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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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Accepted abbreviations:

CS – carbon sorbent;

SSA – 5-sulfosalicylic acid;

Phe – phenylalanine;

Arg – arginine;

CS-SSA – carbon sorbent modified with 0.30 wt.% (3000 mg dm^{-3}) aqueous solution of sulfosalicylic acid;

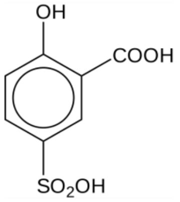
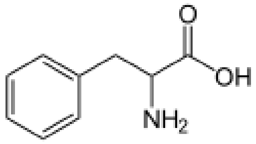
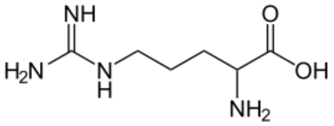
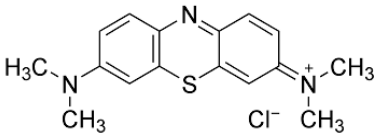
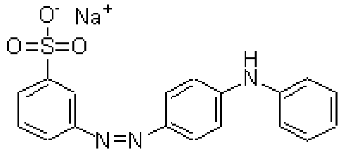
CS-SSA-1500-Phe – carbon sorbent modified with 0.15 wt.% (1500 mg dm^{-3}) aqueous solution of sulfosalicylic acid in the presence of phenylalanine (2000 mg dm^{-3});

CS-SSA-3000-Phe – carbon sorbent modified with 0.30 wt.% (3000 mg dm^{-3}) aqueous solution of sulfosalicylic acid in the presence of phenylalanine (2000 mg dm^{-3});

CS-SSA-1500-Arg – carbon sorbent modified with 0.15 wt.% (1500 mg dm^{-3}) aqueous solution of sulfosalicylic acid in the presence of arginine (2000 mg dm^{-3});

CS-SSA-3000-Arg – carbon sorbent modified with 0.30 wt.% (3000 mg dm^{-3}) aqueous solution of sulfosalicylic acid in the presence of arginine (2000 mg dm^{-3}).

Table S1 Characteristics of adsorptive substances.

Adsorptive, chemical formula	Molecular weight, MW/g mol^{-1}	Structure and size of molecules[*]/nm	Chemical properties
5-Sulfosalicylic acid dihydrate $C_7H_6O_6S{\cdot}2H_2O$ (SSA) CAS 5965-83-3 analytically pure, Omskreaktiv	219.18	0.77×0.71×0.27 	pK_a[**] 2.86 readily soluble in water
L-Phenylalanine $C_9H_{11}NO_2$ (Phe) ultra pure, Omskreaktiv	165.2	0.70×0.50×0.50 	pK_a 2.20 pI[***] 5.48 limited solubility in water (2.83 g/100 ml at 16 °C)
L-Arginine $C_6H_{14}N_4O_2$ (Arg) CAS 74-79-3 PanReac AppliChem	174.2	1.08×0.37×0.3 	pK_a 12.48 pI 10.76 high solubility in water
Methylene blue $C_{16}H_{18}ClN_3S$ (MB) analytically pure, Omskreaktiv	319.9	1.41×1.83×1.14 	Cationic, basic tracer, difficult solubility in water (1:30)
Metanil yellow $C_{18}H_{14}N_3NaO_3S$ (MY) CAS 587-98-4 98 %, Merck Schuchardt OHG	375.4	1.17×1.15×0.59 	Anionic, acidic tracer, soluble in water

[*] Molecular sizes were calculated using the JSmol computer program for 3D molecular modeling of chemical structures. [**] pK_a is the negative decimal logarithm of the acid dissociation constant of the adsorptive in solution. [***] pI is the value of the isoelectric point, *i.e.*, the pH of the medium at which a certain molecule or surface is electrically neutral.

Experimental part

5-Sulfosalicylic acid readily dissolves in ethanol and water and is stable; so, aqueous solutions with the concentration 0.15-99 wt.% can be prepared. The study was performed using solutions of sulfosalicylic acid with the concentrations 0.15-0.30 wt.%. SSA concentrations were chosen to provide possible manifestation of biospecific properties of the acid on the carbon sorbent.[S1-S3]

The initial carbon matrix was represented by a porous carbon sorbent (CS) developed at the Center of New Chemical Technologies BIC (Omsk, Russia). The sorbent has high chemical and microbiological purity; its predominant grain size is 0.5 mm.[S4,S5]

