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PHYSICOCHEMICAL PROCESSES AT THE INTERFACES

Synthesis and Study of Physicochemical Properties of Mesoporous Carbon Sorbent Modified with 3-Phenylpropane Acid

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Abstract—The adsorption of 3-phenylpropanoic acid on a mesoporous carbon sorbent was studied. The optimal ratio and equilibrium time in the sorbent–phenylpropanoic acid solution system were determined. A method for modifying a carbon sorbent with 3-phenylpropanoic acid has been developed. The possibility of migration (desorption) of the modifier into solutions simulating the environment of the stomach and intestines was investigated. The set of physicochemical research methods—low-temperature nitrogen adsorption, IR, NMR, X-ray photoelectron and Raman spectroscopy, spectrophotometry, the titrimetric method of H.P. Boehm, CHNOS elemental analysis—were used to study the properties of a carbon sorbent before and after modification, as well as after desorption of the deposited 3-phenylpropanoic acid. The synthesized modified samples are promising for use as enterosorbents for treating gastrointestinal diseases.

Keywords: carbon mesoporous sorbent, 3-phenylpropanoic acid, adsorption, physicochemical properties, desorption

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INTRODUCTION

In medical practice, phenylcarboxylic acids are used as markers of diseases such as sepsis, immune, chronic, inflammatory diseases, etc. [1–3].

Of particular interest among these acids is 3-phenylpropanoic acid (PPA) (Fig. 1) [2–7]. 3-phenylpropanoic acid ($C_9H_{10}O_2$, MW 150.2 g/mol, average calculated molecule size 0.94 × 0.49 nm) has a wide range of applications, including cosmetics, food additives, and pharmaceuticals. Some physical properties of PPA are presented in Table 1 [8].

It is known that the absolute amount of PPA in circulating human blood is up to 2.5 μmol; in the intestines, up to 600 μmol. It has been established that PPA is absent in the blood serum of septic patients [3, 6, 8]. PPA has a positive effect on the human body, due to antibacterial action, and its esters exhibit antioxidant properties [3, 8–11]. PPA is a moderately toxic substance, and the introduction of 100 μmol (0.0001 M) of 3-phenylpropanoic acid into the human body is considered a relatively safe dose [8].

Application of 3-phenylpropanoic acid as a drug is problematic, since the acid has poor solubility in biological media (the solubility limit in water is 5.9 g/L) [8]. One solution to this problem is to develop multicomponent drugs consisting of a carrier (carbon, polymer, etc.) and an active substance immobilized or adsorbed on its surface [11–13]. When developing such drugs, the therapeutic effect will be achieved due to the gradual release of the modifier (active substance) deposited on the carrier. In the case of a modified PPA sorbent, in order to ensure a therapeutic effect, it is necessary that at least 100 μmol of biologically active substance be released into the biological medium from the sorbent [3, 8, 11]. A very important stage of research in drug development is the study of adsorption–desorption interactions between the modifier and the carrier [14].

Carbon materials have a number of advantages over other sorbents used as carriers for drug delivery: high adsorption surface, biocompatibility, and insolubility in biological media. Various carbon materials are widely used as carriers of medicinal substances: activated carbons [15, 16], carbon nanotubes [17–19], graphene [20, 21], and fullerenes [22, 23]. The possibilities for using carbon materials to immobilize biologically active and medicinal substances are diverse. This is due to the tasks posed and possibilities of regulating the porous structure and chemical nature of surface groups [24–26].

The adsorption and desorption of phenylcarboxylic acids on carbon materials have been little studied in

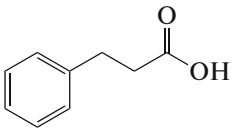

Fig. 1. Structural formula of 3-phenylpropanoic acid.

the literature; there is no data on the creation of drugs containing 3-phenylpropanoic acid for its delivery into the human body. Studies are known on the adsorption and use of active carbons as an inexpensive, accessible, effective and safe carrier for oral delivery of drugs based on the 3-phenylpropanoic acid derivative, ibuprofen [14, 15, 27].

To carry out the research, a mesoporous carbon sorbent was chosen as a carrier, developed at the Central Scientific Research and Technology Institute of the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (CSRT IC SB RAS) (Russia, Omsk) [28, 29]. It is a black spherical granule predominantly 0.5 mm in size. The sorbent is characterized by high chemical purity, neutral pH, biocompatibility, and high-strength granules. Owing to its developed mesoporous structure, it efficiently binds and removes low and medium molecular weight toxic substances (bilirubin, cholesterol, urea, etc.) from the body. In medical practice, on the basis of this material, Enterosorbent carbon VNIITU-2 was produced for binding and removing toxic substances from the gastrointestinal tract in the case of endotoxicosis, acute poisoning, and liver, kidney, autoimmune, and psychoneurological diseases.

The aim of the article is to study the adsorption of 3-phenylpropanoic acid on a mesoporous carbon sorbent: to determine the equilibrium time and the optimal ratio in the sorbent–phenylpropanoic acid solution system, and to study the dependence of the adsorption of organic acid on its concentration in solution.

The objectives are to develop a method for modifying a carbon sorbent with 3-phenylpropanoic acid and to study its physicochemical properties before and after adsorption and desorption of the modifier.

Table 1. Physical properties of 3-phenylpropanoic acid

Property	Value
Molar mass, g/mol	150.17
Density, g/cm^3	1.126
Melting temperature, °C	47–50
Boiling temperature, °C	280
Solubility limit in water at 100°C, g/L	5.9
Acid dissociation constant, (pK_a)	4.66 (H_2O)

EXPERIMENTAL

Materials

For the modification, a mesoporous carbon sorbent (CS) with a specific surface area of 315 m^2/g was selected, produced by CSRT IC SB RAS, Omsk, Russia. 3-phenylpropanoic acid (98%) produced by Sigma-Aldrich, Germany, was used as a modifier.

Study of PPA Adsorption on a Carbon Sorbent

The amount of 3-phenylpropanoic acid in an aqueous solution before and after adsorption on the carbon sorbent was determined by spectrophotometry on a CECIL-1021 instrument (Cecil Instruments Limited, England) using a quartz cell with an absorbing layer thickness of 10 mm at a wavelength of 254 ± 1 nm based on the calibration curve obtained in the concentration range 0.00125–0.02000 M.

The PPA adsorption was calculated using the formula [30, 31]

$$a = \frac{(C_0 - C_x)V}{m}, \quad (1)$$

where a is the value of PPA adsorption by the carbon sorbent (mol/g); C_0 and C_x are, respectively, the initial and equilibrium concentrations of PPA in solution (mol/L); V is the volume of the aqueous solution (L); m is the mass of the carbon sorbent sample (g).

Quantity a_{max} was calculated for $C_x = 0$ (limiting experimental adsorption value). For the obtained PPA adsorption values, the corresponding degree of extraction after contact with the sorbent was calculated [30, 31]:

$$R = \frac{C_0 - C_x}{C_0} \times 100, \quad (2)$$

where R is the degree of PPA extraction, %.

