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NANOCOMPOSITE SYSTEMS PECTIN/SILICA AND THEIR PROPERTIES

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Composite systems based on pectins and silica materials are investigated in the paper. This can be a promising direction in the creation of systems with high adsorption characteristics in relation to molecules of medium and large molecular weight. In particular, the prospects of creating composites based on a mixture of hydrophobic and/or hydrophilic silicas (AM-1 and/or A-300, respectively) with pectin are shown. It has been found that the maximum adsorption of methylene blue occurs from the model solution at pH 5.5 on the surface of all the studied samples. The A-300/AM-1/pectin composite system proved to be the best, regardless of the amount of pectin in the composite (5 or 10%) at different pH values (1.5 and 5.5), compared to other adsorbents.

The purpose of this work was the construction of composite systems based on pectin and silicas (hydrophobic and hydrophilic and their mixtures), the study on their adsorption parameters in relation to the cationic dye methylene blue, and the effect of pectin on the hydration characteristics of silica sorbents.

The peculiarities of the formation of water layers in hydrated nanocomposite systems were investigated by the method of low-temperature ^{1}H NMR spectroscopy. It has been shown that by changing the concentration ratio of pectin and hydrophobic silica, the structure of the interfacial water and the energy of water interaction with the surface can be controlled. Due to this, new types of functionalized materials can be created for use in medical composites.

It has been shown that composite systems containing AM-1 hydrophobic silica are characterized by a decrease in interfacial energy in a weakly polar environment, which is due to the thickening of interfacial water clusters, and the size of surface water clusters decreases during the process of defrosting the system. It has been found that the amount and binding energy of water in heterogeneous systems based on pectin are influenced by the processes of interparticle interactions between heterogeneous components, which likely determine the degree of association of molecules in the water layer.

***Keywords**: composite system, pectin, hydrophobic silica, ^{1}H NMR spectroscopy, adsorption, methylene blue*

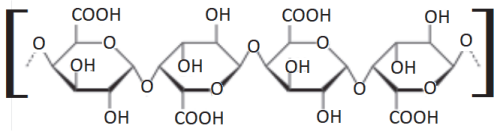
INTRODUCTION

Silica adsorbents are widely used as medical means to cleanse the body of toxic substances, which are metabolic products or those that entered the body as a result of food poisoning [1–3]. Fumed silica belongs to hydrophilic substances and has a high affinity for protein molecules, and also limitedly sorbs organic molecules with an average molecular weight. However, in modern pharmacology there is a demand for the creation of adsorbents in which the surface is formed by natural biopolymeric compounds, such as polysaccharides.

Pectins are a promising natural adsorbent. The largest amount of pectin substances is found in plant tissues: juicy fruits and root crops. The raw materials for the industrial production of pectin are mostly apple and citrus pomace, sugar beet pulp, fodder watermelon, sunflower baskets, pumpkin, i.e. food production waste [4]. Pectin biopolymers have unique biological and functional characteristics. They are widely used in the food, medical and cosmetology industries [5].

A significant disadvantage of poorly water-soluble biopolymers is their low specific surface area. Therefore, the therapeutic dose of pectins used as adsorbents is several tens of grams.

Pectins are polysaccharides of higher plants, responsible for many of their physiological functions [6]. According to their chemical structure, they are compounds of a heterocyclic nature. D-galactopyranosyluronic (D-galacturonic) acid, connected by α-1,4-glycosidic bonds into a filamentous molecule of polygalacturonic acid, is considered the main part of the molecule of pectin substances [7].



The technology for obtaining pectin is based on the classical method of its production: the pulp separated from the stone is homogenized and hydrolyzed at a pH of 2.0–2.5 and a temperature of 75–80 °C for 1.5–2 hours. The mixture is filtered, the hydrolyzate is precipitated with alcohol or acetone. The coagulate is separated in a centrifuge (6000 rpm) with subsequent washing, filtration and drying in a vacuum drying unit. The molecular weight of pectin substances depends, first of all, on the nature and quality of the raw material source, the method of isolation and the method of its preparation for production. The average molecular weight of pectins ranges from 10 to 400 kDa, which corresponds to a degree of polymerization from 50 to 2000. Commercial pectin preparations have an average molecular weight of 30 to 120 kDa depending on the type of preparation [5, 8].

Pectins can be classified as physiologically active substances, since they affect cellular metabolism. In particular, there is evidence of the anticancer activity of pectins [9–12]. Thus, samples of citrus pectins showed a pronounced antitumor effect on adenocarcinoma C127, reducing the metabolic and proliferative activity of its cells, and also demonstrating a pronounced cytotoxic effect. The greatest effect was demonstrated by low-esterified low-molecular pectin. In addition, pectins serve as natural adsorbents capable of removing toxic substances from the body. This makes them a promising component of nanocomposite systems for medical purposes.

