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Comparison of ordered mesoporous materials sorption properties towards amino acids

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Abstract The adsorption of amino acids such as L-phenylalanine and L-histidine was carried out on a series of mesoporous carbons obtained with the use ordered silicas KIT-6, SBA-16, SBA-15 as templates and furfuryl alcohol as carbon precursor. Small angle XRD analysis confirmed the ordered mesoporous structures of all materials obtained. They were also characterised by well-developed surface areas and high pore volumes. Adsorption behaviour of amino acids on ordered mesoporous carbons was investigated in potassium phosphate buffer solutions with adjustable L-phenylalanine and L-histidine concentration, ion strength, and pH. The highest sorption capacity towards the amino acids were observed at pH close to the isoelectric point of L-phenylalanine (pI = 5.48) and L-histidine (pI = 7.59). Electrostatic, hydrophobic and steric interactions had very strong effect on the adsorption of amino acids on mesoporous carbons. The amount of L-phenylalanine and L-histidine adsorbed decreased in the following sequence: $C_{KIT\text{-}6} > C_{SBA\text{-}16} > C_{SBA\text{-}15}$ that was strongly related to their structure, surface areas and average pore diameters.

Keywords Adsorption of L-phenylalanine · L-histidine · Amino acids · Mesoporous carbons · Furfuryl alcohol

1 Introduction

Amino acids, the components of protein, play an important role in many fields, including food industry and solid-phase peptide synthesis (Meng et al. 2004). They are also applied as building blocks for the production of pharmaceutical and agrochemical compounds (O'Connor et al. 2006). In order to make amino acids useful in the above mentioned fields, they should be placed on the surface of solid materials (Vinu et al. 2006), therefore they should be adsorbed. Additionally, the investigation on the adsorption of amino acids can provide important information on separation and purification of these biomolecules (Munsch et al. 2001). Furthermore, the molecular size and zwitterionic nature make amino acids an attractive adsorbate model.

So far the adsorption of amino acids has been investigated on diverse materials such as polymeric adsorbents, active carbon, zeolite, hydroxyapatite, zirconium phosphate, modified silica, silica-gels (Munsch et al. 2001; Vlasova and Golovkova 2004; Imamura et al. 2003; Krohn and Tsapatsis 2005; Palit and Moulik 2001; El Shafei and Moussa 2001; El Shafei 2002). The promising adsorbents are also ordered mesoporous materials because of their excellent physical and chemical properties (Kresge et al. 1992). These materials have high surface areas, narrow pore size distribution, controlled pore volumes and well-defined surface properties (Kresge et al. 1992; Vinu et al. 2003; Vinu et al. 2004; Zhao et al. 1998; Gao et al. 2007) which make them applicable in adsorption process of biomolecules such as amino acids. The adsorption of L-histidine onto porous materials such as SBA-15, CMK-3 and activated carbon has been carried out by Vinu et al. (Vinu et al. 2006). It has been found in this study that the highest amount of L-histidine was adsorbed on CMK-3 near the isoelectric point of the amino acid. O'Connor et al. have investigated the adsorption of lysine on MCM-41 (O'Connor et al. 2006). They proved that the extent of adsorption process strongly depends on the pH and ionic strength of the adsorbate solution because a combination of ion exchange and electrostatic interactions govern the

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adsorption process (O'Connor et al. 2006). Gao et al. (Gao et al. 2007) have investigated the adsorption of arginine (Arg) and phenylalanine (Phe), on a series of SBA-15 materials (such as SBA-15, CH_3 (10 %)-SBA-15, CH_3 (20 %)-SBA-15). They have found that the extent of arginine adsorption is influenced by pH value and the surface charge of adsorbents. The electrostatic interactions were mainly responsible for adsorption of this basic amino acid. However, the adsorption of Phe was strongly related to the degree of organic functionalization of adsorbent. Therefore, the adsorption capacity of phenylalanine was higher when the degree of CH_3-functionalisation on the surface of adsorbents increased (Gao et al. 2007). Similar results have been obtained for the adsorption of glutamic acid (Glu), arginine (Arg), and phenylalanine (Phe), leucine (Leu), and alanine (Ala) on SBA-15-type materials (Gao et al. 2008). It has been found that the adsorption of Glu and Arg on mesoporous silica could be controlled by pH, ion strength of solution and electrostatic property of adsorbents. On the other hand, it has been proved that the extent of adsorption of Phe, Ala and Leu can be increased by changing hydrophobicity of the solid material (Gao et al. 2008).