Methodology for Modifying the Carbon Mesoporous Sorbent PPA

The carbon sorbent was modified by adsorption of 3-phenylpropanoic acid from aqueous solutions of various concentrations (0.01–0.06 mol/L, M). The choice of initial PPA concentrations (0.01–0.06 M) is determined by the minimum amount of PPA required to ensure a therapeutic effect (no less than 0.0001 M), its toxicity (no more than 0.1 M), and solubility in water (0.06 M) [3, 8, 11]. To increase the solubility of PPA, 1–3 mL of ethyl alcohol was added when preparing its aqueous solutions. When preparing PPA solutions with a concentration of 0.04–0.06 M, hot distilled water (80–90°C) was used. The preparation of aqueous solutions of PPA with a concentration of more than 0.06 M is complicated by the limited solubility of the acid in water (Table 1).

The conditions for synthesizing the modified sorbent were: volume ratio in the sorbent–PPA solution system 1/80, contact time 24 h. After modification, the samples were dried in air for 24 h, then in an oven at a temperature of 105°C for 2 h.

As a result of modifying the carbon sorbent, the following samples were obtained: CS-PPA-0.01; CS-PPA-0.02, and CS-PPA-0.06, where in the notation, the numbers 0.01–0.06 indicate the initial concentration of the aqueous solution of PPA in mol/L, selected for modification.

RESEARCH METHODS

The textural properties of the samples were studied by low-temperature nitrogen adsorption (Gemini 2380 analyzer, Micromeritics, USA). The specific surface area was calculated using the BET equation. The qualitative composition of the surface functional groups of the studied samples was examined by IR spectroscopy (IR Prestige-21 spectrometer, Shimadzu, Japan). H.P. Boehm's titrimetric method was used to determine the quantitative content of carboxyl and phenolic groups on the surface of the studied samples. The chemical state of the surface of the samples was studied using X-ray photoelectron spectroscopy (XPS) (spectrometer Surface Science Center, Riber, France). The influence of modification and desorption processes on structural changes in samples was studied by Raman scattering (DXR Smart Raman spectrometer, Thermo Fisher Scientific, USA). The elemental composition of the samples was studied on a Vario El Cube CHNSO analyzer (Elementar Analysen systeme GmbH, Germany).

The desorption of applied PPA from the surface of modified samples was studied in solutions simulating the biological media of the stomach and intestines. The PPA concentration was determined by spectrophotometry (CECIL-1021 spectrophotometer, Cecil Instruments Limited, UK), and the pH of solutions was determined with a SARTORIUS PP-20 pH meter (Sartorius AG, Germany). To simulate the stomach environment, a 0.02 N HCl solution with pH 1.75 was used, and a 0.025 N $NaHCO_3$ with pH 8.2 solution was used to simulate the intestinal environment. Desorption was carried out under static conditions at a sorbent (g)/solution (mL) ratio of 1/5 at a temperature of 36 ± 2°C for 168 h (7 days).

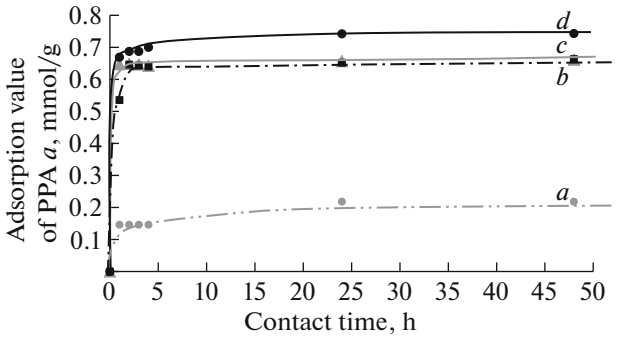

Fig. 2. Dependence of PPA adsorption value (0.02 M aqueous solution) on time of contact with carbon sorbent for studied volume ratios of 1/10 (*a*), 1/25 (*b*), 1/50 (*c*), and 1/80 (*d*).

RESULTS AND DISCUSSION

Study of the Adsorption Properties of the Carbon Sorbent with Respect to PPA

Using the example of a 0.02 M aqueous solution of PPA, the time to reach equilibrium and the optimal ratio in the sorbent–PPA solution system were determined. Using the resulting calibration graph, the adsorption value of PPA was calculated (formula (1)) depending on the time of contact with the carbon sorbent and the corresponding adsorption curves were plotted for the studied ratios 1/10, 1/25, 1/50 and 1/80 (vol) in the sorbent–PPA solution system. The obtained data are presented in Fig. 2.

To confirm the established patterns of PPA adsorption on the carbon sorbent, the textural properties of samples modified with a 0.02 M aqueous solution of 3-phenylpropanoic acid at different sorbent–PPA solution ratios were determined: 1/10, 1/25, 1/50, 1/80 (Table 2). A natural decrease in the specific surface area is observed with an increase in the ratio in the sorbent–PPA solution system.

The maximum value of PPA adsorption from an aqueous solution with a concentration of 0.02 M was 0.74 mmol/g and is achieved at a sorbent–PPA solution ratio of 1/80 (Fig. 2d). Thus, this ratio was taken as optimal for studying PPA adsorption.

The obtained values of adsorption depending on the time of contact of an aqueous solution of PPA

Table 2. Specific surface area of carbon sorbents after adsorption of 3-phenylpropanoic acid (0.02 M aqueous solution) at different sorbent–PPA solution ratios

Sample	Sorbent/PPA solution ratio	Specific surface area S_{BET}, m^2/g
CS-PPA-0, 0210	1/10	227
CS-PPA-0.02-25	1/25	138
CS-PPA-0.02-50	1/50	117
CS-PPA-0.02-80	1/80	111

Table 3. Data on adsorption quantity (a, mmol/g) and degree of extraction* (R, %) of PPA in a given concentration range from aqueous solutions with carbon sorbent as function of time at optimal ratio of 1/80

Time of contact, h	sorbent/PPA solution ratio 1/80			
	PPA concentration, mol/L			
	0.01	0.02	0.04	0.06
	adsorption (a, mmol/g) and degree of extraction (R*, %)			
1	0.69 (57.2)	0.67 (23.1)	0.41 (9.8)	0.82 (10.8)
2	0.73 (59.9)	0.69 (24.0)	0.45 (11.7)	0.83 (11.0)
3	0.67 (55.5)	0.69 (24.0)	0.57 (14.7)	1.70 (21.7)
4	0.69 (57.0)	0.70 (24.2)	0.56 (14.5)	1.90 (24.8)
24	0.74 (61.1)	0.74 (26.0)	0.62 (16.0)	3.40 (44.4)
48	0.75 (62.0)	0.75 (26.0)	0.66 (17.0)	5.20 (68.0)

*Extraction rate is indicated in parentheses.

(0.01–0.06 M) with a carbon sorbent at an optimal ratio of CS/PPA 1/80 are presented in Table 3.

