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Comparative analysis of the adsorption properties of a carbon sorbent modified with sulfosalicylic acid solutions in the presence and absence of amino acids

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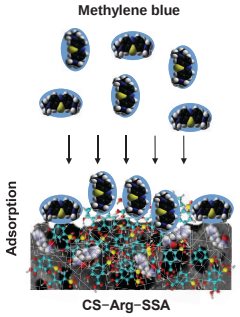
The adsorption properties of a carbon sorbent in relation to sulfosalicylic acid in an individual solution and with an added amino acid (arginine or phenylalanine) were determined. It has been shown that the addition of arginine to an aqueous solution of sulfosalicylic acid leads to an increase in the amount of sulfosalicylic acid adsorbed on the carbon sorbent. The sorbents modified in the presence of amino acids showed high adsorption capacity for the methylene blue dye.



Keywords: carbon sorbent, sulfosalicylic acid, arginine, phenylalanine, modification, physicochemical properties.

5-Sulfosalicylic acid (SSA) belongs to the class of aromatic phenolic acids and combines the properties of carboxylic acids and phenols.[1] There are only a few studies in the literature focusing on SSA, especially its adsorption–desorption properties.[2] SSA is known to have complexing and antibacterial properties; it is used in organic synthesis, analytical chemistry and biochemistry.[1,3–5] Therefore, its application as a biologically active substance for the development of pharmaceuticals is of great interest.

It has been found that toxicity of initial aqueous solutions of SSA increases with increasing its concentration; in connection with this, high concentrations of this preparation are not used in medical practice. However, applying SSA as a modifier to a solid or polymer matrix will solve this problem.

The most promising solution is to use a carbon sorbent as a support. Carbon materials are the promising supports for the immobilization and delivery of biologically active substances due to their large surface area for adsorption, biocompatibility and inertness, insolubility in biological media and availability.[6–8]

It has been shown that the presence of amino acids stabilizes acetylsalicylic acid derivatives and enhances their biospecific properties.[9,10] Amino acids such as arginine and phenylalanine are of greatest interest for research due to their availability, solubility in aqueous solutions and the possibility of quantification by spectrophotometric method.[9,10]

In this work, it is proposed to consider SSA as a promising modifier of a carbon sorbent and to evaluate the effect of adding amino acids on the adsorption of SSA on this sorbent and desorption from it.

The purposes of this work are (i) to evaluate the effect of the sulfo group on the adsorption–desorption properties in carbon sorbent–modifier systems both in individual solutions of SSA and in the presence of amino acids (arginine and phenylalanine), (ii) to investigate the properties of carbon sorbent samples, selected before and after modification as well as after desorption, using various physicochemical methods and (iii) to determine the adsorption properties of the test samples in relation to model toxic substances (methylene blue and metanil yellow).

The research results will make it possible to select modification conditions, obtain the most promising sample for practical application and predict the efficiency of the developed materials for their further use in medical practice.

The results obtained show that SSA is adsorbed better and more completely than salicylic acid.[11,12] Presumably, the solubility of these phenolic acids in water, which is higher for SSA compared to salicylic acid due to the presence of a sulfo group, plays a key role. When adding phenylalanine, the time to establish equilibrium in the CS–Phe–SSA system is 1–4 and 24 h in the SSA concentration ranges of 100–250 and 500–3000 mg dm^{-3}, respectively. In the process, the maximum adsorption of SSA is 91.6 mg g^{-1}. In the case of arginine, the time to establish equilibrium in the CS–Arg–SSA system is 24 h in the SSA concentration range of 100–3000 mg dm^{-3}. The maximum adsorption of SSA on the carbon sorbent in the presence of arginine is 29.13 mg g^{-1} higher than in the presence of phenylalanine and is equal to 120.7 mg g^{-1}.

Under the selected experimental conditions (sorbent/solution volume ratio 1 : 50, contact time 24 h, temperature 25 °C, pH 2, static conditions), concentration dependence curves of SSA adsorption on the carbon sorbent from an individual solution (Figure 1, curve *1*) and in the presence of arginine (curve *2*) or phenylalanine (curve *3*) were obtained.

It was shown that the shape of the experimental curve for the adsorption of SSA on the carbon sorbent from an individual solution (CS–SSA system; see Figure 1, curve *1*) corresponds to the class of Langmuir isotherms (L2 according to the classification of C. H. Giles).[13]

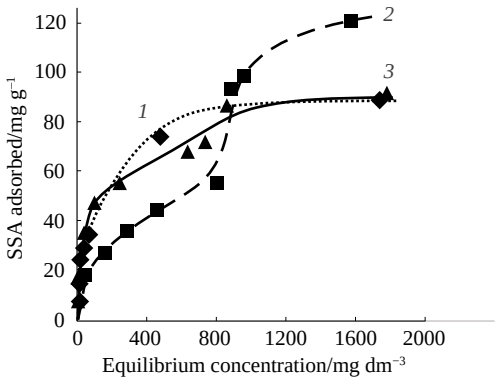


Figure 1 Concentration dependence curves of SSA adsorption on the carbon sorbent (*1*) from individual solutions and in the presence of (*2*) arginine or (*3*) phenylalanine.