In spite of the great potential of mesoporous materials as proper adsorbents of amino acids, only a few of them have been investigated. Therefore, in this study, the adsorption of L-phenylalanine and L-histidine was carried out on a series of ordered mesoporous carbons, obtained with the use of ordered silicas as templates and furfuryl alcohol as carbon precursor. The aim of this research was to compare their sorption properties towards L-Phe and L-His that were chosen as representative amino acids.

2 Experimental

2.1 Synthesis of SBA-15, KIT-6, SBA-16 templates

2.1.1 SBA-15

The synthesis of SBA-15 was performed with the use of 0.5 g of triblock polyoxyethylene-polyoxypropylene-polyoxyethylene copolymer-Pluronic P123 (BASF), 19 ml of 1.6 M HCl (Chempur, 37 %) and 1.1 ml of TEOS (tetraethyl orthosilicate, 98 wt%, Aldrich). The copolymer was dissolved in a solution of hydrochloric acid at 35 °C. Then, to these reagents TEOS as a source of silicon was introduced dropwise under stirring for 8 h. The mixture was placed in a polypropylene bottle and heated in an oven for 24 h at 35 °C and for 6 h at 100 °C. After this time the material was filtered and dried at 100 °C K for 12 h. The template was removed by calcination in a furnace at 550 °C for 8 h in the air in static conditions (Zhao et al. 1998).

2.1.2 SBA-16

The synthesis was carried out according to the procedure proposed by Kim et al. (Kim et al. 2005a). The portions of 0.58 g of Pluronic P123 (BASF) and 2.9 g of Pluronic F127 (Aldrich) were dissolved in 160 ml of distilled water and 10 ml of hydrochloric acid (Chempur, 37 %) at 35 °C. Then, upon stirring 13 ml of TEOS (tetraethyl orthosilicate 98 wt%, Aldrich) was added. After that the mixture was placed in a polypropylene bottle and heated for 24 h at 35 °C and for 24 h at 100 °C in a furnace. The filtered off product was dried in the air at 100 °C for 3 h. The template was removed by calcination at 550 °C.

2.1.3 KIT-6

KIT-6 sample was prepared as follows: 4.0 g of Pluronic P123 (BASF) was dissolved in 144 g of distilled water and 7.9 g of hydrochloric acid (Chempur, 37 %) solution upon stirring at 35 °C (Kim et al. 2005b). After complete dissolution, 4.0 g of 1-butanol was added immediately. After 1 h stirring, 8.6 g of TEOS was added to the homogeneous clear solution. The mixture was kept under vigorous and continuous stirring at 35 °C for 24 h. Subsequently, the reaction mixture was aged at 100 °C for 24 h in static condition. The product was filtered off without washing and dried at 100 °C for 24 h in air oven. Finally, the sample was calcined at 550 °C in the air to remove the template.

2.2 Synthesis of mesoporous carbons

Mesoporous carbons were prepared by hard template method using ordered silicas as templates and furfuryl alcohol as carbon precursor. In a typical synthesis 0.535 ml of furfuryl alcohol (≥98 %, Aldrich) was uniformly infiltrated into ordered mesoporous silicas by incipient wetness impregnation at room temperature. The samples containing furfuryl alcohol were placed in an oven at 35 °C for 1 h and then at 100 °C for 1 h. The resultant polymer/SiO_2 composite samples were further heated under argon for 2 h at 350 °C at a heating rate of 1 °C/min. After the samples were cooled to room temperature, 0.268 ml of furfuryl alcohol was added. The samples were heated at 100 and 350 °C again. The carbonization procedure was performed at 900 °C (8 h) under argon at a heating rate of 2.5 °C/min. The composites obtained were washed with 5 wt% hydrofluoric acid (Chempur) at room temperature for 10 h, to remove the silica template. The carbon products were recovered after filtration, washing with water and ethanol, and drying at 90 °C. The resulting carbon samples contained only traces of silica (<1 %) and were labelled as $C_{SBA\text{-}15}$, $C_{SBA\text{-}16}$, $C_{KIT\text{-}6}$.

2.3 Sample characterization

2.3.1 Powder X-ray diffraction (XRD)

The materials prepared were characterized by X-ray diffraction (XRD) using a D8 Advance diffractometer (Bruker) (CuK_α radiation, $\lambda = 0.154$ nm), with a step size 0.02° in the low-angle range.