It was shown that for the studied conditions in the PPA concentration range 0.01–0.04 M, the equilibrium state in the sorbent–PPA solution system at a ratio of 1/80 is established within 24 h. After 48 h, the adsorption value remains virtually unchanged. Only for a 0.06 mol/L PPA solution after 48 h, the value of adsorption on the carbon sorbent increases significantly from 3.40 to 5.20 mmol/g. The maximum adsorption value of PPA (aqueous solution of PPA 0.01–0.06 mol/L) were 0.75–5.20 mmol/g (extraction degree 17–68%) according to the experiment.

The developed method for modifying the surface of carbon sorbent samples with 3-phenylpropanoic acid includes impregnation of the sorbent with an aqueous solution of PPA with a concentration of 0.01–0.06 M in terms of moisture capacity at the selected optimal volumetric ratio of sorbent–PPA solution of 1/80 for 24 h, followed by drying of the samples in air during the day and in a drying cabinet for 2 h at a temperature of 105°C.

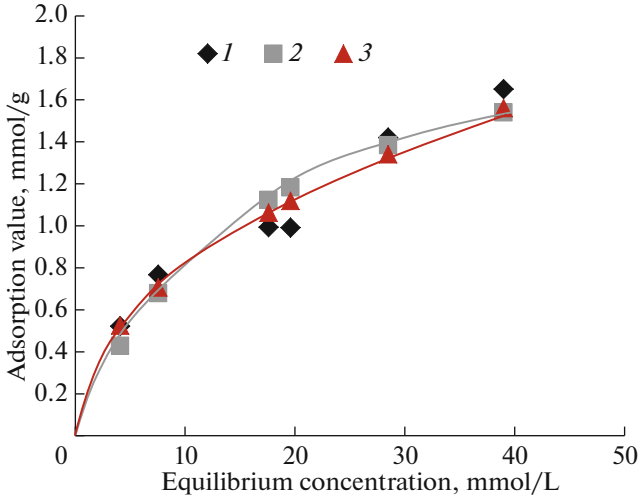

Fig. 3. Isotherm of adsorption of 3-phenylpropanoic acid on carbon sorbent CS: (*1*) experimental data; (*2*) according to Langmuir equation; (*3*) according to Freundlich equation.

Thus, the selected modification conditions make it possible to apply 5.2 mmol of PPA (0.035 mg) to 1 g of sorbent.

The adsorption of 3-phenylpropanoic acid on a carbon sorbent was studied as a function of its concentration (Fig. 3). The adsorption characteristics of the studied carbon with respect to PPA were calculated using the Langmuir equation of monomolecular adsorption and the Freundlich equation (Fig. 3, Table 4).

The type of experimental adsorption isotherm of PPA on the carbon sorbent (Fig. 3, curve *1*), according to the classification of adsorption isotherms from solutions on a solid surface CH Giles, corresponds to the class L1. It has a characteristic curved initial section with respect to the axis of equilibrium concentrations, since with an increase in the proportion of occupied adsorption sites, it is more difficult for PPA molecules to find a vacant place at its higher concentrations 0.04–0.06 mol/L [32, 33]. The maximum amount of PPA, 1.65 mmol/g, is adsorbed from an aqueous solution with an initial concentration of 0.049 mol/L.

According to the analysis of the research results (Fig. 3, Table 4), it is clear that in the range of equilibrium concentrations of 0.004–0.039 mg/L, the experimental adsorption isotherm of PPA on the carbon dioxide is better described by the Freundlich equation (correlation coefficient $R^2 = 0.963$) than the Langmuir equation (correlation coefficient $R^2 = 0.886$).

The adsorption studies carried out made it possible to select the conditions for modifying the carbon sorbent with a biologically active substance and apply 0.035 mg of 3-phenylpropanoic acid to 1 g of sorbent.

Table 4. Parameters of Langmuir and Freundlich equations for adsorption of 3-phenylpropanoic acid on carbon sorbent CS

Parameters	Langmuir equation	Parameters	Freundlich equation
a, mmol/g	2.22	a, mmol/g	1.60
K_L, L/mmol	0.058	K_f	0.265
		$1/n$	0.484
R^2	0.886	R^2	0.963

1. a, maximum calculated adsorption value, mmol/g; R^2, correlation coefficient. 2. K_L, Langmuir equation constant; K_f, n, Freundlich equation constant.

Table 5. Textural properties of studied carbon sorbents

Sample	Specific surface area S_{BET}, m^2/g	Total pore volume, cm^3/g	Mesopore volume, cm^3/g	Micropore volume, cm^3/g
CS	315	0.342	0.332	0.010
CS-PPA-0.01	117	0.183	0.183	–
CS-PPA-0.02	101	0.158	0.158	–
CS-PPA-0.06	26	0.086	0.086	–

Thus, with complete desorption of the modifier from the carbon sorbent, 19 g of sorbent modified by PPA is required to ensure a therapeutic effect.

Physicochemical Properties of the Studied Samples

Textural Properties of the Studied Carbon Sorbents

Using low-temperature nitrogen adsorption, the textural properties of carbon sorbents modified with a 0.01–0.06 M aqueous solution of 3-phenylpropanoic acid were determined for the established optimal parameters (Table 5).

It was found that with increasing concentration of 3-phenylpropanoic acid (from 0.01 to 0.06 M), there is a natural decrease in the specific surface area of the modified samples by 3.1–12.1 times and a corresponding increase in the maximum adsorption value of PPA (from 0.5 to 5.2 mmol/g). All modified samples are characterized by a mesoporous structure.

The amount of adsorbed PPA for the CS-PPA-0.06 sample was 0.035 mg per 1 sorbent. Thus, as a result of modification, this amount of biologically active substance covers 289 m^2/g specific surface area.

Qualitative and Quantitative Composition of Surface Functional Groups of the Studied Carbon Sorbents

According to the H.P. Boehm's titrimetric method, the content of oxygen-containing groups on the surface of carbon sorbent samples before and after PPA adsorption was determined (Table 6).

It was established that with an increase in the concentration of 3-phenylpropanoic acid for all studied samples, there is a natural increase in oxygen-containing groups on the modified carbon sorbent by 2.8–4.0 times, while carboxyl groups predominate in their composition (0.142–0.225 mmol/g).

Using IR spectroscopy, the qualitative composition of the surface functional groups of the studied samples was determined. IR spectra of the studied carbon sorbents CS and CS-PPA-0.01. are presented in Fig. 4.

