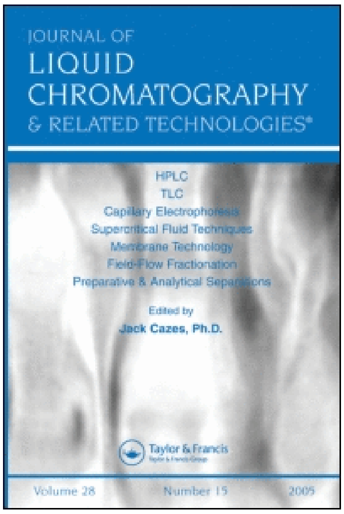

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Preparation and Characterization of Sorption Properties of Porous Microspheres of 1-Vinyl-2-Pyrrolidone-Divinylbenzene

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Abstract: Porous polymeric microspheres of 1-vinyl-2-pyrrolidone–divinylbenzene were prepared using the suspension-emulsion polymerization technique. In their synthesis, the mixture of toluene and n-dodecane was used as a pore forming agent providing materials of different porosities. The obtained copolymers were used as sorbent for solid phase extraction. In order to study the sorption properties of these polymeric materials the breakthrough volumes of phenol were determined. Additionally, these materials were compared with commercially available Strata-X.

Keywords: Polymeric microspheres, Suspension-emulsion Polymerization, Porous structure, Solid phase extraction

INTRODUCTION

Solid phase extraction (SPE) is a well-established technique and, due to its advantages, the most popular method of the preliminary preparation of different kinds of samples before analysis. It is widely used for cleaning up, purification, and preconcentration of analytical samples as well as for removal of toxic or valuable substances from variety of solutions.[1–3] Recently, it has also been used to store and transport the analytes, in combinatorial chemistry and parallel synthesis.[4] SPE can be performed on-line by direct connection to the chromatographic system or off-line. In the latter technique, the sample is separated from the subsequent chromatographic

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analysis. The chemistry and principles are one and the same for both off-line and on-line SPE.[5]

The solid phase extraction can be considered as a chromatographic process: the extraction step can be described as frontal chromatography whereas the desorption step as displacement chromatography. The sorbent plays the role of the stationary phase. For the analytical purposes, SPE is usually performed using a small column or cartridge containing an appropriate packing. Recently, also, SPE discs have become more popular.[6,7] The majority of the commercially available phases are chemically bonded silicas (usually with C_8 or C_{18} organic group) and porous polystyrenes.[8,9] The main limitation of both sorbents is that they must be conditioned with a wetting solvent and not allowed to dry before the loading of an aqueous solvent. The surfaces of polystyrenes and bonded silicas are hydrophobic and, consequently, have poor contact with predominantly aqueous solutions. Considering this fact, it is crucial to incorporate polar functional groups into polymer skeletons. It can be done by employing monomers of more polar character.

In this paper, the preparation of porous polymeric microspheres of 1-vinyl-2-pyrrolidone–divinylbenzene (VP-DVB) is presented. The application of the suspension-emulsion polymerization technique gave microspheres of diameters suitable for SPE applications. Thus, the extraction behaviour of phenol on obtained phases was studied.

EXPERIMENTAL

Chemicals

Divinylbenzene (DVB, Merck, Darmstadt, Germany) was washed with 5% aqueous sodium hydroxide in order to remove inhibitors. 1-Vinyl-2-pyrrolidone (VP), bis(2-ethylhexyl) sulfosuccinate sodium salt (DAC,BP), phenol and α,α'-azobisisobutyronitrile (AIBN) were purchased from Fluka AG (Buchs, Switzerland) and were used without purification. Toluene, n-dodecane, acetone, methanol, and sulphuric acid were from POCh (Gliwice, Poland). Strata X was obtained from Phenomenex, USA.