2.3.2 Transmission electron microscopy (TEM)

For TEM measurements, powdered samples were deposited on a grid with a perforated carbon film and transferred to a JEOL 2000 electron microscope operating at 80 kV.

2.3.3 Nitrogen sorption

Characterization of the pore structure of samples obtained was performed on the basis of low-temperature nitrogen adsorption–desorption isotherms measured on a sorptometer Quantachrome Autosorb iQ. Prior to adsorption measurements, the samples were degassed in vacuum at 300 °C for 2 h. Surface area and pore size distribution were calculated by BET and BJH methods, respectively. Total pore volume and average pore diameter were determined as well.

2.4 Amino acids adsorption process

In adsorption experiments, a series of L-phenylalanine and L-histidine solutions with concentrations ranging from 0.5 to 70 mmol/l were prepared by dissolving different amounts of amino acids in potassium phosphate buffer solutions (pH 5.6–9.4). In each adsorption experiment, 25 mg of adsorbents was suspended in 5 ml of the amino acid solution. At first the time dependence of L-phenylalanine and L-histidine adsorption onto all mesoporous materials was investigated to determine the time required for equilibrium to be reached between the solid and solution. After a chosen contact time (typically 24 h) the resulting mixture was continuously shaken in a shaking bath at 20 °C. The amount of amino acid adsorbed was calculated by subtracting the amount found in the supernatant liquid after adsorption from the amount of amino acid present before addition of the adsorbent by UV absorption at the λ_{max} of L-Phe, 257 nm and at the λ_{max} of L-His, 208 nm.

3 Results and discussion

3.1 Structural characteristics of mesoporous materials

XRD patterns in the low-angle range of mesoporous carbons obtained with the use ordered silicas as templates and furfuryl alcohol as carbon precursor, are shown in Fig. 1. The profile of $C_{SBA\text{-}15}$ indicates three well-developed reflections corresponding to the planes (100), (110) and (200), evidencing that a very ordered hexagonal lattice of mesopores was obtained as expected. The XRD pattern of $C_{SBA\text{-}16}$ shows a narrow single peak centered at $2\Theta \approx 0.9°$ corresponding to the plane (110) which confirms the cubic structure. The XRD profile of $C_{KIT\text{-}6}$ reveals a well-developed and highly intense peak at $2\Theta \approx 1°$ corresponding to the plane (211) and reflections in the range $2\Theta \approx 1.5$–$1.9°$, testifying to a highly ordered cubic structure.

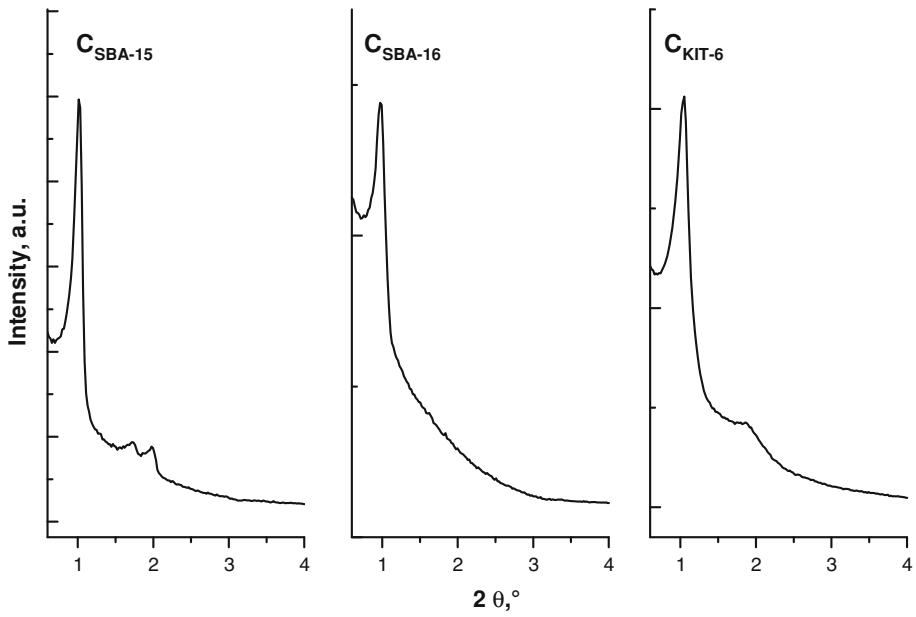

Fig. 1 Low-angle X-ray diffraction patterns of ordered mesoporous carbons

TEM images presented in Fig. 2 confirm that all materials synthesised have mesoporous ordered structures.

