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Research paper

Determination of the mechanism of sorption of Cu^{2+} ions to hydrolyzed fibroin

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Abstract

We were able to obtain hydrolyzed fibroin with sorbing properties from fibrous silk waste. We determined the mechanism of sorption of Cu^{2+} ions into hydrolyzed fibroin using the Dubinin-Radushkevich isotherm. Physical sorption of Cu^{2+} ions to hydrolyzed fibroin has been shown to be predominant. However, it has been observed that the colour of hydrolyzed fibroin, which sorbs Cu^{2+} ions, changes to yellow over time. Analysis of the yellowed sample by IR spectroscopy showed that Cu^{2+} ions formed a coordinate bond with the hydrolyzed fibroin.

Keywords: *Hydrolyzed fibroin ("HF"); sorption; IR spectroscopy; silk; coordinate bond*

1. Introduction

The silk industry produces a lot of fibrous waste. Finding the necessary materials and finding ways to use the fibrous waste of the fibrous natural silk (Bombyx mori) is important. Silk fiber consists of fibroin and sericin proteins. Silk fibroin has specific sorbent properties. Silk fibroin fiber has the property of sorbing various substances.

The initial adsorption rate of Co^{2+}, Ni^{2+}, Cu^{2+}, and Mn^{2+} ions on silk fibroin fibers was studied by Fukashi Shimizu and Ikuzo Sakaguchi. The use of biosorbent from silk fiber fibroin for the separation of Pb^{2+}, CrO_4^{2-}, Cu^{2+} ions was investigated (Huang *et al*. 2021). Silk fibroin/cellulose acetate blend nanofilament membranes were prepared by electrospinning and their performance as sorbents for heavy metal ions was evaluated. The sorption of Cu^{2+} ions into the obtained nanofiber membrane sorbent was studied and it was shown that the sorption capacity is 22.8 mg/g (Zhou *et al.*2010). The sorption of heavy metal ions and dyes using silk fibroin composites was determined. Recommendations have been given for the use of these composite materials in the separation of toxic substances in water (Rastogi & Kandasubramanian, 2020).

The formation of complexes of Cu^{2+} ions with fibroin has been studied (Chen *et al*. 2005). The formation of a complex of Cu^{2+} ions with a silk fibroin molecule was demonstrated by Raman spectroscopy. It is observed that the molecules of silk fibroin in aqueous solution change α-structure to β-structure and form coordination bonds of Cu^{2+} ions (Li *et al*. 2003).

During our research, we were able to obtain powdered "HF" from silk fiber waste (Eshchanov *et al*. 2021). We determined the mechanism of the sorption of Cu^{2+} ions into hydrolyzed fibroin.

2. Experiments

2.1. Materials

In the experiments, powdered "HF", copper(II) sulfate (Carl Roth GmbH+Co. KG, Germany), were used.

2.2. Instrumentation

Nimbus® analytical balance (Germany), "GFL 2104 bidistillator" (Germany), UV-1800 UV-Vis spectrophotometer (Japan), thermostat-Assistant cat. №3180 (Germany), IR-spectrophotometer-JASCO FT/IR-4600 (Japan).

2.3. Determination of the sorption of Cu^{2+} ions in "HF"

“HF” powder weighing 0.05 g was placed in 7 numbered containers. 50 mL of copper(II) sulfate solutions of 0.015, 0.0248, 0.0401, 0.0765, 0.1179, 0.1992, 0.317 and 0.33 mol/L were poured into the containers, respectively. The sorption process was carried out at a temperature of 298 K. To determine the concentrations of copper(II) sulfate solutions, a calibration curve of the relationship between concentration (C_M) and light absorbance (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.

