

Study of the interaction of sorbed silver, gold and copper ions with functional groups on hydrolyzed fibroin using Charmm22 force field calculations

Khushnubek Odilbekovich Eshchanov ^{a, *}, Mukhabbat Matnazarovna Baltaeva ^a

^a Department of Chemistry, Faculty of Natural Sciences, Urgench State University, Urgench, Uzbekistan

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ABSTRACT

We studied the sorption of silver, gold, and copper ions into powdered hydrolyzed fibroin derived from silk fibroin fibers. Metal ions sorbed into hydrolyzed fibroin have been found to interact with active functional groups over time. It was hypothesized that the silver and gold ions sorbed into hydrolyzed fibroin would form nanoparticles as a result of the reduction reaction, while the copper ions would form a coordination bond. Charmm22 force field calculations were performed on this basis. The IR spectral results obtained by calculations were compared with the IR spectral results obtained in practice, and it was proved that silver and gold nanoparticles were formed and that copper ions formed coordination bonds with fibroin.

1. Introduction

The silk industry produces a large amount of fibrous waste that does not meet the requirements of textiles. One of the important issues is to obtain and use materials with sorption properties from the fibrous waste of natural silk.

Silk fiber consists of fibroin and sericin proteins. Silk fibroin has unique sorption properties. Silk fibroin fiber has the property of sorption of various substances. Sorption of Pb^{2+} , Mn^{2+} , Co^{2+} , Cu^{2+} ions into Bombyx mori silk fibroin has been studied [1, 2]. The sorption process of Pd^{2+} ions to silk fibroin has been studied in solutions with the same concentration and mixed ions (Pt^{2+} , Os^{4+} , Ir^{4+} , Rh^{3+} and Ru^{4+}) [3]. The sorption of Cs^{+} ions into silk fibroin is well studied [4].

Samples in the form of powders with sorption properties derived from silk fibroin can be used for technical purposes and in pharmacy [5, 6]. Powdered fibroin samples can be obtained by hydrolysis of silk fibroin fiber under the action of various reagents. The number of amino- and carboxyl groups increases in the discontinuities of the powder sample obtained [7, 8]. Powdered fibroin pores also contain polyfunctional

groups. These functional groups play an important role in the interaction with sorbed substances.

The sorption of Ag^{+} ions into reconstituted fibroin material from a solution of silk fibroin is well studied. The sorption capacity of Ag^{+} ions to the prepared sorbent has been found to be 62.5 mg/g [9]. It is recommended to separate silver ions from wastewater using this type of sorbent. Selective sorption of Cd^{2+} ions on a membrane-based on silk fibroin has been studied [10]. In addition, the sorption of many heavy metal ions and the effects of sorbed ions on the fibroin molecule have been identified [11].

In addition, many quantum chemical calculations have been performed to determine the effect of different media on the structure of silk fibroin [12]. The effect of water on the structure of silk fibroin and the change of crystalline particles have been studied using quantum chemical calculations [13].

In previous editions, we have provided information on how to obtain powdered "HF" [14]. In our study, we studied the sorption of silver, gold, and copper ions into powdered "HF" and changes in post-sorption processes using Charmm22 force field calculations.

* Corresponding author.; e-mail: olmos77@mail.ru

2. Theoretical section

The Charmm22 force field is widely used to simulate and analyze the molecular dynamics of proteins. Quantum chemical calculations of interactions between proteins atomic partial charges, sample compounds, and water are performed in the Charmm22 force field. The Charmm22 force field has the following potential energy function:

$$U = \sum_{\text{bonds}} k_b (b - b_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} k_\phi [1 + \cos(n'\phi - \delta)] + \sum_{\text{impropers}} k_\omega (\omega' - \omega'_0)^2 + \sum_{\text{Urey-Bradley}} k_u (u - u_0)^2 + \sum_{\text{nonbonded}} \left[\varepsilon \left[\left(\frac{R_{\text{min}ij}}{r_{ij}} \right)^{12} - \left(\frac{R_{\text{min}ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{\varepsilon r_{ij}} \right] \quad (1)$$

The first term in the energy function accounts for the bond stretches where k_b is the bond force constant and $b - b_0$ is the distance from equilibrium that the atom has moved. The second term in the equation accounts for the bond angles where k_θ is the angle force constant and $\theta - \theta_0$ is the angle from equilibrium between 3 bonded atoms. The third term is for the dihedrals where k_ϕ is the dihedral force constant, n' is the multiplicity of the function, ϕ is the dihedral angle and δ is the phase shift. The fourth term accounts for the impropers, where k_ω is the force constant and $\omega' - \omega'_0$ is the out of plane angle. The Urey-Bradley component (cross-term accounting for angle bending using 1,3 nonbonded interactions) comprises the fifth term, where k_u is the respective force constant and u is the distance between the 1,3 atoms in the harmonic potential. Nonbonded interactions between pairs of atoms (i, j) are represented by the last two terms. By definition, the nonbonded forces are only applied to atom pairs separated by at least three bonds. The VDW energy is calculated with a standard 12-6 Lennard-Jones potential and the electrostatic energy with a Coulombic potential [15].

