Chemical routes to materials

Adsorption of organic dyes in mesoporous carbon sorbent modified with salicylic acid

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ABSTRACT

For the first time an advanced carbon sorbent modified with salicylic acid for medicinal and veterinary applications was synthesized by the adsorption from solutions. Optimal parameters of the modification were determined: Solvent, "carbon sorbent–modifier" ratio, concentration of salicylic acid, equilibration time of the process in the "sorbent–salicylic acid solution" system, pH, and process temperature. The effect of the drying parameters on stability and amount of oxygen-containing groups on the carbon sorbent surface after modification was established. Physicochemical properties of the carbon sorbent and sorbents modified with different concentrations of salicylic acid were investigated: textural characteristics, qualitative and quantitative compositions of the surface functional groups, and amount of the deposited modifier. The possibility of salicylic acid desorption into the media simulating biological fluids, particularly the gastrointestinal medium, was explored. Adsorption characteristics of the carbon sorbent and sorbents modified with different concentrations of salicylic acid with respect to organic dyes—methylene blue and metanil yellow in a wide range of operating concentrations—were revealed.

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GRAPHICAL ABSTRACT
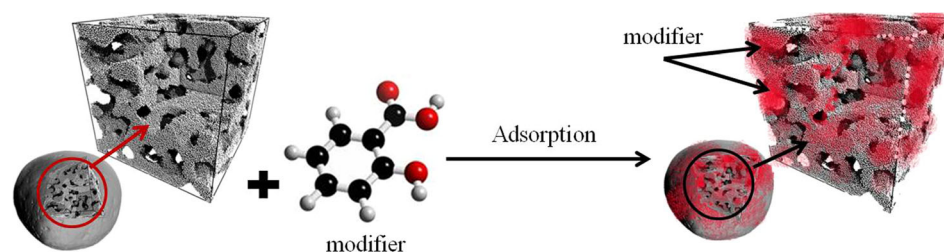
Introduction

The wide application of carbon materials as adsorbents in various fields of science and technology is caused by their unique properties, the variety of structures, and the developed surface area. Carbon materials are used for the adsorption of gases, heavy metals, organic dyes, polymers and biomolecules. Depending on the specified tasks and purposes of carbon materials, it is possible to adjust their pore structure and change chemical features of their surface by modification with various substances [1–13].

The adsorption of biologically active substances on the carbon surface (adsorption modification) is one of the most simple and accessible methods to obtain new modified materials for the sorption processes, which can extend their application field [14]. Promising for such goals are the carbon sorbents having some advantages over other materials: high adsorption surface area, biocompatibility, and insolubility in biological media. Impregnation or immobilization of biologically active substances onto a carbon support is widely employed now [5, 6]. This process increases the number of oxygen- and nitrogen-containing functional groups on the carbon surface, thus enhancing their chemical and adsorption interactions with the deposited modifiers. There are various ways to use carbon sorbents with the biologically active and medicinal substances impregnated or immobilized on them [5, 6].

An increasing interest in salicylic acid and its derivatives is observed now. Such substances possess antibacterial, anti-inflammatory, antimicrobial, antioxidant, wound healing and other biospecific properties [15–20]. However, the possibility to apply salicylic acid and obtain the related medicinal preparations is limited because high concentrations of the acid produce undesirable side effects: a detrimental effect on the gastrointestinal mucosa, disturbance of the kidney functions, and others [21, 22]. At present, 1–2% alcoholic solutions of salicylic acid and ointments with the salicylic acid content from 2 to 10% are used in the national medical practice for outward application [23–25].

Complex preparations based on various matrices (supports) with the deposited salicylic acid or its derivatives have been developed to increase the efficiency, prolong their action and reduce the toxicity. Such preparations include the application hemostatic implants modified with salicylic acid, antibacterial polymeric composites with salicylic and rosemary acids, medicinal preparations containing polysalicylic acid for treatment of osteoporosis, films with antioxidant and antibacterial properties based on chitosan with conjugated salicylic acid, and pharmaceutical compositions based on polysaccharide with salicylic acid [26–30].

The analysis of the literature data demonstrates that carbon materials, particularly the active carbons with high adsorptivity, are widely employed for the adsorption of salicylic acid from aqueous media [31–33]. The revealed regularities and mechanisms of salicylic acid adsorption on the carbon surface allow using the acquired data to develop a method for modifying the carbon sorbents with salicylic acid or its derivatives [2, 34, 35].

Different grades of active carbons, particularly those modified with metal oxides, are applied to concentrate salicylic acid and recover it from aqueous media. Such carbons exhibit high adsorptivity toward salicylic acid (above 240 mg/g). Their drawbacks include long equilibration time, incomplete desorption of the sorbate, and high cost of the carbons [31].

An adsorbent for the removal of methylene blue dye has been developed using steel slag modified with a salicylic acid solution in methanol with the concentration of 100 g/l. The maximum adsorption capacity of the modified sorbent with respect to the dye was 41.6 mg/g (the concentration of methylene blue was 200 mg/l; the equilibration time, 6 h; pH, 7; and temperature, 25 °C) [36].

The quantitative characteristic of the efficiency of carbon sorbents is their adsorptivity toward model substances. The substances used for modeling various compounds with the molecular weight up to 500 D are represented by organic dyes – basic methylene blue and acidic metanil yellow [37–40]. To estimate the operation time of the modified carbon sorbents, the possibility of releasing the modifier was studied in different media and at different pH values [41, 42].

The goal of the work was to develop a method for the adsorption modification of the carbon sorbent surface with salicylic acid. The tasks of the study were as follows. Determination of the optimal modification parameters (solvent, sorbent to modifier ratio, concentration of salicylic acid, equilibration time of the process in the "sorbent–salicylic acid solution" system, pH, and temperature of the process). Investigation of the adsorption properties of the material with respect to salicylic acid used as the modifier and determination of conditions ensuring the deposition of the maximum amount of salicylic acid (the amount of adsorption). The synthesis of the modified samples and investigation of their physicochemical properties. A study on the desorption of the deposited modifier into model solutions.

Investigation of the adsorption properties with respect to organic dyes (methylene blue and metanil yellow), which are used for modeling toxic compounds (model substances), will allow us to estimate the effect of deposited salicylic acid on the properties of the carbon sorbent samples and predict their efficiency as the medicinal and veterinary materials for sorption therapy.

Experimental

Materials

The initial material was represented by a mesoporous carbon sorbent (CS) with the specific surface area 390 m^2/g and the predominant grain diameter 0.50 mm. The micromorphology and microstructure of the carbon sorbent used as a support have been studied and described in our earlier publications [43, 44].