All samples were subjected to nitrogen adsorption/desorption measurements and for all of them type IV adsorption–desorption isotherms according to IUPAC classification were observed. These isotherms are characteristic of mesoporous solid, (Fig. 3). The isotherms of C_{SBA-15}, C_{SBA-16} and C_{KIT-6} show H1 hysteresis loops.

The textural parameters of mesoporous materials presented in Table 1 influence their sorption capacity towards amino acids. All carbons obtained have well-developed surface areas. Sample C_{KIT-6} was characterised by the highest pore volume (1.02 cm^3/g) and pore diameter (4.13 nm), which can indicate its greatest sorption capacity towards large biomolecules. The smallest pore volume of 0.97 cm^3/g and pore diameter of 3.29 nm were found for sample C_{SBA-15}.

3.2 Amino acids adsorption

All ordered mesoporous carbons obtained were tested in the process of L-phenylalanine and L-histidine adsorption.

The time dependence of L-Phe and L-His adsorption on the samples investigated was used to determine the time required for equilibrium to be reached between solid and solution. The amount of amino acids adsorbed increased with contact time, reaching equilibrium within 24 h for C_{SBA-15}, C_{SBA-16} and C_{KIT-6} (Fig. 4). The amount of L-Phe and L-His adsorbed was monitored for longer contact times with amino acids solution. The sorption capacity of carbon samples studied was found not to change upon contact with L-phenylalanine and L-histidine solutions for 100 h.

Figures 5 and 6 present the equilibrium isotherms of adsorption of L-Phe and L-His onto C_{KIT-6}, C_{SBA-15}, C_{SBA-16} mesoporous carbons at different buffer solution pH ranging

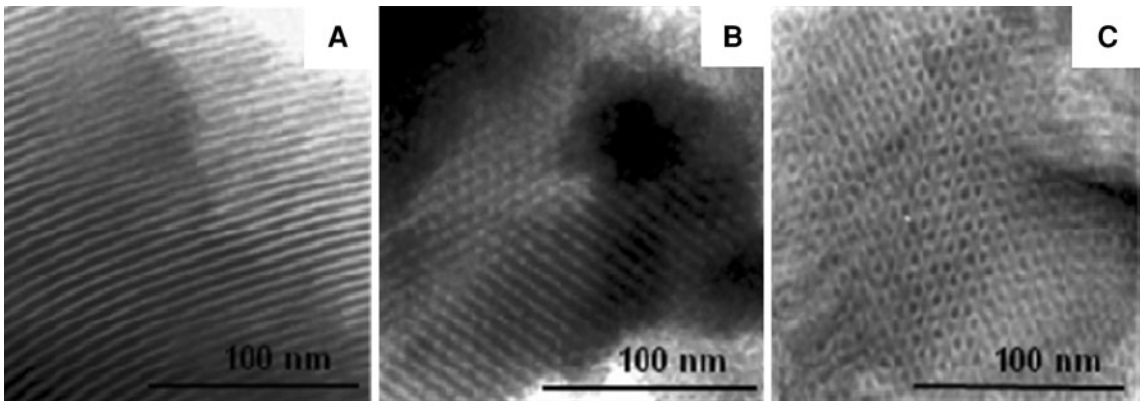

Fig. 2 TEM images of C_{SBA-15} (**a**), C_{SBA-16} (**b**) and C_{KIT-6} (**c**)

