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Physicochemical regularities of the sorption of amino acids on the surface of hydroxylapatite

Biogenic and pathogenic mineral formations contain calcium phosphates. It is known that hydroxylapatite is the main mineral component of bone tissue, tooth enamel, and dentin. The basis of the processes of mineralization is proposed to be in the adsorption interaction of free amino acids and associated protein molecules with inorganic components in body fluids and emerging phases. However, the mechanism of their interaction is not fully understood. In this paper the adsorption of amino acids on the surface of hydroxylapatite has been studied. The synthesis of calcium phosphates from solution has been carried out. According to the results of XRD and IR spectroscopy it has been established that precipitation is represented by the phase of hydroxylapatite. The adsorption of amino acids in a wide range of variation of their concentrations and the pH of the solution has been investigated. It has been established that adsorption of amino acids on the surface of hydroxylapatite reaches saturation. The effect of pH on the maximum adsorption of amino acids on hydroxylapatitehas been considered. It has been established that adsorption of amino acids is described by the Langmuir model. The result of IR spectroscopy confirmed adsorption. It has been determined by the sign of the surface charge of the solid phase of hydroxylapatite. The values of the Gibbs energy have been calculated. It has been revealed that the interaction of amino acids with the surface of the hydroxylapatiteis characterized by physical adsorption.

Keywords: hydroxylapatite, adsorption, amino acid, dissolution, surface charge, solution, Langmuir model, Freundlich model.

Introduction

Calcium phosphates are part of biogenic and pathogenic mineral formations. Biogenic formations are part of different organs and have different functions; they are genetically determined, their place in the body is strictly defined. Pathogenic mineral formations occur in the disruption of the functioning of the whole organism or its separate organs. It is known that hydroxylapatite is the main mineral component of bone tissue, tooth enamel and dentin. The hydroxylapatite plays an important role in many physiological processes in the human body [1–4].

In the papers [5–13] the researchers described that calcium phosphates had an excellent biological activity and had been widely used in bone reconstruction or orthopedic supplements, as the primary inorganic material the composition of the hard tissues of the body.

Interaction of organic and mineral components is important in such processes of biogenic crystallization, as the formation of mammals bone matrix, as well as the emergence and growth of pathogenic entities.

Hydroxylapatite (HA) and dicalcium phosphate dihydrate (DCPD) $CaHPO_4·2H_2O$ are of greatest interest from number of the biocompatible low-temperature calcium phosphates. In nature DCPD expressed in the mineral brushite is the most soluble of biocompatible calcium phosphates, whereas HA is less soluble [14]. In [9] it is examined the differences in stability of calcium phosphates, and also indicated the CA/P ratio, to confirm the differences between the calcium phosphates.

There are a number of assumptions, according to which the basis of the processes of mineralization, is in the adsorption interaction of free amino acids and associated protein molecules with inorganic components in body fluids and emerging phases [15, 16]. The mechanism of their interaction is not fully understood.

In this regard, recent studies aimed at studying the regularities of adsorption of amino acids on the inorganic component of physiognomic and pathogenic neoplasms.

The aim of this work is investigation of peculiarities of adsorption of amino acids on the hydroxylapatite by varying the pH of the solution.

Materials and methods

The synthesis of hydroxylapatite. It is carried out by deposition from aqueous solution at room temperature by the method of spontaneous crystallization in accordance with the following reaction:

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 6H_2O$$

The precipitate is obtained by mixing dilute solutions of calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$, and ammonium hydrogen phosphate $(NH_4)_2HPO_4$ in the ratio of 1.67:1, and aqueous solution of ammonia NH_4OH at room temperature (22–25 ºC). When the synthesis was carried out, to a 500 ml solution containing $Ca(NO_3)_2$, 5 ml of conc. NH_4OH solution, 500 ml of a solution $(NH_4)_2HPO_4$ with a concentration of (50 mmol/l) are rapidly poured. The total volume of the mixture is 1000 ml. After mixing the solutions, the pH of the system is corrected to 12.00 ± 0.05 with solutions of NaOH (20 %) and/or HNO_3 (1:1).