The modification was performed using salicylic acid (SA) (99%, Sigma-Aldrich, Germany) and ethanol (95%, OAO Kemerovo Pharmaceutical Plant, Russia). Methylene blue (MB, analytically pure, Omskreaktiv, Russia) and metanil yellow (MY, 98%, Merck Schuchardt OHG, Germany) served as the adsorbates (model substances).

Physicochemical characterization

Specific surface area of the samples was measured by the low-temperature nitrogen adsorption on a Gemini 2380 (Micromeritics, USA) analyzer. The Boehm titrimetric method was used to estimate the quantitative content of functional groups on the surface of samples under consideration. Adsorption and desorption of the modifier and model substances from the carbon sorbent surface were investigated spectrophotometrically on a CECIL-1021 (Cecil Instruments Limited, UK) spectrophotometer. To perform the adsorption with shaking, an Edmund Buehler SM 30 B (Buehler, Germany) shaker was used. The modification process was controlled by thermal analysis on a DTG-60 (Shimadzu, Japan) thermal analyzer. Heating was carried out in the temperature range of 21–400 °C at a rate of 10 °C/min in a static air medium.

IR spectra were recorded on a Shimadzu IRPrestige-21 spectrometer in a range of 350–7900 cm^{-1} with a resolution 4 cm^{-1} and spectrum accumulation from 50 scans. The spectra were processed using the ORIGIN software package for baseline correction and smoothing. The pH value of solutions was measured on a Sartorius PP-20 (Sartorius AG, Germany) pH-meter.

Adsorption

The concentration of salicylic acid in solutions before and after contacting the sorbent was estimated spectrophotometrically using a quartz cuvette with a 10 mm thick adsorption layer; optical density was measured in the adsorption maximum at a wavelength of 295 nm. To plot a calibration chart, a series of salicylic acid solutions was prepared: in the concentration range of 10–500 mg/l for the aqueous solution and 10–100 mg/l for the alcohol solution.

The adsorption of salicylic acid onto the carbon sorbent was performed from aqueous and alcoholic solutions in the concentration ranges of 100–1500 mg/l and 0.10–60.00 g/l, respectively. The amount of adsorption (a, mg/g) and the degree of recovery (R, %) were calculated by the formula reported in [33, 45]. The effect produced by stirring the aqueous solution of salicylic acid during the adsorption on the equilibration time and degree of recovery under mechanical shaking was estimated at a shaking frequency of 100–150 vibrations/min or without shaking.

The optimal conditions of the adsorption modification were chosen by varying the following parameters:

- The sorbent to salicylic acid solution volume ratio of 1/10, 1/25 and 1/50 (temperature 25 °C, without shaking, the concentration of salicylic acid 100 mg/l);
- The pH value from 2 to 12 (from aqueous solutions, the concentrations of salicylic acid 500 and 1500 mg/l, 1/50 ratio, temperature 25 °C, with shaking);
- The process temperatures of 25 °C, 40 °C and 60 °C (from aqueous solutions, 1/50 ratio, the concentrations of salicylic acid 500 and 1500 mg/l, with shaking).

The adsorption of model substances was studied under static conditions at the sorbent/solution volume ratio 1/10 and temperature 25 °C (with or without shaking). To plot the calibrations charts, a series of initial solutions of the dyes was prepared: methylene blue (0.0007–0.0100 mg/ml) and metanil yellow (0.0063–0.0500 mg/ml). The concentration of substances in the solution was estimated spectrophotometrically using a cuvette with a 10 mm thick adsorption layer; optical density was measured

in the adsorption maximum at a 660 nm wavelength for methylene blue and at 440 nm for metanil yellow.

The following experimental procedure was employed to investigate the adsorption properties of samples toward model substances: 1.0 ml of the carbon sorbent was supplemented with 10.0 ml of an aqueous solution of a dye with the concentration 0.10–2.00 mg/ml for methylene blue and 0.10–0.50 mg/ml for metanil yellow; the adsorbate amount in the solution was measured after a specified contact time (from 1 to 24 h). The concentrations of substances in the solutions were estimated before and after the adsorption using the calibrations charts. The results obtained were used to calculate the amount of adsorption (a, mg/g) and the degree of recovery (R, %).

Desorption study

The possibility of desorption of the modifier in different solvents was examined under static conditions (with or without shaking) at the sorbent (g) to solution (ml) ratio of 1/10 and room temperature. The experiments were carried out in alcoholic and aqueous solutions: an alcoholic solution (95% C_2H_5OH), a 0.9% aqueous solution of NaCl (physiological solution), and an aqueous solution.

Reliability of the data obtained and their statistical treatment

To verify reliability of the data obtained in experimental studies, their statistical treatment was performed using the Statictica 6.0 software package. Sampling of the objects of research complied with the requirements of mathematical statistics.

Every adsorption/desorption experiment was repeated twice, and the average value was reported.

Experimental results

Table 1 lists the data obtained on the adsorption of salicylic acid from aqueous (H_2O) and alcoholic (C_2H_5OH) solutions at different sorbent/solution volume ratios.

The highest static adsorption capacity on the carbon sorbent from aqueous and alcoholic solutions was observed at the volume ratio 1/50. This result is consistent with the literature data: the higher is the concentration of solution, the more pronounced is the

Table 1 Adsorption of salicylic acid from aqueous and alcoholic solutions at different sorbent/solution volume ratios

Sorbent/solution volume ratio	Amount of adsorption, mg/g		Equilibration time, h		Degree of recovery, %	
	H_2O	C_2H_5OH	H_2O	C_2H_5OH	H_2O	C_2H_5OH
1/10	1.5	1.6	8	24	100	99
1/25	3.6	3.2	8	24	99	89
1/50	7.7	4.6	24	24	94	60

competition between salicylic acid molecules and adsorption sites on the carbon sorbent surface, which leads to a decrease in the amount of adsorption [35].

At the 1/50 ratio, a greater amount of salicylic acid was adsorbed from the aqueous solution (7.7 mg/g) as compared to the alcoholic solution (4.6 mg/g). This regularity is observed also when comparing the degree of salicylic acid recovery and equilibration time in the "sorbent-solution" system. The adsorption of organic substances from alcoholic solutions is accompanied by competitive sorption of the solvent (ethanol) on the carbon surface, which complicates the process. Therewith, the diffusion of salicylic acid molecules to the adsorbent becomes slower [2, 46, 47].

It was found that the solvent nature is of great importance in the study of salicylic acid adsorption. The following regularity is known: the more readily the adsorbate dissolves in a solvent, the more difficult is its adsorption; the worse is the adsorbate dissolution, the better is its adsorption [48]. Due to the poor solubility of the adsorbate in water, it is difficult to use an aqueous solution of salicylic acid with the concentration above 1500 mg/l in the study of adsorption on the carbon sorbent. In ethanol, salicylic acid readily dissolves even at high concentrations (0.10–60.00 g/l). Supposedly, salicylic acid on the carbon adsorbent will be adsorbed better from aqueous solution than from alcoholic one.

