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## COMPOSITE MEDICAL SYSTEMS BASED ON HYDROPHOBIC SILICA AND GELATIN

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*The use of hydrophobic silicas as medical adsorbents in comparison with hydroxyl silicas allows to increase the adsorption of some toxins on their surface due to the reduction of water adsorption. The purpose of this study was to find a co-adsorbate that, adsorbed on a hydrophobic surface, would allow the preparation of aqueous suspensions of an enterosorbent based on methylsilica, and, once inside the body, would be easily destroyed by the enzymes of the gastrointestinal tract, freeing its surface for the adsorption of toxins on it.*

*The structure of the hydrate shell and the adsorption capacity of composite materials based on methyl silica and gelatin obtained by different methods were investigated by a set of physical and chemical methods. Low-temperature <sup>1</sup>H NMR-spectroscopy has been used to study of water clusters bound to composite surface. It has been found that the water in the composite on the basis of hydrophobic methyl silica and gelatin gel is present in the form of clusters with a radius of 0.5–15 nm and is in a strongly associated state when measured in air. When a liquid hydrophobic medium is added, the water partially passes into a weakly associated state. The bound water reacts to the presence of chloroform by changing the radial distribution of the adsorbed water clusters. It has been shown that for the composite system methyl silica AM-1/gelatin (5/1), the introduction of chloroform into the interfacial space leads to a significant decrease in the interfacial energy, which indicates a partial displacement of water by the hydrophobic solvent at the interface. At the same time, for composites made on the basis of dry powders, this effect is not observed and its interfacial energy has an intermediate value between the interfacial energies of methyl silica and gelatin containing the same amount of water.*

*Adsorption of Congo red as the medium molecular weight toxins marker from aqueous solutions on the studied composites was studied in comparison with methylsilica. It has been found that gelatin in the composition of composites contributes to increasing dye adsorption. The amount of adsorbed Congo red depends on the method of preparation of the composite and the ratio of silica to gelatin.*

*It is concluded that AM-1/gelatin composite systems can serve as effective adsorbents for removing medium molecular weight molecules from aqueous solutions.*

**Keywords:** *hydrophobic silica, gelatin, composite system, <sup>1</sup>H NMR spectroscopy, adsorption*

### INTRODUCTION

Silica adsorbents are widely used as enterosorbents [1–4], drug carriers [5], excipients in pharmacology [6, 7], and components of composite systems for medical purposes [8–11]. Their high adsorption activity is due not only to the specific surface area, but also to the presence of a large number of hydroxyl groups, which are influential centers of primary adsorption of water and many types of polar organic compounds [12–14]. As a result, a thick film of strongly bound water forms in the inter-particle gaps and on the surface of silica particles, which prevents the adsorption of molecules of medium molecular weight, such as sugar, amino acids, toxic substances and some natural toxins on the surface [15]. The binding of water to the surface can be reduced by partial or complete hydrophobisation

of the silica surface [16–18]. However, this raises the problem of transferring hydrophobic adsorbents to the aqueous medium. Previously, for small amounts of adsorbents (up to 20 g), this problem was solved by the procedure of hydrocompaction under mechanical load [19–21]. Scaling this technology has proven to be not very efficient and requires a lot of mechanical effort.

The aim of this study was to search for a co-adsorbent that, when adsorbed on a hydrophobic surface, facilitates the process of wetting hydrophobic particles with water, and when entering the body as an enterosorbent, is easily destroyed by enzymes of the gastrointestinal tract, freeing its surface for adsorption of toxic substances. One of the most promising materials is food gelatin, which is a product of collagen denaturation. It consists of a mixture of linear polypeptides with different molecular weights

and is a fibrillar protein of animal connective tissue. It is mainly formed by amino acids such as glycine (21 %), proline + hydroxyproline (24 %), alanine (9 %), arginine (8 %), aspartic acid (6 %), and the content of each of the other 10 amino acids in gelatin does not exceed 4 % [22]. Gelatin is registered as food additive E441.

The binding of water to the surface of highly dispersed oxides has been studied using low-temperature  $^1\text{H}$  NMR spectroscopy [23,24], where the value of the chemical shift of interfacial water determines the average number of hydrogen bonds in which each water molecule participates, and the temperature dependence of the non-freezing water concentration determines the distribution of adsorbed water clusters by radii ( $R$ ) and the value of the interfacial energy ( $\gamma_s$ ), which is equal to the total decrease in the free energy of the water/adsorbent system due to the presence of the interface. In composite systems that differ in composition, environment, or concentration of components, an increase in  $\gamma_s$  indicates an increase in water binding, and a decrease in  $\gamma_s$  indicates a decrease in binding energy.

