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Modification of carbon sorbent by sequential adsorption of biologically active phenylalanine and salicylic acid

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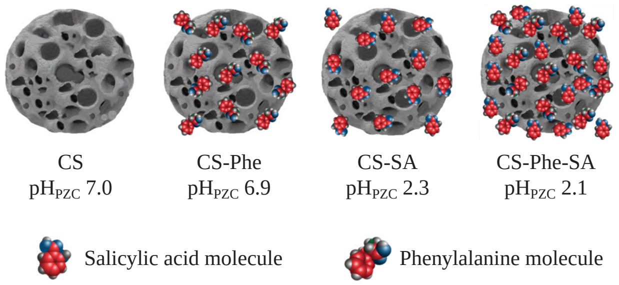
The sequential adsorption of phenylalanine and salicylic acid on a carbon sorbent was studied. The influence of modification conditions, including the sorbent/solution volume ratio, amino acid concentration, temperature and pH, on the adsorption parameters of phenylalanine, as well as the physicochemical properties of the resulting carbon sorbent sample, was established. The effect of sequential adsorption of phenylalanine and salicylic acid on the physicochemical characteristics of sorbents is shown.



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Targeted changes in the physicochemical and adsorption properties of materials are feasible using various methods of their modification.[1–5] Selection of the conditions for the adsorption process of substances of different nature makes it possible to regulate the amount of added substance and introduce several components, sequentially or simultaneously. Successive introduction of modifiers can lead to increased adsorption efficiency.[1–4]

This communication presents the results of a study on the sequential adsorption of an amino acid (phenylalanine) and a carboxylic acid (salicylic acid) onto a mesoporous carbon sorbent (for details, see Online Supplementary Materials). The substances used are biologically active and have anti-inflammatory, antitumor and antimicrobial properties.[6] It is known that salicylic acid is actively used as a component of biodegradable composite films with antibacterial action.[7,8]

The adsorption of amino acids and pharmaceutical compounds has attracted much attention due to its scientific importance and application in many industries, including food, cosmetics, medical, biochemical and others, with the aim of developing new dosage forms and selective adsorbents.[9–11] There are various data in the literature on the adsorption of phenylalanine[10–13] and salicylic acid[14–17] from individual solutions by materials of various natures. In the cited study,[18] phenylalanine was used as a pectin hydrogel modifier to create a long-acting drug carrier. The grafting of phenylalanine onto the surface of chitosan increases antioxidant activity and improves its biocompatibility as a promising biomaterial for the food industry.[19]

Table 1 Effect of the volume ratio of sorbent/phenylalanine solution on adsorption parameters.

Entry	Sorbent/solution volume ratio	Adsorption value/ mg g^{-1}	Time to equilibrium/h
1	1:10	32.1	3
2	1:25	58.6	3
3	1:50	68.9	24

The influence of the sorbent/solution volume ratio on adsorption parameters was studied under the following conditions: phenylalanine concentration 2000 mg dm^{-3}, static conditions (constant stirring), natural pH and temperature 25 °C (Table 1).

From the data obtained it follows that the maximum adsorption of phenylalanine from an aqueous solution onto the carbon sorbent is observed at a volume ratio of 1:50. The increase in adsorption with increasing volume of phenylalanine solution in contact with the carbon material is associated with a decrease in competition between amino acid molecules for adsorption sites on the surface of the adsorbent.

With the established volume ratio of 'sorbent/amino acid solution' of 1:50, the time to reach equilibrium (the time after which no increase in adsorption is observed) in the system was 24 h.

The influence of adsorption conditions (without shaking or with constant shaking) on its parameters was studied (Table 2).

The results obtained indicate that shaking does not have a significant effect on the adsorption parameters. This means that the diffusion of substance molecules from the volume to the outer surface of the carbon sorbent is extremely small and can be neglected in the future.

The effect of temperature on the amount of phenylalanine adsorption on the carbon sorbent was studied (Figure 1).