This hypothesis was supported by the data obtained in our experiments (Table 2): the adsorption of salicylic acid from alcoholic solutions onto the carbon sorbent was characterized by a low degree of recovery, 3–41%.

Taking into account the acquired data, in our study the adsorption of salicylic acid on the carbon sorbent was performed from aqueous solutions under the following conditions: concentration of the acid 100–1500 mg/l, sorbent/solution volume ratio 1/50, and temperature 25 °C.

The effect exerted by stirring the aqueous solution of salicylic acid with the carbon sorbent by mechanical shaking on the equilibration time and degree of recovery was investigated. Shaking led to a considerable decrease in the equilibration time from 24 to 4 h and an increase in the degree of recovery from 94 to 100% at a minor decrease in the amount of salicylic acid adsorption from 7.7 to 7.2 mg/g due to intensification of the process [34, 49].

Figure 1a illustrates the results obtained for the salicylic acid adsorption on the carbon sorbent from aqueous solutions in the concentration range of 100–1500 mg/l versus the contact time. An increase in the concentration is accompanied by an increase in the equilibration time and amount of salicylic acid adsorbed on the carbon sorbent. High degrees of recovery, 90–99%, are observed for all the concentrations.

It was found that the equilibration time in the system "aqueous solution of salicylic acid–carbon sorbent" was reached in 4 h. At the operating concentration of the salicylic acid solution equal to 1500 mg/l, the static adsorption capacity of the adsorbent reached 90.0 mg/g.

The effect produced by the pH value on the adsorption of salicylic acid onto the carbon sorbent from aqueous solutions with the concentration of 500 and 1500 mg/l (Fig. 2a) was revealed.
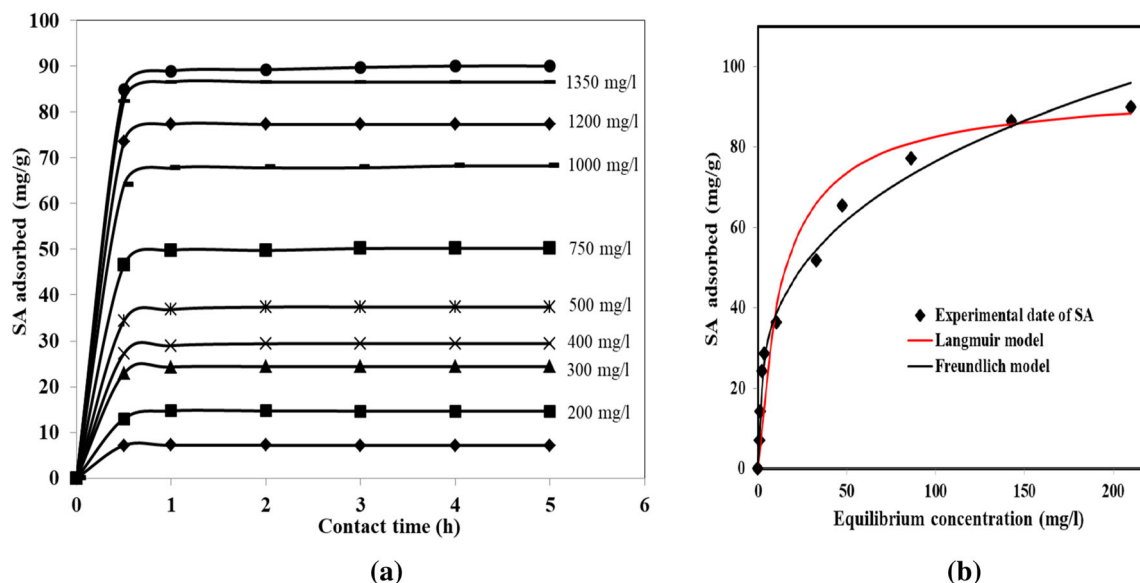
Table 2 Adsorption of salicylic acid from alcoholic solutions on the carbon sorbent

SA concentration, g/l	Amount of adsorption, mg/g	Equilibration time, h	Degree of recovery, %
20	40	3	3
40	410	4	14
60	1070	6	41

Figure 1 Adsorption of salicylic acid on the carbon sorbent versus contact time **a** and equilibrium concentration of the solution **b**.
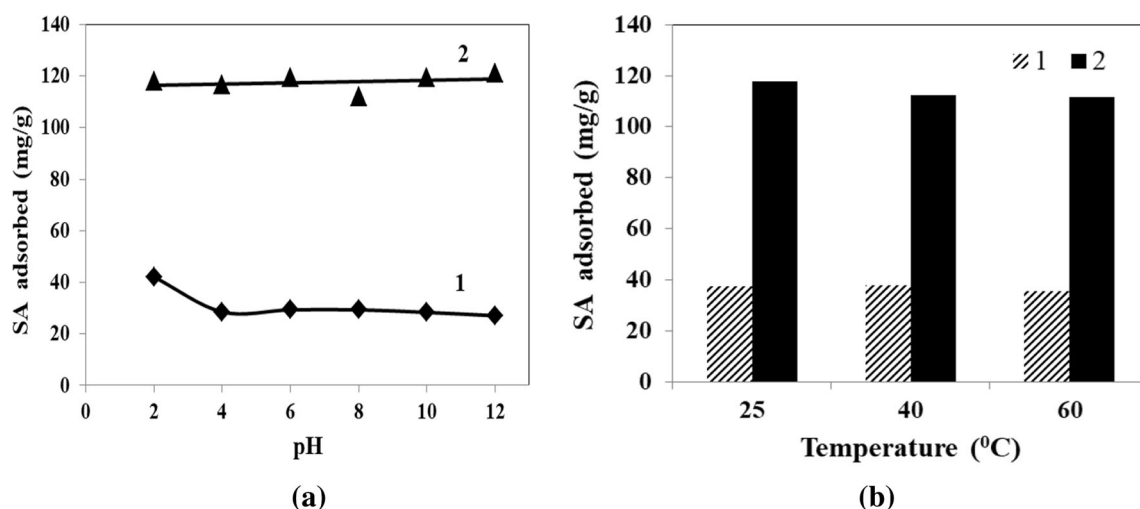

Figure 2 Adsorption of salicylic acid on the carbon sorbent from aqueous solutions with the concentration of 500 mg/l (1) and 1500 mg/l (2) versus the pH value (**a**) and temperature (**b**).