When the atoms in a molecule are displaced, they affect neighbouring atoms. Equations of motion in molecules can be written, and their solutions give the vibrational modes of the molecule. The forces resulting from the displacement of atoms are best represented by the Hessian matrix, which is the second derivative of the potential energy U relative to the oscillations of the atoms [16].

$$H_{K,L} = \left(\frac{d^2 U}{dx_{i,k} dx_{j,l}} \right)_0 \quad (2)$$

where the indices k and l point to the atom (1, 2, ..., N), and the indices i and j point to the Cartesian direction ($1 = x, 2 = y, 3 = z$). The indices K and L are the signs that combine the atomic and Cartesian directions, and $K = 3(k - 1) + i$ and $L = 3(l - 1) + j$.

Equations of motion in terms of the Hessian matrix

$$m_k \frac{d^2 \Delta x_{i,k}}{dt^2} = - \sum_{l=1}^N \sum_{j=1}^3 H_{K,L} \Delta x_{j,l} \quad (3)$$

Here m_k is the mass of the k -atom, $\Delta x_{i,k}$ is the i component of the k -atom's displacement, and N is the number of atoms in the molecule. To calculate the vibration frequencies, a harmonic motion is assumed and the equation is as follows.

$$m_k \omega^2 \Delta x_{i,k} = \sum_{l=1}^N \sum_{j=1}^3 H_{K,L} \Delta x_{j,l} \quad (4)$$

can be rewritten as the eigenvalue equation of the matrix,

$$\left[\omega^2 - m_k^{-1/2} H_{K,L} m_l^{-1/2} \right] = 0 \quad (5)$$

In addition to the interatomic forces described on the right side of Eq. (3), other forces in the atoms include hydrodynamic gravitational forces and forces due to the time-varying electric field of incident electromagnetic radiation acting on charged atoms. The new equations of motion with these additional forces are as follows.

$$m_k \frac{d^2 \Delta x_{i,k}}{dt^2} = - \sum_{l=1}^N \sum_{j=1}^3 H_{K,L} \Delta x_{j,l} - \eta_k m_k \frac{d \Delta x_{i,k}}{dt} + q_k E_i e^{-i\omega t} \quad (6)$$

where E_i is the i th Cartesian component of the electric field and η_k is the damping coefficient. Like a single oscillator housing, a formal solution can be found for shifts at a given ω frequency. The dipole moment, which is now a tensor, and therefore the polarization ability, can be obtained as follows:

$$\alpha(\omega) = \frac{1}{V \varepsilon_0} \left[q (H - m \omega^2 - im \eta \omega)^{-1} q \right] \quad (7)$$

Here, the symbols q , m , H denote matrices or vectors, and V denotes the size of the molecule. The polarity tensor can be calculated from the normal modes of the molecule obtained by diagonalizing the Hessian matrix:

$$\alpha_{i,j}(\omega) = \frac{1}{V \varepsilon_0} \sum_{\text{moden}=7}^{3N} \sum_{\text{atoms } k,l=1}^N \frac{q_k C_{i,k;n} C_{j,l;n} q_l}{m_k^{1/2} (\omega_n^2 - \omega^2 - i \gamma_n \omega) m_l^{1/2}} \quad (8)$$

Here m_k - masses, ω_n and γ_n - real and imaginary parts of the specific frequencies of the Hessian matrix, $C_{i,k}$; n - elements of the eigenvector vector matrix. The symbols i and j refer to directions, k , l to atoms, and n to eigenfrequencies. The charges used to calculate the polarity tensor in Eq. (8) do not have to be the same as those used in the Hessian matrix or the force field used to calculate the molecular dynamics trajectories. The frequency-dependent dielectric function can be obtained from the trace of the polarization tensor

$$\varepsilon(\omega) = \varepsilon_0 \left(1 + N_m \frac{\sum_i \alpha_{ii}}{3} \right) \quad (9)$$

where N_m is the number of molecules. The attenuation is given by

$$\mu(\omega) = \omega \text{Im}(\varepsilon(\omega)) \quad (10)$$

Once Eq.(8) is set, a weakening occurs.

$$\mu(\omega) = \rho \frac{1}{3} \sum_{i=1,3k,l,n} \sum \frac{q_k C_{i,k;n} \gamma_n \omega^2 C_{i,l;n} q_l}{m_k^{1/2} \left((\omega_n^2 - \omega^2)^2 + (\gamma_n \omega)^2 \right) m_l^{1/2}} \quad (11)$$

where ρ is the density of the molecules.