In the IR spectrum of the initial carbon sorbent, the CS (Fig. 4, spectrum *1*) absorption bands (AB) characteristic of stretching vibrations of C=O bonds in carboxylic acids, ketones and esters appear (1700–1760 cm^{-1} region), C=C in the aromatic ring of conjugated systems (1550–1590 cm^{-1} region), C–O in phe-

Table 6. Content of functional oxygen-containing groups on surface of studied samples: total acidic, carboxyl (CG), and phenolic (PG)

Sample	Modifier concentration, mol/L	Total acidic groups, mmol/g	CG, mmol/g	PG, mmol/g
CS	–	0.065	0.032	0.033
CS-PPA-0.01	0.01	0.185	0.142	0.043
CS-PPA-0.02	0.02	0.245	0.205	0.040
CS-PPA-0.06	0.06	0.261	0.225	0.036

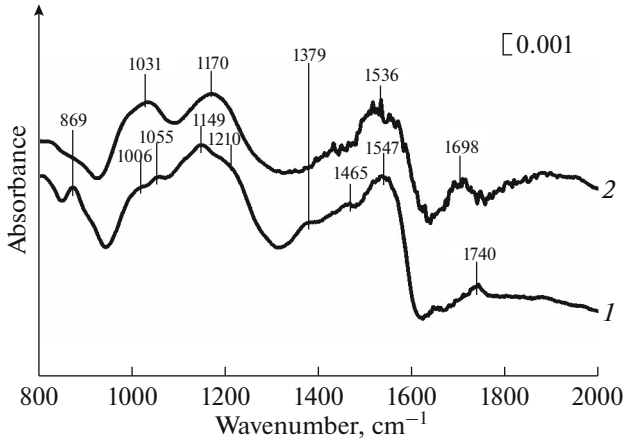

Fig. 4. IR spectrum of studied carbon sorbents CS (*1*) and CS-PPA-0.01 (*2*).

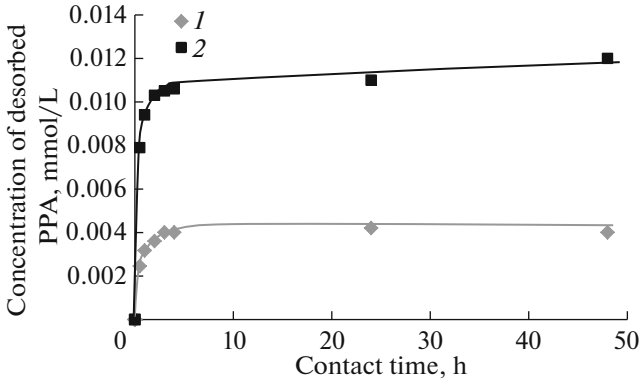

Fig. 5. Desorption of PPA from surface of sample CS-PPA-0.01 at pH 1.5 (HCl) and 8.2 ($NaHCO_3$).

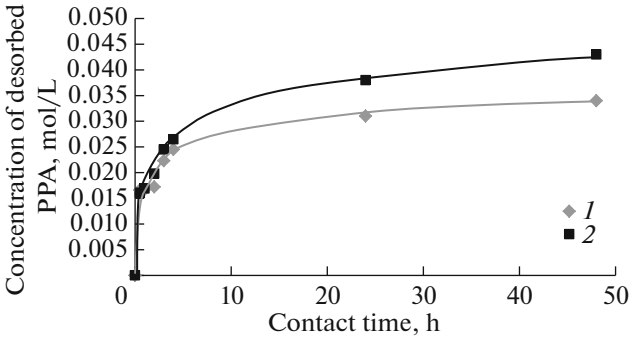

Fig. 6. Desorption of PPA from surface of sample CS-PPA-0.06 at pH 1.5 (HCl) and 8.2 ($NaHCO_3$).

nolic and alcohol structures (1000–1200 cm^{-1} region), and C–O in lactones and phenol esters (1200–1230 cm^{-1} region). Low-intensity absorption bands are also observed in the IR spectrum of the initial CS sample at 1461 and 1373 cm^{-1}, which probably corresponds to ions CO_3^{2-}, as impurity ions upon contact with the atmosphere.

When the sorbent was modified with 3-phenylpropanoic acid, broadening of the absorption band was recorded in the IR spectra in the spectral regions 800–1200 cm^{-1} (C–O in phenolic and alcohol structures) and 1700–1760 cm^{-1} (C=O in carboxylic acids, ketones, and esters) (Fig. 4, spectrum *2*). Also, for the CS-PPA-0.01 sample, broadening of the absorption band is observed in the spectral region 1500–1590 cm^{-1} (C=C in the aromatic ring of conjugated systems).

Study of Desorption of PPA from the Carbon Sorbent under Model Conditions

The desorption (migration) of applied PPA from the surface of modified samples was studied in solutions simulating the biological environments of the stomach (0.02 N HCl solution with pH 1.75) and intestines (0.025 N $NaHCO_3$ solution with pH 8.2). Research for 7 days was carried out for samples CS-PPA-0.01 and CS-PPA-0.06.

The concentrations of PPA desorbed from the carbon sorbent into model solutions were calculated using spectrophotometry. The change in pH of HCl and $NaHCO_3$ solutions was also determined over 48 h.

Using the obtained experimental values, curves were plotted for the dependence of the PPA concentration after desorption on the time of contact with samples CS-PPA-0.01 (Fig. 5) and CS-PPA-0.06 (Fig. 6).

The results of the study (Figs. 5, 6) demonstrate that in an acidic medium—that of the stomach (0.02 N HCl solution)—a small amount of modifier migrates into the solution: the PPA concentration after desorption for the CS-PPA-0.01 sample was 4 mmol/L; for sample CS-PPA-0.06, 34 mmol/L. The pH of the solutions also increased by 0.5.

Desorption of the biologically active substance occurs best in an alkaline environment—the intestinal environment (0.025 N $NaHCO$ solution$_3$): the concentration of 3-phenylpropanoic acid migrating from the surface of the CS-PPA-0.01 sample into the sodium bicarbonate solution was 12 mmol/L, from the surface of the CS-PPA-0.06 sample, 43 mol/L. In this case, the pH of the $NaHCO_3$ solution decreased by 3–4, respectively.

It was found that after 48 h after contact with the modified samples, the concentrations of PPA and the pH of solutions simulating the environment of the human body did not change.

With low-temperature nitrogen adsorption, the values of the specific surface area of the studied samples after desorption of PPA were determined under model conditions (Table 7). The results confirm the desorption of PPA from the surface of the CS-PPA-0.06 sorbent into model solutions: the surface area

Table 7. Specific surface area of carbon sorbent samples after desorption of PPA under model conditions

No.	Sample	S_{BET} after adsorption, m^2/g	Model solution	S_{BET} after desorption, m^2/g
1	CS-PPA-0.01	117	$NaHCO_3$	119
			HCl	116
2	CS-PPA-0.06	26	$NaHCO_3$	44
			HCl	48

increased by 1.9 times (18–22 m^2/g of specific surface area is freed from the applied modifier).

Analysis and calculation of the results of a study on the desorption of PPA from a modified sample CS-PPA-0.06 showed that when hydrochloric acid and sodium bicarbonate are used as solutions simulating the biological medium of the stomach and intestines, 6–7% (0.0022–0.0026 mg from 1 g of sorbent) is desorbed modifier from the applied amount (if we take 0.035 mg of PPA as 100%, calculated from experimental data on acid adsorption).

Thus, complete desorption of the modifier from the carbon sorbent is not observed under the studied conditions. According to the desorption results, to ensure the minimum therapeutic effect (the concentration of PPA released into the body is 10 μmol), 19 g of sorbent modified by PPA is not required, but 27–31 mg of the drug. That is, the approximate dosage of the drug can be calculated as 10 g three times a day.