Polymeric substances, such as pectins or other biopolymers in their natural form, are materials with a small specific surface area. Therefore, to increase it, it is possible to create composite systems with synthetic adsorbents, in particular with silicas, which have not only a high specific surface area, but also a high affinity for polymer molecules [1, 2, 13, 14]. Particularly noteworthy is the prospect of using organosilicon adsorbents, which, in addition to high adsorption characteristics, have increased biocompatibility [15–18]. Their disadvantage, however, is their hydrophobic properties, which complicate the process of their use in aqueous environments. In recent years, simple methods have been developed for wetting hydrophobic powders under mechanical load [19, 20]. It should be noted that in the case of using combined materials consisting of a hydrophobic carrier adsorbent modified by a hydrophilic agent, such as pectin, the possibility of wetting the composite with water is significantly facilitated.

The purpose of this work was the construction of composite systems based on pectin and silica (hydrophobic and hydrophilic and their mixtures), the study of their adsorption parameters in relation to the cationic dye methylene blue, and the effect of pectin on the hydration characteristics of silica sorbents.

MATERIALS AND METHODS

Materials. Apple pectin (China, IMDICATE A COMPANY), hydrophilic compacted silica brand A-300 ($S_{БЕТ}$ = 295 м^2/г) and hydrophobic silica AM-1 ($S_{БЕТ}$ = 175 м^2/г) (Kalush, Ukraine), as well as a mixture of A-300 with AM-1 in a ratio of 1/1 were used in the research. To obtain compacted silica, hydrophilic A-300 was used according to the method described in works [21, 22]. The composite system A-300/pectin, AM-1/pectin and A-300/AM-1/pectin was prepared by thoroughly grinding compacted A-300 and/or hydrophobic AM-1 with pectin to a homogeneous state. The amount of pectin in the composite was 5 or 10 %. Wetting of systems containing AM-1 was carried out by grinding with water according to the method described in [19, 20].

Hydrated pectin and two types of Pectin/H_2O/AM-1 composite systems with component ratios of 1/1.25/5 and 1/2/0.5 were used for NMR studies. Hydrated pectin was prepared by adding the required amount of water to dry pectin and equilibrated for 24 h. Composites were prepared by grinding pectin and AM-1, followed by adding the required amount of water with which the composite was ground for another 5–10 min. Deuterated chloroform and

trifluoroacetic acid (TFAA) were used as organic components for NMR studies.

Adsorption from solutions. Adsorption of methylene blue (MB) dye (M = 319.85 g/mol, manufactured by Khimlaborreaktiv LLC) on silica-containing media was studied under static conditions at $T = 23 \div 25$ °C. For this purpose, aqueous solutions of different concentrations (from 15.63 to 156.32 μmol/l) in a volume of 10 ml were added to the weighing of the corresponding sample (m = 100 mg) and mixed for ~1 hour. The solutions were adjusted to the desired pH using standard HCI or NaOH titers. The solid phase was separated by centrifugation for 20 min at the speed of 3000 rpm. The concentration of MB in the solution was determined spectrophotometrically by measuring its absorption spectra on a spectrometer (Specord M-40, Carl Zeiss Jena, Germany) at a wavelength of 660 nm (l = 1 cm). The amount of dye adsorption (A_∞) was determined by the difference between its initial and equilibrium concentration in the solution before and after contact with the sorbents.

^{1}H NMR spectroscopy. The NMR spectra were measured using a high-resolution NMR spectrometer (Varian "Mercury") with an operating frequency of 400 MHz. Eight 60° probing pulses with a duration of 1 μs and a bandwidth of 20 kHz were used. The temperature in the sensor was regulated with an accuracy of ± 1 degree. Signal intensities were determined by measuring the peak area using the procedure of decomposing the signal into its components assuming a Gaussian waveform and optimising the zero line and phase with an accuracy of ± 10 %. To prevent overcooling of the water in the studied objects, the concentration of non-freezing water was measured by heating the samples, which were previously cooled to 210 K. The temperature dependence of the NMR signal intensity was carried out in an automated cycle, when the sample was held at a constant temperature for 9 min and the measurement time was 1 min. NMR measurements were performed in an air environment.

Since the water concentration in the samples is known, the water signal intensities (I) can be used to calculate the non-freezing water concentration (C_{uw}) at any temperature: $C_{uw} = I_T/I_{T>273}\ h$ (mg/g). The process of freezing (melting) of interfacial water localised in a solid porous matrix occurs in according to changes in the Gibbs free energy caused by the influence of the surface [23]. They are the smaller, the farther from the surface is the studied layer of water. At $T = 273$ K, water freezes, the properties of which do not differ from volumetric water, and when the temperature decreases (excluding the effect of overcooling), the layers of water close to the surface freeze, and besides for interfacial water the following proportion holds true:

$$\Delta G_{\text{ice}} = -0{,}036(273.15 - T), \quad (1)$$

where the numerical coefficient is a parameter related to the temperature coefficient of variation of the Gibbs free energy for ice. Then, in accordance with the methodology described in detail in [24–27], the amounts of strongly and weakly bound water (SBW and WBW, respectively), as well as the thermodynamic characteristics of these layers, can be calculated.