Each eigenfrequency is bent by Lorentzian, the full width of which is half the maximum γ_n damping constant.

$$\mu(\omega) = \rho \frac{1}{3} \sum_{k,l,n} \frac{q_k C_{i,k;n} \gamma_n C_{i,l;n} q_l}{m_k^{1/2} (4\delta^2 + \gamma_n^2) m_l^{1/2}} \quad (12)$$

when the γ_n damping constant is small compared to eigenfrequency ω_n and

$$\omega = \omega_n + \delta \quad (13)$$

For frequencies comparable to the damping constant in the THz range, the motion decreases critically ($\gamma_n = \omega_n$) or decreases excessively ($\gamma_n > \omega_n$) [17].

Fibroin protein particles that bind silver, gold nanoparticles, and copper ions were simulated in the Charmm22 (BIO+) force field in HyperChem Professional 8.0.8.

3. Experimental

3-1. Materials

In the experiments, powdered fibroin, silver nitrate ampule (Chimreaktivinvest, Uzbekistan), tetrachloroauric acid trihydrate (Carl Roth GmbH+Co. KG, Germany), KSCN-ampule, iron(III) nitrate crystal hydrate ampule (Chimreaktivinvest, Uzbekistan) were used.

3-2. Instruments

"GFL 2104 bidistillator" (Germany), UV-1800 UV-Vis spectrophotometer (Japan), thermostat-Assistant cat. №3180 (Germany), IR-spectrophotometer-JASCO FT/IR-4600 (Japan), 2 mL micro burette (TU 64-2-403-89).

3-3. Research procedure

3-3-1. Sorption of Ag^+ ions into "HF"

In order to study the sorption of Ag^+ ions to "HF", experiments were performed in solutions of AgNO_3 at a concentration of 0.006, 0.0215, 0.04, 0.06 and 0.1 mol/L. The sorption process was carried out at a temperature of 298 K.

The amount of silver in the solutions after the sorption process was determined by titration with a solution of 0.02 mol/L KSCN using a 2 mL micro burette (to the nearest 0.01 mL). Samples obtained after the sorption process was analyzed by IR spectroscopy.

3-3-2. Sorption of $[\text{AuCl}_4]^-$ ions into "HF"

To study the sorption of gold ions into "HF" $[\text{AuCl}_4]^-$ from solutions containing ions 0.00025, 0.0003, 0.0005, 0.001, 0.00258, 0.003322, 0.008, 0.015 and 0.017 mol/L used. The sorption process was carried out at a temperature of 298 K. The absorption values of the post-sorption solutions were determined using a UV-1800 UV-Vis spectrophotometer (Shimadzu) at a wavelength of 300 nm.

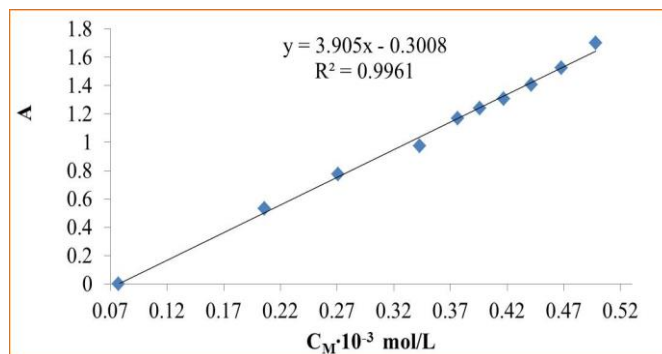


Figure 1. $[\text{AuCl}_4]^-$ calibrated graph for a solution containing ions ($\lambda = 300$ nm)

"HF" powder, which sorbs gold ions in low concentration solutions, turns red. This was seen as a sign that the gold ions were returned to the nanoparticle state by fibroin molecules. The IR spectra of the samples, which are thought to contain gold nanoparticles, were obtained.

3-3-3. Sorption of Cu^{2+} ions into "HF"

The sorption process was carried out at a temperature of 298 K in copper(II) sulfate solutions with a concentration of 0.015, 0.0248, 0.0401, 0.0765, 0.1179, 0.1992, 0.317 and 0.33 mol/L. In order to determine the concentrations of copper(II) sulfate solutions, a calibration graph of the relationship between concentration (C_M) and light absorption (A) was constructed. The graph is based on the results obtained using a UV-1800 UV-Vis spectrophotometer (Shimadzu) at a wavelength of 810 nm.