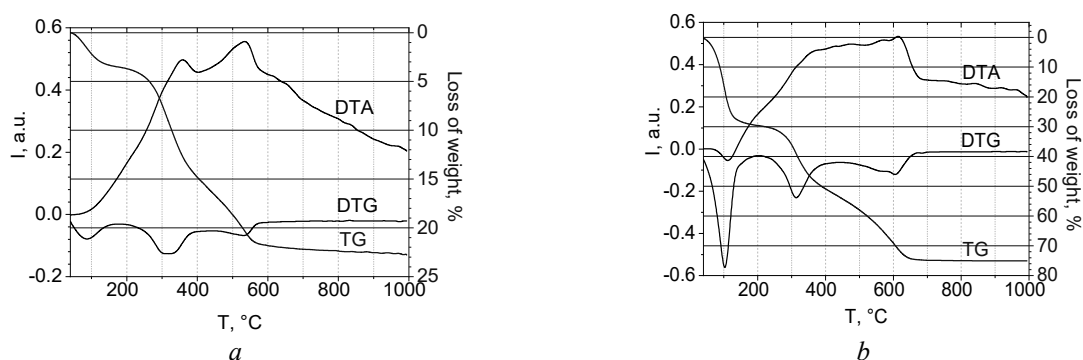
#### EXPERIMENTAL PART MATERIALS

For the experiments, pharmacopoeial gelatin (Belgium) containing 4 wt. % residual water, methyl silica AM-1 (Kalush, Ukraine) and Congo red (CR) dye ( $M = 697$  g/mol) (Reapharm) was used. The composite systems were prepared in

two ways. According to the first method, the gelatin was ground in a porcelain mortar to form a fine powder. It was then mixed with an equal amount of methyl silica by weight. Then the mixture was ground dry for 10–15 min. It was compacted and a composite with a bulk density of  $C_d = 350$  mg/cm<sup>3</sup> was formed. 0.428 g/g was final containing of water in the composite and additionally ground in a mortar for 2 min. It was equilibrated with 24 h of water at 280 K.

In the second method, a 2 % gelatin gel was prepared. For this purpose, 5 ml of distilled water was added to 100 mg of dry gelatin at 360 K. The solution was stirred for 3 min until the opalescence disappeared. After that, it was cooled to 280 K for 2 h. As a result, a solid gel was formed, which was mixed with a suspension of AM-1 and ground for 10 min. A liquid homogeneous suspension was formed. It was kept for 2 h at  $T = 280$  K, which eventually turned into a solid gel, which was then dried at  $T = 293$  K and 20 % relative humidity for 24 hours. After such drying, the composite contained 4 wt. % residual water. The water content in the composite was increased to 428 mg/g or 1 g/g by adding distilled water (without grinding) and holding the sample at 285 K for 2 h. The mass ratio of AM-1 to gelatin was 1/1 and 1/5 when preparing composite systems by both ways.

Fig. 1 *a, b* shows the data for composites, which contained 4 (*a*) and 30 wt. % of H<sub>2</sub>O (*b*).



**Fig. 1.** Thermogravimetric studies of AM-1/gelatin composite containing 4 wt. % (*a*) or 30 wt. % (*b*) of water

The adsorption of Congo red dye from aqueous solution onto AM-1 methyl silica and composites was studied under static conditions at a temperature of 20–25 °C, a weight of the adsorbent was added to 5 ml of the dye solution (with concentrations ranging from 0.005 to 0.05 %), pH ~ 5. Since methyl silica AM-1 and

the created composites exhibit hydrophobic properties and are not wetted by water, mechanical loading was used to obtain their suspensions [19–21]. 28 mL of water was gradually added in small portions to 0.56 g of the composite or methyl silica AM-1 with constant grinding in a mortar. As a result of grinding with

a high mechanical load, air is squeezed out of the inter-particle gaps of hydrophobic adsorbents, which is replaced by water and concentrated suspensions are formed. To 2.5 ml of these suspensions were added 2.5 ml of CR solutions so that the initial concentration of the dye was 0.005–0.05 %. After stirring for 2 h, the solutions were centrifuged for 20 min at 3000 rpm and the supernatant was collected. The optical properties of the obtained solutions were studied using a Specord M-40 spectrometer (Germany) at a maximum absorption band of  $\lambda = 498$  nm in a 1 cm cuvette. The equilibrium concentration of the CR was calculated using the previously obtained calibration graph. The amount of adsorption of dye  $A$  (mg/g) was calculated by formula (1), and the degree of its extraction ( $E$ , %) was calculated by formula (2):

$$A = (C_0 - C_p) \cdot V/m, \quad (1)$$

$$E = ((C_0 - C_p)/C_p) \cdot 100\%, \quad (2)$$

where  $C_0$  and  $C_p$  are the initial and equilibrium concentrations of Congo red in solution, mg/ml;  $V$  is the volume of the test solution, l;  $m$  is the adsorbent weight, g.

**Microscopy.** The morphology of samples was analyzed using a JEOL JSM6490 scanning electron microscope (SEM).

**Thermogravimetry (TG) with differential thermal analysis (DTA).** Thermograms (TG, differential TG (DTG), and DTA) were recorded using a Derivatograph Q-1500 D apparatus (MOM, Hungary) upon heating of samples (~0.2 g) in air at a heating rate of 10 °C/min (average errors for TG and DTA measurements are  $\pm 0.1$  %).