The interfacial energy of solids or biopolymers was defined as the modulus of the total decrease in the free energy of sorbed water due to the presence of an internal water-polymer interface according to the formula:

$$\gamma_S = -K \int_0^{C_{\text{uw}}^{\max}} \Delta G(C_{\text{uw}}) dC_{\text{uw}} . \quad (2)$$

The Gibbs-Thomson formula [28, 29] could be used to determine the geometric dimensions of nanoscale liquid aggregates confined to a solid surface, which relates the radius of spherical or cylindrical pores (R) to the value of the freezing temperature depression:

$$\Delta T_m = T_m(R) - T_{m,\infty} = \frac{2\sigma_{sl} T_{m,\infty}}{\Delta H_f \rho R}, \quad (3)$$

where $T_{\text{m}}(R)$ is the melting temperature of ice localised in pores of radius R, $T_{\text{m},\infty}$ is the melting temperature of bulk ice, ρ is the density of the solid phase, σ_{sl} is the energy of interaction between the solid and the liquid, and ΔH_{f} is the volume enthalpy of fusion.

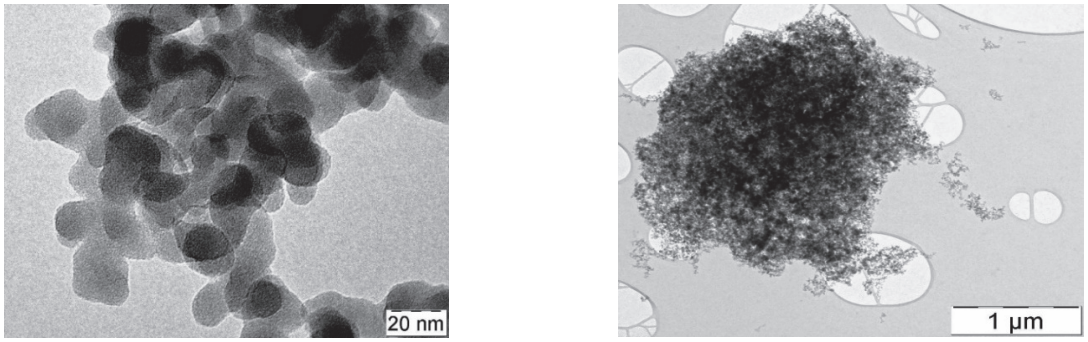
The value (ΔG), as well as the interfacial energy (γ_S), were calculated according to formulas (2, 3). The part of the interfacial water for which the decrease in the Gibbs free energy $\Delta G < 0.5$ kJ/mol was considered to be strongly bound.

High resolution transmission electron microscopy (TEM) (JEM-2100F, Japan) images

were recorded for initial A-300 and AM-1 as representative samples. A powder sample was added to acetone and sonicated. Then a drop of the suspension was deposited onto a copper grid with a thin carbon film. After acetone evaporation, sample particles remained on the film were studied with TEM.

RESULTS AND DISCUSSION

Fumed silicas belong to nonporous adsorbents, however, due to significant interparticle interactions, primary particles with a diameter of 10^{-3} nm form a mesoporous structure in which the pore volume can reach 1–1.2 cm^3/g [13, 16]. TEM micrographs of particles of a mixture of hydrophilic (A-300) and hydrophobic (AM-1) silicas are shown in Fig. 1. In general, the particles of the agglomerates are 1–20 μm, in which the mesoporous structure of the interparticle spaces is very well observed. Unlike "hard" porous silicas of the silica gel type, in pyrogenic silicas the porous structure is unstable, and the surface and total volume of pores can change under the influence of mechanical loads, which are used as a factor for their structural modification [20, 22]. The "soft" nature of pyrogenic silicas also allows replacing air in the interparticle gaps with water by using mechanical processing in the presence of an aqueous phase [19, 20].



a *b*

Fig. 1. TEM microphotographs of the mechanically activated mixture of hydrophobic and hydrophilic silicas

For testing most medical sorbents, pharmacopoeial standards recommend marker substances [30]. They include differently charged dyes with different molecular weights. The sorption properties of the created composite systems were studied for their ability to bind the cationic dye MB, which has a hydrophobic aromatic fragment and is used to study the adsorption of positively charged substances with a low molecular weight on surfaces that, like silica A-300, have a negative charge [31].

Based on the optical density data of a series of solutions with different concentrations of MB, a calibration curve was constructed that reflects the linear growth of its optical density with an increase in the concentration of the solution (Fig. 2).

The adsorption isotherms of MB from a model solution at pH = 5.5 and a solution with pH = 1.5, which simulates the physiological environment of the stomach are shown in Fig. 3. The contact time (1 h) of the studied samples with MB corresponded to the time of silica stay in the gastrointestinal tract and represents the duration of its maximum effective action [32, 33]. At the same time, measurements of MB adsorption on the surface of individually taken AM-1 did not reveal a change in the optical density of the solution, which can be interpreted as the absence of adsorption.