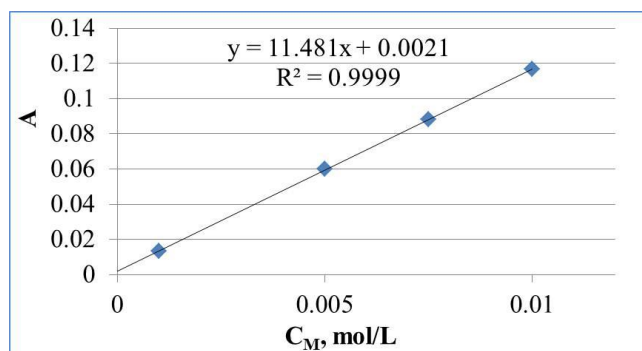


Figure 2. The calibrated graph to determine the concentration of Cu^{2+} ion in aqueous solution (light absorption values determined at $\lambda = 810$ nm)

4. Results and Discussion

Sorption of Ag^+ ions into “HF” and post-sorption processes were studied. At a temperature of 298 K, the maximum sorption capacity of Ag^+ ions to “HF” powder was found to be 247.7 mg/g.

Washing of the “HF” sample sorbing the Ag^+ ions with distilled water resulted in the complete removal of the sorbed Ag^+ ions from the “HF”. This phenomenon confirms that Ag^+ ions are not chemically bound to “HF”.



Figure 3. The IR spectrum of “HF” containing silver

Vibrations in the IR spectrum of 3283.21, 3078.8, 2978.52 cm^{-1} indicate a decrease in the polyassocytic state of -OH and a structural change. The sharp increase in the vibrational intensities in the 1339.32 cm^{-1} region is due to the vibrations of the C-H group in the Phe amino acid residue. The valence vibration in the 1167.69 cm^{-1} regions is specific to the C-N bond in the Tyr amino acid residue [18, 19]. Changes in absorption in the 600 and 825 cm^{-1} regions are symmetrical vibrations characteristic of silver nanoparticles [20, 21]. The actual IR spectra of the “HF” containing the silver nanoparticles were compared with the IR spectra obtained on the basis of calculations in the HyperChem professional 8.0.8 program and the Charmm22 (BIO+) force field.

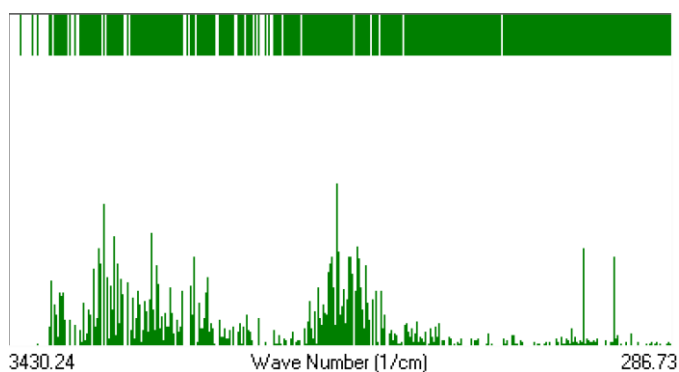


Figure 4. IR spectrum calculated in HyperChem program (AgNPs-“HF”)

Based on the IR spectra obtained from calculations and the IR spectra obtained in practice, it can be concluded that silver nanoparticles were formed in “HF”.

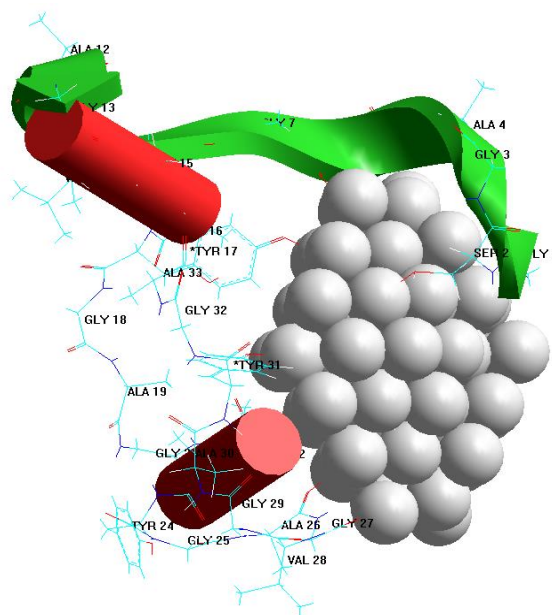


Figure 5. Model of silver nanoparticles bonded with “HF”

Table 1. Comparison of IR spectrum results obtained by calculation and in practice in HyperChem program (AgNPs-“HF”)