### <sup>1</sup>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  $\pm 1$  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  $\pm 10$  %. 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 the temperature of 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 freeze-thaw water concentration ( $C_{iw}$ ) at any temperature:  $C_{iw} = I_T/I_{T>273h}$  (mg/g). The process of freezing (melting) of interfacial water localised in a solid porous matrix occurs in accordance with changes in the Gibbs free energy caused by the influence of the surface. At  $T = 273$  K, water freezes, the properties of which do not differ from those of bulk water, and as the temperature decreases (without taking into account the effect of supercooling), water layers closer to the surface freeze, with the same ratio for interfacial water:

$$\Delta G_{ice} = -0.036(273.15 - T), \quad (3)$$

where the numerical coefficient is a parameter related to the temperature coefficient of variation of the Gibbs free energy for ice [25]. Then, in accordance with the methodology described in detail in [23, 24], 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:

$$\gamma_S = -K \int_0^{C_{uw}^{max}} \Delta G(C_{uw}) dC_{uw}. \quad (4)$$

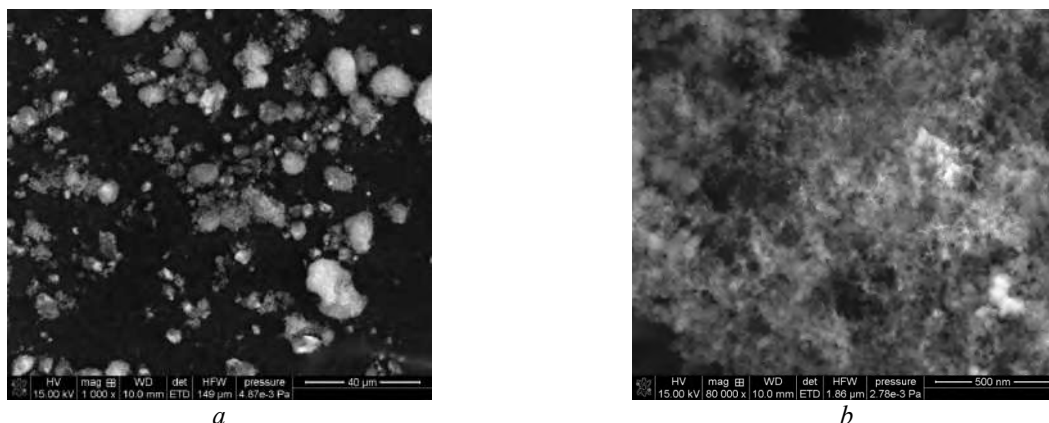
The Gibbs-Thomson equation [26, 27] can be used to determine the geometric dimensions of nanoscale liquid aggregates confined to a solid surface, which relates the radius of spherical or cylindrical pores ( $R$ ) to the value of the freezing point depression:

$$\Delta T_m = T_m(R) - T_{m,\infty} = \frac{2\sigma_{sl}T_{m,\infty}}{\Delta H_f \rho R}, \quad (5)$$

where  $T_m(R)$  is the melting point of ice localised in pores of radius  $R$ ,  $T_{m,\infty}$  is the melting point of

bulk ice,  $\rho$  is the density of the solid phase,  $\sigma_{sl}$  is the energy of interaction between the solid and the liquid, and  $\Delta H_f$  is the volumetric enthalpy of melting.

The value ( $\Delta G$ ), as well as the interfacial energy ( $\gamma_s$ ), were calculated according to equations (3, 4). 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.



**Fig. 2.** SEM micrographs of the initial (uncompacted) methyl silica AM-1

The  $^1\text{H}$  NMR spectra of water in gelatin gel and AM-1/gelatin composite systems obtained at different temperatures are shown in Figs. 3, 4. When the amount of water in gelatin is 30 wt. % (428 mg/g), it is observed as a single signal (Fig. 3 *a*), the chemical shift of which increases from  $\delta_H = 5$  ppm at  $T = 283$  K to  $\delta_H = 8$  ppm at  $T = 210$  K. According to the classification given in [23], such water is strongly associated water (SAW), since each molecule participates in the formation of several hydrogen bonds. As the temperature drops, the intensity of the water signal decreases due to its partial freezing. The replacement of the air medium with deuteriochloroform helps to reduce the SAW signal width due to a decrease in the signal broadening associated with the sample heterogeneity and the appearance of a weakly intense weakly associated water (WAW) signal in the region  $\delta_H = 1$  ppm, which practically does not participate in the formation of hydrogen bonds. The appearance of WAW in a heterogeneous system is due to the formation of surface-stabilised water-chloroform hydrates [23,24].