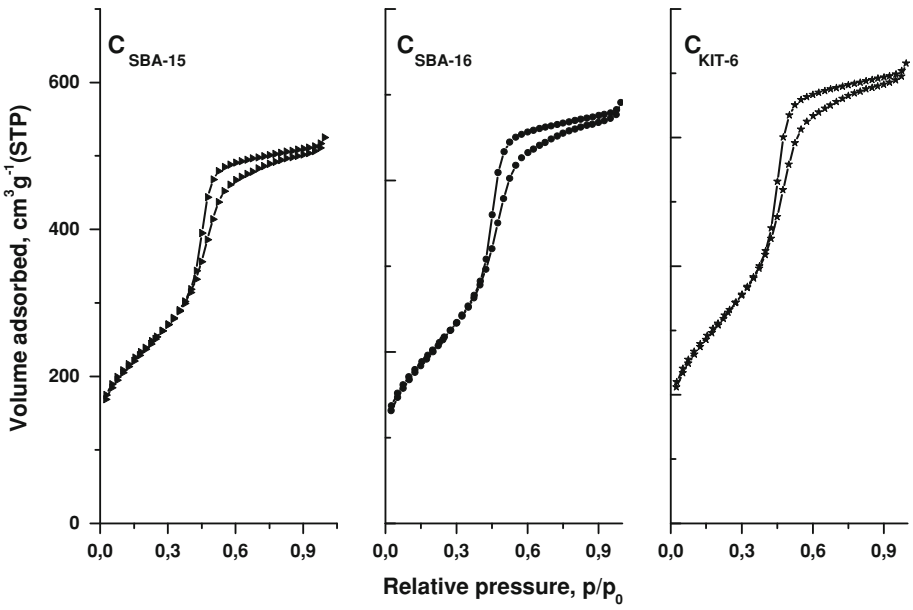

Fig. 3 Nitrogen adsorption isotherms of mesoporous materials

Table 1 Textural parameters of mesoporous materials

Sample	Total surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
C_{KIT-6}	1,210	1.02	4.13
C_{SBA-16}	1,101	0.98	3.62
C_{SBA-15}	1,074	0.97	3.29

from 5.6 to 9.4. The amount of adsorption is given in micromoles of amino acid per gram adsorbents measured at 20 °C. All isotherms are Type L (Langmuir isotherms). The amount of amino acid adsorption significantly increases with increasing initial concentration of both L-phenylalanine and L-histidine solution. At low concentrations of the buffer solutions the amino acid adsorption on the surface of the materials studied is a random process. With increasing concentration the nonpolar functional groups of two or more amino acids approach each other at the closest distance allowed by their van der Waals radii leading to close packing of amino acids on the adsorbents surface. Additionally, it was found that extent of L-Phe and L-His adsorption was related to the pH value of the adsorbing solution. The carbon materials showed the highest sorption capacity towards L-phenylalanine, at pH 5.6, which is relatively close to the isoelectric point of this amino acid (pI = 5.48). The highest sorption capacities were 1,856 μmol/g for C_{KIT-6}, 1,734 μmol/g for C_{SBA-16} and 1,656 μmol/g for C_{SBA-15}. The coulomb repulsion of L-phenylalanine molecules at pH close to the isoelectric point is minimum, which determines the highest sorption capacity at this pH. Above pH 5.6 the amount of adsorbed amino acid decreases. As follows from the low-temperature nitrogen adsorption measurements, the surface areas and pore volumes of the carbon materials significantly decrease after adsorption of L-phenylalanine. For sample C_{KIT-6} after loading with 1,856 μmol/g of L-phenylalanine, the surface area was reduced from 1,210 to 732 m^2/g, while the pore volume from 1.02 to 0.60 cm^3/g. For the other samples after adsorption of amino acid, the surface area decreased from 1,101 to 689 m^2/g for C_{SBA-16}, and from 1,074 to 656 m^2/g for C_{SBA-15}. Pore volume decreased from 0.98 to 0.56 cm^3/g for C_{SBA-16}, while from 0.97 to 0.53 cm^3/g for C_{SBA-15}. Such a significant decrease in the surface area and pore volume of mesoporous carbons can be attributed to the tight packing of amino acid molecule in the mesopores of materials.

The greatest sorption capacity towards L-histidine were observed at pH 7.5, which is also close to the isoelectric point of this amino acid (pI = 7.59). In these conditions, the electrostatic interactions between host and guest are negligible that enables more intensive adsorption of biomolecules when compared to the other pH ranges. In the range of equilibrium concentration, the adsorption capacities towards L-His of the various ordered carbons at pH 7.5 change in the following order: C_{KIT-6} (1,602 μmol/g) > C_{SBA-16} (1,447 μmol/g) > C_{SBA-15} (1,332 μmol/g). Similarly as after adsorption of L-phenylalanine, also after adsorption of L-histidine the surface area of C_{KIT-6} decreased to 889 m^2/g, while those of samples C_{SBA-16} and C_{SBA-15} decreased to 823 and 756 m^2/g. The pore volume of the samples also decreased as a result of adsorption.