IR spectral results obtained by calculation in HyperChem 8.0.8	Practical IR spectral results	A functional group in which silver nanoparticles are bonded
2871.66 cm^{-1}	2876.31 cm^{-1}	O=C-Tyr, Ar(C=C), Ag-NH-
1338 cm^{-1}	1339.32 cm^{-1}	Ag-O=C-Tyr*, Ag-O=C, Ag-NH-
831 cm^{-1}	830 cm^{-1}	Ag-Ag, Au-O=C-Tyr*, Ag-O=C
826.63 cm^{-1} 829 cm^{-1}	825.324 cm^{-1}	Ag-NH-Ag-Ag, Ag-NH ₂ -, Ag-O=C, Ag-NH-, Ag-HO-Ser
702.97 cm^{-1} 688 cm^{-1}	687.498 cm^{-1}	Ag-O=C, Ag-NH-

The maximum sorption capacity of gold ions to “HF” was observed in 0.008 mol/L solution and was 265.47 mg/g. In solutions with a concentration of less than 0.005 mol/L, $[\text{AuCl}_4]^-$ ions sorbed into “HF” react with phenolic groups of the amino acid residue Tyr to form

gold nanoparticles. Therefore, after sorption, the color of “HF” particles changes to red over time. After the sorption process, IR spectra of “HF” powder obtained from solutions with a concentration of 0.00025, 0.0003, 0.0005 mol/L were obtained and analyzed.

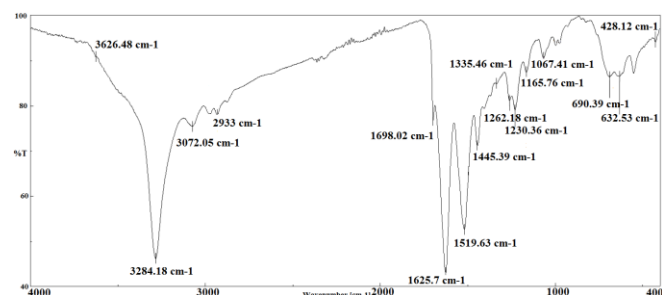
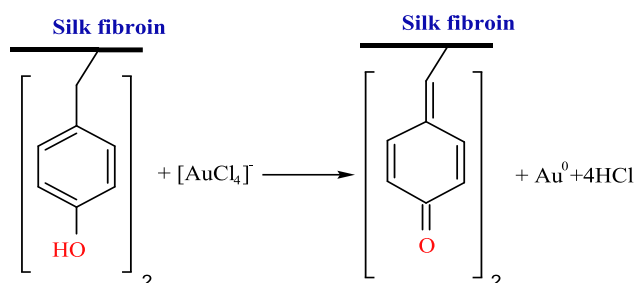


Figure 6. IR spectrum of “HF” bonded with gold nanoparticles

The decrease in the intensity of absorption of 3284.18 cm^{-1} peaks in the IR spectrum explains the change in -NH- in the -OH and amide groups. The vibration in the 3072.05 cm^{-1} regions is related to the C-H vibrations in the aromatic ring, which reduces the absorption intensity in that area. Based on these data, it can be concluded that the -OH and phenylene groups in the amino acid residue of Tyr have undergone structural changes. The reaction of $[\text{AuCl}_4]^-$ ions is as follows.



The displacement of the 1167.69 cm^{-1} region in the IR spectrum of the bonded gold nanoparticle to the 1165.76 cm^{-1} valence vibration region shows. Vibration in the 690.39 cm^{-1} area confirms the existence of an Au-N and Au-O bond.

IR spectra of a fibroin molecule bound to a gold nanoparticle were obtained and analyzed based on calculations.

The results of the analysis confirmed the above data. Calculations were performed in the HyperChem professional 8.0.8 program and in the Charmm22 (BIO+) force field optimized molecule. The IR spectra obtained by calculations were compared with the results of the IR spectra obtained in practice.

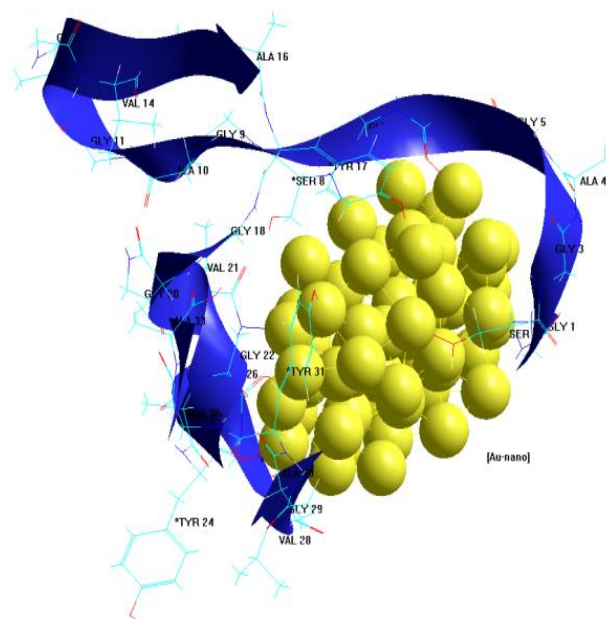


Figure 7. Model of gold nanoparticles bonded with “HF”