With increasing temperature, a decrease in the equilibrium adsorption of phenylalanine is observed. This indicates the exothermic nature of the adsorption of the amino acid on the carbon sorbent. The process is reversible and occurs due to van der Waals interactions characteristic of physical adsorption.[20]

Table 2 Conditions for the adsorption of phenylalanine on the carbon sorbent.

Entry	Adsorption conditions	Adsorption value/ mg g^{-1}	Extraction degree (%)
1	Without shaking	66.1	38
2	With shaking	68.9	42

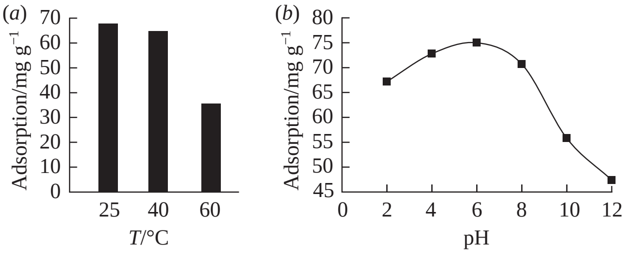

Figure 1 The amount of phenylalanine adsorption on the carbon sorbent depending on (*a*) the temperature and (*b*) pH of the solution.

The effect of pH on the adsorption parameters of phenylalanine is shown in Figure 1(*b*). Maximum amino acid adsorption is observed at pH 4–6. At pH < 2, the surface of the carbon sorbent and the phenylalanine molecules are positively charged, which leads to electrostatic repulsion and a decrease in the amount of adsorbed amino acid. At pH 4–6, the amino acid has both a positive and negative charge, and the electrostatic attraction between the protonated amino groups and the negatively charged carbon surface promotes adsorption. In the pH range of 8–12, the decrease in adsorption capacity occurs due to the repulsion of negatively charged surfaces of the carbon sorbent and phenylalanine molecules from each other.

The adsorption of phenylalanine from an aqueous solution onto the carbon sorbent was studied in the concentration range of 100–2500 mg dm^{-3} under previously established optimal static conditions with the sorbent/solution volume ratio of 1:50, temperature of 25 °C, pH 4–6 and 24-h time to equilibrium. The dependence of the adsorption of phenylalanine on the carbon sorbent on its concentration was determined [Figure 2(*a*)].

A direct proportional relationship is observed: with increasing concentration of phenylalanine, the amount of amino acid adsorbed on the carbon sorbent increases. At maximum phenylalanine concentrations of 2000 and 2500 mg dm^{-3}, no significant increase in adsorption is observed. The maximum amount of amino acid (69.6 mg g^{-1}) is adsorbed from a phenylalanine solution with a concentration of 2000 mg dm^{-3}.

The adsorption curve of phenylalanine on the carbon sorbent, constructed from experimental data, belongs to type L2 according to the Giles classification of adsorption isotherms from solutions on a solid surface.[21,22]

The adsorption characteristics of the carbon sorbent with respect to the adsorption of phenylalanine were calculated using the Langmuir monomolecular adsorption equation and the Freundlich equation (Table 3).

It has been shown that for the carbon sorbent in the range of equilibrium phenylalanine concentrations of 1.0–1586.0 mg dm^{-3}, the adsorption isotherm is described by the Langmuir equation.

As a result of the adsorption of phenylalanine on the carbon sorbent from an aqueous solution with a concentration of 2000 mg dm^{-3}, a sample of the carbon sorbent with pre-adsorbed phenylalanine (CS-Phe) was obtained.

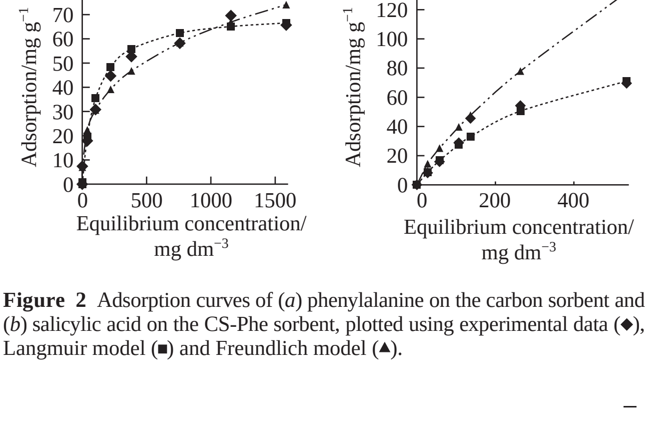

Figure 2 Adsorption curves of (*a*) phenylalanine on the carbon sorbent and (*b*) salicylic acid on the CS-Phe sorbent, plotted using experimental data (◆), Langmuir model (■) and Freundlich model (▲).