In the dried 5/1 AM-1/gelatin composite (4 wt. % residual water), a weakly associated

## RESULTS AND DISCUSSION

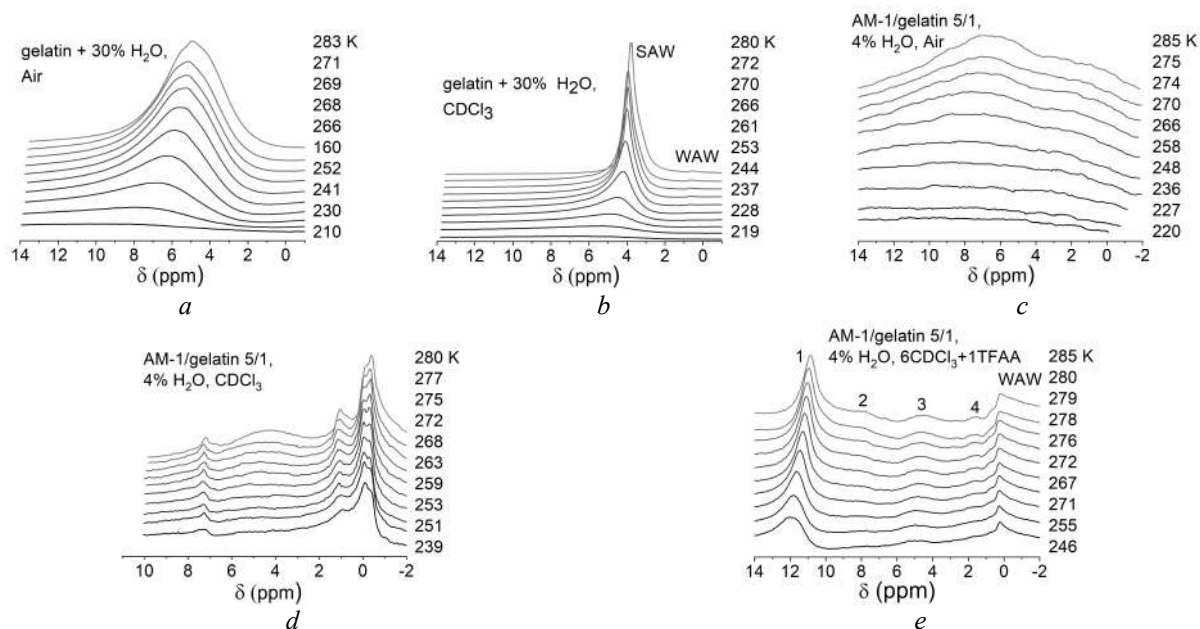
SEM micrographs of the initial methyl silica are shown in Fig. 2. The powder consists of agglomerates ranging in size from 1 to 15  $\mu\text{m}$  (Fig. 2 *a*). A mesoporous structure is clearly visible on the surface (Fig. 2 *b*), which is caused by effective interactions between the primary particles. As a result, the bulk density of AM-1 is low and amounts to about 50  $\text{mg}/\text{cm}^3$ .

water signal is observed in the air environment (Fig. 3 *c*). Consequently, its partially hydrophobic surface is capable of exerting a disordered (chaotropic) effect on water [18, 28, 29]. In a hydrophobic medium ( $\text{CDCl}_3$ ), several signals of weakly associated water are observed (Fig. 3 *d*), and the chemical shift of the strongly associated water signal decreases to  $\delta_H = 4$  ppm. There is also an increase in the intensity of the WAW signal due to a decrease in the intensity of the SAW signal. The addition of deuteriochloroform partially eliminates this effect (Fig. 3 *e*). The WAW signal decreases (but does not disappear), and several water signals with different associations appear in the spectra. Signal 1 in the weakest field ( $\delta_H = 12$  ppm) corresponds to a concentrated water-acid solution [30, 31], signal 2 to a more dilute acid solution, and signals 3 and 4 to water clusters that do not dissolve TFAA.