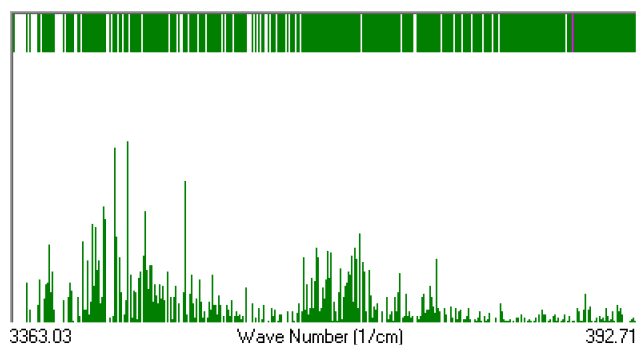


Figure 8. IR spectrum calculated in HyperChem program (AuNPs-“HF”)

Table 2. Comparison of IR spectrum results obtained by calculation and in practice in HyperChem program (AuNPs-“HF”)

IR spectral results obtained by calculation in HyperChem 8.0.8	Practical IR spectral results	A functional group in which silver nanoparticles are bonded
3285.96 cm^{-1}	3284.18 cm^{-1}	Au-O=C, Au-O=C-Tyr
3081.47 cm^{-1} 3079.53 cm^{-1}	3072.05 cm^{-1}	Au-O=C, Au-NH ₂ -Ar(C=C), Au-HO-Ser
2935.13 cm^{-1}	2933 cm^{-1}	Au-O=C-Tyr Ar(C=C)
1340 cm^{-1} 1335.97 cm^{-1} 1335.66 cm^{-1}	1335.46 cm^{-1}	Au-O=C-Tyr* Au-O=C
692.41 cm^{-1} 696.45 cm^{-1} 629.43 cm^{-1}	690.39 cm^{-1} 632.537 cm^{-1}	Au-NH- Au-O=C, Au-NH-

Based on the IR spectra obtained as a result of calculations and the IR spectra obtained in practice, it was concluded that gold nanoparticles were formed.

The maximum sorption capacity of Cu^{2+} ions to “HF” was observed in a solution with a concentration of 0.317 mol/L and was found to be 56.88 mg/g.

Once the sorption of Cu^{2+} ions is complete, the copper ions in the powdered “HF” can be desorbed. However, when the copper ions were retained in the powdered “HF” for 1 week, the “HF” turned yellow and the sorbed copper ions could not be desorbed. From these changes, it can be concluded that Cu^{2+} ions are initially sorbed to the surface and pores of powdered “HF”, and over time, Cu^{2+} ions sorbed form chemical bonds with the multifunctional groups of “HF”. IR-spectroscopy analysis was performed to determine whether the sorbed Cu^{2+} ions formed a chemical bond with the polyfunctional groups in the “HF”.

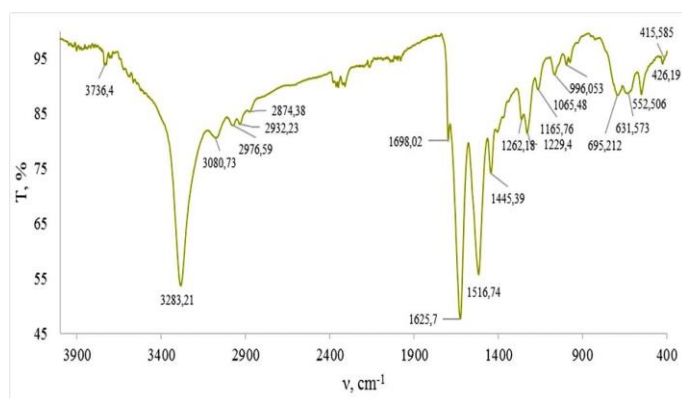


Figure 9. IR spectrum of “HF” bound to Cu^{2+} ions

Analysis of the IR spectrum of “HF” bound by Cu^{2+} ions showed a partial increase in peak intensity in the area of 426.191 cm^{-1} . It is known from the literature [22, 23] that in the IR spectra of proteins bound by copper coordination bonds, vibrations related to Cu-N, Cu-O bonds are observed in the absorption of $470\text{--}350\text{ cm}^{-1}$ areas. Absorption in the 426.191 cm^{-1} region of the “HF” IR spectrum indicates the formation of a Cu-N and Cu-O bond.

An increase in the absorption intensity of “HF” in the area of 1625.7 cm^{-1} indicates that it binds to copper ions with amide I groups in the β -structure of fibroin. It can be explained that the changes in the peaks in the area of 3080.73 cm^{-1} , 2976.59 cm^{-1} are also associated with copper ions in the carboxyl group “-O-”.