Preparation of the VP-DVB Microspheres

Copolymerization was performed in an aqueous medium. In a typical experiment, 195 mL of distilled water and 2.2 g of bis(2-ethylhexyl)sulfosuccinate sodium salt were stirred for 1 h at 80°C in order to dissolve the surfactant. Then, the solution containing 15 g of monomers (VP and DVB), and 0.2 g of α,α'-azoisobutyronitrile in 22.5 mL of diluents (toluene and n-dodecane) was prepared and added, while stirring, to the aqueous medium. The mole ratio of VP to DVB was 0.5:0.5. Copolymerization was performed for 20 h at 80°C. Porous beads formed in this process were sucked off, washed with hot water, and extracted in a Soxhlet apparatus with acetone, toluene, and methanol. The purified beads were separated into fractions by sedimentation from methanol-acetone (90:10; v/v).

Characterization of Porous Structure

Characterization of the porous structure was performed using nitrogen adsorption-desorption measurements. In a dry state, such parameters as specific surface areas, pore volumes, pore size distributions, and the most probable pore diameters were determined by the method of nitrogen adsorption. These determinations were made using an adsorption analyzer ASAP 2405 (Micrometrics Inc., USA). The specific surface area was calculated by the BET method, assuming that the area of a single nitrogen molecule is 16.2 $Å^{2.}$ The measurements of the surface properties of the copolymers were preceded by activation of the samples at 200°C for 2 h. This method allows detecting all pores of diameters 10–2,000 Å.

Column Preparation

PEEK columns (50 mm × 4 mm I.D.) were packed with dry VP-DVB microspheres. Diameter of the beads was always 30–40 μm. As a reference material Strata-X (33 μm) was used, which was kindly offered by Phenomenex, USA. This material was packed in the PEEK column in the same procedure.

Apparatus for Breakthrough Volume Determinations

Breakthrough volumes for phenol were determined using a set equipped with 260D syringe pomp (ISCO, Lincoln, USA), high-pressure pomp model 305 (Gilson Inc., Middleton, USA), thermostat model 831 (Gilson Inc., Middletown, USA), UV/Vis detector 155 (Gilson Inc., Middletown, USA), PEEK column packed with the examined polymer and ten-way valve C10W (VICI, Valco Instruments Co. Inc., Houston, USA) maintained in the thermostat, and integrator model DP 700 (Carlo Erba Instruments, Milan, Italy). The block diagram of this set is presented in Figure 1.

Chromatographic Measurements

When the column was installed in the apparatus, 10 mL of methanol with the flow rate 1 mL/min, was pumped over the packing material. During this

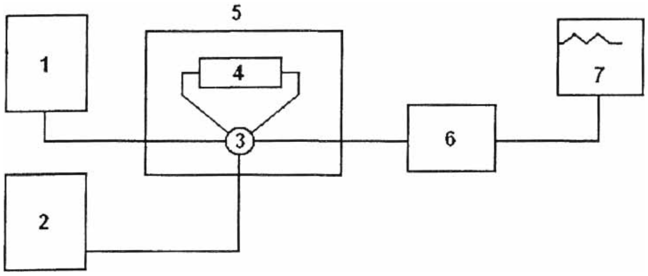

Figure 1. The block diagram of apparatus for breakthrough volume determinations. 1 = syringe pump; 2 = high-pressure pomp; 3 = ten-way valve; 4 = column; 5 = thermostat; 6 = UV/V is detector; 7 = integrator.

treatment, salvation of the studied polymers took place. Consequently, The polymer swelled and residual impurities were removed from its structure. Then, the column was conditioned for 10 min. using Milli-Q (Millipore, Bedford, USA) aqueous solution of sulfuric acid (pH 2.55) with the flow rate 1 mL/min. Phenol solution was directed to the column switching ten way valve. The solution of 0.001% phenol in water acidified to pH 2.55 was used in these studies. Its flow rate was 1 mL/min.

The measurements were carried out till the plateau on the breakthrough curve appeared. Monitoring of phenol concentration in the leak of the column and registration of absorbance changes was the basis of breakthrough volume determinations.

Measurements of breakthrough volumes were carried out at 30°C. Detection was performed at wavelength t 280 nm.