After the heterogeneous system settling for two days, the solution was filtered using a water-jet pump, Bunsen flask and a Buchner funnel (using two filters, a blue ribbon). After filtration, the filter cake was washed with water (V=50 ml), dried in a drying box at a temperature of ~ 100 ºC until complete removal of water. The dried precipitate is ground in a porcelain mortar into a powder, transferred into a special marked container and weighed on an analytical balance.

It is the determination of the sign of the charge of the particles of the sols of hydroxylapatite by the method of capillary analysis. When a piece of filter paper is immersed in water, thin wall paper is charged negatively. These allow determining the sign of the charge of the colloidal particles. Negatively charged particles rise through the capillaries.

We used the direct potentiometric method for pH measurements. The measurements were carried out in a glass beaker, which pre-processes. The measurement error is ±0.01 pH units.

Determination of the concentration of calcium ions in the experiment performed by direct potentiometry using ion-selective electrode and calibration schedule determined by the value of $[Ca^{2+}]$.

Determination of phosphate ions was carried out by the molybdenum blue method (State Standard 18309–72) on the *KFK*-2 device, using the red filter (λ_{ef} = 690 nm) and cuvettes with a layer thickness of 2 cm. The determination is repeated three times and the average values of optical densities to build a calibration curve: $D = f\{C(PO_4^{3-})\}$, calculate the regression equation.

Error determinations are found within 2-4 Rel. %. X-ray diffraction (XRD) is used to study the mineral (phase) composition of synthesized solid phases of hydroxylapatite. A diffractogram was obtained by the «method of powder» for stationary x-ray apparatus DRON-3 [17, 18]. Phase identification was performed using ASTM international indexes and tables [18]. The sensitivity of the XRD method for these measurements is 3 %.

The infrared spectroscopy method was used for more information on the composition of the samples obtained. IR spectrum was obtained on the FSM 2201 spectrophotometer. Mathematical processing of the data was carried out using statistical software Statistica 10 and Static2 from the StatSoft statistical package. The sensitivity of the method of IR-spectroscopy for the measurement data was < 5 %.

The method of area measurement was used to analyze the specific surface of synthetic calcium phosphates. Analysis of the specific surface of the samples according to the BET method (SBET-N2) was carried out using techniques of single-point standard gas adsorption equilibrium at an absolute pressure in the adsorption unit Sorbtometr, IK SB RAS (OSC SB RAS, Omsk). The limit of permissible relative error of measurement of the specific surface in the mode of multiple measurements is not more than 5 %.

The adsorption experiment. 0.5 g of hydroxylapatite sample was placed in a flask and the solution of amino acids was poured. The concentration of amino acids was varied as follows: 2, 4, 6, 8, 10, 15, 20, 25, 30 mmol/l and pH range 5.00–8.00 ± 0.05 (except 6.50) in increments of 0.50. Shaking is carried out for 30 minutes, then it was left for 48 hours. After the specified time the content of the flasks was filtered and there was determined the content of amino acids in the filtrate by the method of transfer of amino acids in a soluble copper salt and subsequent photometric determination, the pH after adsorption was measured, the mass of precipitation was determined.

Determination of the concentration of amino acids in the experiment was assessed by the photometric determination of amino acids. The essence of the method fordetermination of the concentration of amino acids used in the analysis is based on the conversion of amino acids into soluble copper salts and their subsequent photometric determination. KFK-2photoelectric colorimeter was usedfor measurements. Determination of optical density of standard solutions is carried out in the wavelength interval that includes the value of 670 nm. A calibration curvewasbuiltfor measurements. Determining the unknown concentration of amino acids was performed using a calibration chart.

Results and discussion

1. The results of the synthesis of crystals of hydroxylapatite. The methods of XRD and IR spectroscopy were established that the precipitation obtained after 48 hours of crystallization, represented by the phase of hydroxylapatite (Fig. 1), belonging to the hexagonal crystal structure (2 Θ corresponds to 31.8, 32.9, 39.9).). The crystallite size was calculated of equal to D = 13 nm [19], which is consistent with the data [2].