In the presence of phenylalanine in solution, the adsorption curve in the CS–Phe–SSA system remains virtually unchanged compared to the CS–SSA system. However, the shape of the SSA adsorption curve changes when arginine is added to the solution (CS–Arg–SSA system), with the amount of SSA adsorbed increasing by 55%. Arginine and SSA are jointly adsorbed from solution onto the carbon sorbent via a donor–acceptor mechanism. In this interaction, no steric hindrance is observed, in contrast to the adsorption of phenylalanine and SSA molecules.

The adsorption of SSA by the carbon sorbent from an individual solution proceeds with the formation of a monolayer and is described by the Langmuir equation with values of maximum theoretical adsorption (a_{theor}) of 90.1 mg g^{-1}, the Langmuir constant (K_L) of 0.021 dm^3 mg^{-1} and correlation coefficient of 0.996.[14]

Our calculations revealed that in the presence of phenylalanine, the experimental curve for SSA adsorption on the carbon sorbent in the equilibrium concentration range of 1.9–1780.0 mg dm^{-3} is better described by the Freundlich equation (correlation coefficient $R^2 = 0.99$) than by the Langmuir equation (correlation coefficient $R^2 = 0.98$). Therewith, in the Freundlich equation, the maximum theoretical amount of adsorption was 92.8 mg g^{-1}, the Freundlich constant K_F was 15.481, and the parameter $1/n$ was 0.239.

It is noteworthy that in the region of low initial SSA concentrations of 100–500 mg dm^{-3} in the presence of phenylalanine with a concentration of 2000 mg dm^{-3}, an adsorption peak of phenylalanine is observed in the spectra. At SSA concentrations above 500 mg dm^{-3}, the phenylalanine adsorption peak may overlap with the SSA signal.

Thus, when phenylalanine is adsorbed in the presence of SSA at a concentration of 100–250 mg dm^{-3}, equilibrium in the system is established within 4 h, while in the presence of SSA at a concentration of 500 mg dm^{-3}, this requires 24 h. It has been established that with increasing the SSA concentration from 100 to 500 mg dm^{-3}, the degree of phenylalanine recovery decreases from 41 to 33%, while the amount of adsorption decreases from 60.4 to 49.7 mg g^{-1}, respectively, at the same initial phenylalanine concentration of 2000 mg dm^{-3}. In this case, the time required to establish equilibrium in the system increases.

The established patterns can be explained by the competitive interaction of Phe and SSA molecules at the adsorption sites of the carbon sorbent. With increasing SSA concentration, the proportion of free sites for the adsorption of phenylalanine molecules gradually decreases. This may be due to the steric effect, the spatial arrangement of SSA and Phe molecules (the presence of a sulfo group in the SSA structure), which interfere with each other when they are jointly adsorbed on the carbon surface.

According to our calculations, when arginine is added to the CS–SSA system, the experimental SSA adsorption curve in the equilibrium concentration range of 5.8–1570.0 mg dm^{-3}, as in the presence of phenylalanine, is better described by the Freundlich equation (correlation coefficient $R^2 = 0.95$) than the Langmuir equation (correlation coefficient $R^2 = 0.66$).

Thus, the adsorption of SSA in the presence of an amino acid (phenylalanine or arginine) on the carbon sorbent in the range of initial concentrations from 100 to 3000 mg dm^{-3}, which corresponds to equilibrium concentrations of 1.9–1780.0 mg dm^{-3}, differs from the adsorption of the modifier by the carbon sorbent from an individual solution. The amount of SSA adsorption in the presence of arginine (Figure 1, curve *2*) reaches a maximum experimental value of 121 mg g^{-1}.

Data on the textural characteristics and amount of deposited modifier for the tested samples are listed in Table 1.

All the samples under consideration have a mesoporous structure with a mean pore diameter of 4–7 nm. With increasing the initial SSA concentration from 1500 to 3000 mg dm^{-3}, the textural characteristics of the modified samples decrease from 311 to 104 m^2 g^{-1} (see Table 1). The smallest specific surface area, which is 3 times lower compared to the initial sample, is observed in samples with a maximum initial modifier concentration of 3000 mg dm^{-3}. Note that the CS–SSA–Phe and CS–SSA–Arg samples have comparable specific surface area and pore volume values.

