

Brief Analysis of Selected Sorption and Physicochemical Properties of Three Different Silica-Based Adsorbents

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ABSTRACT

An important role in the retention/adsorption mechanisms are both the interactions between the liquid phase components and the adsorbent surface, and the effects connected with the fluid flow through the bed. Unfortunately, the retention mechanism in most adsorption systems (e.g. liquid chromatography) is unknown and further investigations are needed. In this work, the sorption mechanism of caffeine and phenol as test substances in various adsorption systems has been analyzed. Investigations were conducted using three adsorbents. On the basis of appointed adsorption isotherms, the adsorption energy distributions have been determined. In addition, particle size distributions and SEM-EDS analysis have been performed. The obtained results show the presence of diverse active sites on the surfaces of adsorbents, which may significantly affect the sorption mechanism. One of the reasons for this phenomenon may be the presence on the tested adsorbent surfaces of metal atoms. The particle size distribution of tested adsorbents is polydisperse, which can affect the adsorption/mass transfer mechanisms and separation efficiency.

Keywords: Adsorption; Adsorbent; Energetic Heterogeneity; Particle Size Distribution; SEM-EDS

Abbreviations: HPLC: High Performance Liquid Chromatography; PSD: Particle Size Distribution; SEM: Scanning Electron Microscopic; SEM-EDS: Scanning Electron Microscopy with Energy Dispersive Spectrometry; AED: Adsorption Energy Distribution; MeOH: Methanol; ACN: Acetonitrile

Introduction

Mass exchange in various adsorption processes (including various types of High-Performance Liquid Chromatography, (HPLC) and closely related to it, the retention mechanism of adsorbed substance(s) has been and still is the subject of investigations by many research teams. It is a very complex process that depends not only on the physicochemical properties of the fluid phase components, but also on the structure and properties of the adsorbent [1-4]. Even approximate knowledge of this mechanism can facilitate the correct selection of the adsorption system and thus obtain the appropriate mixture separation selectivity. Although the literature contains research

results on the retention mechanism related to e.g. the adsorption energy distribution on the adsorbent surface, there are relatively few official data about e.g. adsorbent particle size distributions of commercial adsorbents. Manufacturers are also reluctant to share such data despite the fact that they are important from a practical point of view. As mentioned above, a significant role in different adsorption processes, which determines the efficiency of mixture separation is played by the physical and physicochemical properties of the adsorbent. Therefore, since powder adsorbents are used in liquid chromatography, it is important to accurately determine their material properties. One such parameter is particle size, or more precisely, Particle Size Distribution (PSD).

There are many methods for determining the PSD. Some of the more widely used are electrical sensing zone method (Coulter principle), sedimentation, laser light diffraction (analysis of light scattering pattern) and analysis of Scanning Electron Microscopic (SEM) images. Mechanical screening is effective for granular materials from 30 μm to 125 mm in size, laser diffraction is suitable for materials with fine particles [5]. Particles of different sizes differ in surface area and may also differ in pore structure. The process of migration of analyte particles to pores inside the interior of an adsorbent particle can be considerably longer for larger particles. Consequently, the particle size distribution can affect the adsorption process. This process can be affected by the width or span of the particle size distribution. Wide particle size distributions have significant effect on the separation efficiency of molecules [3]. Literature data indicate that the presence of fine particles also plays an important role which significantly determines the performance of particular adsorption/chromatographic columns [1]. Some investigations of commercial HPLC adsorbent particle types shows a strong trend between the PSD of the stationary phases and the typically employed "goodness of packing" parameters. The performance of the current generation of fully porous particle columns could be significantly improved if the PSD of these particles could be reduced [6].