The pH of the solution was shown to affect the adsorption of salicylic acid on the carbon sorbent from aqueous solutions only at the initial concentration of 500 mg/l at pH 2. With a further increase in the pH value, the amount of adsorption virtually did not change and remained equal to 27–29 mg/g. The adsorption of salicylic acid from a solution with the concentration of 1500 mg/l did not change with the pH of the solution and was equal to 112–121 mg/g. It should be noted that at the initial concentration of salicylic acid of 500 mg/l the equilibrium was

reached within 2–4 h, while at the concentration of 1500 mg/l–within 24 h.

It is known that almost all salicylic acid molecules in the solution with pH 2 are not dissociated and can form strong hydrogen bonds with the oxygen-containing surface functional groups of the sorbent; they are not repelled from the positively charged surface of the sorbent (the pH of the carbon sorbent point of zero charge is 7.0) [32, 34, 50, 51].

The effect of temperature on the adsorption of salicylic acid from an aqueous solution was studied

(Fig. 2b). The analysis of the data revealed that an increase in temperature virtually does not affect the adsorption of salicylic acid on the carbon sorbent.

Elevation of the process temperature was shown to increase the equilibration time in the "adsorbate-adsorbent" system. This indicates that the adsorption of salicylic acid by the carbon sorbent is an exothermic process [35, 49, 52]. The optimal temperature is taken equal to 25 °C.

Adsorption characteristics of the carbon sorbent with respect to salicylic acid were estimated at the equilibration time of 4 h (Fig. 1b) [1, 53, 54]. According to the C.H. Giles classification of adsorption isotherms from solutions on the solid surface, the form of the adsorption isotherm of salicylic acid on the carbon sorbent, which was plotted with the experimental data, corresponds to type L2. This type of isotherms is analyzed using the Freundlich, Langmuir or Dubinin-Astakhov equations, whereas the linear isotherms are analyzed using the Henry equation [55–57]. The analysis of adsorption curves in Fig. 1b shows that the experimental adsorption curve in the range of equilibrium concentrations 1.0–210.0 mg/l is better described by the Freundlich equation (the correlation coefficient 0.99) than by the Langmuir equation (the correlation coefficient 0.97).

Parameters of the Freundlich equation for the adsorption of salicylic acid by the carbon sorbent were calculated: the maximum theoretical amount of adsorption $a_{theor} = 96$ mg/g and constants for the Freundlich equation $K_f = 18.65$ and $1/n = 0.31$.

Table 3 lists comparative data on the adsorption of salicylic acid by various carbon materials [58–61].

The adsorption of salicylic acid on the studied carbon sorbent is higher as compared to the data reported in the literature for various carbon materials.

Two samples containing salicylic acid were prepared with different initial concentrations of the modifier: CS-SA-1 (the initial concentration of salicylic acid 500 mg/l) and CS-SA-2 (the initial concentration of salicylic acid 1500 mg/l). Various

physicochemical methods were employed to investigate their properties: textural characteristics, amount of the deposited modifier, qualitative and quantitative composition of functional groups on the surface of samples.

According to the thermal analysis data, for the CS-SA-2 sample modified with salicylic acid, a 10.6% weight loss with a maximum at 63 °C is observed on the DTG curve in the low-temperature region up to 100 °C, which may be related to the removal of highly volatile compounds and adsorbed water (Fig. 3a). In the temperature region of 130–350 °C the weight loss is 5.6% and the maximum decomposition rate is observed at 251 °C (Fig. 3b). Decomposition of the modifier is known to occur in this temperature range [62, 63]. One can see in the thermogram that 150 °C is the optimal temperature for the removal of highly volatile compounds and adsorbed moisture from the CS-SA-2 sample after the impregnation step. As the temperature is increased up to 180 °C, partial decomposition of the modifier is observed, which is undesirable.

The effect exerted by the thermal treatment step on the content of oxygen-containing groups on the surface of modified samples was established (Fig. 4). The amounts of oxygen-containing groups on the surface of modified samples before and after thermal treatment were compared. Thus, in comparison with the unmodified (initial) sorbent sample CS, the modified samples CS-SA-1 and CS-SA-2 showed a 2–threefold increase in the total number of oxygen-containing groups on the surface of samples. An increase from 0.065 to 0.200 mmol/g was observed for the CS-SA-1 sample, and from 0.065 to 0.130 mmol/g–for CS-SA-2. The study showed that thermal treatment of CS-SA-1 and CS-SA-2 samples at different temperatures led to a decrease in the content of functional groups on the surface; the maximum decrease was observed for the thermal treatment at 180 °C.

Thus, it is necessary to introduce a step of additional thermal treatment at 150 °C in a drying oven

Table 3 A comparison of the adsorption capacity toward salicylic acid of various adsorbents found in the literature

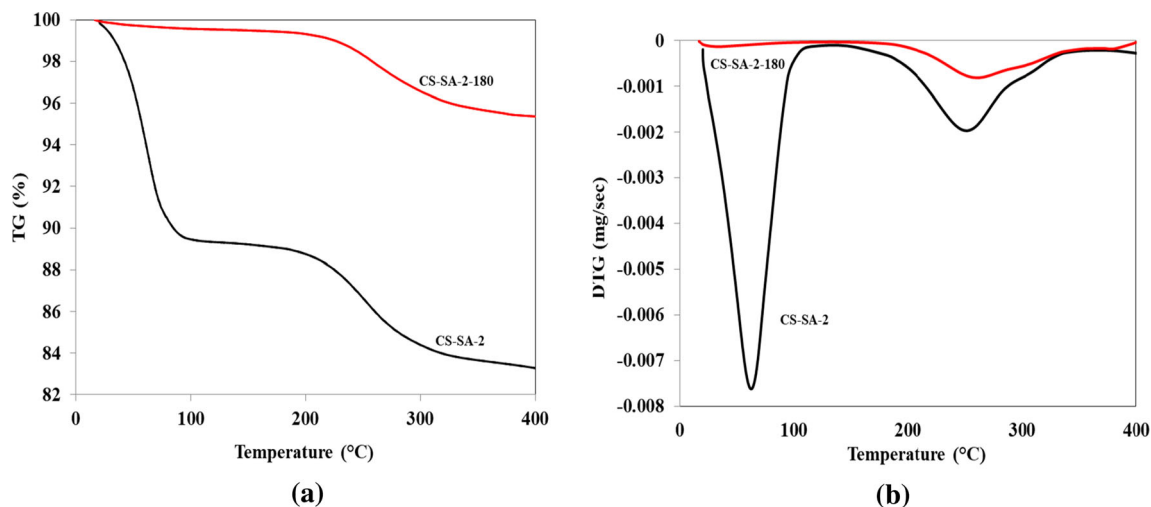| Adsorbent	SA adsorbed, mg/g	Reference
Carbon sorbent	90.0	This work
Pine wood biochar	22.7	[58]
Sibunit	80.0	[59]
Activated carbon Cloth	50.0	[60]
Modified activated carbon CA–TiO$_2$	4.0	[61]

Figure 3 Thermogravimetric **a** and differential thermogravimetric **b** curves for carbon sorbents after the adsorption of salicylic acid.