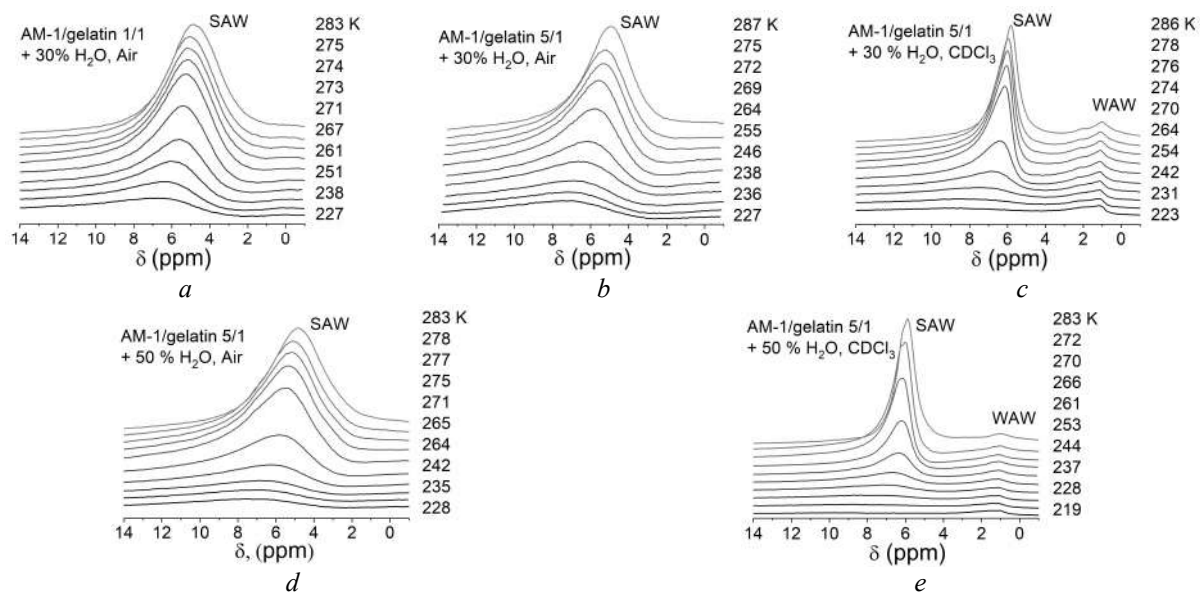
Previously, similar results were obtained on samples of hydrated silica A-300 in  $\text{CDCl}_3$  medium containing additives of hydrochloric or phosphoric acids [23]. The results show that for water adsorbed in the inter-particle gaps of

nanostructures silica, a system of water clusters is formed, in which the formation of strong acid solutions is thermodynamically disadvantageous. For water adsorbed in AM-1/gelatin = 1/1 (Fig. 4 a) and 5/1 (Fig. 4 b–e) composite systems,

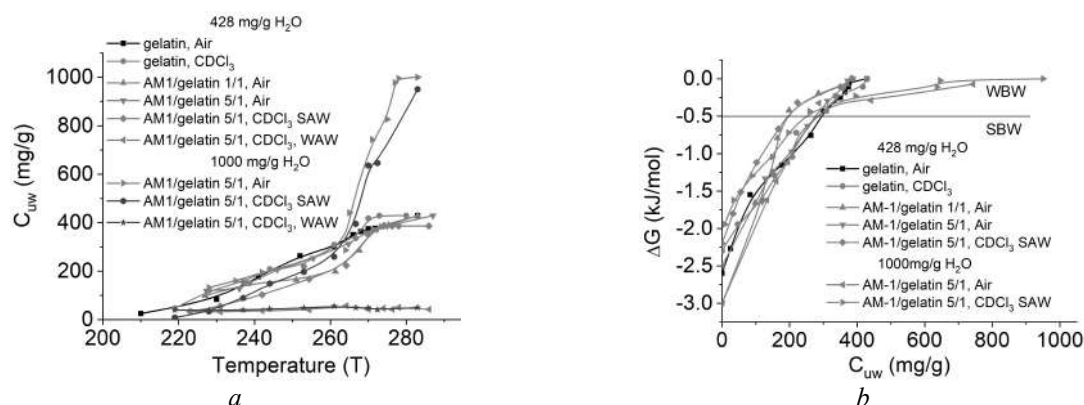
the  $^1\text{H}$  NMR spectra are characterized by the presence of only strongly associated water in the case of measurements in air (Fig. 4 a, b, d) and SAW and WAW signals in  $\text{CDCl}_3$  (c, e).



**Fig. 3.**  $^1\text{H}$  NMR spectra of water in a gelatin gel containing 30 wt. % water (a, b) and a 5/1 AM-1/gelatin composite system (c, d, e) measured at different temperatures, in air (a, c),  $\text{CDCl}_3$  (b, d) and  $\text{CDCl}_3+\text{TFAA}$  (e)



**Fig. 4.**  $^1\text{H}$  NMR spectra of water in AM-1/gelatin 1/1 (a) and 5/1 (b–e) composite measured at different temperatures, in air (a, b, d),  $\text{CDCl}_3$  (c, e) containing 30 (a–c) and 50 wt. % (1 g/g) of water



**Fig. 5.** Dependences of the non-freezing water concentration on temperature (a) and the dependences of the Gibbs free energy on the non-freezing water concentration (b) built on their basis

Fig. 5 shows the dependence of the measurement of the concentration of non-freezing water on temperature (a) and the dependence of the change in the Gibbs free energy on the concentration of non-freezing water  $\Delta G(C_{uw})$  (b), built on their basis, according to formula (3), and Table 1 shows the characteristics of the bound water layers in the studied systems. The table also contains data on hydrated methyl silica powder AM-1 taken from [32]. The concentrations of strongly and weakly bound water ( $C_{uw}^S$  and  $C_{uw}^W$ ,

respectively), the maximum decrease in free energy in the layer of strongly bound water, which was measured by extrapolating the dependence  $\Delta G(T)(C_{uw})$  to the ordinate axis  $\Delta G$ , and the value of interfacial energy calculated in accordance with formula (4) were measured. 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 [23,24]. The radial distribution of the adsorbed water clusters was calculated according to formula (5) (Fig. 6).