RESULTS AND DISCUSSION

Porous copolymer VP-DVB was prepared by heterogeneous free radical polymerization. The chemical structure of the obtained copolymer is presented in Figure 2a. Additionally, Figure 2b shows the functional group of strata-X sorbent. The received VP-DVB copolymers contain hydrophilic pyrrolidone moieties in their internal structure, whereas strata-X contains piperidin 4-one group. Both types of copolymers consist of two different types of monomers. These monomers construct a hydrophilic lipohilic balance so they can be used for preconcentration of polar and non-polar compounds from aqueous solution.

Another problem connected with preparation of SPE packings is the shape and size of polymeric beads. They should be rigid, porous, uniform in size, and have diameters about 40 μm. To meet these requirements, suspension-emulsion was employed. This technique gave a product in the form of regular microspheres. In their synthesis, the mixture of toluene and

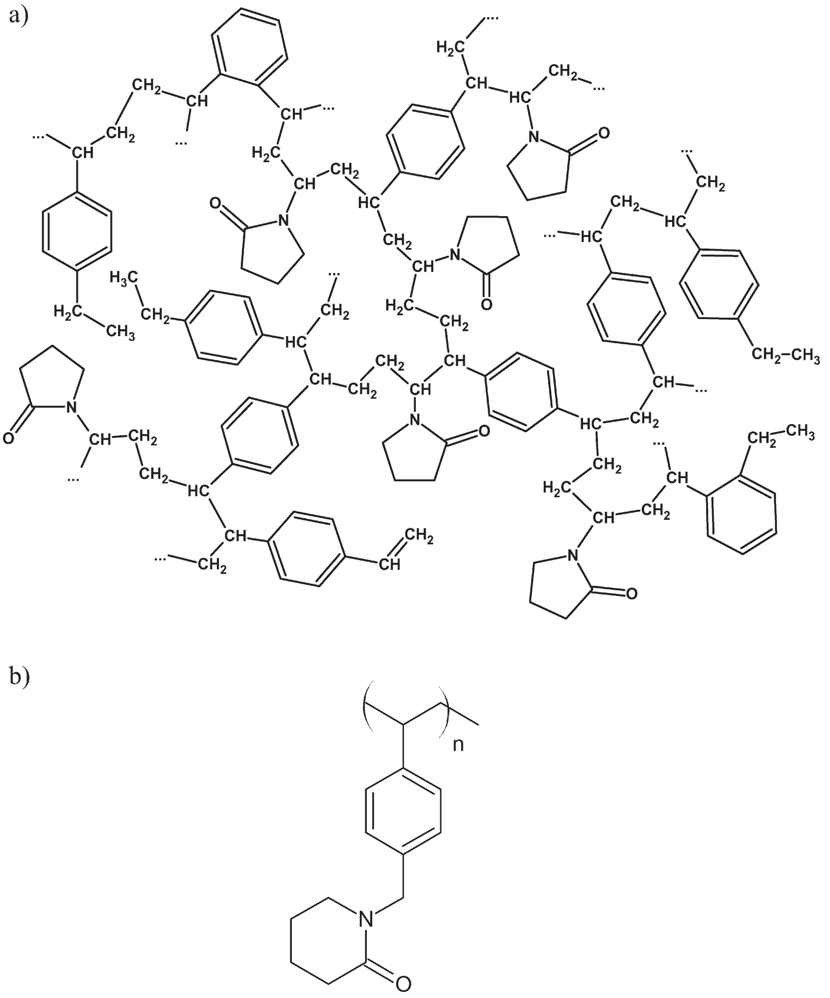

Figure 2. Chemical structure of a) VP-DVB copolymer. b) Strata-X.

n-dodecane was used as a pore forming agent. The choice of proper diluent ensures formation of materials with the highly developed porous structure suitable for SPE purposes. In the used mixture, toluene is a good solvent for the polymer and n-dodecane is a non-solvent. A non-solvent is responsible for the formation of meso- and macropores in the internal structure of the polymeric particle, whereas good solvent is responsible for its microporous structure. In the syntheses of VP-DVB microspheres different concentrations of toluene in the mixture with n-dodecane were used, provided that other parameters such as mole ratio of monomers and volume ratio of diluents to monomers were constant (Table 1). Products obtained in the presence of