The observed results of studies on PPA desorption in model media differing in pH can be explained as follows. The point of zero charge of the carbon sorbent is 7.4 (pH_{TNZ} 7.4). At pH 1.5, PPA molecules are neutral (pKa(PPA) = 4.7), and the surface of the sorbent has a positive charge. Thus, the equilibrium in an acidic environment will shift towards adsorption of the modifier on the carbon surface: adsorption occurs due to the dispersion interaction between the modifier molecules and functional groups on the surface of the sorbent. At pH 8.5, the PPA molecules and surface of the carbon sorbent are negatively charged; in this system, electrostatic repulsion of the adsorbate molecules from the carbon surface occurs. Accordingly, the equilibrium in an alkaline environment will shift towards desorption of the modifier from the carbon surface [27, 34].

After studying the desorption of CS-PPA-0.06-D-$NaHCO_3$ and CS-PPA-0.6-D-HCl, the samples were studied by XPS and Raman spectroscopy (RS). Their comparative analysis was carried out with the initial carbon sorbent CS and the modified sample CS-PPA-0.06.

Figure 7 shows overview XPS spectra of carbon sorbents measured in the binding energy range 0–1050 eV. In all spectra, photoelectron lines of carbon (C1s) and oxygen (O1s), as well as the line of the Auger transition of oxygen O KLL, are observed. No lines of other elements are observed in the spectra, which indicates the purity of the samples.

During the modification process, the amount of oxygen in the surface layer of the samples decreases, possibly due to the quantitative redistribution of oxygen in the sample [35]. During desorption at different pH values, the oxygen concentration decreases in equal amounts for the samples CS-PPA-0.06-D-$NaHCO_3$ and CS-PPA-0.06-D-HCl.

The structural and chemical state of the surface was analyzed from the XPS spectra of the carbon (C1s) and oxygen (O1s) lines. Figure 8 shows that the value of the full width at half-maximum (FWHM) of the parameter of the C1s line decreases in the spectrum of the sample after modification with CS-PPA-0.01. According to the literature data, this may indicate an increase in the degree of ordering of the carbon structure [36].

The carbon spectra were approximated using several components denoted C1–C5 in accordance with [37–40]. The most intense component of the spectrum (C1) at a binding energy of ~284.5 eV corresponds to the states of carbon included in the C=C bonds (sp^2-carbon). The spectral component at a binding energy of ~285.5 eV (C2) corresponds to the states of hydrogenated carbon (C–H); carbon found

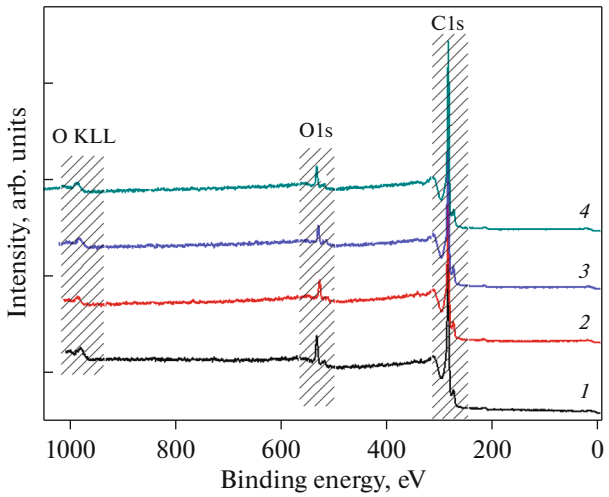

Fig. 7. Overview XPS spectra of samples: (*1*) CS; (*2*) CS-PPA-0.06; (*3*) CS-PPA-0.06-D-NaHCO3; (*4*) CS-PPA-0.06-D-HCl.

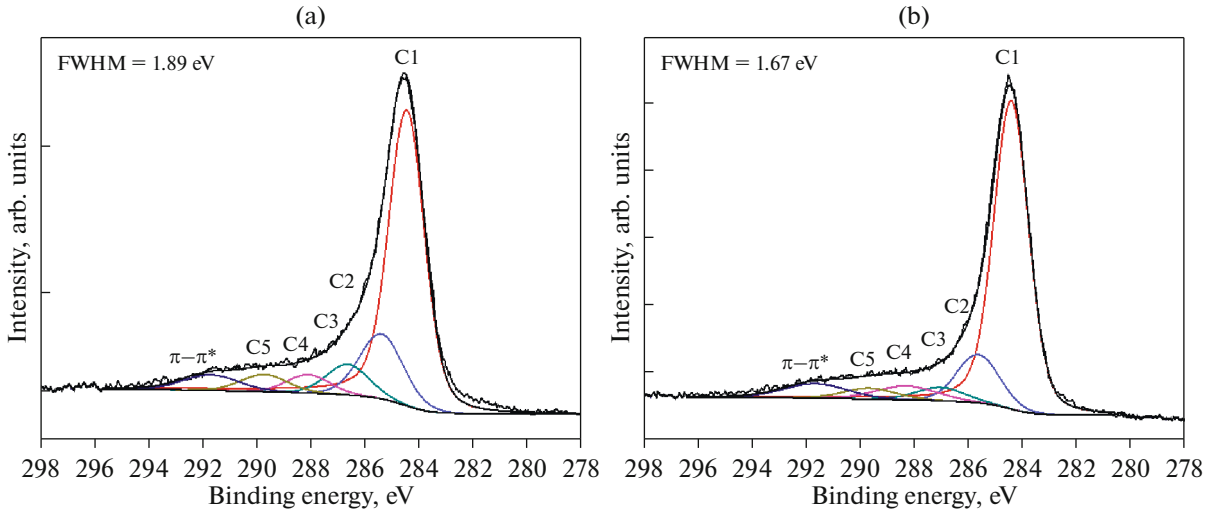

Fig. 8. XPS C1s spectra of samples: (a) CS; (b) CS-PPA-0.06.

in the sp^3-hybridized state (C–C); and carbon atoms located directly next to oxidized carbon (C*–C(O)). The component with the maximum at a binding energy of ~287 eV (C3) corresponds to carbon in the composition of single C–O bonds (epoxy, hydroxide, ether, carbonyl, and other functional groups). At binding energies of ~288 and 289.5 eV, there are states corresponding to carbon in the C=O and COOH groups, respectively (C4 and C5). The local maximum at a binding energy of ~292 eV corresponds to the so-called "shake up" satellite (π–π*), the presence of which is characteristic of the spectra sp^2-of carbon materials with a low content of structural defects. The quantitative results of the decomposition are presented in Table 8.

The increase in the proportion of component C1 (corresponding to C=C bonds) in the spectrum of the CS-PPA sample is consistent with the results of quantitative analysis, which showed a decrease in the oxygen concentration on the surface of this sample after impregnation with a modifier (Table 8).

A decrease in the relative intensity of component C2 indicates a decrease in the degree of defectiveness of the crystal structure in the surface layers of the carbon sorbent. A change in the intensity of components corresponding to different carbon-oxygen chemical bonds is also observed. The proportion of component C3, corresponding to single C–O bonds, significantly decreases, and the proportion of component C5 (C=O bond) decreases less so, while the proportion of component C4 (corresponding to COOH groups) somewhat increases.