On the other hand the PSD may have direct physical impact on eddy dispersion and column efficiency [2]. Therefore, it is important to conduct further research to clearly determine the effect of adsorbent particle size distribution in e.g. the liquid chromatography process. Particle size distribution can also affect particle packing in a chromatography column. Small particles tend to settle in the flow-through pores surrounding the larger particles, leading to very high packing densities and also negatively influencing the column permeability as well as the band broadening [7]. On the other hand, the presence of various impurities (e.g., metals) in the adsorbent structure may be one of the reasons for the presence of energetically different active sites on the adsorbents surface, which also significantly influences the separation selectivity. Scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) is the only affordable analytical technique that can define/discriminate both morphology and elemental composition of inorganic materials (what as mentioned is important in such investigations).

The aim of this study has been to analyse:

- A. The particle size distribution to determine the properties of the selected adsorbents,
- B. The chemical composition of the surface of the tested adsorbents,
- C. The adsorption equilibrium and
- D. The evaluation of the Adsorption Energy Distribution (AED) of the tested stationary phases. The investigations have been conducted using three silica-based polar stationary phases in sys-

tems with two test compounds (phenol and/or caffeine) solved in acetonitrile – water and/or methanol – water mixtures.

Materials and Methods

Materials

Phenol and caffeine, both from Merck, were applied as test analytes. The test compounds belonging to miscellaneous chemical classes. Therefore, they could interact diversely with the stationary phase and allow a wider and more objective assessment of the retention/sorption mechanism of the tested adsorbents. All chromatographic grade organic solvents i.e., methanol (MeOH) and acetonitrile (ACN) were purchased from Merck. Distilled, deionized and demineralized water was prepared on SolPure-78Z (ELKAR) water deionizer. An ultrasonic bath (from ULTRON) was used to degas the solvents for 5 minutes immediately after mixing. As adsorbents were used: MCM-41 (mesoporous silica), which was newly synthesized in the Department of Industrial and Materials Chemistry at Rzeszow University of Technology using the modified procedure described previously by Fujita [8], LiChrospher 4000 Si (10 μm) and Silica gel 60 (0.015-0.04 mm) - both from Merck. The experiments were carried out using MeOH–water and ACN–water solvent systems containing 95% volume fractions (v/v) of the appropriate organic component. As a dispersing liquid used for particle size distribution for adsorbents was distilled water.

Experimental – Measurement of Particle Size Distribution

The PSD of each sample was measured with a Mastersizer (Malvern Instruments, Malvern, Worcestershire, UK). This device infers particle size via dynamic light scattering. The output data from the analyzer is PSDs, normalized with respect to the volume of the particle collective for each sample. Measurements were carried out in suspension, placing a small amount of the adsorbent under test in a beaker filled with deionized water which was the dispersing liquid. The measurements were carried out with continuous, intensive mixing and using at least 4 series of ultrasound, each of 30 s. Ultrasound was used to break up agglomerates in samples. Additionally the parameters were determined, as follows: $d(0.5)$ is the median diameter where 50% of the distribution is above and 50% is below, $d(0.X)$ is the volume diameter where X% of the particles is below X%,

Span is calculated as follows: $[d(0.9) - d(0.1)] / d(0.5)$, $D[4.3]$ is the volume weighted mean diameter, $D[3.2]$ – is the surface weighted mean diameter, SSA is the external specific surface area, uniformity is the total variance from the median.

Experimental – SEM-EDS Analysis

The chemical composition and images of powders were taken by using a scanning electron microscope (SEM) MIRA3 from TESCAN, equipped with energy dispersive X-ray spectrometer (EDS) X-MaxN from OXFORD Instruments. The SEM images and EDS maps and area

spectra were taken at 20 keV electron beam accelerating voltage. Working distance was 15 mm, as per specifications of the manufacturer. Detector used for SEM images was the Back Scattered Electron (BSE) unit. The powdered samples were deposited on aluminium tables covered with a carbon tape. The carbon tape can be seen as a black background on the SEM images (Figure 1). The acquisition time of the EDS maps was 30 minutes. The acquisition time of the separate spectra used for determining the chemical composition was 180 seconds. For each sample there were ten spectra acquired.