Figure 4 The content of oxygen-containing groups on the surface of tested carbon sorbents before and after thermal treatment.
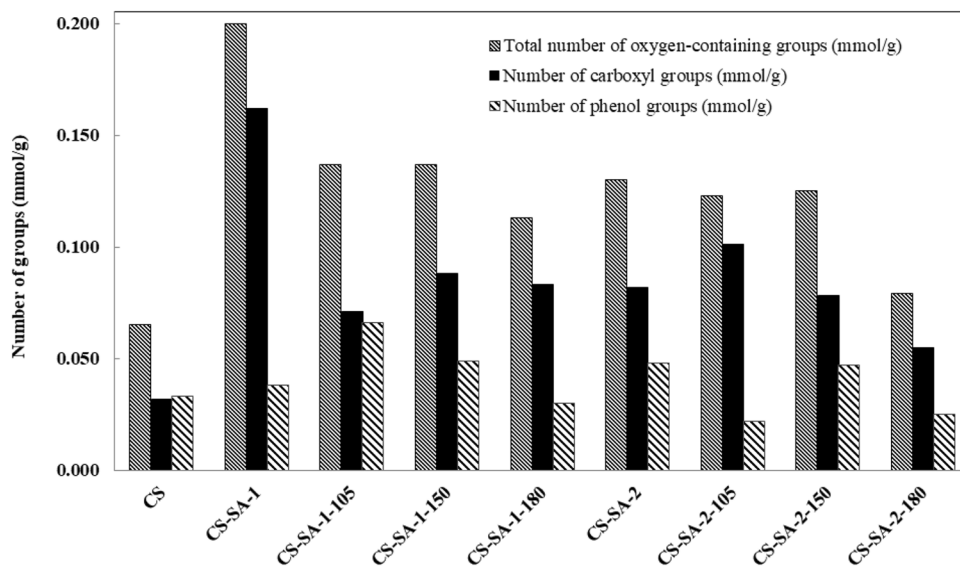
for 1 h into the procedure of carbon sorbent modification with salicylic acid.

The data obtained made it possible to determine the optimal conditions for modification of the carbon sorbent with salicylic acid by its adsorption from an aqueous solution: sorbent/solution ratio SA = 1/50, solution pH 2, temperature 25 °C, and drying of samples at 150 °C in a drying oven for 1 h.

Table 4 Textural characteristics of the tested samples

Sample	Specific surface area, m²/g	Total pore volume, cm³/g	Mesopore volume, cm³/g	Micropore volume, cm³/g	Mean pore size, nm
CS	390	0.340	0.330	0.010	4
CS-SA-1	260	0.289	0.284	0.005	4
CS-SA-2	180	0.234	0.234	-	5

Figure 5 IR spectra of the initial carbon sorbent CS and sorbents after the adsorption of salicylic acid: CS-SA-1 and CS-SA-2.
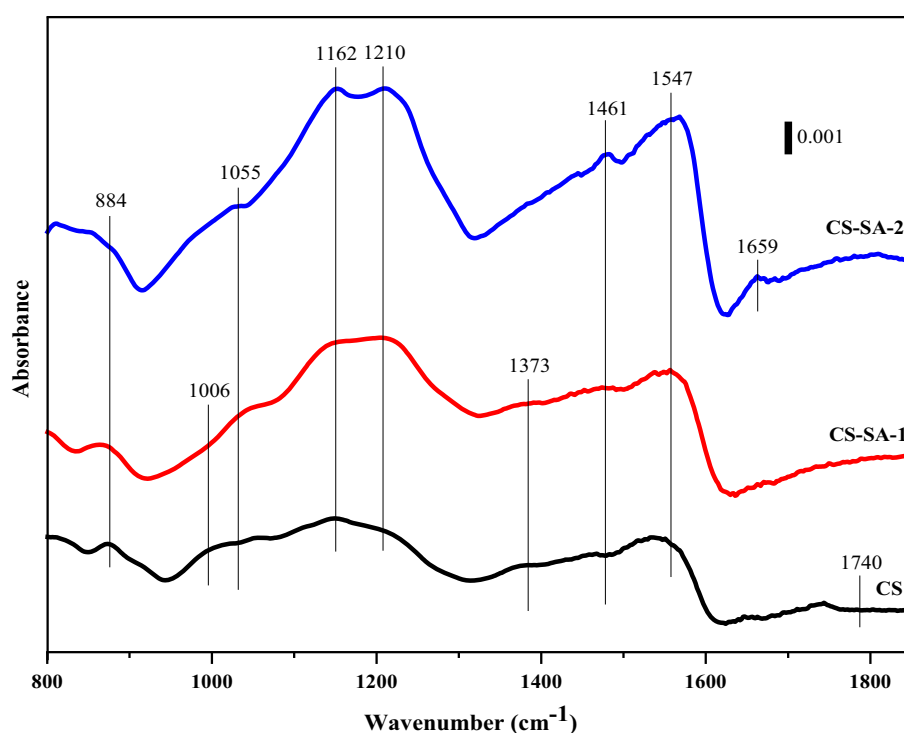

Table 5 Adsorption of model substances on the tested sorbents

Model substance	Adsorption conditions	Sample								
		CS			CS-SA-1			CS-SA-2		
		a, mg/g	τ, h	R, %	a, mg/g	τ, h	R, %	a, mg/g	τ, h	R, %
Methylene blue	Without shaking	7.4	26	100	6.8	27	100	6.1	24	100
	With shaking	7.2	3	100	7.1	3	100	6.0	4	100
Metanil yellow	Without shaking	7.3	7	100	7.0	7	99	5.5	7	99
	With shaking	7.7	0.5	99	7.3	0.5	99	5.6	0.5	100

a The amount of adsorption, τ The equilibration time, R The degree of recovery

The specific surface area was studied during modification of the carbon sorbent with a salicylic acid solution of different concentrations. A 1.5-fold decrease in the specific surface area was observed for CS-SA-1 sample and a 2.2-fold decrease – for CS-SA-2 (Table 4). It should be noted that the mesoporous structure of the samples is retained during the modification. Along with the textural characteristics, the adsorption properties of the modified samples also depend on the qualitative composition of surface functional groups and the pH value of the sorbent point of zero charge.