Figure 9 shows the XPS O1s spectra of the initial and modified samples. The spectra contain three components corresponding to the states of oxygen in single C–O bonds, as well as in water molecules adsorbed on the surface (~533 eV), double C=O bonds (~531.5 eV) and COOH bonds (~530.5 eV) , denoted O1, O2 and O3, respectively [40–42]. As can be seen from Fig. 7, the integral intensity of the components corresponding to oxygen in the O1 and O3 bonds significantly decreases in the spectrum of the sample after modification. The decrease in the relative proportion of the O1 component in the spectrum of the modified sorbent agrees with the results of decomposition of the XPS C1s spectrum, which showed a decrease in the proportion of carbon in the composition of the C–O bond for this sample.

Figure 10 shows the results of analyzing the XPS C1s spectra of samples after desorption under model conditions.

Table 8. Quantitative results of decomposition of C1s spectra

Sample	Relative area of component, %				
	[C1]	[C2]	[C3]	[C4]	[C5]
CS	66.6	16.1	8.4	4.4	4.5
CS-PPA-0.06	76.2	12.7	3.2	4.5	3.4
CS-PPA-0.06-D-$NaHCO_3$	78.3	9.5	4.5	4.0	3.7
CS-PPA-0.06-D-HCl	78.1	9.7	4.1	4.1	4.0

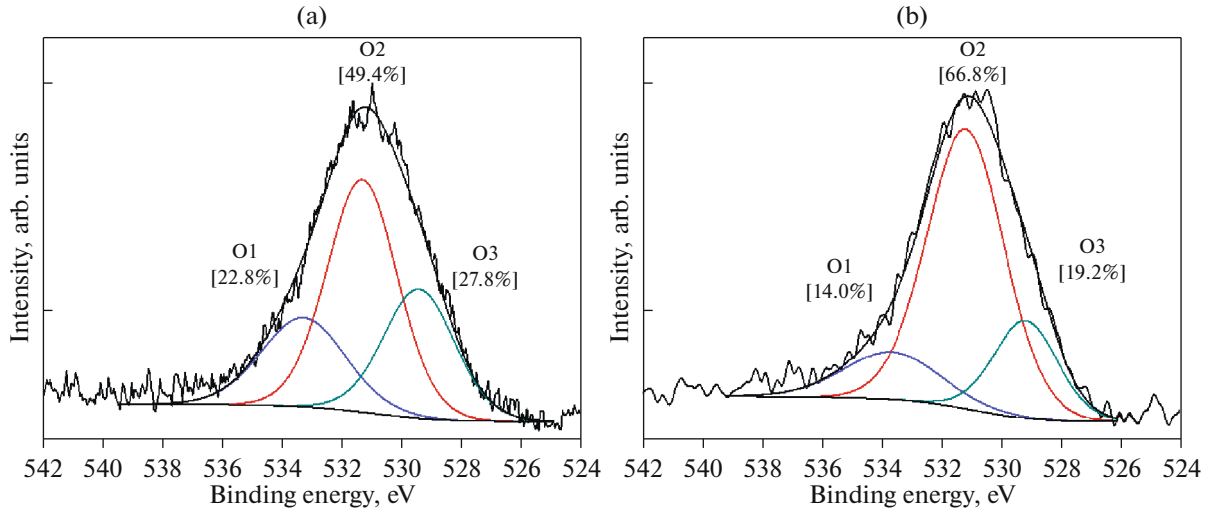

Fig. 9. XPS of O1s spectra: (a) CS; (b) CS-PPA-0.06.

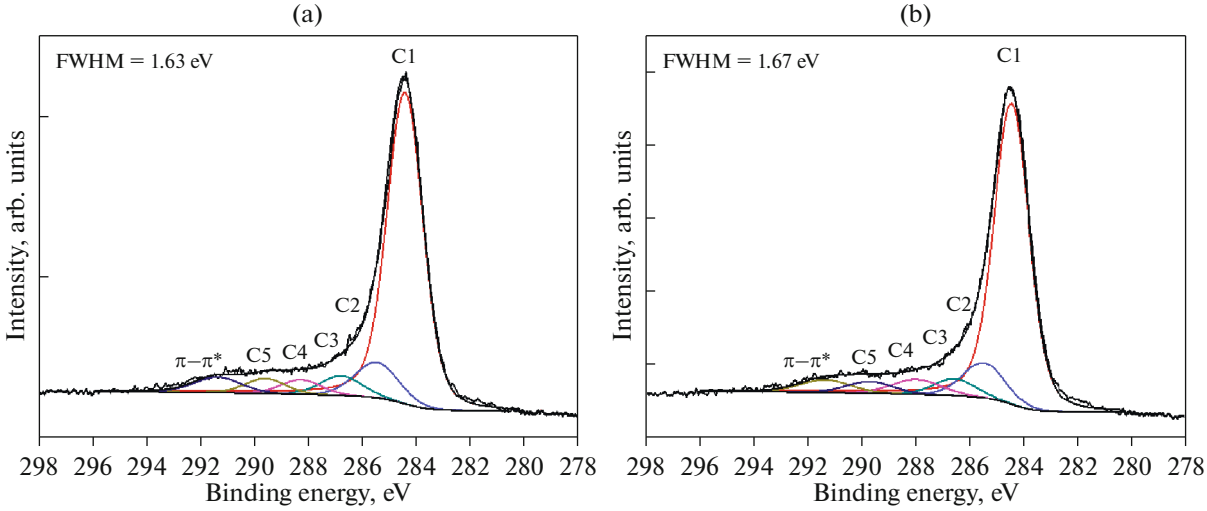

Fig. 10. XPS of C1s spectra of samples after desorption: (a) CS-PPA-0.06-D-$NaHCO_3$; (b) CS-PPA-0.06-D-HCl.

The quantitative results of decomposition of C1s spectra for the studied samples are presented in Table 8. The results indicate a similar state of carbon after desorption under model conditions. It has been shown that after desorption, the state of carbon on the surface differs from its state on the surface of the initial carbon sorbent. The proportion of component C1 corresponding to C=C bonds in the spectra of samples after different desorption variants exceeds the proportion of this component in the spectrum of the initial sorbent. The proportion of component C3, corresponding to the states of carbon in single C–O bonds in the samples after desorption, increases slightly with respect to its proportion in the spectra of the modified sample (Table 8).

XPS analysis of the O1s spectra also indicates a similar chemical state of the surface of the samples after desorption in different media (Fig. 11). In these spectra, an increase in the proportion of components O1 and O3 is observed compared to the spectrum of the modified sample (Fig. 9b).

Figure 12 shows the Raman spectra of the studied samples. It can be seen that typical lines at 1323 cm^{-1} (D-band) and 1601 cm^{-1} (G-band) are recorded in the Raman spectra. The ratio of their intensities is given in Table 9. It can be seen that ID/IG > 1 do not differ significantly from each other. It was established that the studied sorbents have an amorphous structure and there were no changes in it after modification.