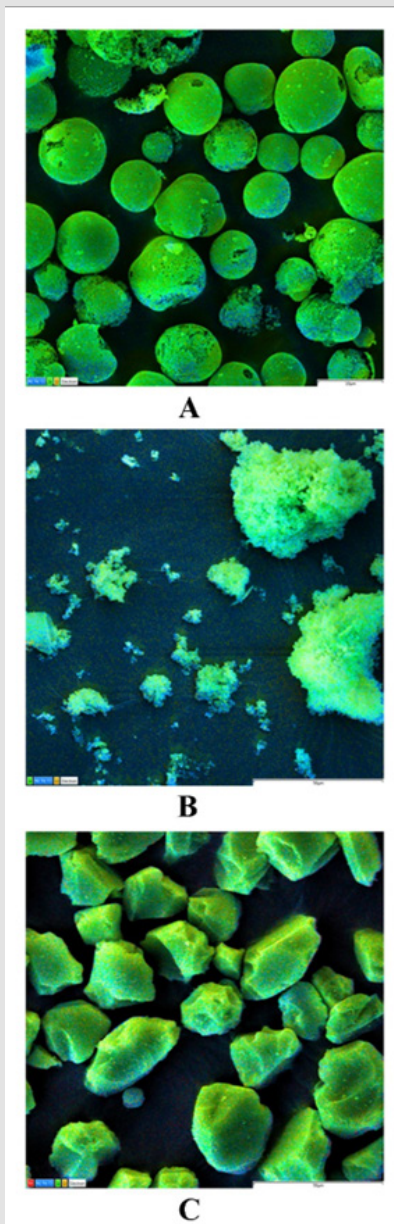


Figure 1: SEM-EDS photograph of
 A - LiChrospher 4000 Si (mag. 2500x)
 B - MCM-41 (mag. 1000x)
 C - of Silica gel 60 (mag. 1000x)

Experimental – Determination of Adsorption Isotherms

Adsorption isotherms (i.e. the equilibrium dependencies of solute concentration in the stationary phase, q , as a function of sample concentration in fluid phase, C : $q=f(C)$) were determined using a static method described in literature – e.g. [9,10]. Different concentrations of solutions of 3 cm³ each for phenol and caffeine in methanol/water and acetonitrile/water were prepared: for phenol 1; 6; 10; 20; 30; 40; 50; 60; 70; 80; 90; 100; 120 g/dm³ and for caffeine 0.1; 0.5; 0.8; 1; 2; 3.5; 5; 6.75; 8.25; 10.5; 12; 13.5; 15 g/dm³. In the next step, adsorbents (MCM-41, LiChrospher 4000 Si and Silica gel 60) were weighed into flasks in the amount of 0.3 g. The aforementioned solutions were then poured over the weighed adsorbents. In order to achieve the appropriate dynamics of the adsorption process and constant conditions of the temperature, an Orbital Shaker-Incubator ES-20/60 shaker was used. The device is equipped with a direct drive mechanism that allows the platform to move, which provides stable measurement conditions for long-term experiments.

The rotational speed was set at 100 rpm, samples were taken one hour at a time using a syringe with a filter (with a pore diameter of 0.2 μ m) and then placed in test tubes. The concentrations of the resulting solutions and concentration of the test compound after adsorption C were determined on a HPLC chromatograph using bypass mode. All measurements were carried out under isocratic conditions at an eluent flow rate of 0.5 cm³/min for a given solvent mixture composition. The injection volume of the sample was 0.02 cm³. Retention times were read for phenol at wavelength 294 nm while for caffeine at 303 nm. The HPLC system consisted of Primaide Merck–Hitachi pump (model 1110), Primaide Merck–Hitachi UV detector (model 1410), Primaide Merck–Hitachi column oven (model 1310).