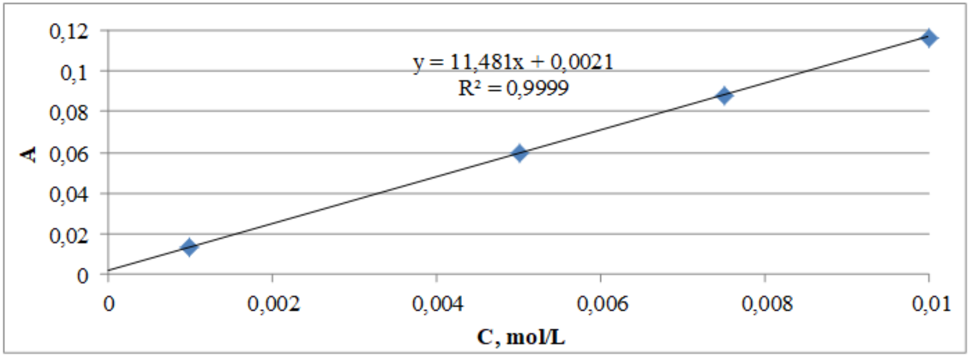

Fig. 1: Calibrated graph for determining the concentration of Cu^{2+} ions (light absorption values determined at λ=810 nm).

The results obtained were obtained through isothermal sorption diagrams of Cu^{2+} ions to “HF”, maximum sorption capacity (Q_{max}) and Langmuir constant (K_L). Samples sorbing copper ions were analyzed by IR spectroscopy (JASCO 4600 FTIR spectrophotometer).

3. Discussion and results

Sorption indices of Cu^{2+} ions on “HF” in solutions of copper(II) sulfate at concentrations of 0.015, 0.0248, 0.0401, 0.0765, 0.1179, 0.1992, 0.317 and 0.33 mol/L were determined. Based on the results, a concentration-dependence diagram of the sorption of Cu^{2+} ions on “HF” at a temperature of 298 K was drawn.

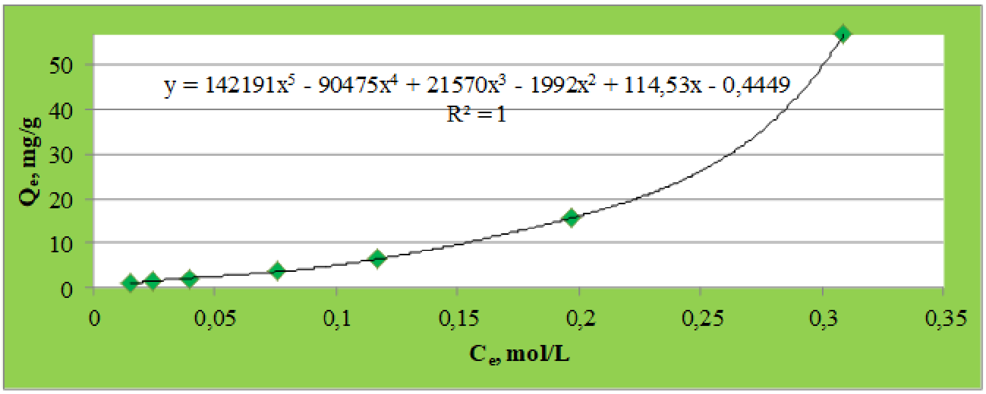

Fig. 2: Sorption isotherm of Cu^{2+} ions on “HF”.

From the diagram it can be seen that the relationship between the sorption capacity of “HF” for Cu^{2+} ions at a temperature of 298 K and the concentration of the solution at equilibrium after sorption is $Q_e=142191C^5-90475C^4+21570C^3-1992C^2+114.53C-0.4449$ is equivalent to the function. The results showed that the maximum sorption capacity of Cu^{2+} ions of “HF” is 56.88 mg/g. During the sorption process, it was found that the concentrations of solutions containing Cu^{2+} ions above 0.317 mol/L remained unchanged. Due to the low pH value in highly concentrated solutions, the amorphous parts of the pores crystallize out on the surface of the "HF" and the inner pores are closed. The sorption of Cu^{2+} ions on “HF” was considered consistent with the Langmuir isotherm model. Using the isotherm diagram, Q_{max} and other parameters were determined.