**Table 1.** Characteristics of non-freezing water layers in gelatin gel and AM-1/gelatin composite system with different hydration

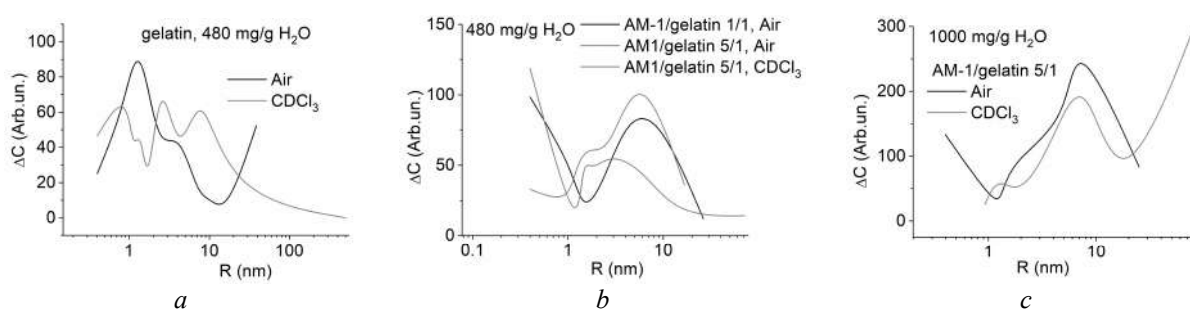
Adsorbent	Medium	h, g/g	$C_{uw}^S$ , mg/g	$C_{uw}^W$ , mg/g	$\Delta G^S$ kJ/mol	$\gamma_s$ , J/g
Gelatin	Air	0.428	290	138	-2.6	23.6
	CDCl <sub>3</sub>	0.428	280	148	-2.3	23.7
AM-1/gelatin= 1/1	Air	0.428	200	228	-2.5	19.6
	Air	0.428	275	153	-3.0	25.3
AM-1/gelatin= 5/1	CDCl <sub>3</sub>	0.428	200	228	-2.2	15.5
	Air	1	280	720	-3.0	31.0
	CDCl <sub>3</sub>	1	250	750	-2.0	20.1
AM-1	Air	0.540	80	460	-2.0	9.6
		1	110	890	-2.0	14.0

The data in Table 1 show that the energy of water binding by hydrated gelatin practically does not change when the air medium is replaced by CDCl<sub>3</sub> (the interfacial energy is the same). It is possible that the water is tightly bound to gelatin and that the diffusion of chloroform to the polymer molecules requires reorganisation of both the hydrate shell and the polymer chains. However, the bound water reacts to the presence of chloroform by changing the radial distribution of the adsorbed water clusters (Fig. 6 a). In air,

the main maximum of the distribution is located at  $R = 1$  nm, while in chloroform, the maximums are recorded at  $R = 0.8, 3$  and  $10$  nm. For the composite system AM-1/gelatin = 5/1, the introduction of chloroform into the inter-particle gaps leads to a significant decrease in the value of  $\gamma_s$  (at  $h = 0.428$  g/g from 25.3 to 15.5 J/g, and at  $h = 1$  g/g from 31 to 20.1 J/g). That is, in the composite, chloroform molecules partially displace the water bordering the surface. This process is accompanied by a decrease in the

amount of strongly bound water and an increase in the amount of weakly bound water (Table 1). This process is manifested in the curves of distribution by radii of water clusters in the form of a decrease in the amount of water included in small clusters ( $h = 0.428$  g/g, Fig. 6 *b*) or an increase in the amount of water in large clusters ( $h = 1$  g/g, Fig. 6 *c*). If we compare the water binding of the starting materials at equal water content, we can conclude that the addition of five parts of AM-1 to one part of gelatin (the

introduction of AM-1 into the gelatin gel) leads to an increase, not a decrease, in the water binding energy. This is probably due to a significant restructuring of the polymer/silica system. For the composite obtained by preliminary grinding of the dry mixture of ingredients (AM-1/gelatin = 1/1), this effect is not observed, and the value of  $\gamma_S$  has an intermediate value between hydrated silica AM-1 and gelatin (Table 1). In this case, there may be separated phases of hydrated polymer and hydrated AM-1 on the micro level.



**Fig. 6.** Radius distribution of adsorbed water clusters in hydrated gelatin (*a*) and AM-1/gelatin composites (*b*, *c*)

To determine the optimal adsorption time, 5 ml of CR solution with a concentration of 0.025 mg/g was added to 50 mg of the AM-1/gelatin composite created by the first method at the ratio of methylsilica AM-1/gelatin = 1/1. The optical density of the solutions was measured after 0.5, 1, 2, 3, 4 and 24 hours.