Thermogravimetric analysis of the samples revealed that the largest amount of adsorbed modifier, 5.8 and 8.2 wt%, is deposited from solutions with an initial SSA concentration of 3000 mg dm^{-3} in the presence of amino acids for samples CS-SSA-3000-Phe and CS-SSA-3000-Arg, respectively. This is consistent with the results of adsorption studies and data on the textural characteristics of the samples (see Table 1).

The Boehm titration method was used to estimate the number of oxygen-containing groups on the surface of the carbon sorbents under consideration (Figure 2). For all the modified samples, the number of oxygen-containing groups, predominantly

Table 1 Textural characteristics and amount of deposited modifier for the tested samples.

Entry	Sample[a]	Specific surface area S_{BET}/m^2 g^{-1}	Total pore volume/ cm^3 g^{-1}	Mesopore volume/ cm^3 g^{-1}	Micropore volume/ cm^3 g^{-1}	Amount of deposited modifier (wt%)
1	CS	311	0.294	0.253	0.041	–
2	CS-SSA-1500	222	0.255	0.253	0.002	2.7
3	CS-SSA-3000	170	0.207	0.207	0	3.8
4	CS-SSA-1500-Phe	123	0.196	0.196	0	4.6
5	CS-SSA-3000-Phe	104	0.162	0.162	0	5.8
6	CS-SSA-1500-Arg	115	0.195	0.195	0	5.8
7	CS-SSA-3000-Arg	111	0.172	0.172	0	8.2

[a] The numbers 1500 and 3000 in the sample designation indicate the concentration of the SSA modifier (in mg dm^{-3}) in the initial solution.

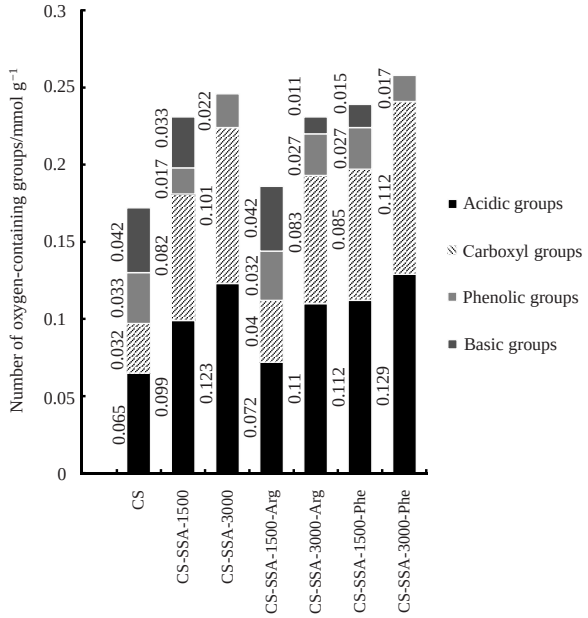


Figure 2 Content of oxygen-containing groups on the surface of the tested carbon sorbents.

the carboxyl ones, increased in comparison with the initial sorbent by 1.5–2 times, depending on sample synthesis conditions.

The pH value of the point of zero charge[7] of carbon sorbents was determined by the pH drift method (Table 2). According to the presented data, the adsorption of the modifier on the carbon sorbent in this concentration range leads to a shift in pH to the acidic region from 7.00 to 2.07, which is due to the acidic nature of the adsorptive. The addition of amino acids exerts virtually no effect on the pH_{PZC} of the modified CS-SSA-3000 sample (see Table 2); this may be related to the high initial concentration of the modifier, which plays a key role for this parameter.

Table 2 also lists data on the adsorption of methylene blue and metanil yellow on the carbon sorbents under consideration.

Table 2 pH_{PZC} and dye adsorption values for the tested carbon sorbents.

Entry	Carbon sorbents	pH_{PZC}	Adsorption of dyes[a]/mg g^{-1}	
			Methylene blue	Metanil yellow
1	CS	7.00	18 ± 2	34 ± 2
2	CS-SSA	2.09	28 ± 2	28 ± 2
3	CS-SSA-3000-Phe	2.07	40 ± 3	28 ± 2
4	CS-SSA-3000-Arg	2.08	46 ± 3	28 ± 2

[a] The concentration of dyes is 2.0 g dm^{-3}, the equilibration time is 24 h, and the sorbent/dye solution volume ratio is 1 : 10.