The IR spectrum of the samples contained the whole spectrum of the bands characteristic forhydroxylapatite (Fig. 2) and have a complex structure. The presence of absorption at 1113, 1019, 958 cm^{-1} and 604, 573, 469 cm^{-1}correspond to vibrations of a group PO_4^{3-} as well as trough sat 3576, 3400 cm^{-1} that are characteristic for OH- stretching vibrations of molecules of structurally bound water. One can also notice that the spectrum contains absorption bands of CO_3^{2-} with the peaks at 1460, 1420 and 865 cm^{-1}. In addition, a broad band in the region of 2700–3700 cm^{-1} and peak at 3540 cm^{-1}can be attributed to the stretching vibrations of H-O-H and OH^-, respectively.

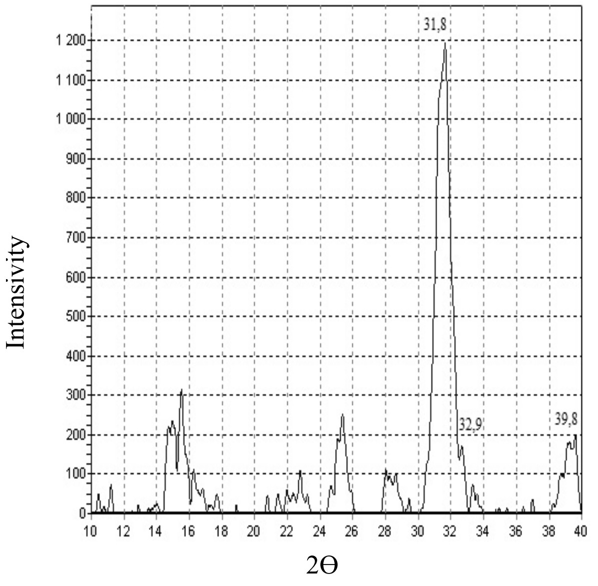


Figure 1. The diffraction pattern of the synthesized sample of hydroxylapatite at pH = 5.50±0.05 (48 hours)