It was found that 1.56 mg/g of CR was adsorbed during the first hour (Fig. 7 *a*). From the second hour of adsorption and during the day, the adsorption was 1.41–1.47 mg/g. It is known that during the adsorption of dyes on various types of adsorbents, an increase in adsorption is observed over time [33, 34]. However, in the case of using adsorbents with a non-rigid structure, for example, pyrogenic silica, some internal rearrangement of aggregates is possible over time, which changes the equilibrium state of the adsorbent-adsorbate system [32], which can lead to a decrease in adsorption. Thus, 2 h was taken as the optimal time for establishing the adsorption equilibrium, since a further increase in the adsorption time did not affect its value. Further, adsorption of the dye on all investigated sorbents was carried out for 2 hours.

The adsorption isotherms of the CR on the studied composites from aqueous solution are shown in Fig. 7 *b*. Table 2 shows the values of

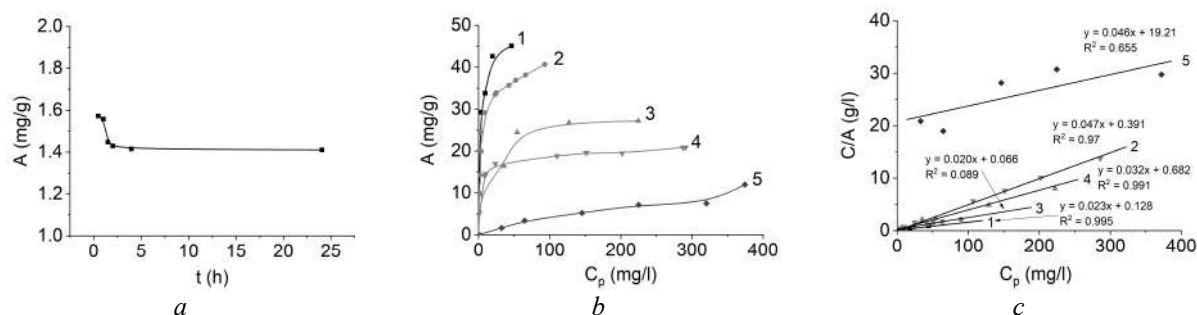
adsorption capacity ( $A$ , mg/g) and the degree of dye removal ( $E$ , %) at the maximum value of its initial concentration ( $C_0 = 0.5$  mg/ml).

It should be noted that the adsorption activity of the initial methyl silica AM-1 towards the CR is insignificant, since the gentle increase in the adsorption isotherm (Fig. 7 *b*, curve 5) with a gradual reaching of the “plateau” indicates a weak bonding of the dye molecules with the surface, mainly due to hydrophobic and Van-der-Waals forces. In this case,  $A = 12.5$  mg/g, and  $E$  is 12 % (Table 2). Preliminary modification of the silica surface with protein increases the adsorption activity towards the dye. The best sorption activity among the studied adsorbents was recorded for the composite prepared by method 2, at the ratio of AM-1/gelatin 1/1. For this adsorbent,  $A = 45.4$  mg/g, and the degree of dye removal is maximum, amounting to 90.8 % (Table 2). Thus, pre-gelation promotes a change in the conformation of the gelatin molecule, which increases the number of adsorption centers in relation to the dye. A 5-fold increase in the silica component of the composites leads to a decrease in the adsorbed CR in the systems created by methods 1 and 2 by 1.9 and 1.6 times, respectively (Table 2), which indicates partial adsorption of the dye by gelatin. The experimental adsorption isotherms of the CR on the studied

composites can be described by the Langmuir adsorption equation (6):

$$A = A_{\infty}(KC/(1 + KC), \quad (6)$$

where  $A_{\infty}$  is the limiting monomolecular adsorption – the capacity of the monolayer, mg/g;  $K$  is the adsorption equilibrium constant characterising the affinity of the adsorbed substance for the surface, l/mol.



**Fig. 7.** The dependence of the amount of adsorption of Congo red on the composite AM-1/gelatin from time (a); Congo red adsorption isotherms on composite (b) and congo red adsorption isotherms, represented in inverse coordinates in accordance with the Langmuir equation(c), on composite (way 1) with a ratio of AM-1/gelatin 1/1 (1) and 5/1 (2), composite (way 2) with a ratio of AM-1/gelatin 1/1 (3) and 5/1 (4) and AM-1 (5)

**Table 2.** Adsorption characteristics of AM-1 and created composites relative to CR at  $C_0 = 0.5$  mg/ml

No	Adsorbent	Magnitude of adsorption $A$ , mg/g	The degree of extraction $E$ , %	$A_{\infty}$ , mg/g	$K$ , l/g
1	AM-1	12.5	25.0	21.37	2.44
<b>Composites are created by way 1</b>					
2	AM-1/gelatin 1/1	40.8	81.7	42.19	184.58
3	AM-1/gelatin5/1	21.1	42.2	21.14	120.85
<b>Composites are created by way 2</b>					
4	AM-1/gelatin 1/1	45.4	90.8	49.02	304.93
5	AM-1/gelatin 5/1	27.5	55.0	30.40	48.23