In order to verify the above results, it was assumed that Cu^{2+} ions formed a coordination bond with silk fibroin, and calculations were performed on this compound. The calculations were performed in HyperChem professional 8.0.8 software and in the case of optimizing the molecule in the Charmm22 (BIO+) force field. Using the program, the IR spectra of the compound were

obtained on the basis of calculations. The IR spectra obtained using calculations were compared with the IR spectral results obtained in practice. Using the program, it was determined which spectrum was observed in which functional groups.

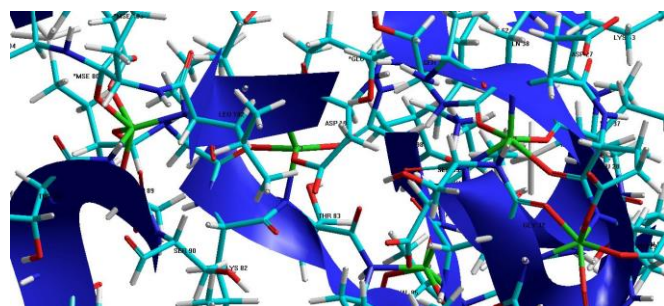


Figure 10. Model of molecular structure of “HF” bound to Cu^{2+} ions

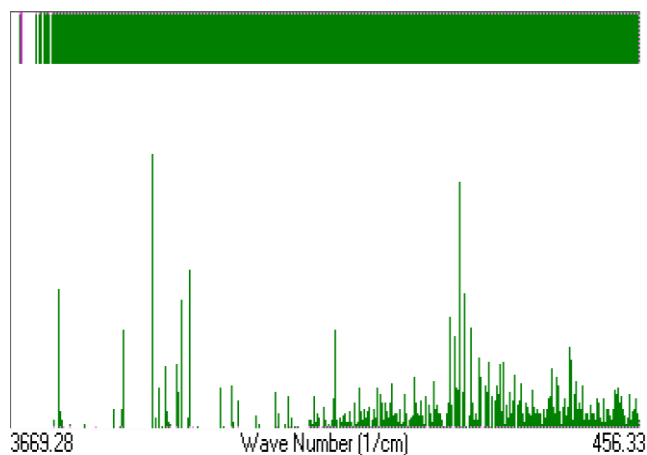


Figure 11. IR spectrum of “HF” bound to Cu^{2+} ions

Table 3. Comparison of IR spectrum results obtained by calculation and in practice in HyperChem program (Cu^{2+} -“HF”)

IR spectral results obtained by calculation in HyperChem 8.0.8	Practical IR results	A functional group in which silver nanoparticles are bonded
3283.22 cm^{-1} 3293.69 cm^{-1}	3283.21 cm^{-1}	Cu-O-CO-, Cu-NH Cu-O=C
1626.37 cm^{-1}	1625.7 cm^{-1}	Cu-O=C-Gly, Cu-NH-Gly
427.11 cm^{-1}	426.191 cm^{-1}	Cu-O=C, Cu-NH-

It can be seen that the IR spectrum obtained using calculations and the IR spectrum obtained in practice is close to each other. Based on these results, it can be assumed that Cu^{2+} ions formed a complex compound by

coordinating with the functional groups in the β -chain part of "HF". Based on the results of the analysis, it was concluded that copper ions with polyfunctional groups of "HF" sorbent formed a polymer-metal complex.

5. Conclusion

The formation of nanoparticles from silver and gold ions in "HF" pores and the formation of coordination bonds by copper ions were proved using Charmm22 force field calculations. The peaks in the 600–825 cm^{-1} region of the IR spectra practical obtained from the silver-bearing "HF" were characteristic of silver nanoparticles, and the results of the spectra obtained on the basis of theoretical calculations were compared. The peak in the 690.39 cm^{-1} region characteristic of the Au-N and Au-O bonds in gold nanoparticles was compared with the theoretically calculated peaks. It was observed that the IR spectral results obtained in theoretical calculations that copper ions were not converted to nanoparticles in the composition of "HF" corresponded to the actual results. Based on the results of such research, it will be possible to draw preliminary conclusions about the composition of the obtained substance.