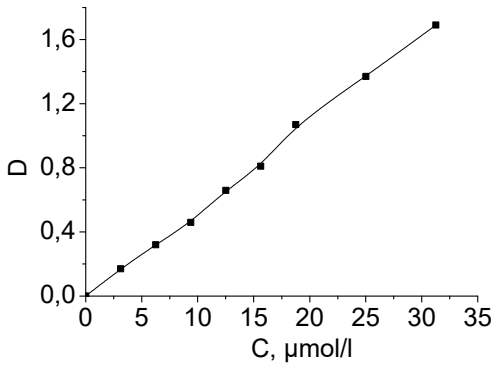


Fig. 2. Calibration curve of methylene blue

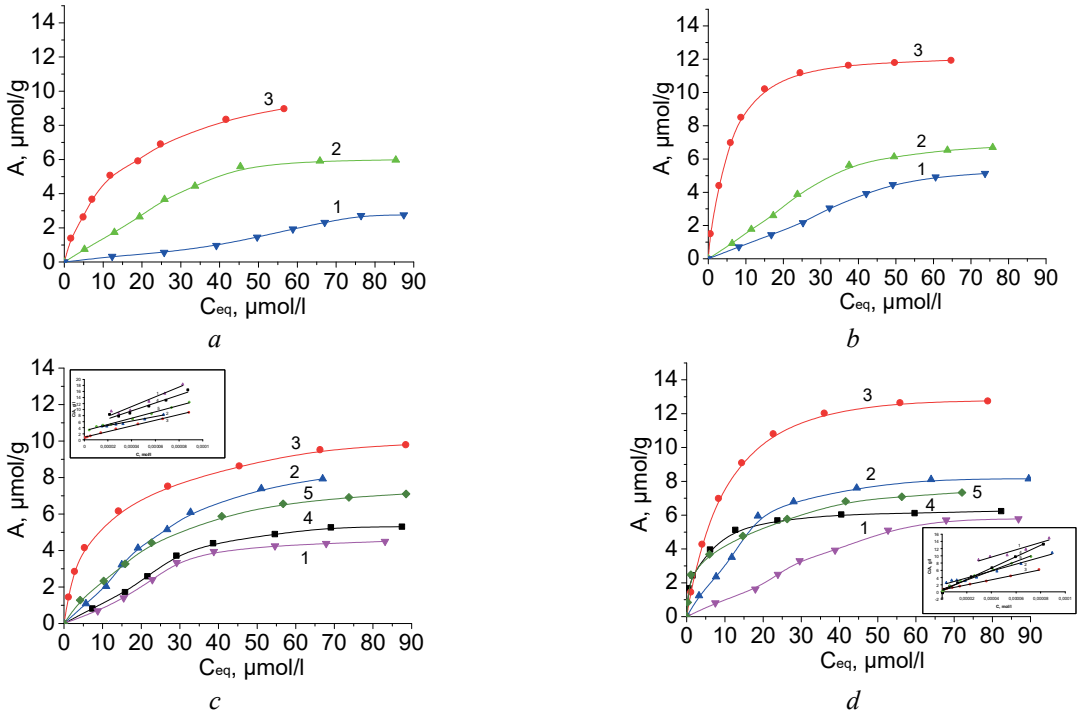


Fig. 3. Adsorption isotherms of MB on the surface of AM-1/pectin (*1*), A-300/pectin (*2*), A-300/AM-1/pectin (*3*), A-300 (*4*) and A-300/AM-1 (*5*) at pH 1.5 (*a*, *c*) and 5.5 (*b*, *d*). Pectin content in the composite: 5 % (*a*, *b*) and 10 % (*c*, *d*)

According to the adsorption data, it was determined that the adsorption isotherms of the dye on the surface of all the studied samples have the form of Langmuir isotherms (Fig. 3). They have a fairly steep initial section and quickly reach saturation. This form of the isotherm could be indicated a strong interaction of the dye with the surface [34].

Linearization of the obtained adsorption isotherms made it possible to determine the value of the limiting adsorption (A_∞) of MB for the studied samples (Table 1).