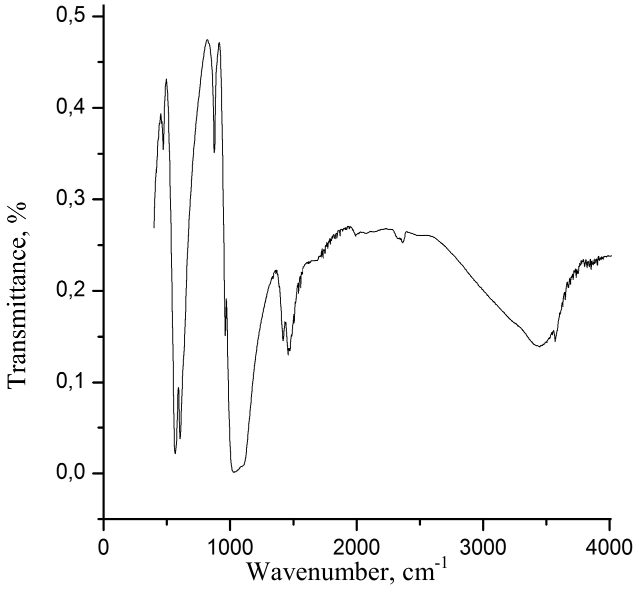
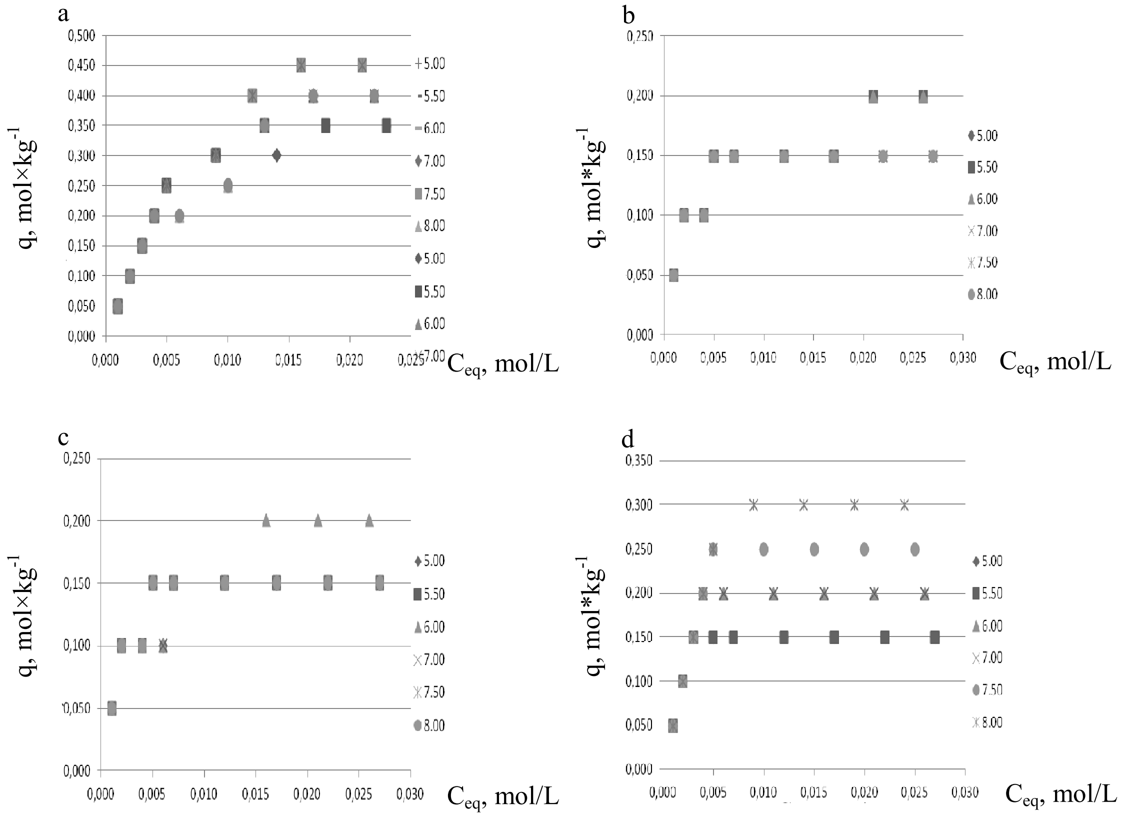


Figure 2. The IR spectrum of the sample of hydroxylapatite synthesized at pH = 5.50±0.05 (48 hours)

The specific surface of hydroxylapatite was calculated by the method of BET, and its value was 72.0 m^2/g. Analysis of the supernatant liquid and calculation of the Ca/P ratio showed that the Ca/P in the synthesized hydroxylapatite was equal to 1.67 that corresponded to the ideal HA.

2. The results of adsorption experiment. As a result of the adsorption experiment, isotherms of adsorption of amino acids to hydroxylapatite were obtained (Fig. 3). Referring to the curves, it can be concluded that the adsorption reaches saturation. This allows for C_{am} = 0.030 mol×L^{-1} to compare the values of adsorption while varying the pH of the solution to finding the values of maximum adsorption (Table 1).



a — glycine; *b* — arginine; *c* — alanine; *d* — aspartic acid

Figure 3. Isotherms of adsorption of amino acids on hydroxylapatite

Table 1

The maximum adsorption of amino acids at varying pH, q, mol×kg^{-1}

Amino acid	pH					
	5.00	5.50	6.00	7.00	7.50	8.00
Glycine	0.400	0.350	0.400	0.400	0.450	0.400
Alanine	0.150	0.150	0.200	0.150	0.150	0.150
Aspartic acid	0.150	0.150	0.200	0.200	0.250	0.300
Glutamic acid	0.300	0.250	0.250	0.200	0.200	0.200
Arginine	0.200	0.200	0.200	0.150	0.150	0.150