It was found that the modified samples CS-SSA-3000-Phe and CS-SSA-3000-Arg have a higher adsorption capacity with respect to the basic dye methylene blue compared to the initial sorbent and the CS-SSA sample (see Table 2). These samples contain the largest amount of deposited SSA and, accordingly, general acid groups, predominantly the carboxyl ones, which can serve as active adsorption sites (see Figure 2). The pH_{PZC} values of the samples are also strongly shifted towards the acidic region (see Table 2). Presumably, physical adsorption of the positively charged dye methylene blue on the surface of modified sorbents occurs via a donor–acceptor mechanism.[15] This is promoted by the negative charge of their surface, since the pH_{PZC} of the samples (2.1) is lower than the pH of the dye solution (3.4).[16]

Table 3 lists the results of studies of SSA desorption from sorbents modified with an initial SSA concentration of 3000 mg dm^{-3}. For the tested samples, it was shown that during a 48-h desorption *ca.* 68–72% and *ca.* 61–82% of the initial concentration of SSA deposited under the specified conditions pass into an aqueous 0.025 M sodium hydrogen carbonate solution, simulating the intestinal medium, and into 96% ethanol, respectively. As a results of SSA desorption, the pH of the initial solutions decreases by 5–6 units. In a 0.02 M hydrochloric acid solution, simulating the stomach medium, *ca.* 11–21% of SSA passes into the solution. The pH of the initial hydrochloric acid solution remains virtually unchanged.

A small amount of SSA, no more than 21% of the initial concentration, passes into an acidic medium, simulating the environment of the stomach. This happens because the optimal medium for the adsorption of the modifier by the carbon sorbent is an acidic medium with a pH of 2. The amount of adsorption greatly decreases with increasing pH of the medium.[14] Accordingly, the higher the pH of the initial SSA solution, the less its adsorption and, consequently, the more pronounced the reverse process, desorption.

In this study, five samples of modified sorbents were obtained using a carbon sorbent and SSA with an initial concentration of 1500 and 3000 mg dm^{-3}, both in individual solutions and in the presence of the amino acid arginine or phenylalanine with a concentration of 2000 mg dm^{-3}. The properties of the samples were investigated by various physicochemical methods. It was found that the largest amounts of the modifier, 5.8 and 8.2 wt%, are deposited in the CS–Phe–SSA and CS–Arg–SSA systems, respectively. This is consistent with the experimental adsorption data of the samples (91.6–120.7 mg g^{-1}) and measurements of their textural characteristics. Compared to the initial carbon sorbent, the adsorption of SSA on modified sorbents leads to a 1.5–2 times increase in the number of oxygen-containing groups, predominantly the carboxyl ones, depending on the adsorption conditions. It was shown that the adsorption of SSA from an

Table 3 SSA concentration and pH value of solutions after desorption in different media for various times.[a]

Entry	Sample	Desorption medium	24-h SSA concentration/ mg dm^{-3}	48-h SSA concentration/ mg dm^{-3}	48-h relative concentration of SSA (%)[b]	Initial pH	24-h pH	48-h pH
1		96% ethanol	2071	2449	82	8.4	1.8	1.9
2	CS-SSA-3000	0.02 M HCl	67	421	14	1.9	1.9	1.8
3		0.025 M $NaHCO_3$	72	2038	68	10.6	4.2	4.2
4		96% ethanol	2338	2332	78	8.4	2.7	2.7
5	CS-SSA-3000-Phe	0.02 M HCl	676	630	21	1.9	2.0	1.9
6		0.025 M $NaHCO_3$	2278	2047	68	10.6	4.7	4.7
7		96% ethanol	273	1838	61	8.4	3.0	2.8
8	CS-SSA-3000-Arg	0.02 M HCl	69	320	11	1.9	2.0	2.0
9		0.025 M $NaHCO_3$	69	2159	72	10.6	5.5	5.0

[a] The amounts of phenylalanine and arginine after the desorption were not measured. [b] Relative to the value of 3000 mg dm^{-3}.

individual solution by the carbon sorbent occurs with the formation of a monolayer and is described by the Langmuir equation. When amino acids are added, typical signs of polymolecular adsorption are observed for the CS–Arg–SSA and CS–Phe–SSA systems at initial amino acid concentrations of 1000 and 1500 mg dm^{-3}, respectively. The capacity of the monolayer is reduced due to the concomitant competitive adsorption of SSA and amino acid molecules.

Desorption studies of the samples revealed that for the tested samples, during desorption for 48 h, *ca.* 68–72% and *ca.* 61–82% of the initial concentration of deposited SSA passes into an aqueous 0.025 M $NaHCO_3$ solution, simulating the intestinal medium, and into 96% ethanol. This is accompanied by a decrease in the initial pH of these solutions by 5–6 units.

The adsorption properties of the samples in relation to model toxic substances methylene blue and metanil yellow were investigated. Modified samples CS-SSA-3000-Phe and CS-SSA-3000-Arg, obtained in the presence of amino acids, showed high adsorption capacity for methylene blue dye, 40 and 46 mg g^{-1}, respectively. This may be due to the greatest amount of the modifier deposited on the sorbents, as well as the high content of acidic oxygen-containing groups on the surface, which act as active adsorption sites. Adsorption of the dye is also facilitated by the negative charge of their surface, since the pH_{PZC} of the samples is lower than the pH of the dye solution.

The results obtained indicate the promise of the developed materials and expand the possibilities of their application in sorption therapy.

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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.2024.09.043.

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