Table 1. Parameters of methylene blue adsorption on the investigated adsorbents at different pH

Adsorbent	contents pectin, %	pH	A_∞, μmol/g	ω_∞, nm^2	θ, %	$-\Delta G$, kJ/mol	R
A-300/pectin	5	1.5	5.92	2.9	41.2	25.07	0.98
		5.5	6.54	2.4	49.2	24.71	0.98
	10	1.5	7.4	1.8	67.8	23.94	0.99
		5.5	8.11	2.3	53.3	25.69	0.99
AM-1/pectin	5	1.5	2.72	8.8	13.6	21.04	0.97
		5.5	4.92	2.8	43.2	23.75	0.98
	10	1.5	4.38	3.8	31.4	24.99	0.98
		5.5	5.71	2.4	50.3	23.32	0.97
A-300/AM-1/pectin	5	1.5	8.35	2.1	56.5	26.57	0.99
		5.5	11.8	1.8	65.2	29.38	0.99
	10	1.5	9.53	2.2	54.1	27.73	0.99
		5.5	12.65	1.6	73.0	27.8	0.99
A-300	-	1.5	5.27	3.1	38.8	24.54	0.98
		5.5	6.12	3.7	32.0	31.57	0.99
AM-1	-		0				
A-300/AM-1	-	1.5	6.91	2.5	48.5	24.95	0.99
		5.5	7.09	3.1	39.1	28.93	0.99

It is possible to reveal some regularities in the influence of the composition of the composite on the amount of cationic dye adsorption. There is a tendency for MB adsorption to increase with a decrease in pH from 5.5 to 1.5 (Fig. 3, Table 1). This is usually associated with a change in the surface charge of silica in an acidic environment from negative to positive [34]. However, as follows from the data in the Table 1, for most of the studied systems the difference in the value of A_∞ with a change in pH is quite small. That is, electrostatic interactions of dye molecules with the surface are not decisive. Since the MB molecule has hydrophobic fragments, and the surface of hydrophobic silica AM-1, which is used for the preparation of composites, is hydrophobic, it could be assumed that hydrophobic (dispersion) interactions can be dominant in adsorbent-adsorbate interactions. However, cationic dye adsorption was not observed on the surface of hydrophobic AM-1. Adding pectin to AM-1 promotes dye adsorption on such a composite due to the appearance of new types of adsorption centers. Thus, for AM-1/pectin with a pectin content of 5 %, the lowest MB adsorption is observed, compared to other studied samples. When increasing the amount of pectin to 10 % in the AM-1/pectin composite at an acidic pH value, MB adsorption increases by 1.6 times, in contrast to pH 5.5. Adsorption of MB on the surface of A-300/pectin composite with 10 % pectin content is 7.4 and 8.1 μmol/g at pH 1.5 and 5.5, respectively. This is 1.4 and 1.3 times more than on the surface of the initial compacted A-300 without the addition of pectin. It was noted that MB on the surface of A-300 and A-300/pectin with 5 % pectin in the composite exhibits similar adsorption activity. At all pH values, dye adsorption is greatest on the surface of the A-300/AM-1/pectin composite at a pectin content of 10 %. A decrease in the amount of pectin in the composite to 5 % is accompanied by a slight decrease in MB adsorption. From the analysis of these data, it can be concluded that the adsorption activity of nanocomposite systems to MB, which contain hydrophobic silica, is largely determined by the features of the formation of the boundary layer of water that fills the interparticle space.

Mathematical processing the adsorption isotherms of MB made it possible to obtain equations describing the adsorption process with high linear correlation coefficients (R). The values of the correlation coefficient when linearizing the adsorption isotherms show that its sorption is described with maximum probability by the Langmuir equation.

The calculated dye adsorption parameters for each case are presented in Table 1. The values of the change in Gibbs free energy (ΔG) for all the studied samples are slightly different. This allows us to expect that the degree of affinity of the dye to the surface of the adsorbents will also differ. The degree of surface coverage of MB samples was calculated according to adsorption data, taking into account the size of the dye molecule. The calculations show that for 1 molecule adsorbed from an aqueous solution, there are quite large values of the area occupied by the molecule in the adsorbed state ($\omega_\infty > 1.2$ nm^2). This may indicate the planar orientation of MB molecules during adsorption. This is confirmed by literature data [34] and the obtained degree of surface coverage (θ) of the adsorbents by the dye, calculated from the adsorption parameters at the flat position of the MB.

Features of the formation of aqueous layers in hydrated nanocomposite systems containing AM-1 and pectin were investigated by the method of low-temperature ^{1}H NMR spectroscopy [24–27]. The ^{1}H NMR spectra of water in hydrated pectin (Fig. 4 *a*, *b*) and Pectin/AM-1/H_2O composites (*c*–*g*) obtained at different temperatures in the presence of air (*a*, *c*, *e*), deuterochloroform (*b*, *d, f*) and $5CDCl_3 + 1CF_3COOD$ mixture (*g*) are shown in Fig. 4. The main signal of water in the spectra is observed in the form of a broad signal with a chemical shift in the range of 4–6 ppm. As the temperature decreases, the signal intensity decreases due to partial freezing of the interfacial water. Chemical shift values shows that almost all water is strongly associated (SAW) [24–26], that is, its molecules form a spatial network of hydrogen bonds in which each water molecule is involved in at least two hydrogen bonds. In the environment of chloroform, and in some systems also in air (Fig. 4 *c*), signals of weakly associated water (WAW), which does not participate in the formation of hydrogen bonds, appear in the spectra.