Table 1. An influence of the pore-forming diluent composition on the porous structure of the VP-DVB copolymers

Copolymer	Toluene concentration in the mixture with n-dodecane (%)	Product	Specific surface area (m^2/g)	Pore volume (mL/g)	The most probable pore diameter (Å)
VP-DVBrD	0	Coagulated	—	—	—
VP-DVBrA	15	Coagulated	—	—	—
VP-DVBrB	50	Microspheres	813	2.38	150/500
VP-DVBrC	85	Microspheres	792	1.52	170
VP-DVBrE	100	Microspheres	746	1.05	80
Strata-X	—	Microspheres	800	1.20	85

pure n-dodecane and in the mixture containing 15% toluene coagulated. An increase of toluene concentration resulted in formation of regular microspheres. As shown in Figure 3, the composition of diluents affects size and size distribution obtained microspheres. Beads with the narrowest diameter distribution were produced in the presence of 50% of toluene. The diluent composition also influenced the parameters of porous structures. A increase of toluene concentration in the mixture with n-dodecane causes the decrease of a specific surface area. The most developed specific area is observed for the copolymer obtained in the presence of 50% (v/v) toluene (VP-DVBrB). Its value is a bit larger than that for strata −X. The pore volume of this copolymer is almost two times higher compared with this reference material. For the copolymers prepared in the presence of 85% toluene (VP-DVBrC), the value of the specific surface area slightly decreases. The more significant drop is observed in the pore volume; however, their value is still higher than in the case of Strata-X. The copolymer obtained in pure toluene as a pore forming agent (VP-DVBrE) possesses an insignificantly less developed surface.

Since the determination of the porous structure was performed in a dry state, micropores are not observed in any of the studied copolymers. Nevertheless, the shape and position of a hysteresis loop for the copolymer obtained in the presence of 100% toluene (Figure 4) indicates the possibility of the appearance of micropores in its internal structure.

The diluent mixture composition also affected the average pore diameters. The system with a higher concentration of toluene produces a structure with smaller pores. Consequently, the pore size distribution function becomes narrower, shifting towards smaller diameters (Figure 5). Figure 6 presents an AFM imagine of the porous structure copolymer obtained in the presence of 85% toluene. Changes of pore volume of all the