Calculation of Adsorption Energy Distribution (AED)

In order to first evaluation of obtained equilibrium data it is most common to represent the data in form of the Scatchard plot. The Scatchard plot (i.e. $\frac{q}{C} = f(q)$ graphical dependence) is most suited for a qualitative evaluation of the experimental information. The non-linear – concave Scatchard dependence corresponds to energetically heterogeneous interactions of the adsorbing substance with the stationary phase, while the homogeneous interactions correspond to the linear course of this relationship [11]. Basing on the acquired raw adsorption data the degree of heterogeneity of the stationary phases were determined by calculation of the AED. These findings were realized using a mathematical method elaborated by Stanley and Guiochon [12,13]. The calculations carried out with this method provide model-independent information about a number of different adsorption sites and their respective energy levels. The thermodynamic data cannot provide a valid microscopic picture of the adsorption mechanisms but with an excellent degree of confidence they can supply information on distribution of the adsorption sites, i.e. the degree of adsorbent surface heterogeneity. The AED can be solved by many dif-

ferent methods. The one used in this study is the expectation maximization (EM) method [12,13], where the integral equation (1) is discretized to an adequate sum and solved in an iterative manner.

$$q(C) = \int_{k_{\min}}^{k_{\max}} f(\ln k) \theta(C, K) d \ln k$$

where: $\theta(C, K)$ is the local adsorption model (usually the Langmuir model) and $f(\ln k)$ is the AED, K_{\min} and K_{\max} are governed by $1/10C_{\max}$ and $1/C_{\min}$, respectively, where C_{\min} and C_{\max} are the lowest and the highest sample concentrations used in experiments.

Results and Discussion

In the first step, in order to accurately characterize the adsorbents, their particle size distributions and the properties associated

with it were determined. The results of the particle size distribution measurements are shown in (Figure 2 & Table 1) Of the tested adsorbents, the smallest particles are characterized by LiChrospher 4000 Si, the mean diameter of this adsorbent $d(0.5)$ is $8.62 \mu\text{m}$, besides, the particle size distribution is similar in shape to a Gaussian curve, and its span is relatively small and is 0.82. Other adsorbents are characterized by larger particle size and more irregular distribution. Adsorbent silica gel 60 is characterized by a bimodal distribution and its distribution is relatively wide, with particle sizes between $2 \mu\text{m}$ and as large as $60 \mu\text{m}$. The mean diameter of this adsorbent $d(0.5)$ is $23.88 \mu\text{m}$ and this is the highest value of all the adsorbents tested. MCM-41 adsorbent is characterized by monomodal distribution, mean diameter $d(0.5)$ is equal to 17.85 and its span is 1.74 and this is the highest value of all samples tested (Figure 1) shows a SEM-EDS photography of the LiChrospher 4000 Si, MCM-41 and Silica gel 60 adsorbent. LiChrospher 4000 Si is characterized by regular grains with a near spherical shape.