The pH values, at which the maximum adsorption of amino acids on the surface of hydroxylapatiteoccurs, are shown in the table 1. These amino acids are in charged ionic formsat given pH values of the solution.To determine the equation describing the adsorption, the experimental data were processed from the position of the Langmuir theory (1) and the Freundlich theory (2) (Table 2):

$$q = \frac{q_m K_L C}{1 + K_L C}, \tag{1}$$

where q_m — is the limiting amount of adsorption, mol×kg^{-1}; K_L — is the adsorption equilibrium constant; C — is equilibrium concentration of adsorbate, mol×L^{-1}.

$$q = K_F C^{\frac{1}{n}}, \tag{2}$$

where K_F — is coefficient of proportionality; n — is exponent, $n<1$.

Table 2

Equations described by the models of Freundlich and Langmuir, for adsorption of amino acids on hydroxylapatite by varying the pH of the solution

Amino acid	q_{max}, mol×kg^{-1}	pH$_{max}$	Equation model of		R^2	
			Langmuir	Freundlich	Langmuir	Freundlich
Glycine	0.450	7.50	$q = 0.749 \times \frac{46.49 \times C}{1 + 46.49 \times C}$	$q = 9.158 \times C^{0.722}$	0.960	0.958
Alanine	0.200	6.00	$q = 0.239 \times \frac{11.40 \times C}{1 + 11.40 \times C}$	$q = 0.938 \times C^{0.401}$	0.958	0.899
Aspartic acid	0.300	8.00	$q = 0.368 \times \frac{33.47 \times C}{1 + 33.47 \times C}$	$q = 2.965 \times C^{0.534}$	0.969	0.831
Glutamic acid	0.300	5.00	$q = 0.368 \times \frac{33.15 \times C}{1 + 3 = 33.15 \times C}$	$q = 2.966 \times C^{0.534}$	0.969	0.831
Arginine	0.200	5.00–6.00	$q = 0.216 \times \frac{13.08 \times C}{1 + 13.08 \times C}$	$q = 0.782 \times C^{0.361}$	0.957	0.846

The obtained values of q_m are adequate, as all practical values of q are less than q_m. As can be seen from Table 2, adsorption of amino acids has a good correlation in the linear coordinates of the model of Langmuir.

It was further used to calculate the change of Gibbs energy according to the formula (3) (Table 3):

$$\triangle G = -RT \times \ln K, \tag{3}$$

where R — is the universal gas constant, R = 8.314 kJ/(Kmol×K); K — is the constant of adsorption equilibrium.

Table 3

The value of the Gibbs free energy for adsorption of amino acids, $-\Delta G$, kJ×mol^{-1}

Amino acid	pH					
	5.00	5.50	6.00	7.00	7.50	8.00
Glycine	8.94	8.87	9.08	9.08	9.51	8.80
Alanine	6.47	7.42	6.03	6.47	7.42	7.42
Aspartic acid	8.53	8.53	8.50	8.50	8.56	8.70
Glutamic acid	8.67	8.53	8.53	8.46	8.46	8.46
Arginine	6.37	6.37	6.37	7.42	7.42	7.42

The values of the Gibbs energy were calculated and there was revealed that the interaction of amino acids with the surface of the hydroxylapatitewas characterized by physical adsorption due to forces of electrostatic interaction of positively and negatively charged centers, as well as due to the formation of hydrogen bonds.

Analysis of the surface charge of the solid phase of hydroxylapatite at pH = 5.00, 6.50, 8.00 ± 0.05 has shown that its surface is positively charged under the given pH values of the solution. It can be seen that after adsorption (C_{aa} = 4 mmol/l), glycine addition does not change the sign of the surface charge, because it is possible to incorporate glycine into the hydroxylapatite structure. With the addition of alanine, there is also no surface recharge, since physical adsorption binds its positive and negative groups at the ends, and as a result, the uncharged side group does not affect the charge of the surface. When adsorption of arginine is also binding its end groups, but at these pH values it is in the form of positively charged zwitterions, and as a result, outside the surface is it's charged positively side group, which does not change the charge of the surface. However, with the addition of aspartic and glutamic acids, it can be seen that the surface is recharging, they are at the given pH values of the solution in the form of negatively charged zwitterions. Because of this, adsorption on the surface has a negatively charged side group that forms a layer on the surface, which as a result changes the charge of the surface of the hydroxylapatite (Table 4).

