose, presented in Figure 5, shows an almost linear increase; higher values of removed polyphenols concentration can be obtained increasing the mesoporous silica SBA-15 dose.

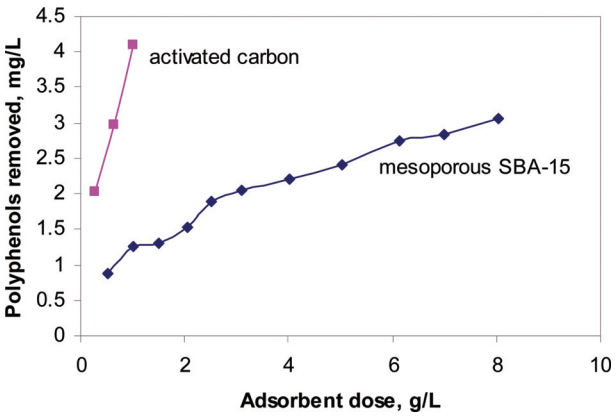

Fig. 5: Variation of polyphenols removed by mesoporous silica SBA-15 and activated carbon as a function of adsorbent dose

The identification of the phenolic compounds adsorbed by SBA-15 mesoporous silica was carried with HPLC. In this case, 500 ml of red wine were mixed with 4.0273 g of SBA-15 for 30 minutes and kept for 24 hours at a temperature of 5 °C. The solid adsorbent was filtered, dried at room temperature and then treated with 50 ml of methanol. Afterwards the methanolic extract was used for the qualitative analysis of phenolic compounds removed by the silica. The chromatograms of the original red wine and of the methanolic extract of phenols removed by SBA-15 are shown in Figures 6 and 7.

The chromatographic analysis shows that SBA-15 selectively retains the phenolic compounds from wine, following the order: quercitin > trans-resveratrol > cis-resveratrol. In the wine chromatogram it was observed that the characteristic peak for quercitin is very low, while in the chromatogram of the extract the quercitin corresponding peak is very high. This demonstrates that mesoporous silica SBA-15 is capable to remove quercitin selectively from the wine.

Conclusions

The activated carbon retains a larger amount of phenolic compounds in comparison to SBA-15, but the SBA-15 material has a selective effect on the phenolic compounds, retaining specific molecules in a larger