One should especially focus on the system containing pectin and a small amount of AM-1 (Fig. 4 *e*). A splitting of the water signal into two closely spaced signals with slightly different values of the chemical shift is observed in this system in the spectra, and its value is somewhat

smaller than that for the other studied systems. This could be indicated the presence of clusters with a partially destroyed network of hydrogen bonds at the interface boundary.

Since the amount of water in the samples (*h*) is known, based on the measurement of NMR signal intensities at different temperatures, can be used to calculate the temperature dependences of the amount of non-freezing water (C_{uw}), and according to formulas (1)–(3) to determine the dependences of the change in Gibbs free energy (ΔG) from C_{uw} and distributions by radii of adsorbed water clusters $\Delta C(R)$ (Fig. 5 *a*–*c*). According to the method described in [24–27], the thermodynamic parameters of interfacial water layers could be calculated (Table 2), in which $C_{uw}{}^{S}$ and $C_{uw}{}^{W}$ are the concentrations of strongly and weakly bound water, respectively, ΔG^{S} is the maximum change in Gibbs energy in layers of strongly bound water, which characterize the maximum decrease in free energy due to adsorption interactions (or clustering), γ_S is the interfacial energy, which refers to the overall decrease in free energy due to adsorption interactions (or clustering) applied to all interfacial water, and γ_S* is interfacial energy per unit mass (expressed in g/g) of interfacial water.

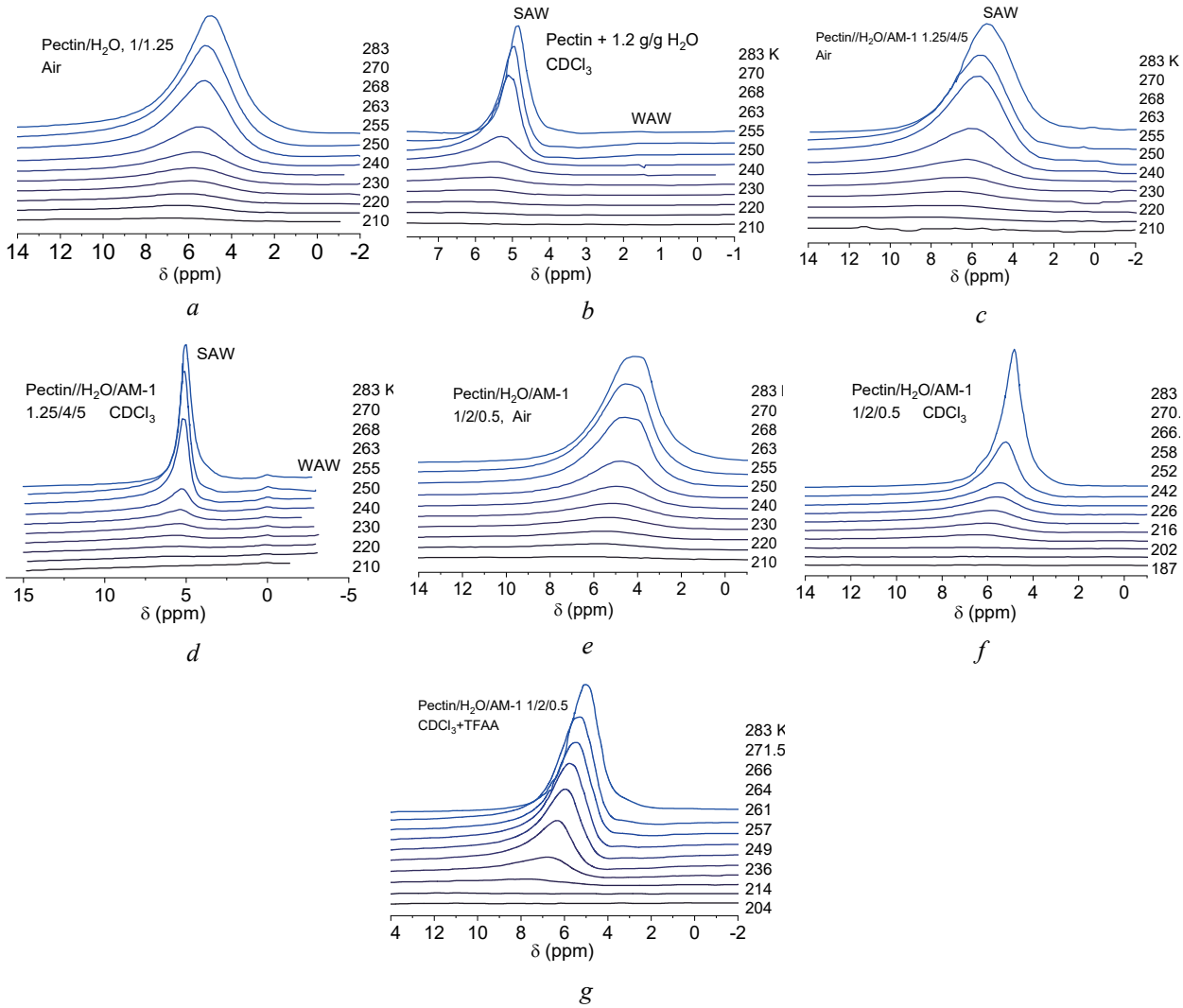


Fig. 4. ^{1}H NMR spectra of water in hydrated pectin (*a*, *b*) and pectin/AM-1/H_2O composites (*c*–*f*) measured at different temperatures, in the presence of air (*a*, *c*, *e*), deuterochloroform (*b*, *d*, *f*) and mixtures $5CDCl_3 + 1CF_3COOD$ (*g*)