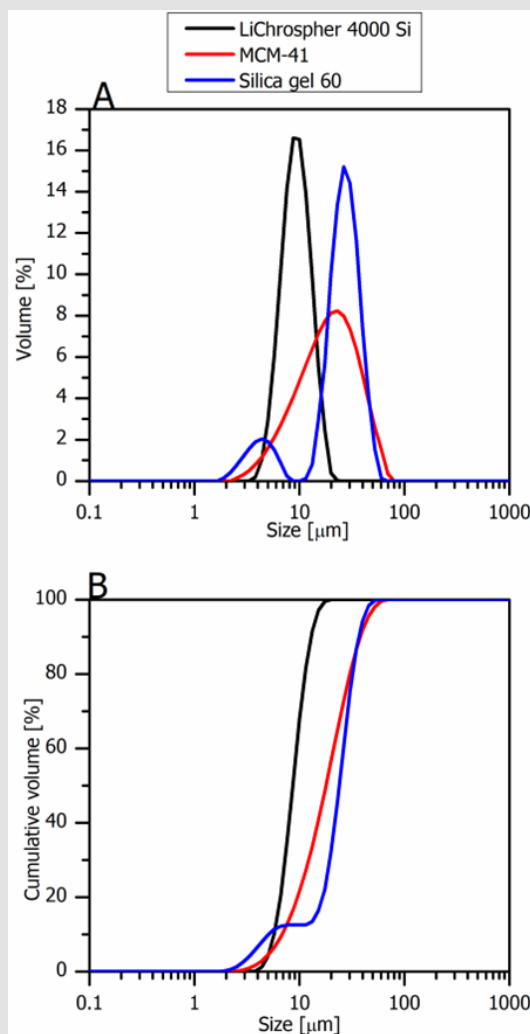


Figure 2: Particle size distribution of adsorbents:

A - differential curve

B - cumulative curve

Table 1: Properties of adsorbents.

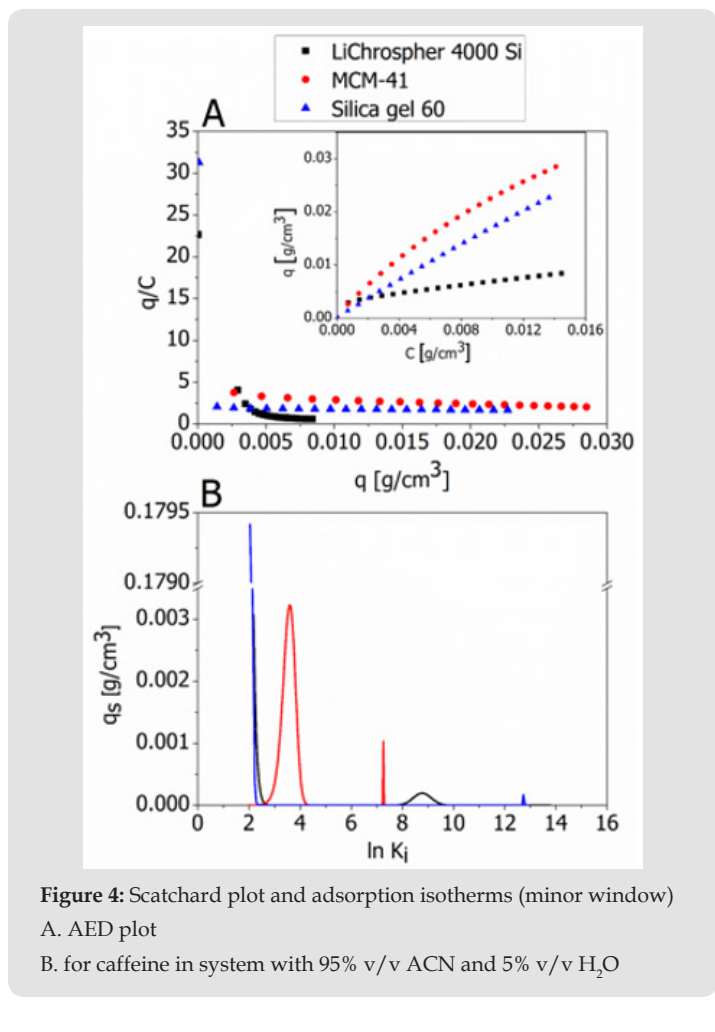
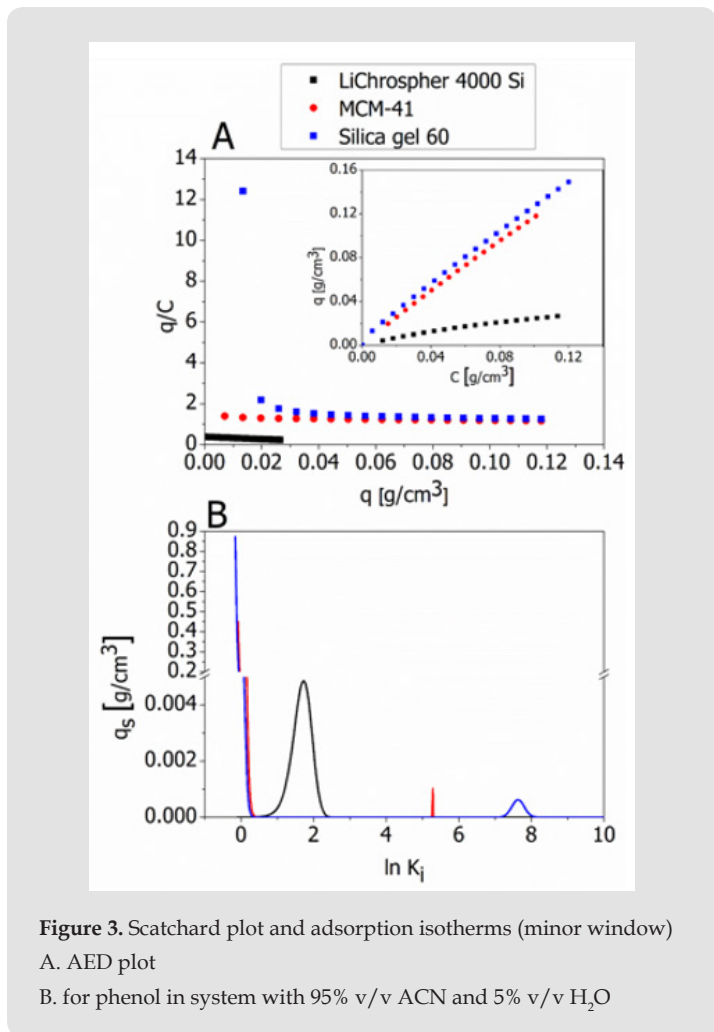
Adsorbent	$d(0.1)$ μm	$d(0.5)$, μm	$d(0.9)$, μm	Span
LiChrospher 4000 Si	5.72	8.62	12.83	0.82
MCM-41	6.81	17.85	37.88	1.74
Silica gel 60	5.06	23.88	36.39	1.31
Adsorbent	D[4,3], μm	D[3,2], μm	SSA, m^2/g	Uniformity
LiChrospher 4000 Si	9.00	8.18	0.73	0.26
MCM-41	20.40	13.41	0.44	0.54
Silica gel 60	23.59	14.14	0.42	0.34