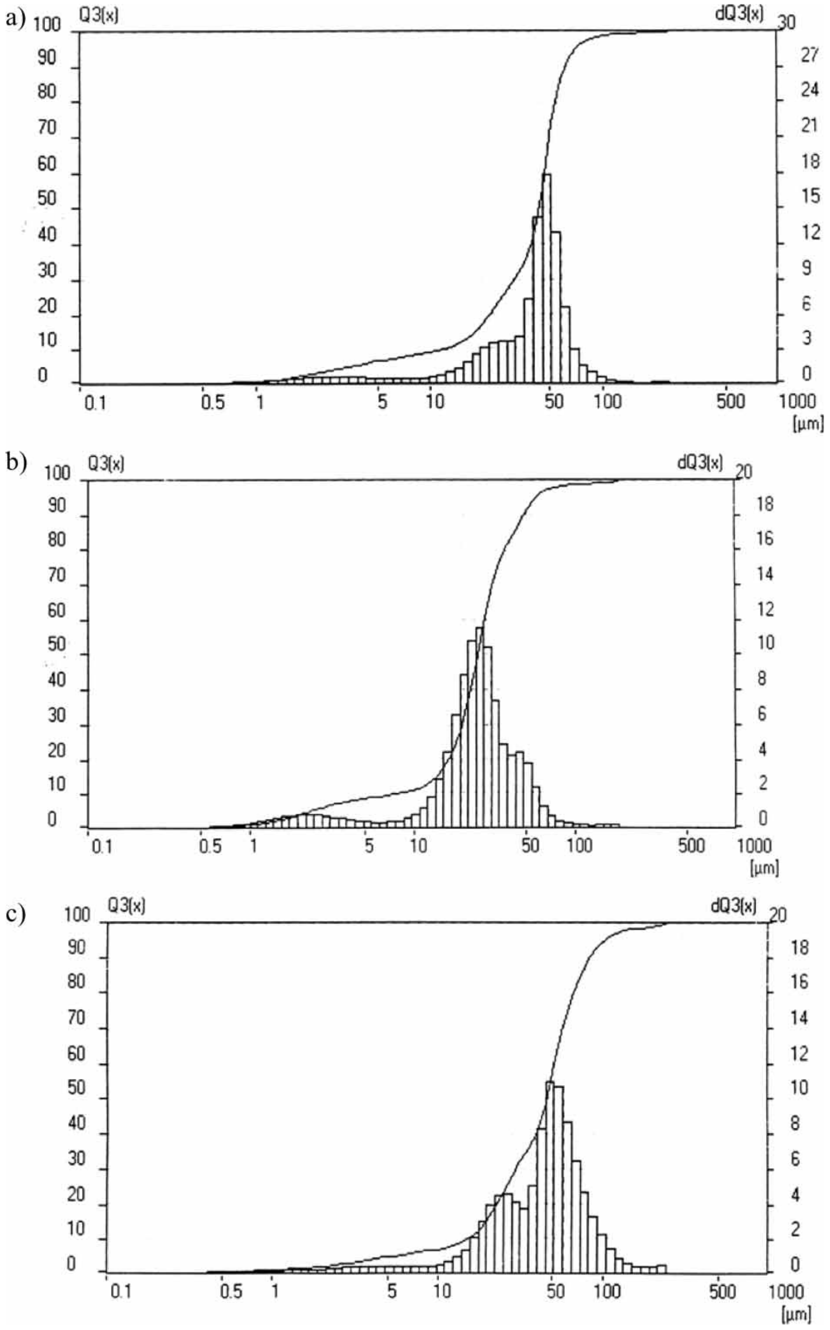

Figure 3. Distribution of microspheres diameters obtained in presence a) 50%, b) 85%, c) 100% toluene.

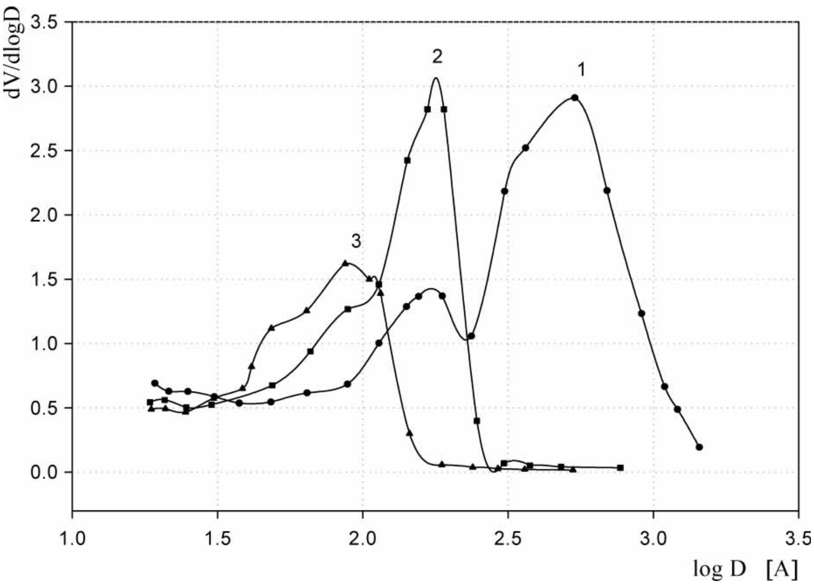

Figure 4. Hysteresis loops.