Table 3 Parameters of the Langmuir and Freundlich equations for the adsorption of phenylalanine by the carbon sorbent.[a]

Entry	Equation	a_{th}/mg g^{-1}	K_{L}/dm^3 mg^{-1}	K_{F}/mg$^{1-1/n}$ g^{-1} dm$^{3/n}$	1/*n*	r^2
1	Langmuir	70.9	0.01			0.991
2	Freundlich	74.1		6.82	0.324	0.976

[a] Here, a_{th} is the maximum theoretical adsorption value, K_{L} is the Langmuir constant, K_{F} is the Freundlich constant, *n* is the correction factor in the Freundlich equation, and r^2 is the correlation coefficient.

The adsorption of salicylic acid on the CS-Phe sorbent from an aqueous solution in the concentration range of 100–1500 mg dm^{-3} was studied under static conditions at a sorbent/solution volume ratio of 1:50, temperature of 25 °C, pH 2 and 24-h time to equilibrium. The resulting adsorption isotherm of salicylic acid on CS-Phe is presented in Figure 2(*b*). From the adsorption curve it is clear that with increasing salicylic acid concentration, the adsorption value increases. The maximum amount of adsorbed salicylic acid on the CS-Phe sorbent was 69.6 mg g^{-1}.

The adsorption characteristics of the CS-Phe sorbent with respect to the adsorption of salicylic acid were determined using the Langmuir monomolecular adsorption equation and the Freundlich equation. It has been shown that for the CS-Phe sorbent in the equilibrium concentration range of 27.5–534.4 mg dm^{-3}, the adsorption isotherm of salicylic acid is described by the Langmuir equation with the parameters $a_{\mathrm{th}} = 71.1$ mg g^{-1}, $K_{\mathrm{L}} = 0.0029$ dm^3 mg^{-1} and $r^2 = 0.981$. According to the Giles classification of adsorption isotherms from solutions on a solid surface, the experimental curve of adsorption of salicylic acid on the CS-Phe sorbent corresponds to type L1.[21,22]

As a result of the adsorption of salicylic acid on the CS-Phe sorbent from an aqueous solution with a concentration of 1500 mg dm^{-3}, a CS-Phe-SA sample was obtained.

A comparison of the adsorption capacity of various adsorbents found in the literature and the studied carbon sorbent CS showed that in adsorption properties with respect to phenylalanine it is superior to activated carbon from sunflower meal functionalized with sulfo groups,[23] activated defective coffee beans[20] and spherical carbon aerogels[24] by 1.1–2.7 times, and with respect to salicylic acid, it is 1.2–3.0 times superior to activated carbon cloth,[25] pine wood biochar[26] and wheat straw biochar.[26] At the same time, there is no data in the literature on the sequential adsorption of phenylalanine and salicylic acid on any materials.

The concentration of oxygen-containing groups on the surface of the studied carbon sorbents was determined by the Boehm titration method (Figure 3). There is a natural increase in the concentration of oxygen-containing groups by 1.4–1.6 times due to the applied modifiers. As it turned out, the nature of the modifier affects the quantitative ratio of oxygen-containing surface groups.

The textural characteristics of carbon sorbents were determined by the method of low-temperature nitrogen adsorption (Table 4). In the process of sequential adsorption of components, a decrease in the specific surface area by 2.1 times is observed, but the predominance of mesopores remains.

It was found that when the CS-Phe sorbent comes into contact with an aqueous solution for 48 h, desorption of phenylalanine does not occur, and the specific surface area (S_{BET}) of the sorbent after desorption (CS-Phe-D) was 207 m^2 g^{-1}.