References

- [1] Huang, Y, Farooq, MU, Kundu, P, Hazarika, S, Feng, X. Use of fibroin polypeptide from silk processing waste as an effective biosorbent for heavy metal removal. *Can J Chem Eng.*, (2021) 1–11.
- [2] Fukashi Shimizu, Ikuzo Sakaguchi. Adsorptive rate of metal cations on silk fibroin fiber, *Sen'i Gakkaishi*, 36(3), (1980) 127-131.
- [3] Tsukasa Sato, Saki Abe, Shinko Ito, Tatsuo Abe. Silk fibroin fiber for selective palladium adsorption: Kinetic, isothermal and thermodynamic properties. *Journal of Environmental Chemical Engineering*, 7(2), (2019) 102958.
- [4] Tsukasa Sato, Tsugumi Seki, Shino Yokoyama, Shinko Ito. Adsorption of Cesium Ion on Silk Fibroin in Aqueous Solution, *Trans. Mat. Res. Soc. Japan*, 42(2), (2017) 19-22.
- [5] Tomeh MA, Hadianamrei R, Zhao X. Silk Fibroin as a Functional Biomaterial for Drug and Gene Delivery. *Pharmaceutics*, 11(10), (2019) 494.
- [6] A. Bozorgian, Z. Arab Aboosadi, A. Mohammadi, B. Honarvar, A. Azimi, Optimization of determination of CO₂ gas hydrates surface tension in the presence of non-ionic surfactants and TBAC, *Eurasian Chemical Communications*, 2 (2020), 420-426.
- [7] Eshchanov K. , Baltayeva M. Determination of the molecular mass of hydrolyzed fibroin obtained from natural silk fibroin by spectrophotometry. *Journal of the Turkish Chemical Society Section A: Chemistry*, 9(1), (2022) 115-120.
- [8] N.I. Semenov, V. P. Yanukovych. Method for obtaining powder from natural silk. *USSR Patent*, (1991) No. 1826999 A3.
- [9] Nitayaphat W., Jintakosol T. Adsorption of Ag(I) from Aqueous Solutions Using Regenerated Silk Fibroin Adsorbent Beads. *Journal of Natural Fibers. Bellwether Pub., Ltd.* (2020) 1-13.
- [10] Gao Ai Qin, Xie Kong Liang, Song Xi Yu, Zhang Kai, Hou Ai Qin. Removal of the heavy metal ions from aqueous solution using modified natural biomaterial membrane based on silk fibroin. *Ecological Engineering*, 99 (2017) 343-348.
- [11] Rastogi, S., Kandasubramanian, B. Ipak fibroin kompozitlari yordamida og'ir metall ionlari va bo'yoqlarning adsorbsiyasidagi progressiv tendentsiyalar. *Environ Sci Pollut Res*, 27(2020) 210–237.
- [12] Patel, Mrinal & Dubey, Devendra & Singh, Satinder. Phenomenological models of Bombyx mori silk fibroin and their mechanical behavior using molecular dynamics simulations. *Materials Science and Engineering: C*. 108 (2019) 110414.
- [13] A. Samimi, K. Kavosi, S. Zarinabadi, A. Bozorgian, Optimization of the Gasoline Production Plant in order to Increase Feed, *Progress in Chemical and Biochemical Research*, 3 (2020), 7-19.
- [14] Eshchanov K., Baltayeva M. Determination of the molecular mass of hydrolyzed fibroin obtained from natural silk fibroin by spectrophotometry. *Journal of the Turkish Chemical Society Section A: Chemistry*, 9(1), (2022) 115-120.
- [15] M.B. Sadr, A. Bozorgian, An overview of gas overflow in gaseous hydrates, *Journal of Chemical Reviews*, 3 (2021) 66-82.
- [16] Hayward S, Kitao A, Go N. Harmonic and anharmonic aspects in the dynamics of BPTI—a normal-mode analysis and principal component analysis. *Protein Science*, 3, (1994) 936–943.
- [17] Mott, A. J., & Rez, P. Calculation of the infrared spectra of proteins. *European biophysics journal*, 44(3), (2015) 103–112.
- [18] Davidson R.S. The photodegradation of some naturally occurring polymers. *J Photochem Photobiol B Biol*; 33(1), (1996) 3-25.
- [19] Wyeth P.R. Scientific analysis of ancient and historic textiles informing preservation display and interpretation. *Archetype Publications*, (2004) 137-42.
- [20] Widyaningtyas, Ariffinisa & Yulizar, Yoki & Bagus Apriandanu, Dewangga. Ag₂O nanoparticles fabrication by Vernonia amygdalina Del . leaf extract: synthesis, characterization, and its photocatalytic activities. *IOP Conference Series: Materials Science and Engineering*. 509 (2019) 012022.
- [21] Daye Sun, Jonathan Turner, Nan Jiang, Songsong Zhu, Li Zhang, Brian G. Falzon, Colin P. McCoy, Paul Maguire, Davide Mariotti, Dan Sun. Atmospheric pressure microplasma for antibacterial silver nanoparticle/chitosan nanocomposites with tailored properties. *Composites Science and Technology*, 186 (2020) 107911.
- [22] Kazuo Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory*

and Applications in Inorganic Chemistry, New Jersey (2008).

Allowance for universities, "Higher. School", Moscow (1971).

[23] Kaznitsyna L.A., Kupletskaya N.B. *Application of UV, IR and NMR spectroscopy in organic chemistry*. Proc.