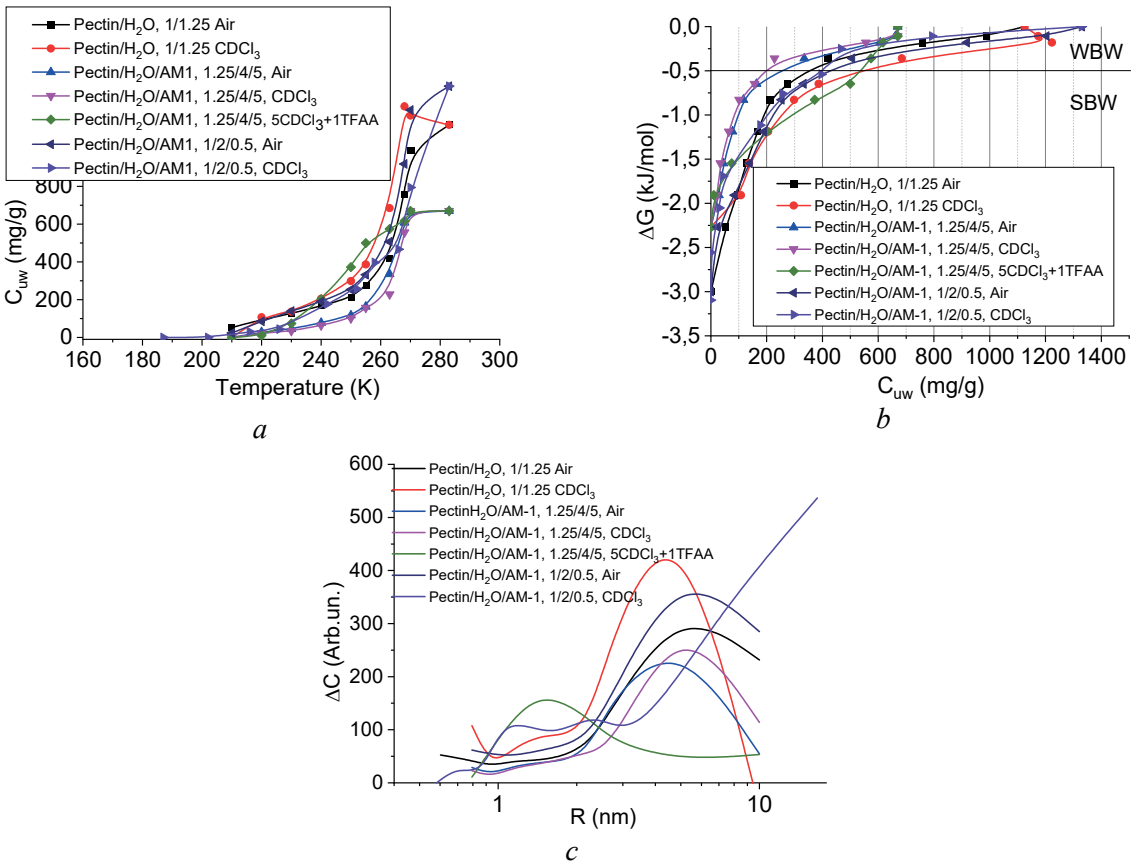


Fig. 5. Temperature dependences of the amount of non-freezing water (C_{uw}) (*a*), dependences of the changes in the Gibbs free energy (ΔG) on C_{uw} (*b*) and distributions of adsorbed water cluster radii $\Delta C(R)$ (*c*)

Table 2. Characteristics of interfacial water in hydrated pectin and its composites with hydrophobic silica AM-1 in different environments

Sample	Medium	*h*, (mg/g)	C_{uw}^S, (mg/g)	C_{uw}^W, (mg/g)	ΔG^S, (kJ/mol)	γ_S/γ_S^* (J/g)
Pectin/H_2O	Air	1125	350	775	-3.0	35.1/31.2
	$CDCl_3$		550	575	-2.27	42.4/37.7
Pectin/H_2O/AM-1 1.25/4/5	Air	670	250	420	-2.3	20.7/30.9
	$CDCl_3$		200	470	-2.3	18.2/27.2
	$5CDCl_3$+1TFAA		550	120	-2.3	35.0/52.2
Pectin/H_2O/AM-1 1/2/0.5	Air	1300	430	870	-3.0	40.4/35.7
	$CDCl_3$		410	890	-2.6	31.3/27.7