The surface of these grains is the smoothest of all adsorbents. MCM-41 has grains with a distinctly irregular shape. Numerous pores can be seen, and the surface of the grains is very rough. Silica gel 60 has grains of irregular shape and the particles are polyhedral and their surface is smooth. SEM-EDS analysis confirmed the results with respect to the particle size distribution obtained by laser diffraction (Table 2) shows the chemical composition of the surface of the ad-

sorbents obtained from SEM-EDS investigations. LiChrospher 4000 Si contains the most oxygen while Silica gel 60 contains the most silicon. MCM-41 contains the most Fe and Silica gel 60 is the only one that contains Sn. The presence of metals (Cr, Fe, Ni, Sn) on the surface of the adsorbents may be one of the reasons for the observed heterogeneity in energy of the studied adsorbents. These metals may act as additional active centres at adsorbent surface and in different way interact with the components of the studied systems - e.g. [12,13]. The example results of the adsorption equilibrium states and adsorbent surfaces energetic heterogeneity investigations (i.e. Scatchard plots, adsorption isotherms and AEDs calculations results) were presented in (Figures 3-5).

Table 2: Chemical composition of the adsorbents surface.

Adsorbent	SEM-EDS - Wt., %					
	O	Si	Cr	Fe	Ni	Sn
LiChrospher 4000 Si	61.3	36.1	0.4	1.9	0.2	0
MCM-41	59.1	37.1	0.7	2.7	0.3	0
Silica gel 60	54.7	42.5	0.4	1.8	0.1	0.4



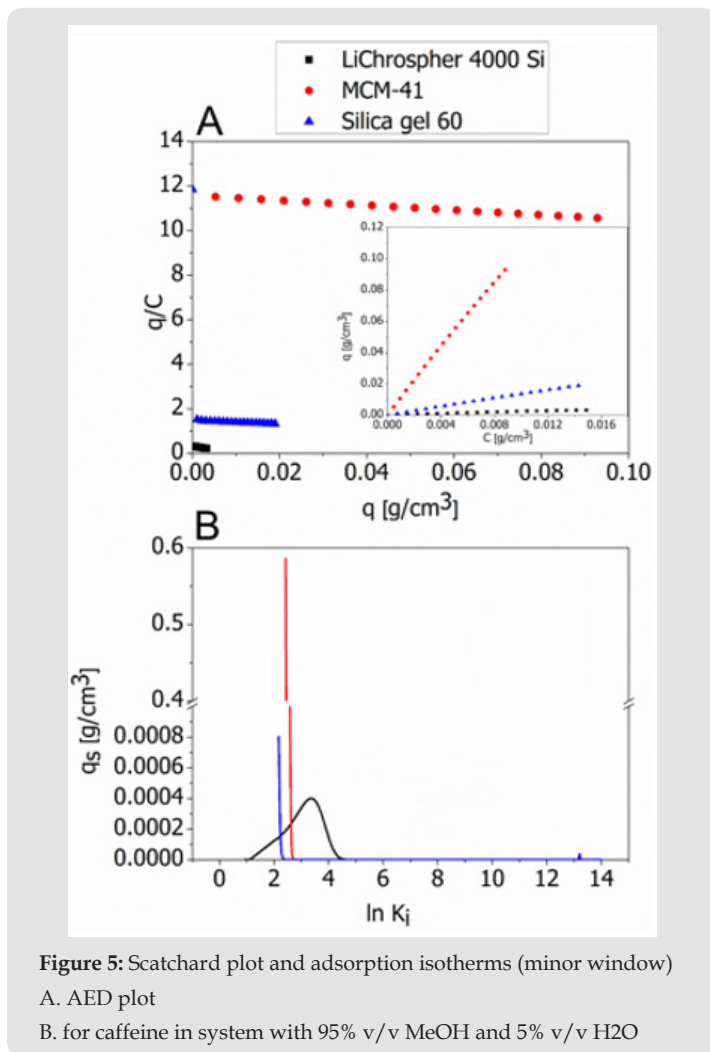


Figure 5: Scatchard plot and adsorption isotherms (minor window)

A. AED plot

B. for caffeine in system with 95% v/v MeOH and 5% v/v H₂O

By analyzing the adsorption isotherms obtained, it can be seen that the type of adsorbent used and the composition of the organic-water phase affect the sorption process of the test substances. The obtained results show that adsorbents with different particle sizes may have different effects on the adsorption see (Figures 3-5) and also on the mass-transfer process. Since mass dispersion is a phenomenon of fluid mixing during flow through porous material, the polydisperse particle size distribution can significantly affect the concentration distribution of fluid components, what in chromatography results usually in blurring the shapes of chromatographic peaks. This may lower the efficiency of a column. LiChrospher 4000 Si shows the smallest sorption capacity and also has the smallest grain size and narrowest distribution. Adsorbents with larger grain sizes have a higher sorption capacity. In most cases, the largest sorption capacity is shown by MCM-41 adsorbent, it also has the widest particle size distribution. Results for system containing 95% v/v ACN and 5% v/v H₂O are shown in (Figure 3) for phenol. In the case of MCM-41 and Sil-

ica gel 60 adsorbent, a non-linear Scatchard dependence is observed while for LiChrospher 4000 Si it is linear.