Salicylic acid desorption from the CS-Phe-SA sample into ethanol and model solutions was studied by spectrophotometry (Table 5). It was established that salicylic acid passes into both aqueous and alcoholic solutions, reaching within 24 h a concentration of ~10% of the initial concentration in an aqueous solution of salicylic acid before adsorption. As a result of desorption, acidification of the solutions to pH 2–4 is observed due to the transition of the modifier into the solution.

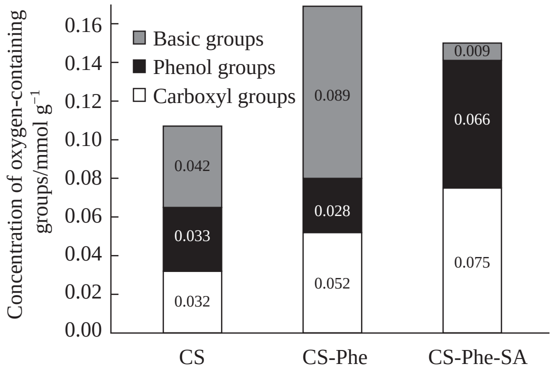

Figure 3 Concentration of oxygen-containing groups on the surface of carbon sorbents.

Table 4 Changes in the textural characteristics of the CS sorbent as a result of sequential adsorption of phenylalanine and salicylic acid.

Entry	Sorbent	Specific surface area S_{BET}/m^2 g^{-1}	Pore volume/cm^3 g^{-1}			Average pore size/nm
			Total	Mesopores	Micropores	
1	CS	311	0.294	0.253	0.041	4
2	CS-Phe	180	0.238	0.238	-	5
3	CS-Phe-SA	146	0.198	0.198	-	5

Using the pH drift method,[27,28] the pH values at the point of zero charge (pH$_{PZC}$) of carbon sorbents CS, CS-Phe and CS-Phe-SA after adsorption were determined to be 7.0, 6.9 and 2.1, respectively. It was previously established that the CS-SA sorbent is characterized by a pH$_{PZC}$ of 2.3.[29] From the presented data it follows that the absorption of salicylic acid leads to a shift in pH to the ‘acidic’ region, which is due to the acidic nature of salicylic acid itself. Adsorption of phenylalanine from an individual solution and with salicylic acid does not significantly affect the pH$_{PZC}$ value of the carbon sorbent.

The process of applying a carbon sorbent by sequential adsorption of components makes it possible to purposefully regulate the physicochemical and adsorption properties of the materials being developed.

Thus, it has been shown that the adsorption curves of both phenylalanine in the range of equilibrium concentrations of 1.0–1586.0 mg dm^{-3} on the intact carbon sorbent, and salicylic acid in the range of equilibrium concentrations of 27.5–534.4 mg dm^{-3} on the carbon sorbent with pre-adsorbed phenylalanine are described by the Langmuir equation. Phenylalanine does not desorb into aqueous solution within 48 h. Salicylic acid passes into model solutions in an amount of ~10% in 24 h. The physicochemical properties of carbon sorbent samples after adsorption of modifiers were studied. The specific surface area for carbon sorbents CS-Phe and CS-Phe-SA is 180 and 146 m^2 g^{-1}, respectively. The concentration of oxygen-containing groups on the surface of CS-Phe and CS-Phe-SA was measured to be 0.169 and 0.150 mmol g^{-1}, respectively. The pH value of the point of zero charge of the carbon sorbent is 6.9 after the adsorption of phenylalanine and 2.1 after the sequential adsorption of phenylalanine and salicylic acid.

Table 5 Data on salicylic acid desorption from the CS-Phe-SA sample into model solutions.

Entry	Model solution	Concentration of salicylic acid after desorption/mg dm^{-3}	pH	
			Initial	After desorption
1	EtOH	148	8.1	4.4
2	HCl	140	1.7	2.0
3	$NaHCO_3$	150	8.5	3.3

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.04.021.

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