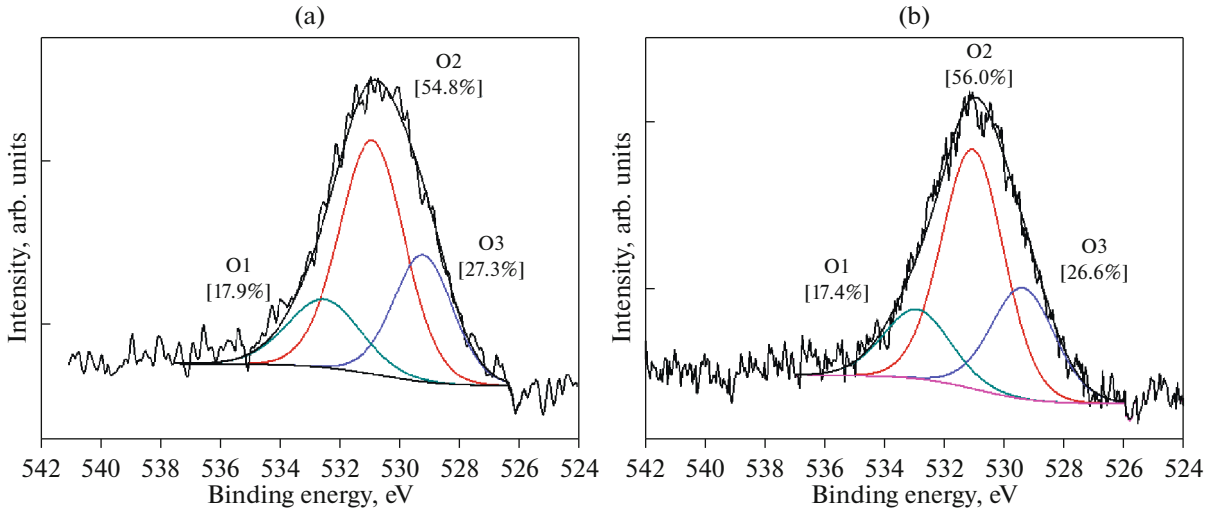

Fig. 11. XPS of O1s spectra of samples after desorption: (a) CS-PPA-0.06-DNaHCO$_3$; (b) CS-PPA-0.06-DHCl.

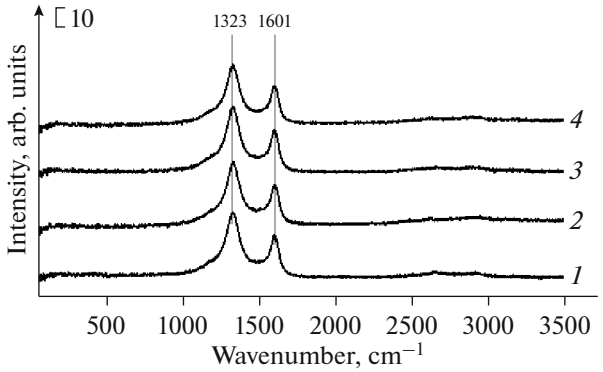

Fig. 12. Raman spectra of studied sorbents: (*1*) CS; (*2*) CS-PPA-0.06; (*3*) CS-PPA-0.06-DHCl; (*4*) CS-PPA-0.06-DNaHCO$_3$.

Table 10 presents the results of quantitative elemental analysis of the studied samples. When the carbon sorbent is modified with 3-phenylpropanoic acid, an increase in oxygen content is observed from 0.85 to 2.67 wt % and hydrogen from 0.16 to 0.67 wt %, while the carbon content decreases from 98.43 to 96.23 wt %. With increasing concentration of the PPA solution, a further increase in the oxygen and hydrogen content and a decrease in the carbon content in the modified samples are observed. After desorption, no significant changes in the quantitative composition of the samples are observed with this analysis method.

Thus, modification and desorption do not affect the initial structure of the carbon sorbent, which is a positive result when choosing it as a carrier for development of a long-acting drug based on it.

CONCLUSIONS

Based on the results of adsorption studies, a method for modifying a mesoporous carbon sorbent with 3-phenylpropanoic acid was developed: optimal synthesis conditions were determined (PPA concentration 0.01–0.06 mol/L, volume ratio "sorbent–PPA solution" 1/80, contact time 24 h, temperature 25 °C, static conditions (constant stirring).

The obtained results of physicochemical studies made it possible to establish that the carbon sorbent modified with 3-phenylpropanoic acid with a concentration of 0.06 M (sample CS-PPA-0.06), is the most promising sample, since it contains the largest amount of adsorbed biologically active substance—PPA (5.20 mmol/g)—with a high content of oxygen-containing groups (0.261 mmol/g). The adsorption stud-

Table 9. Intensities of D- and G-bands of studied carbon sorbents

Sample	Intensity		Ratio of D-band intensity to G-band intensity
	G-band	D-band	
CS	11.717	17.878	1.53
CS-PPA-0.06	11.145	17.607	1.58
CS-PPA-0.06-D-NaHCO$_3$	10.533	16.008	1.52
CS-PPA-0.06-D-HCl	11.514	18.213	1.58

Table 10. Quantitative elemental composition of studied samples

Sample	Content of elements, wt %		
	C	N	O
CS	98.43 ± 0.10	0.16 ± 0.05	0.85 ± 0.15
CS-PPA-0.01	96.23 ± 0.35	0.67 ± 0.02	2.67 ± 0.03
CS-PPA-0.01-D-HCl	96.88 ± 0.20	0.54 ± 0.03	2.30 ± 0.15
CS-PPA-0.06	95.21 ± 0.17	0.76 ± 0.06	3.18 ± 0.06
CS-PPA-0.06-D-$NaHCO_3$	94.94 ± 0.11	0.83 ± 0.01	3.28 ± 0.21

ies made it possible to select the conditions for modifying the carbon sorbent with a biologically active substance and apply 0.035 mg of 3-phenylpropanoic acid to 1 g of sorbent.

Using sample CS-PPA-0.06 as an example, the desorption of PPA in solutions simulating the biological media of the stomach and intestines was studied. The set of physicochemical analysis methods has established the following:

– the most intense desorption of 3-phenylpropanoic acid occurs under conditions simulating the intestinal environment, at pH 8.5 for 48 h;

– after contact with solutions simulating the biological environment of the stomach and intestines, the surface area increased by 1.9 times (18–22 m^2/g is freed from the applied modifier specific surface area, which is 6–7% of the applied amount of modifier or 0.0022–0.0026 mg per 1 g of sorbent);

– desorption processes under the studied conditions do not affect the initial structure of the carbon sorbent.

Thus, complete desorption of the modifier from the carbon sorbent CS-PPA-0.06 is not observed when using hydrochloric acid and sodium bicarbonate as solutions simulating the biological environment of the stomach and intestines.

It can be suggested that in real conditions, when studying the desorption of the modified sample CS-PPA-0.06 in biological media in the human body, which are more complex systems than those selected in this study, the migration of the biologically active substance 3-phenylpropanoic acid will proceed more completely, since greater desorption of PPA from the carbon carrier can be facilitated by enzymes, salts, amino acids, glucose, and other biological substances present in the biological fluid of the gastrointestinal tract.