The Langmuir equation in linear form (7) was used to graphically determine the values of  $A_{\infty}$  and  $K$ :

$$C/A = 1/(A_{\infty}K) + C/A_{\infty}. \quad (7)$$

In the  $(C/A)/C_p$  coordinates, the experimental isotherms look like straight lines (Fig. 7 c). The parameters of the CR isotherms calculated within the Langmuir model are presented in Table 2. The lowest value of the adsorption equilibrium constant was found for the adsorption of the dye on the initial hydrophobic silica, which indicates a weak energy of interaction between the adsorbent and the adsorbate (Table 2). The modification of the AM-1 surface with protein increases the values of the dye adsorption limit and the adsorption equilibrium constant.

Thus, the preliminary sorption of gelatin on the surface of methyl silica AM-1 significantly increases the adsorption properties of the material in relation to the anionic dye Congo red, especially in the case of preliminary dispersion of dry gelatin in the presence of AM-1.

## CONCLUSION

The composite systems of methyl silica AM-1/gelatin obtained by different methods were investigated. It has been found that the water in the composite is present in the form of clusters with a radius of 0.5–15 nm and is in a highly associated state when measured in air. When a liquid hydrophobic medium is added, the water becomes weakly associated. The bound water reacts to the presence of chloroform by changing the radial distribution of the adsorbed water



clusters. It has been shown that for the composite system methyl silica AM-1/gelatin (5/1), the introduction of chloroform into the inter-particle gaps leads to a significant decrease in interfacial energy, which indicates a partial displacement of water by a hydrophobic solvent at the interface.

A homogeneous gel-like composite can be created on the basis of gelatin gel and hydrophobic methylsilica, which, after drying, is saturated with water in direct contact. The water in the AM-1/gelatin composite exists in the form of clusters with a radius of 0.5–15 nm and is in a strongly associated or weakly associated state. The latter is stabilised by contact with a liquid hydrophobic medium. The addition of five parts of hydrophobic silica to the gelatin gel does not reduce but increases water binding (interfacial energy increases by 20 %). At the same time, for composites made on the basis of dry powders, this effect is not observed and its interfacial energy

has an intermediate value between the interfacial energies of methyl silica and gelatin containing the same amount of water.

It has been found that gelatin in the composition of composites contributes to increasing dye adsorption. The amount of adsorbed Congo red depends on the method of preparation of the composite and the ratio of silica to gelatin.

It is shown that the AM-1/gelatin composite systems can serve as effective adsorbents for the removal of medium molecular weight molecules from aqueous solutions.

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## Композитні медичні системи на основі гідрофобного кремнезему та желатину

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*Використання гідрофобних кремнеземів як адсорбентів медичного призначення у порівнянні з гідроксильними кремнеземами дозволяє підвищити адсорбцію деяких токсинів на їхній поверхні внаслідок зниження адсорбції води. Метою даного дослідження був пошук такого ко-адсорбата, який, адсорбуючись на гідрофобній поверхні, дозволить готувати водні суспензії ентеросорбента на основі метилкремнезему, а потрапивши в організм, легко руйнуватиметься ферментами шлунково-кишкового тракту, звільняючи його поверхню для адсорбції на ній токсинів. Розроблено два способи отримання композитних систем на основі метилкремнезему та харчового желатину. Комплексом фізико-хімічних методів досліджено структуру гідратної оболонки та адсорбційну здатність композитів. Методом низькотемпературної  $^1\text{H}$  ЯМР-спектроскопії досліджено будову кластерів води, зв'язаної з поверхнею композитів. Встановлено, що вода в композиті на основі метилкремнезему і гелю желатини існує у вигляді кластерів радіусом 0.5–15 нм і знаходиться в сильно- або слабоасоційованому стані. Останній стабілізується при контакті з рідким гідрофобним середовищем. Додавання п'яти частин гідрофобного кремнезему до желатинового гелю не зменшує, а збільшує зв'язування води (міжфазна енергія збільшується на 20 %). У той же час для композитів, виготовлених на основі сухих порошків метилкремнезему і желатину, цей ефект не спостерігається і міжфазна енергія має проміжне значення між міжфазними енергіями метилкремнезему та желатини, що містить однакову кількість води.*

*Досліджено адсорбцію конго червоного як середньомолекулярного маркера токсинів із водних розчинів на досліджуваних композитах у порівнянні з метилкремнеземом. Встановлено, що желатин у складі композитів сприяє підвищенню адсорбції барвника. Кількість адсорбованого конго червоного залежить від способу отримання композиту та співвідношення кремнезему і желатини.*

*Зроблено висновок, що композитні системи AM-1/желатин можуть слугувати ефективними адсорбентами для видалення з водних розчинів молекул середньої молекулярної маси.*

**Ключові слова:** гідрофобний кремнезем, желатин, композитна система,  $^1\text{H}$  ЯМР-спектроскопія, адсорбція

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