Due to the tight packing of the amino acid molecules in the mesopores, the differences in pore volumes of the adsorbents would result in different adsorption capacities. A comparison between three-dimensional cubic C_{KIT-6} with C_{SBA-16} reveals that a decrease in the pore volume by ca. 3.9 % causes a decrease in the adsorption capacity towards L-His (at pH = 7.5) of ca. 9.7 % and towards L-Phe (at pH = 5.6) of ca. 6.6 %. However, the adsorption capacity loss as high as 7.9 % for L-His and 4.5 % for L-Phe is observed as corresponding to a pore volume decrease as low as 1 % when C_{SBA-15} (two-dimensional hexagonal) is compared with C_{SBA-16}.

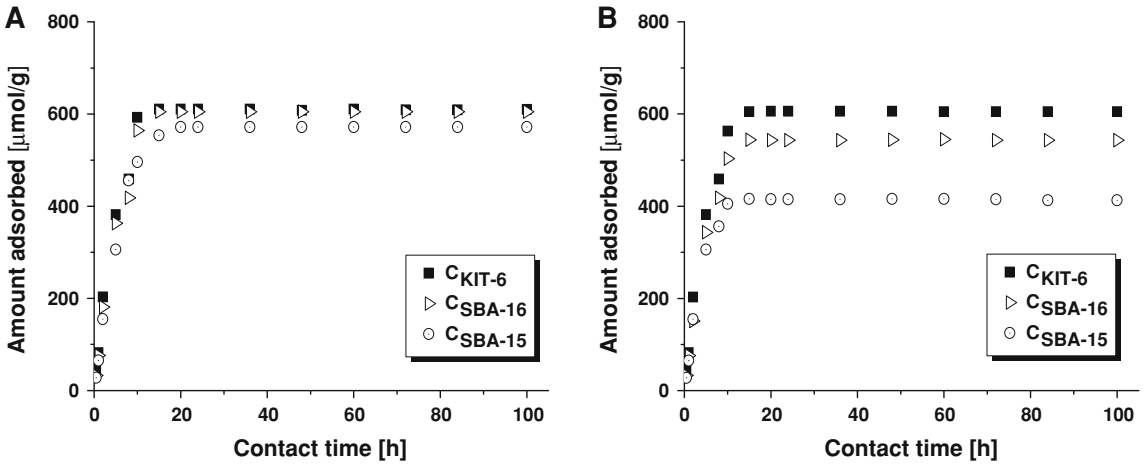

Fig. 4 Amount of L-phenylalanine (**a**) and L-histidine (**b**) adsorbed onto mesoporous carbons as a function of contact time (initial solution concentration of amino acids—5 mmol/l)