The adsorption-desorption properties of carbon sorbents were studied spectrophotometrically on a CECIL-1021 (Cecil Instruments Limited, UK) spectrophotometer. Shaking of samples was performed using an Edmund Buehler SM 30 B (Buehler, Germany) shaker with the frequency of 100-130 vibrations min^{-1}. The studies were performed using three sorbent–adsorbate systems: CS–SSA (adsorption of sulfosalicylic acid by the carbon sorbent), CS–Phen–SSA (adsorption of sulfosalicylic acid by the carbon sorbent in the presence of phenylalanine), CS–Arg–SSA (adsorption of sulfosalicylic acid by the carbon sorbent in the presence of arginine). Adsorption characteristics of carbon sorbent in the tested systems were estimated by calculation using the Langmuir equation of monomolecular adsorption and the Freundlich equation.[S6]

Textural characteristics of the samples (specific surface area, pore volume and diameter) before and after the adsorption/desorption were determined by the low-temperature nitrogen adsorption on a Gemini 2380 (Micromeritics, USA) analyzer.

The modification process and the amount of deposited modifier were controlled by thermal analysis on a DTG-60 (Shimadzu, Japan) thermal analyzer (air atmosphere, heating rate 10 ºC min^{-1}, temperature range up to 500 ºC).

The H.P. Boehm titrimetric method was used to estimate quantitatively the content of functional groups on the surface of tested samples.[S7,S8] The pH drift method[S9,S10] was employed to determine the pH values of the point of zero charge (pH_{PZC}) of the sorbents using a pH-meter (Sartorius, Germany). To this end, the dependence of pH_{fin}-pH_{init} on pH_{init} was obtained. The point where the curve intersects the *x*-axis corresponds to the pH value of the point of zero charge of the sample (Fig. S1).

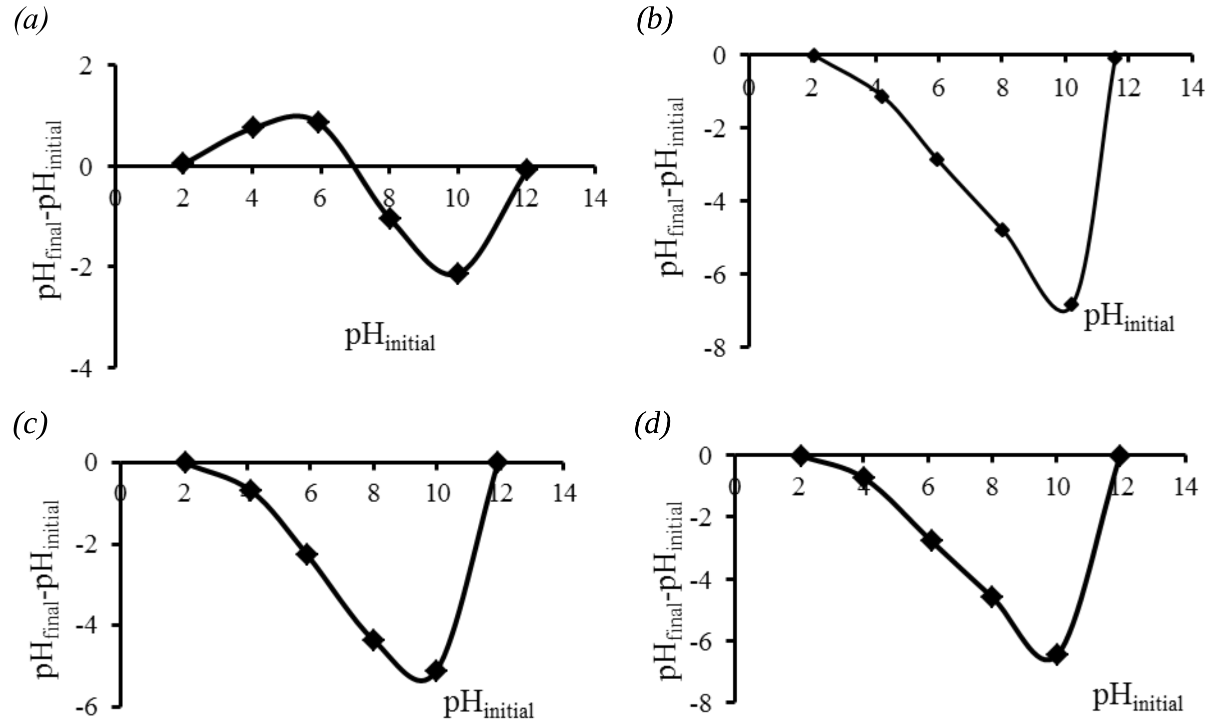


Figure S1 pH of the point of zero charge of the tested carbon sorbents: *(a)* CS, (*b*) CS-SSA-3000, *(c)* CS-SSA-3000-Phe, (*d*) CS-SSA-3000-Arg.