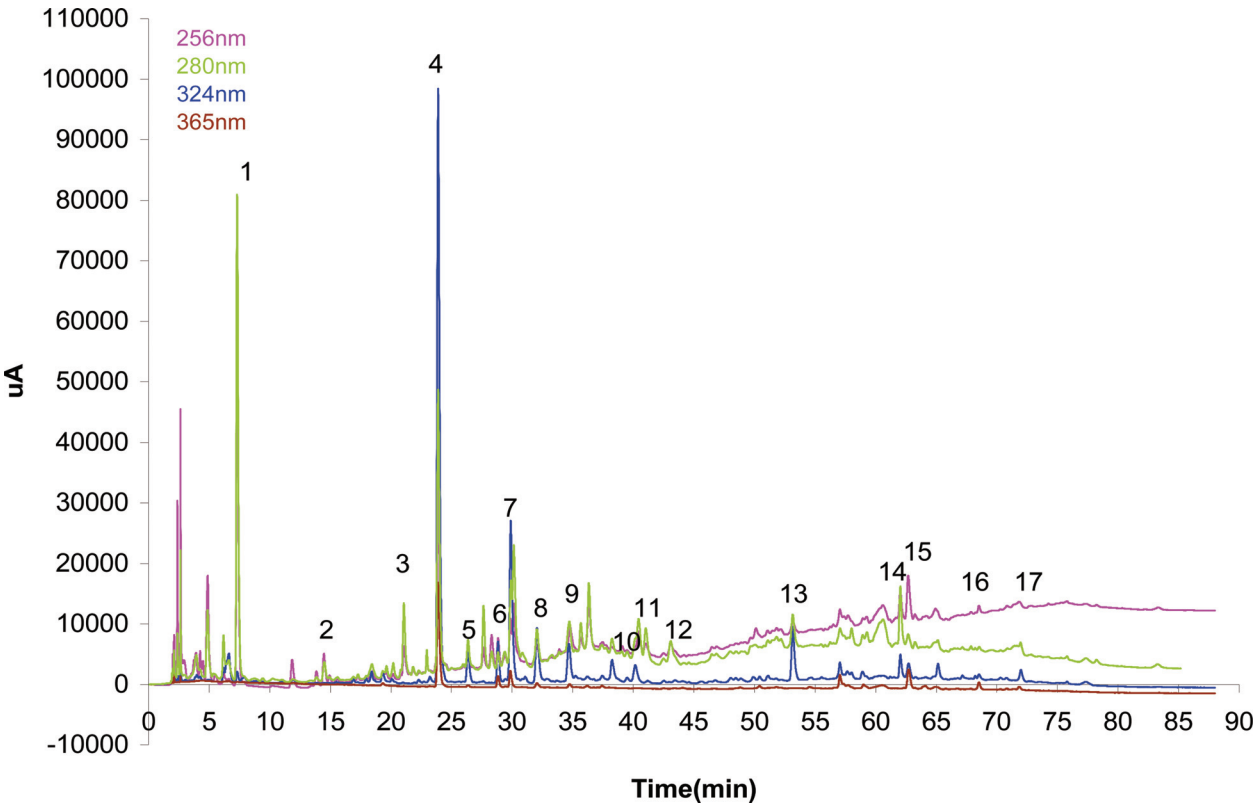

Fig. 6: The chromatogram of the red wine: 1-gallic acid; 2-protocatechic acid; 3-para-hydroxybenzoic acid; 4-gentisic acid; 5-meta-hydroxybenzoic acid; 6-vanillic acid; 7-catechin; 8-caffeic acid; 9-clorogenic acid; 10-para-coumaric acid; 11-epicatechin; 12-salicylic acid; 13-sinapic acid; 14-trans-resveratrol; 15-rutin trihydrate; 16-cis-resveratrol; 17-quercitin

quantity due to its structure. In the wine chromatogram it was observed that the characteristic peak for quercitin is very low, while in the extract chromatogram the same peak was very high. This demonstrates that SBA-15 is able to remove quercitine from wine.

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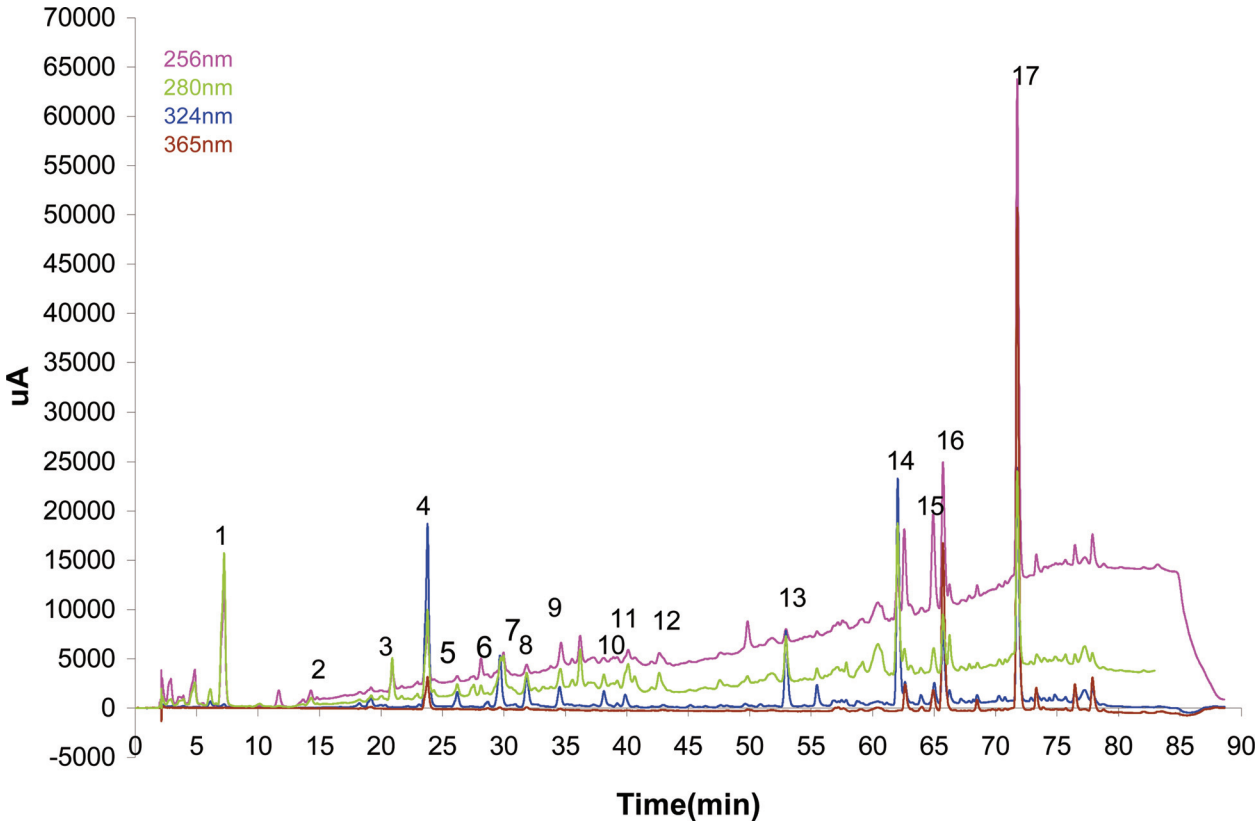

Fig. 7: The chromatogram of the methanolic extract of polyphenols adsorbed by SBA-15 mesoporous silica: 1-gallic acid; 2-protocatechic acid; 3-para-hydroxybenzoic acid; 4-gentisic acid; 5-meta-hydroxybenzoic acid; 6-vanillic acid; 7-catechin; 8-caffeic acid; 9-clorogenic acid; 10-para-coumaric acid; 11-epicatechin; 12-salicylic acid ;13- sinapic acid; 14-trans-resveratrol; 15-rutin trihydrate; 16-cis-resveratrol; 17-quercitin

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