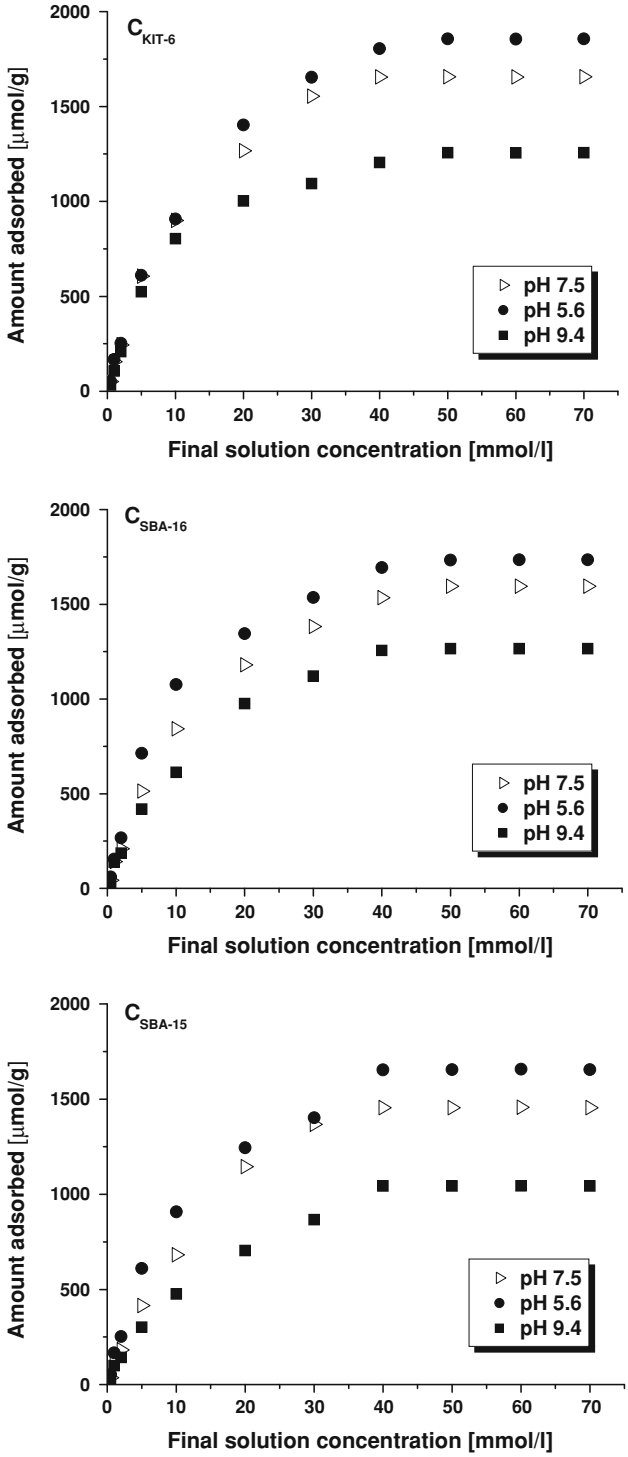

Fig. 5 Adsorption isotherms of L-phenylalanine on ordered mesoporous carbons at various pH conditions

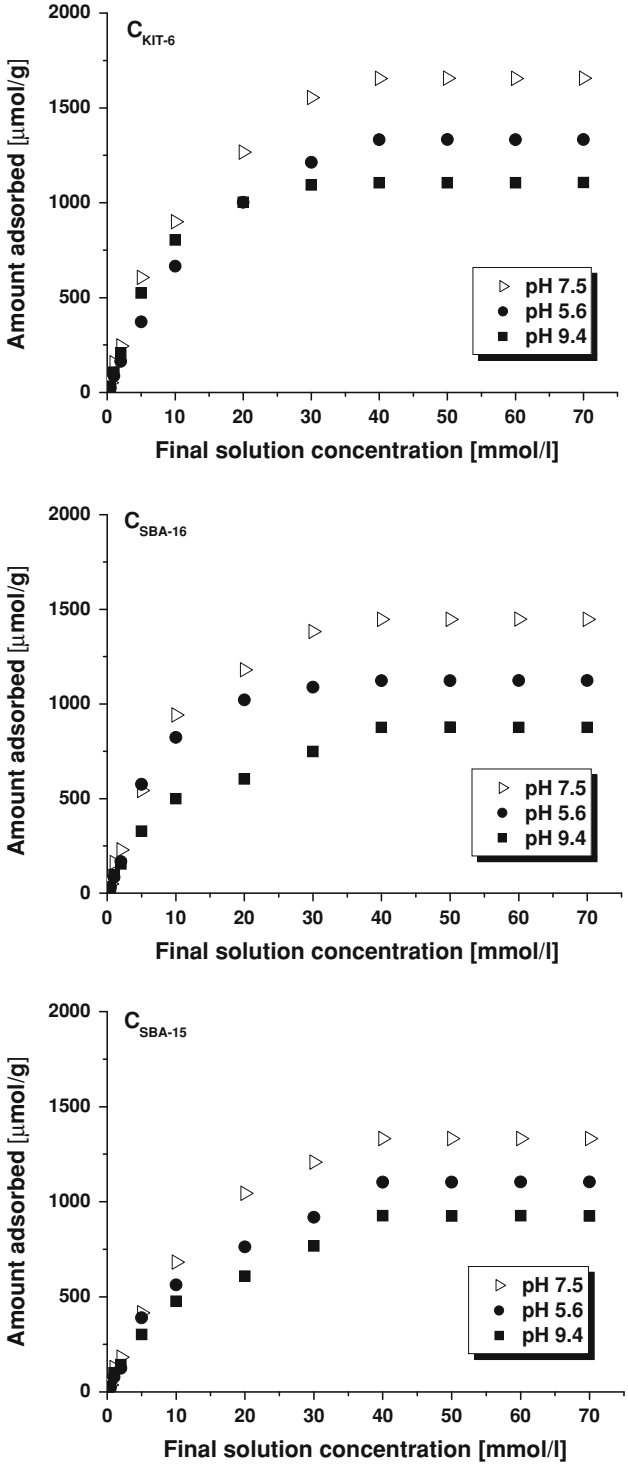

Fig. 6 Adsorption isotherms of L-histidine on ordered mesoporous carbons at various pH conditions

Moreover, it was found that electrostatic and hydrophobic interactions are very important in amino acid adsorption on mesoporous molecular sieves. According to O'Connor et. al (O'Connor et al. 2006) the extent of adsorption is strongly related to the pH and ionic strength of the adsorbate solution because of, a combination of ion exchange and electrostatic interactions governing the adsorption process.