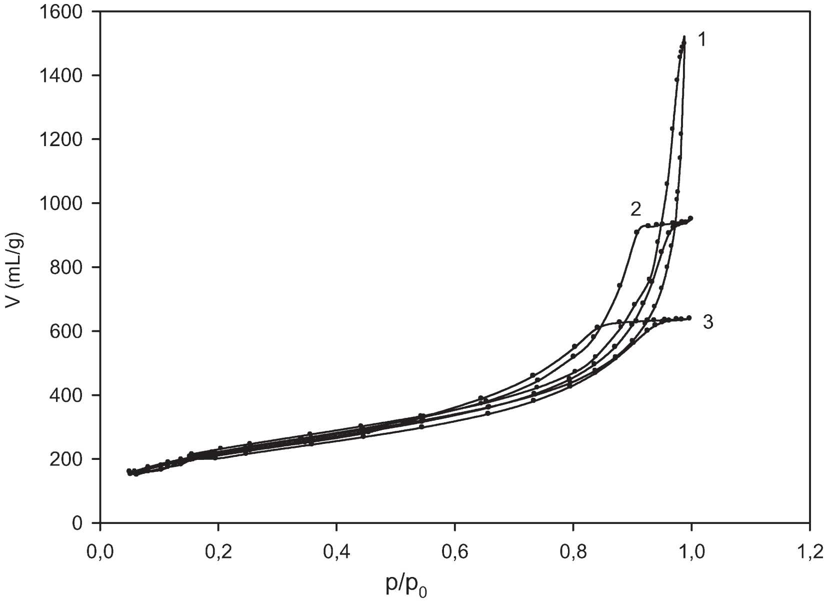

Figure 5. Differential pore size distribution as a function of log of pore diameter, D_p, for the studied copolymers obtained in the presence of the diluent containing different amounts of toluene: 1= 50%; 2 = 85%; 3 = 100%.

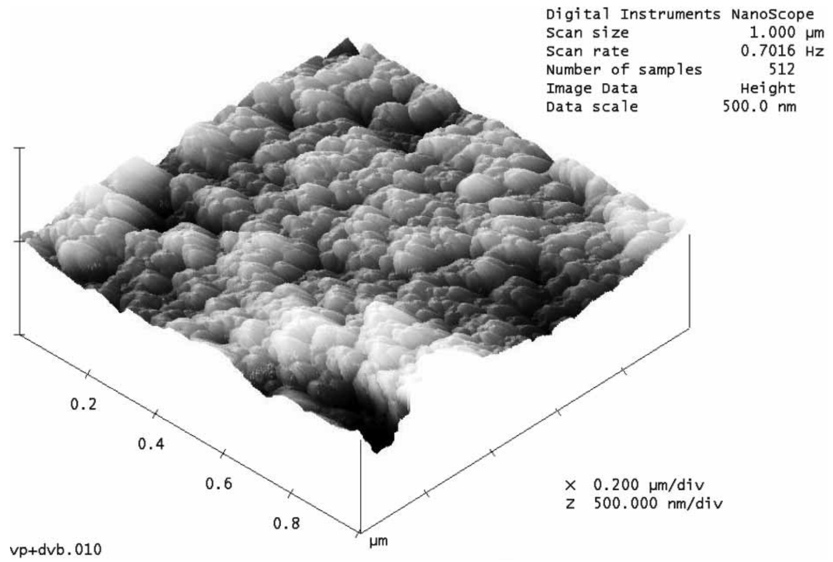

Figure 6. AFM micrographs of the VP-DVB copolymer obtained in the presence of 85% toluene.

studied copolymers are the same as observed by Sederel et al.[10] The largest values of pore volume are obtained for the copolymers that are synthesized in the presence of diluent containing high concentrations of the component precipitating the copolymer, e.g., n-dodecane.

Table 2 contains the basic chromatographic parameters obtained in breakthrough experiments: the retention volume of analyte-V_R, the breakthrough volume $-V_B$ (at 10% level) and the standard deviation parameter-$\sigma_{v.}$ The standard deviation parameter was determined graphically from the curves according to procedure described by Gelencser et al.[11] σ_v is in direct relation to the efficiency of the SPE column, i.e., the number of theoretical plates (N). Purnell[12] has shown that N is inversely proportional to the value of σ_v. The results presented in Table 2 argue that the best adsorption properties towards phenole indicate copolymer VP-DVBrE. The value of breakthrough volume is higher compared not only with two other VP-DVB

Table 2. The basic chromatographic parameters obtained in breakthrough experiments