Table 4

The sign of the charge hydroxylapatite in the presence of amino acids of a similar concentration

Amino acid	pH		
	5.00	6.50	8.00
Without amino acid	+	+	+
Glycine	+	+	+
Alanine	+	+	+
Aspartic acid	–	–	–
Glutamic acid	–	–	–
Arginine	+	+	+

The result of IR spectroscopy confirmed adsorption. On the IR spectrum of the sample after the adsorption experiment (Fig. 4), the vibration band at 1650 cm^{-1} should be considered as the total, reflecting the vibrations of C = O, N–H, O–H bonds in amino acid and OH-ions in hydroxylapatite. Also, the appearance of specific absorption bands associated with the vibrations of N–H and C–N bonds, which appear in the 3500–3300, 1650–1500, 1360–1000 cm^{-1} regions, is registered, which confirms the possibility of adsorption of amino acids on hydroxylapatite.

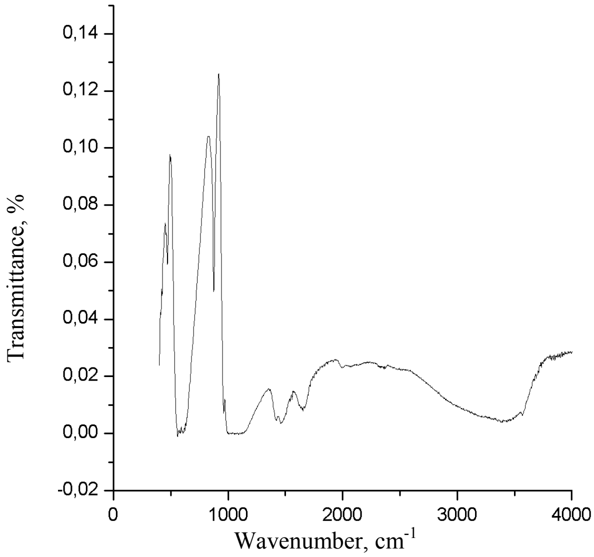


Figure 4. The IR spectrum of the sample after the adsorption experiment (48 hours)

Previously we have found that glycine, aspartic and glutamic acids adsorption is described by Freundlich model. For alanine and arginine adsorption is described by the model of Langmuir [20, 21].

Conclusions

1. It was carried out the synthesis of hydroxylapatite, the structure of which was confirmed by XRD and IR spectroscopy. The values of the sign of the surface charge of hydroxylapatite were found to be positive. т

2. The processes of adsorption of amino acids on the hydroxylapatite were investigated. There was identified that the values of pH of maximum adsorption were as follows: glycine at pH = 7.50 ± 0.05, the alanine at pH = 6.00 ± 0.05, aspartic acid at pH = 8.00 ± 0.05, glutamic acid at pH = 5.00 ± 0.05, arginine at pH = 5.00–6.00 ± 0.05.

3. Adsorption of amino acids was described by the Langmuir model.

4. The values of the Gibbs energy were calculated.There was revealed that the interaction of amino acids with the surface of the hydroxylapatite was characterized by physical adsorption.

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Гидроксилапатит бетінде аминқышқылдар сорбциясының физика-химиялық заңдылықтары