On the dependences $\Delta G(C_{uw})$ (Fig. 5 *b*), the horizontal line drawn at the level of $\Delta G = 0.5$ kJ/mol determines the amount of strongly and weakly bound water. The data in Table 2 show that for hydrated pectin, the use of an organic weakly polar medium, in contrast to most heterogeneous systems studied earlier [24–27], leads to a significant increase in the value of the interfacial energy γ_S and γ_S*. Probably, under the influence of the organic environment, the restructuring of pectin polymer molecules is carried out, aimed at reducing the total amount of free energy, which is characterized by smaller sizes of water clusters located in the intermolecular (or interparticle) space of pectin (Fig. 5 *c*). Composite systems containing hydrophobic silica AM-1 are characterized by a decrease in values γ_S* in a weakly polar

environment, which is due to an increase in interphase water clusters (Fig. 5 *c*). In the presence of a strong acid in the dispersion medium, the value of γ_S* increases (Table 2) due to solvation effects. At the same time, the size of the surface clusters of water decreases in the process of defrosting the system.

For the composite system containing a small amount of AM-1 additive in the air environment the maximum value of the interphase energy is observed (Table 2). This is due to a significant amount of strongly bound water, which is concentrated in small clusters (Fig. 5 *c*). That is, the amount and energy of water binding in heterogeneous systems based on pectin is primarily influenced not by the amount of hydrophobic substance forming the composite, but by the processes of interparticle interactions between disparate components. They probably also determine the degree of association of molecules in the water layer. These results also agree with the data obtained during the study of adsorption from the MB solution on the surface of various composite systems. Direct adsorption measurements did not reveal certain regularity between the hydrophobic properties of the matrix and the ratio of component concentrations.

CONCLUSION

The construction of composite systems containing pectins and silica materials can serve as a promising direction in the creation of nanomaterials with high adsorption characteristics in relation to molecules of medium and large molecular weight.

In particular, it shows the prospects of creating composites based on a mixture of hydrophobic and/or hydrophilic silicas (AM-1 and/or A-300, respectively) with pectin. It has been shown that the maximum adsorption of MB occurs from the model solution at pH 5.5 on the surface of all the studied samples. The A-300/AM-1/pectin composite system proved to be the best, regardless of the amount of pectin in the composite (5 or 10 %) at different pH values, compared to other adsorbents.

It is possible to control the structure of interfacial water and the energy of interaction between water and the surface by changing the concentration ratio of pectin and hydrophobic silica. In this way, new types of functionalized materials can be created for use in medical composites.

Нанокомпозитні системи пектин/кремнезем і їхні властивості

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В роботі досліджено композитні системи на основі пектинів та кремнеземних матеріалів. Це може бути перспективним напрямком у створенні систем із високими адсорбційними характеристиками по відношенню до молекул середньої та великої молекулярної маси. Зокрема, показано перспективність створення композитів на основі суміші гідрофобного або/та гідрофільного кремнеземів (АМ-1 або/та А-300, відповідно) з пектином. Виявлено, що максимальна адсорбція метиленового синього відбувається з модельного розчину при pH 5.5 на поверхні всіх досліджених зразків. Найкраще себе зарекомендувала композитна система А-300/АМ-1/пектин незалежно від кількості пектину в композиті (5 або 10%) при різних значеннях pH (1.5 та 5.5), порівняно з іншими адсорбентами.

Метою даної роботи було конструювання композитних систем на основі пектину та кремнеземів (гідрофобного та гідрофільного і їхніх сумішей), вивчення їхніх адсорбційних параметрів по відношенню до катіонного барвника метиленового синього та вплив пектину на гідратаційні характеристики кремнеземних сорбентів.

Досліджено особливості формування водних шарів у гідратованих нанокомпозитних системах методом низькотемпературної ^{1}H ЯМР-спектроскопії. Показано, що змінюючи співвідношення концентрацій пектину та гідрофобного кремнезему, можна керувати структурою міжфазної води та енергією взаємодії води з

поверхнею. За рахунок цього можуть бути створені нові типи функціоналізованих матеріалів для використання в композитах медичного призначення.

В роботі показано, що для композитних систем, які містять гідрофобний кремнезем АМ-1, характерне зниження величин міжфазної енергії у слабкополярному середовищі, що обумовлено укрупненням кластерів міжфазної води, а розмір поверхневих кластерів води в процесі розморожування системи зменшується. Виявлено, що на кількість і енергію зв'язування води в гетерогенних системах на основі пектину впливають процеси міжчастинкових взаємодій між різноріднимі складовими, які ймовірно визначають ступінь асоційованості молекул у шарі води.

***Ключові слова**: композитна система, пектин, гідрофобний кремнезем, ^{1}H ЯМР-спектроскопія, адсорбція, метиленовий синій*

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