In order to investigate the influence of ionic strength, L-Phe and L-His adsorption isotherms were determined at

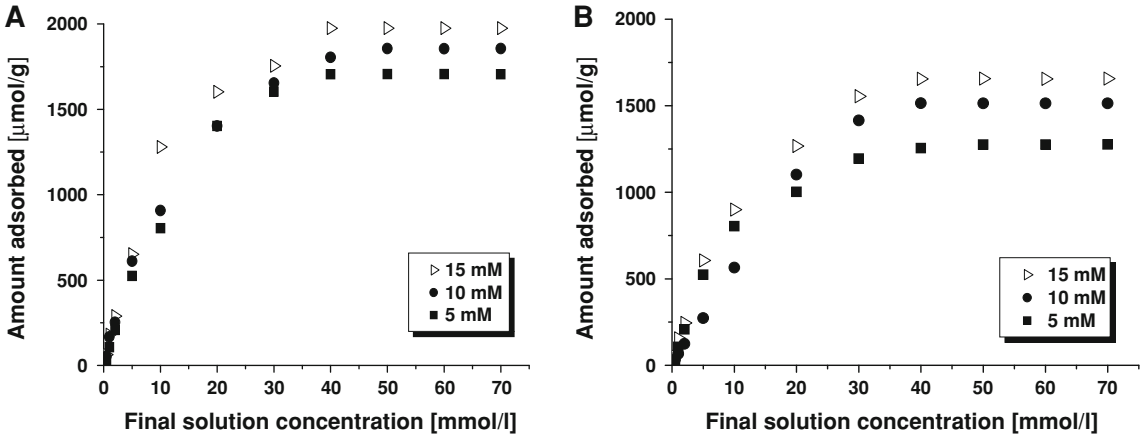

Fig. 7 L-Phe (**a**) and L-His (**b**) adsorption isotherms on $C_{KIT\text{-}6}$ mesoporous carbon at different ionic strengths

different concentrations of phosphate buffer (5, 10, 15 mM) at pH close to the isoelectric points of the amino acids studied. The amount of amino acids adsorbed on $C_{KIT\text{-}6}$ increases with increasing concentration of the buffer (Fig. 7). A similar relation was observed for $C_{SBA\text{-}15}$ and $C_{SBA\text{-}16}$ samples. Vinu et al. (Vinu et al. 2006) have proposed the following interpretation of this behaviour. When the concentration of buffer increases, the repulsive electrostatic interactions between the phosphate ions increase, thereby increasing the interaction between the amino acid molecule and can then operate toward aggregation. Consequently, the amount of amino acid adsorbed onto mesoporous carbon is increased. Furthermore it should be mentioned that at pH close to isoelectric point (of L-Phe or L-His) the hydrophobic interactions between the appropriate amino acid and the surface of mesoporous material and the intra-molecular interaction between amino acids molecules are generally high. Thus, the close packing of either L-Phe or L-His on the mesopores of the adsorbents (near the pI) can be explained.

4 Conclusion

A series of mesoporous carbons was obtained by hard template method with the use of ordered silicas KIT-6, SBA-16, SBA-15 as matrices and furfuryl alcohol as carbon precursor. The structural and textural properties of the carbon materials have been studied by XRD and nitrogen adsorption. The occurrence of ordered mesoporous structure of all the materials studied was confirmed. The materials were also characterised by well-developed surface area and large pore volume. The adsorption of L-phenylalanine and L-histidine on the mesoporous carbons follows the Langmuir type isotherm with a maximum capacity at pH close to the isoelectric points of these amino acids. The strength of coulomb repulsive interactions between amino acid molecules at a pH close to the isoelectric point is minimum, which means that at this pH the sorption capacity of the ordered mesoporous carbons is the greatest. The amount of L-phenylalanine and L-histidine adsorbed decreases in the following sequence: $C_{KIT\text{-}6} > C_{SBA\text{-}16} > C_{SBA\text{-}15}$ that was strongly related to their structure, surface area and average pore diameter. Adsorption of amino acids on mesoporous carbon samples studied led to a decrease in their surface area and pore volume.

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