Кальций фосфаттары физиогендік және патогендік минералды түзілімдердің бір бөлігі болып табылады. Гидроксилапатит сүйектің, тіс эмалі және дентиннің негізгі минералды компоненті болып табылатыны белгілі. Органикалық және минералды компоненттердің өзара әрекеті биогенді кристалдану үрдістерінде сүтқоректілердің сүйек матрицасын қалыптастыру, сондай-ақ патогенді түзілістердің нуклеациясын және өсуін қамтамасыз етуде үлкен маңызға ие. Мұнда минералдану процестерінің негізінде биофлуидтердің бейорганикалық компоненттері мен қалыптастырушы фазалары бар ақуыз молекулаларына байланыстырылған бос аминқышқылдардың және ақуыз молекулаларының адсорбциялық өзара әрекеттесуінің бірнеше болжамдары бар. Алайда олардың өзара әрекеттесулерінің тетігі толық зерттелмеген. Мақалада гидроксилапатит бетінде аминқышқылдардың адсорбциясы зерттелді. Кальций фосфатын ерітіндіден синтездеу жүргізілді. РФА және ИҚ спектроскопиясының нәтижелеріне сүйене отырып, тұнба гидроксилапатит фазасы арқылы анықталған. ВЭТ әдісімен гидроксилапатиттың бетінің ауданы 72,0 м^2/г болатыны анықталды. Аминқышқылдардың адсорбциясы олардың концентрациялары мен ерітінділер рН-нің кең ауқымында зерттелген. Гидроксилапатит бетіндегі аминқышқылдардың адсорбциясы қанықтылық қажет ететіндігі анықталды. Аминқышқылдардың максималды адсорбциясына гидроксилапатит бетіндегі ерітіндінің pH-ның әсері қарастырылды. Аминқышқылдардың гидроксилапатит бетіндегі адсорбциясы Ленгмюр үлгісімен сипатталғаны зерттелді. ИҚ-спектроскопия нәтижелері адсорбция фактісін растау үшін берілген. Гидроксилапатиттің қатты фазасының бетіндегі зарядтың белгісі анықталды. Гидроксилапатит бетінің зарядының белгісі оң болғаны расталды. Гиббс энергиясының мәндерін есептеу жүргізілді және аминқышқылдардың гидроксилапатит пен өзара әрекеттестігі физикалық адсорбциямен сипатталатыны дәлелденді.

Кілт сөздер: гидроксилапатит, адсорбция, аминқышқылы, ерігіштігі, бетінің заряды, ерітінді, Ленгмюр моделі, Фрейндлих моделі.

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Физико-химические закономерности сорбции аминокислот на поверхности гидроксилапатита

Фосфаты кальция входят в состав физиогенных и патогенных минеральных образований. Известно, что гидроксилапатит является основной минеральной составляющей костной ткани, зубной эмали и дентина. Взаимодействие органической и минеральной составляющих имеет большое значение в таких процессах биогенной кристаллизации, как формирование костного матрикса млекопитающих, а также зарождение и рост патогенных образований. Существует ряд предположений, согласно которым в основе процессов минерализации лежит адсорбционное взаимодействие свободных аминокислот и связанных белковых молекул с неорганическими компонентами биожидкостей и формирующихся фаз. Однако механизм их взаимодействия до конца не изучен. В работе изучена адсорбция аминокислот на поверхности гидроксилапатита. Осуществлен синтез фосфатов кальция из раствора. По результатам РФА и ИК-спектроскопии установлено, что осадки представлены фазой гидроксилапатита. С помощью метода БЭТ рассчитали удельную поверхность гидроксилапатита, равную 72,0 м^2/г. Исследована адсорбция аминокислот в широком интервале варьирования их концентраций и pH раствора. Доказано, что адсорбция аминокислот на поверхности гидроксилапатита достигает насыщения. Рассмотрено влияние pH раствора на значение максимальной адсорбции аминокислот на поверхности гидроксилапатита. Доказано, что адсорбция аминокислот на поверхности гидроксилапатита описывается моделью Ленгмюра. Результаты ИК-спектроскопии приведены для подтверждения факта адсорбции. Проведено определение знака заряда поверхности твердой фазы гидроксилапатита. Получено, что значение знака заряда поверхности гидроксилапатита положительное. Осуществлен расчет значений энергии Гиббса и выявлено, что взаимодействие аминокислот с поверхностью гидроксилапатита характеризуется физической адсорбцией.

Ключевые слова: гидроксилапатит, адсорбция, аминокислота, растворение, поверхностный заряд, раствор, модель Ленгмюра, модель Фрейндлиха.

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