



# ADSORPTION OF HIGH-MOLECULAR-WEIGHT HYALURONIC ACID ON CARBONATE HYDROXYAPATITE

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Cite this: *INEOS OPEN*,  
2025, 8 (1–3), 117–118  
DOI: 10.32931/io2544a

Received 12 November 2024,  
Accepted 3 December 2024

<http://ineosopen.org>

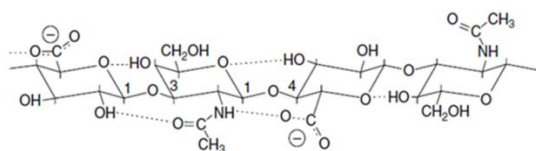
## Abstract

In this work, the interaction of hyaluronic acid (HA) with the surface of carbonate hydroxyapatite is studied. The process of the polysaccharide adsorption is described by the Freundlich model. Effective interaction of HA with the apatite surface occurs at the polysaccharide concentrations in the reaction mixture not exceeding 0.25 wt %. There are physical and chemisorption bonds between the HA molecules and the solid phase. The active centers of the polysaccharide molecules can act as nuclei for the deposition of the mineral component on the formed carbonate hydroxyapatite–polymer layer.

**Key words:** hydroxyapatite, hyaluronic acid, adsorption, polymers, biocompatible materials.

## Introduction

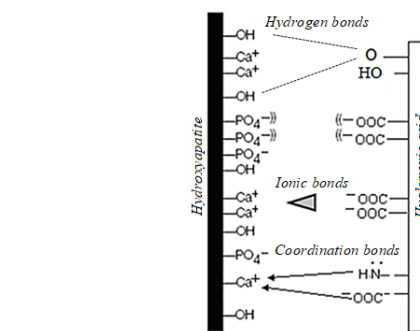
In the last decade, the technologies for obtaining polymeric compositions of calcium phosphates biocompatible with human bone tissue have been intensively developed [1]. Natural polysaccharides find extensive use as organic components since they are well resorbed by cells *in vivo*, without having a negative toxic effect [2]. Hyaluronic acid ( $C_{14}H_{21}NO_{11}$ )<sub>n</sub> is a functional glycosaminoglycan with unique viscoelastic and hygroscopic properties. This is a structure-forming linear anionic glycosaminoglycan, the molecules of which, owing to functional groups and hydrogen bonds, collect the components of the intercellular matrix into a single ordered system (Fig. 1). Polysaccharide solutions are a framework—a "net" along which the dissolved substances diffuse at a limited rate [3–7].



**Figure 1.** Fragment of the HA molecule in solution consisting of the residues of D-glucuronic acid and D-N-acetylglucosamine connected by  $\beta$ -(1-3)- and  $\beta$ -(1-4)-glycosidic and hydrogen bonds.

It is known that the conformation of the HA macromolecules and therefore the properties of the biomaterial strongly depend on the molecular weight of the polysaccharide and its ionic environment in solution. In this regard, a detailed study of the processes of interaction of the polysaccharide molecules with apatite in viscoelastic media will allow obtaining new compositions with specified properties for bone implantology.

The purpose of this work was to study the adsorption of



high-molecular-weight hyaluronic acid on carbonate hydroxyapatite.

## Results and discussion

To conduct adsorption experiments, calcium phosphate powder was synthesized using a patented technique [8] from a model medium similar in electrolyte composition, ionic strength, and pH to human synovial fluid. The sample was analyzed using X-ray diffraction (D8 Advance, Bruker) and IR spectroscopy (FSM-2202). It was shown that the main phase is poorly crystallized nanocarbonate HA, with crystallite sizes of  $22.09 \pm 0.01$  nm. The specific surface area of the crystals, determined using the BET method (Gemini 2380), was  $130 \pm 0.07$  m<sup>2</sup>/g.

To study the adsorption process, a sample of the obtained apatite ( $0.3000 \pm 0.0001$  g) was poured into 15 mL of a solution of HA in the form of sodium hyaluronate ( $2.0 \cdot 10^6$  Da, Germany) with a concentration of 0.025 to 0.250 wt %. Shaking was carried out for 30 min, the contact time was selected experimentally and composed 48 h, pH =  $7.40 \pm 0.05$ . Adsorption on the surface of the adsorbent from the solution was determined by the difference in the polysaccharide concentrations before and after the contact. After filtration, the HA content in the liquid phase was determined spectrophotometrically by the reaction of carbazole with the oxidation product of D-glucuronic acid (PE 5400UF,  $\lambda = 530 \pm 2$  nm) [4]. To determine the equation describing the adsorption, the experimental data were processed using the Langmuir and Freundlich models [9].

Based on the resulting experimental data, the values of molecular ( $G$ ) and limiting adsorption ( $G_{\infty} = 5.26$  mg/g) as well as the degree of filling of the adsorbent surface (fraction of the occupied surface  $\theta = G/G_{\infty}$ ) were calculated (Table 1).