The amount of sulfosalicylic acid in an aqueous solution after the adsorption/desorption was determined using a quartz cuvette with a 10 mm thick adsorption layer at a 297±5 nm wavelength; a calibration chart obtained in the concentration range of 100-500 mg dm^{-3} was employed. A calibration chart for phenylalanine was obtained in the concentration range of 125-2000 mg dm^{-3} at a 254±5 nm wavelength. Arginine cannot be determined directly by spectrophotometry. The amount of adsorption (*a*/mg g^{-1}) and the degree of recovery (*R*/%) were calculated by the formulas.[S4,S5,S10] The test result was taken as the arithmetic mean of the results of three parallel determinations performed by one researcher, the absolute difference between which did not exceed 1.0 mg g^{-1} (relative measurement error 3-5%).

Earlier it was shown that the higher is the pH of the SSA solution, the weaker is its adsorption on the carbon sorbent. The maximum adsorption of SSA on the carbon adsorbent is observed in the acidic medium at pH 2.[S3] Before recording the adsorption isotherms, it was found that equilibrium in the SSA–CS system was reached within 24 hours (the initial concentration of SSA 100-3000 mg dm^{-3}, from individual solutions and in the presence of amino acids with the concentration 2000 mg dm^{-3} at the sorbent/solution ratio 1:50 (by volume) in the tested systems). Therewith, the maximum amount of SSA adsorption for the initial concentration 3000 mg dm^{-3} was equal to 88.8 mg g^{-1}.[S3]

To desorb SSA from the surface of sorbents, the following model solutions were used: 96% ethanol solution as an accessible alternative solvent for SSA for complete removal of the modifier from the pores and surface of the support; solutions of hydrochloric acid (0.02 M) and sodium hydrocarbonate (0.025 M), which model, respectively, the stomach and intestine media. A more detailed description of the technique can be found elsewhere.[S3]

Concentrations of the model substances, methylene blue (MB) and metanil yellow (MY) dyes, after contacting carbon sorbents in an aqueous solution were measured spectrophotometrically using a cuvette with a 10 mm thick adsorption layer at a 660 nm wavelength for MB and 440 nm for MY using the corresponding calibration charts. The amount of adsorption of the dyes was then calculated. The indicated dyes model toxic substances with the molecular weight up to 500 g mol^{-1}, particularly creatinine, uric acid, bilirubin and others.[S11-S13] It is known that the adsorption of dyes on solid porous materials is affected mostly by their textural characteristics (specific surface area, pore volume) and chemical composition of the surface.[S11]

The adsorption studies allowed us to develop techniques for modification of the carbon sorbent with sulfosalicylic acid from individual solutions and in the presence of amino acids: arginine and phenylalanine. First, we carry out the incipient wetness impregnation of the carbon sorbent with an aqueous solution of SSA with the initial concentration 1500-3000 mg dm^{-3} (0.15-0.30 wt. %) for 24 h at room temperature and volume ratio 1:50, pH 2 under static conditions from individual solution and in the presence of amino acid with the concentration of 2000 mg dm^{-3}. This is followed by drying the sorbent in air for 24 h and then in a drying oven at 110 ºC for 2 h.

Five samples have been synthesized:

CS-SSA − carbon sorbent modified with an aqueous solution of sulfosalicylic acid with the concentration 3000 mg dm^{-3} from individual solution;

CS-SSA-1500-Phe and CS-SSA-3000-Phe − carbon sorbents modified with an aqueous solution of sulfosalicylic acid with the concentrations 1500 and 3000 mg dm^{-3} in the presence of phenylalanine with the concentration 2000 mg dm^{-3};

CS-SSA-1500-Arg and CS-SSA-3000-Arg − carbon sorbents modified with an aqueous solution of sulfosalicylic acid with the concentrations 1500 and 3000 mg dm^{-3} in the presence of arginine with the concentration 2000 mg dm^{-3}.

The calculated values of phenylalanine adsorption versus contact time are listed in Table S2.

Table S2 The amount of adsorption (a/mg g^{-1}) and the degree of recovery (R/%) Phe from the aqueous solution with the concentration 2000 mg dm^{-3} by the carbon sorbent versus contact time in the presence of SSA with the initial concentration from 100 to 500 mg dm^{-3}.