Figure 5 displays IR spectra of the initial and modified samples. The IR spectra of the tested sorbents (Fig. 5, spectra 1–3) contain the adsorption bands (a.b.) that are typical of the stretching vibrations of C = O bonds in carboxylic acids, ketones and esters (the region of 1690–1760 cm^{-1}), C = C bonds in the aromatic ring of conjugated systems (the region of 1500–1590 cm^{-1}), C–O bonds in phenolic and alcoholic structures (the region of 1000–1200 cm^{-1}), and C–O bonds in lactones and phenol esters (the region of 1200–1300 cm^{-1}). Low-intensity a.b. at 1461 and 1373 cm^{-1} are observed in the IR spectrum of the initial sample; they may correspond to CO_3^{2-} as the impurity ions that emerge upon contacting the atmosphere. For the samples after adsorption of salicylic acid, a.b. in the spectral region of
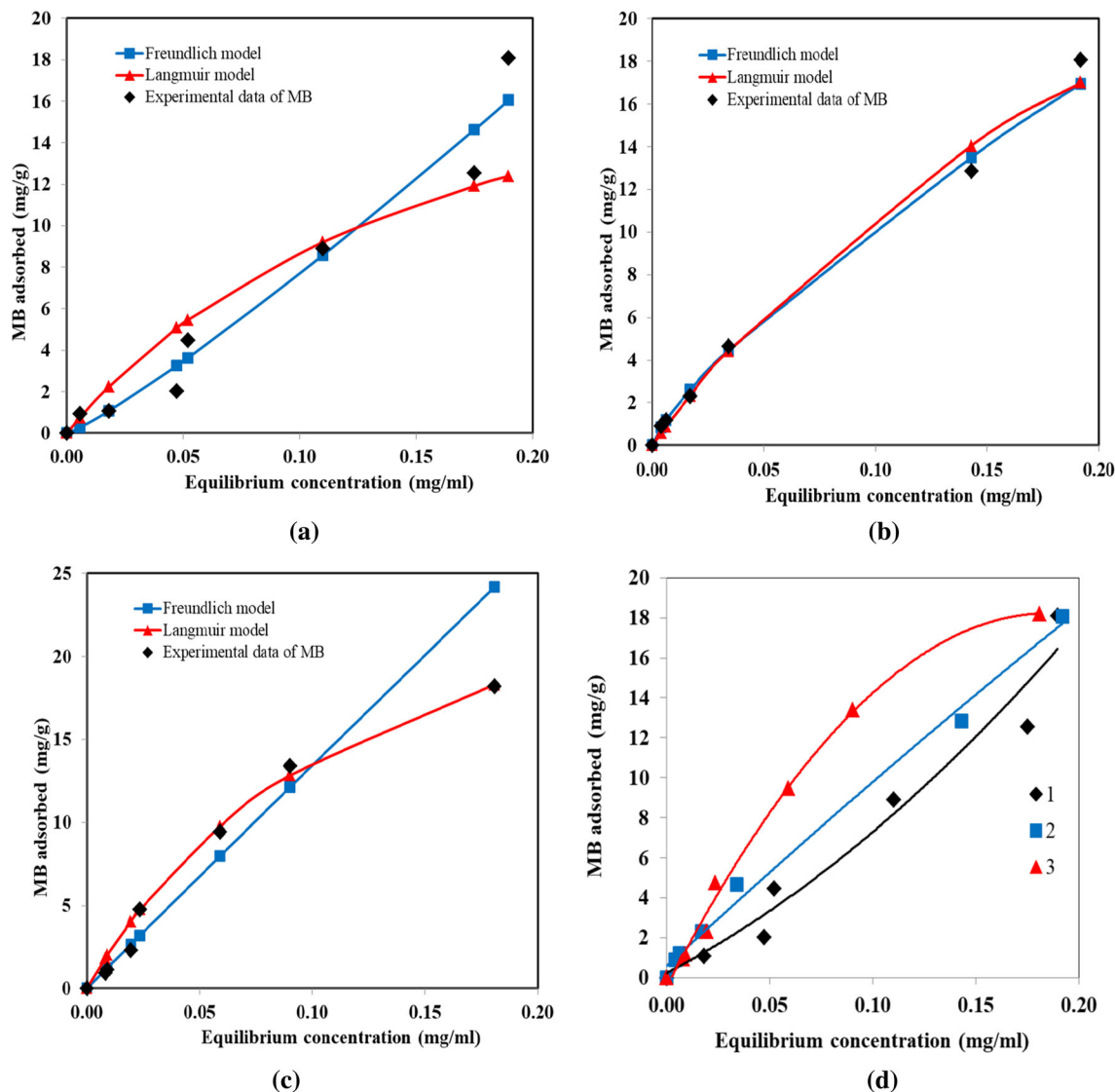
Figure 6 Isotherms of methylene blue adsorption from aqueous solutions on the tested carbon sorbents. A comparison of experimental adsorption curves with the data calculated by Langmuir and Freundlich equations: CS (**a**), CS-SA-1 (**b**), and CS-SC-2 (**c**). A comparison of experimental adsorption curves on the tested samples (**d**): CS (1), CS-SA-1 (2), and CS-SA-2 (3).

1700–1760 cm^{-1} disappeared from the IR spectra (Fig. 5, spectrum 2–3).

The pH values of the point of zero charge for the initial carbon sorbent (CS) and carbon sorbents modified with salicylic acid (CS-SA-1 and CS-SA-2) were determined by the pH drift method [50, 51]. A considerable shift of the pH value for the point of zero charge toward the acidic region from 7.0 to 2.3 is observed only for the CS-SA-2 sample (the carbon sorbent modified with an aqueous solution of salicylic acid with the concentration of 1500 mg/l). This may be caused by a large amount of the deposited

modifier and its acidic properties. In the case of CS-SA-1 sample, the pH value for the point of zero charge did not change.

The adsorption of model substances from aqueous solutions with the concentration of 0.50 mg/ml on the initial and modified carbon sorbents was studied in dependence on the contact time (Table 5).

The adsorption of all the model substances was shown to have the same order of magnitude for the initial carbon sorbent and those modified with salicylic acid. A minor decrease in the adsorption amount in the series CS > CS-SA-1 > CS-SA-2 is

Table 6 Parameters of the Langmuir and Freundlich equations for the adsorption of methylene blue

Parameters	CS	CS-SA-1	CS-SA-2
Langmuir equation			
a_{theor}, mg/g	12.4	17.0	18.3
K_L, l/mg	5.78	3.32	7.48
r^2	0.791	0.883	0.990
Freundlich equation			
a_{theor}, mg/g	16.1	17.0	24.2
K_f	108.30	60.62	131.33
$1/n$	1.149	0.772	0.990
r^2	0.992	0.997	0.961

where a_{theor} is the maximum theoretical amount of adsorption, r^2 The correlation coefficient, K_L The Langmuir equation constant, K_f, n The Freundlich equation constants

caused by a decrease in specific surface area of the modified samples compared to the initial carbon sorbent. The main difference in the adsorption of marker substances with and without shaking is the equilibration time. Without shaking, an equilibrium in the "sorbent-adsorbate" system is established during 7–24 h, while with shaking, during 0.5–4 h.