The AED plots confirm the conclusions resulting from the analysis of the Scatchard charts. In the systems with LiChrospher 4000 Si, a homogeneous AED is observed that means there is a strong, single, low-energy active center. In the system with MCM-41 and Silica gel 60, there are two well separated and different active sites of low and high energy. (Figure 4) presents the results collected for the system with 95% v/v of ACN and 5% v/v of H₂O for caffeine. Nonlinear Scatchard dependence is observed for MCM-41, Silica gel 60 and LiChrospher 4000 Si stationary phase. The non-linear Scatchard dependences correspond to heterogeneous distributions of the adsorption energy in the AED diagrams, the presence of two well-separated active centers is evident (Figure 5) presents the results collected for the system with solvent containing 95% v/v of MeOH and 5% v/v of H₂O for caffeine. Linear Scatchard dependence is observed for MCM-41, Silica gel 60 and LiChrospher 4000 Si stationary phase and AEDs are homogeneous. For LiChrospher 4000 Si, MCM-41 and Silica gel 60 stationary phases, for phenol in systems with methanol, similar results were obtained as in the system with acetonitrile (data not presented in this study).

It was observed that in systems where the AEDs are heterogeneous, the high energy adsorption sites (measured as the values of $\ln K_i$, i.e. the interaction energy of an analyte with a stationary phase) have low saturation capacities, q_s , resulting from the area under the AED peak. Thus, it seems that in these cases the main role in adsorption mechanism play the low energy active sites with much higher capacity.

Concluding Remarks

In this work, the adsorption behavior of phenol and caffeine as test analytes in different systems was analyzed. Besides, in order to accurately assess the phenomena observed in the experiments, the particle size distributions and chemical compositions (using the SEM-EDS method) were determined for adsorbents applied in the examined systems.

The conclusions resulting from the conducted research can be summarized as follows:

- (i) The obtained results confirms the possibility of presence of diverse active sites on surface of tested adsorbents,
- (ii) The heterogeneity of adsorbent surface may significantly affects the sorption mechanism in analyzed systems,
- (iii) In analyzed systems the main role in sorption mechanism play low-energy sites,
- (iv) The adsorption capacity of high-energy sites on tested adsorbents is relatively low,
- (v) The particle size distribution of tested adsorbents is het-

erogeneous (polydispersive), what may be affected both on the adsorption, mass transfer mechanisms and separation efficiency, (vi) One of the reasons for the observed energy heterogeneity of the tested adsorbents may be the presence of metals (Cr, Fe, Ni, Sn) on their surface, which may interact in different way with the components of the tested systems.

List of the More Important Symbols and Abbreviations

- ACN - acetonitrile
- C - sample concentration in fluid phase, g/dm³
- C_{min} and C_{max} - the lowest and the highest sample concentrations used in experiments, g/dm³
- d(0.9) - volume diameter where 90% of the particles is below, μm
- d(0.5) - median diameter, μm
- d(0.1) - volume diameter where 10% of the particles is below, μm
- d(3.2) - surface weighted mean diameter, μm
- d(4.3) - volume weighted mean diameter, μm
- D[4.3] - the volume weighted mean diameter, μm
- D[3.2] - the surface weighted mean diameter, μm
- f(lnK) - the adsorption energy distribution (AED)
- K_{min} = 1/10C_{max} - constant
- K_{max} = 1/C_{min} - constant
- MeOH - methanol
- q - solute concentration in the stationary phase, g/dm³
- q_s - saturation capacity, g/dm³
- SSA - external specific surface area, m²/g
- Wt., % - weight percent
- Greek Symbols
- θ(C, K) - the local adsorption model (usually the Langmuir model)
- Subscripts
- i - number of AED peak

Conflict of Interest

The authors have declared no conflict of interest.

Data Availability Statement

The authors confirm that the data supporting the findings of this study are available from the corresponding author upon reasonable request.

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