On the adsorption isotherm (Fig. 2), constructed based on the data from Table 1, two sections with different curve patterns can be distinguished. It is evident that at low concentrations of the polysaccharide in solution (< 0.25 wt %), the quantitative adsorption occurs, that is, the adsorption is directly proportional to the equilibrium concentration of the polysaccharide (linear dependence, Henry plot, ( $r^2 = 0.95$ )). With a further increase in the content of HA, the proportion of the free surface of the adsorbent decreases and the value of  $G$  changes exponentially ( $r^2 = 0.98$ ). At the polysaccharide concentrations > 0.25 wt %, the saturation occurs. Consequently, a further increase in the polysaccharide content will not affect the adsorption value. Thus, effective interaction of HA with the active centers of carbonate hydroxyapatite occurs at the polysaccharide concentrations in the reaction mixture not exceeding 0.25 wt %.

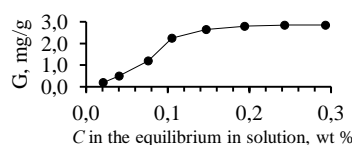


Figure 2. Adsorption isotherm of HA on apatite.

The experimental data were processed according to the Langmuir and Freundlich theories. The coefficients of the equations were calculated graphically (Fig. 2, Table 2). The resulting values of  $G_{\infty}$  are adequate since the practical values of  $G$  are less than  $G_{\infty}$ . The Freundlich (1) and Langmuir (2) equations were obtained:

$$G = 28.92 \cdot C^{0.79} \quad (1)$$

$$G = 5.26 \cdot \frac{2.16 \cdot C}{1 + 2.16 \cdot C} \quad (2)$$

It is shown that the adsorption of the polysaccharide on carbonate hydroxyapatite at pH = 7.4 obeys the Freundlich equation ( $r^2 = 0.97$ ). According to this model, the surface of the synthesized hydroxyapatite is energetically non-uniform, first of all, the filling of sorption centers with maximum energy occurs, the active centers are not completely independent of each other and act as nuclei for subsequent crystallization of hydroxyapatite. Lateral interactions are possible between the fragments of HA macromolecules sorbed on mineral particles.

## Conclusions

Thus, it was established that the main mechanism of inclusion of HA in the solid phase is the physical and chemisorption interaction of the polysaccharide functional groups with the hydroxyapatite surface. The polymer adsorption process is preferably described by the Freundlich model. Effective interaction of the polysaccharide with the HA surface occurs at the HA concentrations in the reaction mixture not exceeding 0.25 wt %. At the initial stage of adsorption, the polysaccharide molecules are bound to the solid phase. Subsequently, the active centers of the polysaccharide molecules themselves can act as nuclei for the deposition of the mineral component on the formed carbonate hydroxyapatite–polymer layer. In the gel-like media, most of the solid phase surface is occupied by the biopolymer molecules, and crystallization processes are hindered.

Table 1 Results of polysaccharide adsorption on the surface of apatite

HA concentration $C$ , wt %			$G$ , mg/g	$\theta = G/G_{\infty}$
Initial sol.	equilibrium in sol. after adsorption	equilibrium in the layer of the adsorbent surface		
0.025	0.021 ± 0.002	0.004 ± 0.002	0.20 ± 0.01	0.04 ± 0.01
0.050	0.040 ± 0.001	0.010 ± 0.001	0.50 ± 0.02	0.10 ± 0.02
0.100	0.076 ± 0.003	0.024 ± 0.003	1.20 ± 0.02	0.23 ± 0.01
0.150	0.105 ± 0.005	0.045 ± 0.005	2.25 ± 0.03	0.43 ± 0.01
0.200	0.147 ± 0.005	0.053 ± 0.005	2.65 ± 0.02	0.50 ± 0.02
0.250	0.194 ± 0.002	0.056 ± 0.002	2.80 ± 0.04	0.53 ± 0.01
0.300	0.243 ± 0.001	0.057 ± 0.001	2.85 ± 0.03	0.54 ± 0.02
0.350	0.293 ± 0.002	0.057 ± 0.002	2.85 ± 0.03	0.54 ± 0.02

Table 2. Freundlich and Langmuir equations for the adsorption of HA on apatite

Freundlich model					
Curve equation	1/n	n	lnK	K	$r^2$
$y = 1.26 \cdot x + 3.36$	1.26	0.79	3.36	28.82	0.97
Langmuir model					
Curve equation	$1/G_{\infty}$ g/mg	$G_{\infty}$ mg/g	$1/b \cdot G_{\infty}$ g/mg	b	$r^2$
$y = -0.19 \cdot x + 0.09$	0.19	5.26	0.09	2.16	0.36

## Acknowledgements

This work was supported by the Russian Science Foundation (project no. 23-23-00668).

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