Entry	Initial data on SSA concentration/ mg dm^{-3}	Contact time/h						
		1	2	3	4	5	24	48
1		Residual concentration C_{Phe}/mg dm^{-3}						
	C_{init}(SSA) = 100 mg dm^{-3}	119.2	1176.7	-	1175.6	1176.7	**1172.2**	1172.2
		a_{Phe}/mg g^{-1} (degree of recovery R/%)						
	a_{max}(Phe)* = 145.9 mg g^{-1}	58.9 (40.4)	60.1 (41.2)	-	60.1 (41.2)	60.1 (41.2)	**60.4** **(41.4)**	60.4 (41.4)
2		Residual concentration C_{Phe}/mg dm^{-3}						
	C_{init}(SSA) = 250 mg dm^{-3}	1297.8	1270.0	-	1266.7	1266.7	**1265.6**	1302.2
		a_{Phe}/mg g^{-1} (degree of recovery R/%)						
	a_{max}(Phe) = 143.6 mg g^{-1}	50.4 (35.1)	52.4 (36.5)	-	52.7 (36.7)	52.7 (36.7)	**52.7** **(36.7)**	50.1 (34.9)
3		Residual concentration C_{Phe}/mg dm^{-3}						
	C_{init}(SSA) = 500 mg dm^{-3}	-	1422.2	1388.9	-	1384.4	**1340.0**	1353.3
		a_{Phe}/mg g^{-1} (degree of recovery R/%)						
	a_{max}(Phe) = 150.6 mg g^{-1}	-	43.5 (28.9)	46.0 (30.6)	-	46.3 (30.8)	**49.7** **(33.0)**	48.7 (32.3)

* Here, a_{max} is the limiting experimental amount of adsorption calculated at the equilibrium concentration $C_x = 0$

By way of example, Fig. S2 shows the obtained thermograms of the modified samples CA-SSA-1500-Phe and CS-SSA-3000-Phe. Several steps of weight loss are observed on DTG curves of the modified samples.

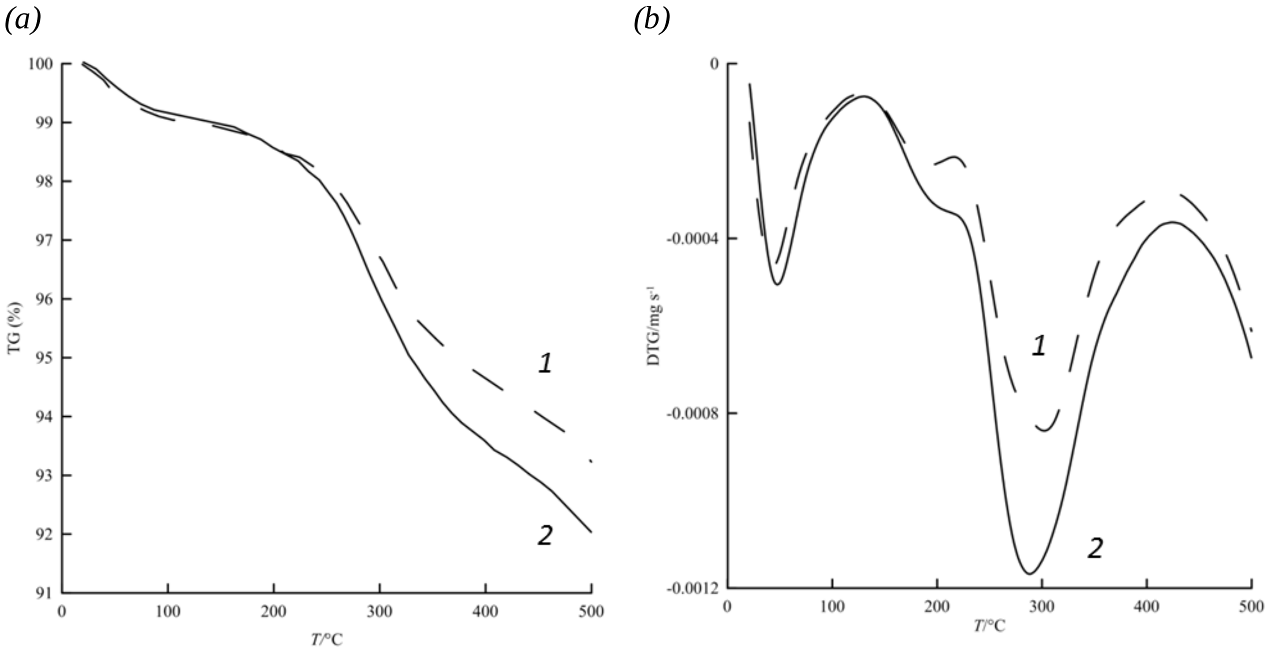


Figure S2 Thermograms of the modified samples CS-SSA-1500-Phe (curve *1*) and CS-SSA-3000-Phe (curve *2)*: thermogravimetric *(a)* and differential thermogravimetric curves of the samples *(b)*.

In the temperature range from 20 to 100 °C, some weight loss occurs due to the removal of adsorbed moisture (hygroscopic moisture) in an amount of 0.97 wt. %. A weight loss of the sorbent in the temperature range from 130 to 420 °C corresponds to decomposition of sulfosalicylic acid and amino acid adsorbed on the carbon sorbent in the amount of 4.6-5.8 wt. %. This is consistent with the literature data.[S14,S15]

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