Future research plans include studying desorption processes in more complex model environments similar to the biological media of the gastrointestinal tract—in biorelevant media. Such media are as close in composition and physicochemical properties as possible (pH, osmolality, buffer capacity, surface tension, and composition) [43]. The use of these media makes it possible to most reliably simulate the behavior of drugs under in vivo conditions.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. Koh, A., Vadder, F.De., Kovatcheva-Datchary, P., and Backhed, F., *Cell,* 2016, vol. 165, p. 1332.
2. Kumar, N. and Goel, N., *Biotechnol. Rep.,* 2019, vol. 24, p. 00370.
3. Beloborodova, N.V., Moroz, V.V., Osipov, A.A., et al., *Biochemistry* (Moscow), 2015, vol. 80, p. 374.
4. Beloborodova, N.V., *Gen. Reanimatol.,* 2019, vol. 15, no. 6, p. 62.
5. Martínez-Oca, P., Robles-Vera, I., Sánchez-Roncero, A., et al., *J. Nutr. Biochem.,* 2020, vol. 81, p. 108383.
6. Kirby, T.O., Ochoa-Reparaz, J., Roullet, J.-B., and Gibson, K.M., *Mol. Genet. Metab.,* 2021, vol. 132, no. 1, p. 1.
7. Pautova, A.K., Sobolev, P.D., and Revelsky, A.I., *Clin. Mass Spectrom.,* 2019, vol. 14, p. 46.
8. National Center for Biotechnology Information. PubChem Compound Summary for CID 107, 3-Phenylpropionic acid PubChem. https://pubchem.nc-

bi.nlm.nih.gov/compound/3-Phenylpropionic-acid. Accessed January 11, 2023.

9. Cueva, C., Moreno-Arribas, M.V., Martín-Álvarez, P.J., et al., *Res. Microbiol.,* 2010, vol. 161, p. 372.
10. Lee, I., Han, M., Kim, D., and Yun, B., *Bioorg. Med. Chem. Lett.,* 2014, vol. 24, p. 3503.
11. Gisbert-Garzarán, M., Manzano, M., and Vallet-Regi, M., *Bioengineering,* 2017, vol. 4, p. 3.
12. Devnarain, N., Osman, N., Fasiku, V.O., et al., *Rev. Nanomed. Nanobiotechnol.,* 2021, vol. 13, p. 1664.
13. Deirram, N., Zhang, C., Kermaniyan, S.S., et al., *Macromol. Rapid Commun.,* 2019, vol. 40, p. 1800917.
14. Dong, P., Rakesh, K.P., Manukumar, H.M., et al., *Bioorg. Chem.,* 2019, vol. 85, p. 325.
15. Miriyala, N., Ouyang, D., Perrie, Y., et al., *Eur. J. Pharm. Biopharm.,* 2017, vol. 115, p. 197.
16. Yadavalli, T., Ames, J., Agelidis, A., et al., *Sci. Adv.,* 2019, vol. 5, p. 1.
17. Mehra, N.K. and Palakurthi, S., *Drug Discovery Today,* 2016, vol. 21, p. 585.
18. Falank, C., Tasset, A.W., Farrell, M., et al., *Nanomedicine,* 2019, vol. 20, p. 102025.
19. Zhua, S., *Aquaculture,* 2019, vol. 512, p. 734377.
20. Muthoosamy, K., Bai, R.G., and Manickam, S., *Curr. Drug Delivery,* 2014, vol. 11, p. 701.
21. Campbell, E., Hasan, Md.T., and Pho, C., *Sci. Rep.,* 2019, vol. 9, p. 416.
22. Kumar, M. and Raza, K., *Pharm. Nanotechnol.,* 2017, vol. 5, p. 169.
23. Grebinyk, A., Prylutska, S., and Grebinyk, S., *Nanoscale Res. Lett.,* 2019, vol. 14, p. 61.
24. Thambiliyagodage, C., Mirihana, S., and Gunathilaka, H., *Biomed. J. Sci. Tech. Res.,* 2019, vol. 22, p. 16905.
25. Zhao, Q., Lin, Y., Han, N., et al., *Drug Delivery,* 2017, vol. 24, p. 94.
26. Maiti, D., Tong, X., Mou, X., and Yang, K., *Front. Pharmacol.,* 2019, vol. 9, p. 1.
27. Guedidi, H., Reinert, L., Soneda, Y., et al., *Arabian J. Chem.,* 2017, vol. 10, p. 3584.
28. P'yanova, L.G., Likholobov, V.A., Sedanova, A.V., and Drozdetskaya, M.S., *Russ. J. Gen. Chem.,* 2020, vol. 90, no. 3, p. 550.
29. Likholobov, V.A., P'yanova, L.G., Danilenko, A.M., et al., *J. Fluorine Chem.,* 2019, vol. 227, p. 109372.
30. Sedanova, A.V., P'yanova, L.G., Delyagina, M.S., et al., *Chem. Sustainable Dev.,* 2022, vol. 30, p. 543.
31. Vezentsev, A.I., Thuy, D.M., Goldovskaya-Peristaya, L.F., and Glukhareva, N.A., *Indones. J. Chem.,* 2018, vol. 18, p. 733.
32. Alaqarbeh, M.M., *Rhazes: Green Appl. Chem.,* 2021, vol. 13, p. 43.
33. Giles, C.H., Macewan, C.H., Nakhwa, S.N., and Smith, D., *J. Chem. Soc.,* 1960, p. 3973.
34. Popov, A.Yu., Blinnikova, Z.K., Tsyurupa, M.P., and Davankov, V.A., *Sorbtsionnye Khromatogr. Protsessy,* 2017, vol. 17, no. 2, p. 183.
35. Eleftheriadis, G.K., Filippousi, M., Tsachouridou, V., et al., *Int. J. Pharm.,* 2016, vol. 515, p. 262.
36. Xu, C., Shi, X., Ji, A., et al., *PLoS One,* 2015, vol. 15, p. 1.
37. Chen, X., Wang, X., and Fang, D., *Fullerenes, Nanotubes, Carbon Nanostruct.,* 2020, vol. 28, no. 2020, p. 1048.
38. Yamada, Y. and Sato, S., *Carbon,* 2015, vol. 269, p. 181.
39. Kovtun, A., Jones, D., Dell'Elce, S., et al., *Carbon,* 2019, vol. 143, p. 268.
40. Bobenko, N.G., Bolotov, V.V., Egorushkin, V.E., et al., *Carbon,* 2019, vol. 153, p. 40.
41. Sotoma, S., Akagi, K., Hosokawa, S., et al., *RSC Adv.,* 2015, vol. 5, p. 13818.
42. Zhang, L., Tu, L., Liang, Y., et al., *RSC Adv.,* 2018, vol. 8, p. 42280.
43. Ramenskaia, G.V., Shokhin, I.E., Savchenko, A.Iu., and Volkova, E.A., *Biomed. Khim.,* 2011, vol. 57, no. 5, p. 482.