Adsorption characteristics of the tested carbon sorbents with respect to the methylene blue adsorption in the concentration range of 0.1–2.0 mg/ml were determined using the Langmuir monomolecular adsorption equation and the Freundlich equation at the equilibration time of 24 h (Fig. 6a–c).

The analysis of curves in Fig. 6a–c and a comparison of correlation coefficients for the equations (Table 6) revealed changes in the adsorption of methylene blue: for the initial CS sample (in the range of equilibrium concentrations 0.006–0.190 mg/ml), the curve is better described by the Freundlich equation; for the CS-SA-1 sample (in the range of equilibrium concentrations 0.004–0.192 mg/ml), the adsorption curve is well described by the Freundlich equation; and for the CS-SA-2 sample (in the range of equilibrium concentrations 0.008–0.181 mg/ml), the experimental curve is better described by the Langmuir equation.

Figure 6d displays the experimental adsorption isotherms of methylene blue by the initial sorbent (CS) and those modified with salicylic acid (CS-SA-1 and CS-SA-2) at the equilibration time of 24 h.

The adsorption isotherms of methylene blue by the tested carbon sorbents have different shapes, which indicate differences in the adsorption mechanisms of methylene blue by the initial and modified sorbents. This is caused by the presence of a modifier and by its different amounts in the modified samples.

The shape of the adsorption isotherm of methylene blue on the carbon sorbent CS, which was plotted using the experimental data, corresponds to type S according to the C.H. Giles classification of adsorption isotherms from solutions on the solid surface. The shape of the adsorption isotherm of methylene blue on the CS-SA-1 and CS-SA-2 carbon sorbents modified with salicylic acid, which was plotted using the experimental data, corresponds to type L1 [55–57].

Adsorption characteristics of the tested carbon sorbents with respect to the adsorption of metanil yellow in the concentration range 0.10–0.50 mg/ml were determined using the Langmuir monomolecular adsorption equation and the Freundlich equation at the equilibration time of 7 h (Fig. 7a–c). Parameters of the Langmuir and Freundlich equations for the adsorption of metanil yellow by the carbon sorbents are listed in Table 7.

It is difficult to reveal differences between experimental and calculated adsorption curves in Fig. 7 by their visual comparison. However, the analysis of the calculated correlation coefficients (Table 7) leads to a conclusion that the adsorption isotherms of metanil yellow for all the samples under consideration are better described by the Freundlich equation than by the Langmuir one: for the CS sample–in the range of equilibrium concentrations 0.0030–0.0168 mg/ml, for CS-SA-1–0.0030–0.0128 mg/ml, and for CS-SA-2–0.0062–0.0444 mg/ml.

Figure 7d illustrates a comparison of the adsorption isotherms of metanil yellow by the initial sorbent (CS) and those modified with salicylic acid (CS-SA-1, CS-SA-2) at the equilibration time of 7 h. An essential difference of the adsorption isotherm of metanil yellow by the CS-SA-2 sample may be caused by a more acidic nature of the modified sorbent surface (the pH of the point of zero charge is 2.3) and the acidic nature of the dye.

The desorption of salicylic acid from the surface of modified samples into the model solutions was studied (Fig. 8).

The maximum amount of the modifier passes into ethanol due to a better solubility of salicylic acid in
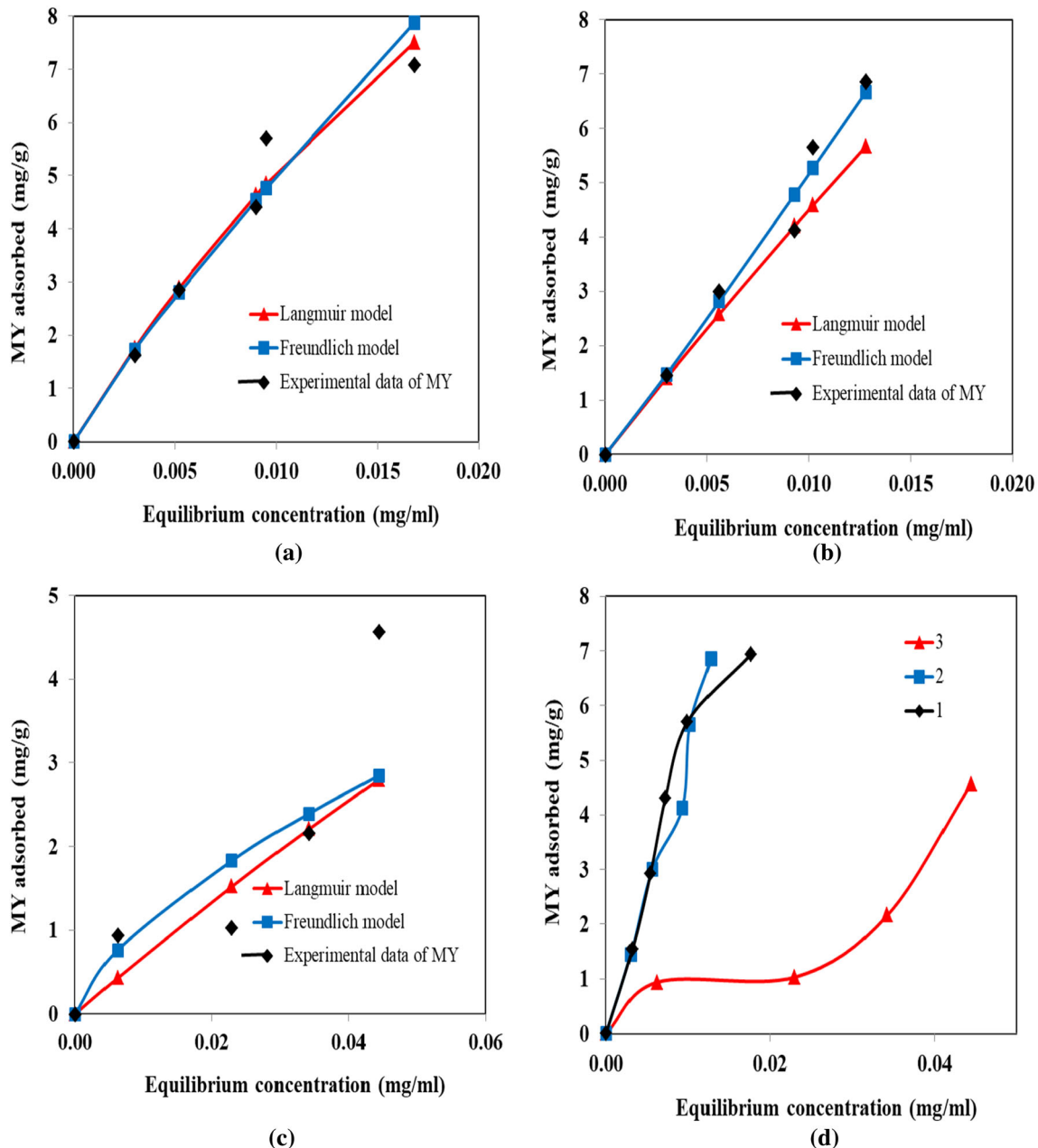
Figure 7 Isotherms of metanil yellow adsorption from aqueous solutions on the tested carbon sorbents. A comparison of experimental adsorption curves with the data calculated by Langmuir and Freundlich equations: CS (**a**), CS-SA-1 (**b**), and CS-SC-2 (**c**). A comparison of experimental adsorption curves on the tested samples (**d**): CS (1), CS-SA-1 (2), and CS-SA-2 (3).