Copolymer	V_R (mL)	V_B (mL)	σ_v
VP-DVBrB	51.5	65	14
VP-DVBrC	137	125	9.8
VP-DVBrE	171	160	7.2
Strata-X	225	151	64

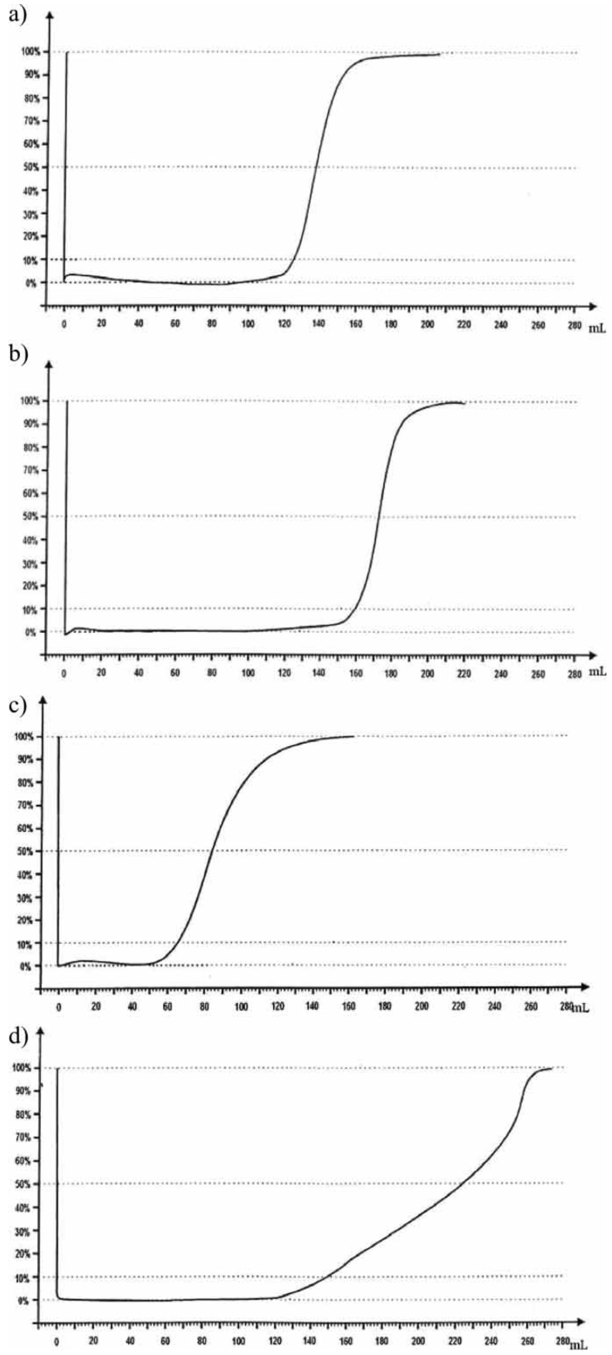

Figure 7. The breakthrough curves across the different adsorbents: a) VP-DVBrC, b) VP-DVBrE, c) VP-DVBrB, d) Strata-X.

adsorbents studied but also with commercially available Strata-X. The comparison of the σ_v values shows that this copolymer possesses the highest number of theoretical plates.

Surprisingly, the discussed adsorbent has the smallest values of the specific surface area and the pore volume. The most probable explanation of its excellent adsorption properties is the shape and proper diameter of its pores. Figure 7 shows the course of breakthrough curves for phenol obtained on the studied sorbents. It is important that on VP-DVBrC and VP-DVBrE copolymers breakthrough volumes for phenol exceed 100 mL, while on the sample VP-DVBrB smaller amounts of phenol can be preconcentrated. These values are comparable to that obtained on Strata-X sorbent. Additionally, the curves for the VP-DVB copolymers have a sharp course. In comparison, the breakthrough curve for Strata-X is rather shallow.

The presented results strongly suggested that VP-DVB copolymers show high affinity toward phenols and, due to this fact, can be used as SPE packings. Their adsorption properties are closely connected with their internal structure.

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