alcoholic solutions as compared to aqueous ones. For the CS-SA-1 sample modified with the 500 mg/l salicylic acid solution, 49–50 rel.% of SA passes into alcoholic solution. For the CS-SA-2 sample modified with the 1500 mg/l salicylic acid solution—16–17 rel.% of SA. For the alcoholic model solution, stirring of the solution during the desorption of salicylic acid was shown to exert no effect.

For the CS-SA-1 sample, ca. 3 rel.% of the modifier (relative to the 500 mg/l concentration of salicylic acid solution chosen for modification) passes into physiological and aqueous solutions with or without shaking. For the CS-SA-2 sample, ca. 10 rel.% of the modifier (relative to the 1500 mg/l concentration of salicylic acid solution chosen for modification) passes into physiological and aqueous solutions with or

Table 7 Parameters of the Langmuir and Freundlich equations for the adsorption of metanil yellow by the carbon sorbents

Parameters	CS	CS-SA-1	CS-SA-2
Langmuir equation			
a_{theor}, mg/g	7.5	5.7	2.8
K_L, l/mg	23.75	5.90	2.64
r^2	0.548	0.067	0.007
Freundlich equation			
a_{theor}, mg/g	7.9	6.7	2.9
K_f	290.01	626.03	22.84
$1/n$	0.883	1.042	0.668
r^2	0.965	0.979	0.629

where a_{theor} is the maximum theoretical amount of adsorption, r^2 The correlation coefficient, K_L The Langmuir equation constant, K_f, n The Freundlich equation constants

without shaking. Thus, the amount of deposited modifier that passes into solution is greater for the CS-SA-2 sample.

Conclusion

Physical adsorption from solutions was used to obtain a carbon sorbent modified with salicylic acid. Optimal conditions of the modification were determined. The adsorption of salicylic acid on the carbon sorbent is adequately described by the Freundlich equation; the maximum adsorbed amount was 90.0 mg/g, which compares well with the published data on the adsorption of salicylic acid on the surface of carbon materials.

The pore structure and the presence of oxygen-containing groups on the surface of the modified carbon sorbent ensure high adsorption capacity toward organic dyes. The adsorption of methylene blue and metanil yellow on the surface of the modified carbon sorbent is adequately described by the Freundlich equation. The maximum adsorbed amount was 18.2 mg/g for methylene blue and 24.7 mg/g for metanil yellow.

The desorption of salicylic acid from the surface of the modified carbon sorbent into model solutions

Figure 8 Changes in the concentration of salicylic acid **a**, **c** and pH of the solution **b**, **d** upon contact of the modified sorbents CS-SA-1 **a**, **b** and CS-SA-2 **c**, **d** with the model solutions of NaCl (1), C2H5OH (2) and H2O (3).
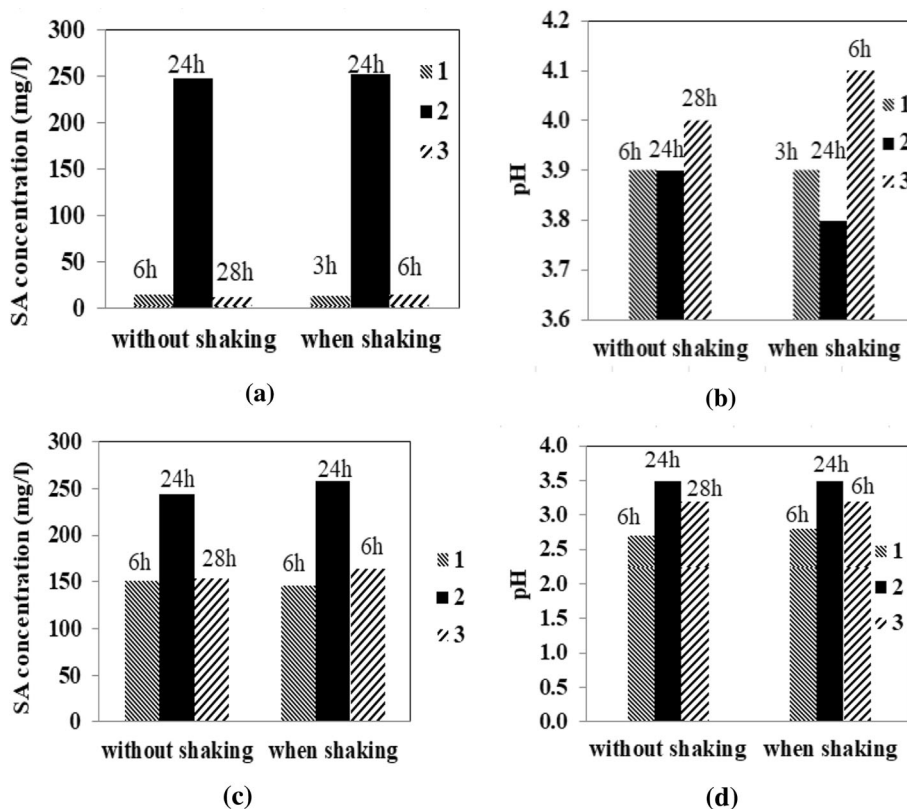
makes it possible to use the modified sorbent in medicinal and veterinary applications as a prolonged action material.

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Author contribution

AVS: Conceptualization, Methodology, Data curation, Writing—review & editing, Validation. LGP': Methodology, Visualization. NVK: Methodology, Investigation, Writing—original draft, Visualization, Writing—review & editing. MSD: Methodology, Visualization, Investigation, Writing—review & editing. VAD: Methodology, Visualization. AVV: Investigation, Methodology, Visualization. NNL: Supervision. MSM: Formal analysis, Writing—review & editing. AVL: Project administration. All authors have read and agreed to the published manuscript.

Data availability

No data was used for the research described in the article.

Declarations

Conflict of interest   The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors declare that they have no conflict of interest.

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