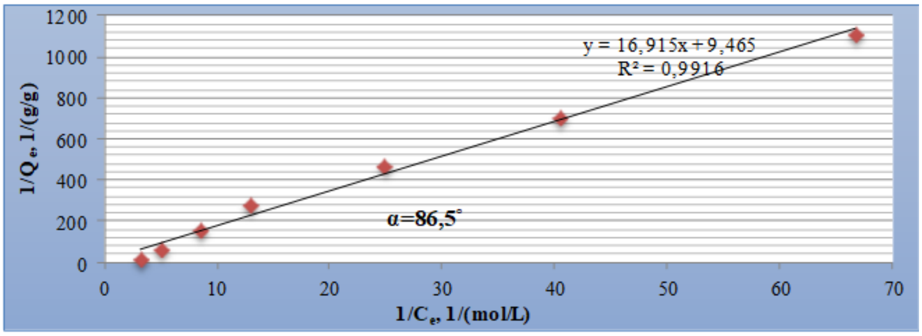

Fig. 3: Langmuir isotherm of Cu^{2+} ion sorption in “HF”.

Table 1: Indicators based on the Langmuir isotherm

Q_{max} (mg/g)	K_L	α
105,6	0,57919	86,5°

According to Langmuir isotherm refers to the sorption capacity of Cu^{2+} ions 105.6 mg/g. The Dubinin-Radushkevich (D-R) isotherm is the first to be explained with the mechanism of sorption of Cu^{2+} ions at "HF" (Dubinin, 1960; Chaudhry *et al.* 2016). A diagram of the dependence of $\ln Q_e$ and ε^2 was created, in which to determine the maximum sorption capacity of the Cu^{2+} ion on the Dubinin-Radushkevich isotherm.

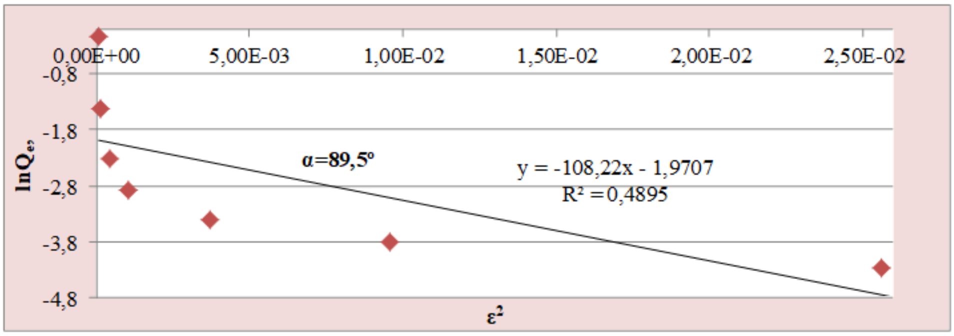

Fig. 4: Linearized Dubinin-Radushkevich isotherm for Cu^{2+} sorption on the "HF".

Based on the obtained results, the sorption energy of Cu^{2+} ions on "HF" from solutions of different concentrations was determined using the Dubinin-Radushkevich (D-R) isotherm.

Table 2: Indicators of the Dubinin-Radushkevich (D-R) isotherm

$Q_{D\text{-}R}$ (mmol/g)	β ($mol^2 \cdot kJ^{-2}$)	E (kJ/mol)
0,13935	114,5886	0,066056

Since the sorption energies of Cu^{2+} ions are less than 8 kJ/mol, it was concluded that the physical sorption process is superior to the chemisorption process. The values of the sorption energy prove that the process did not proceed according to the chemisorption mechanism.

Once the sorption of Cu^{2+} ions is complete, the copper ions can be desorbed into the powdered "HF". However, when the copper ions were retained in the powdered "HF" for 1 week, the colour of the "HF" changed to yellow and the Cu^{2+} ions could not be desorbed. From these changes, it can be concluded that first Cu^{2+} ions are sorbed to the surface and pores of powdery "HF", and then over time, the sorbed Cu^{2+} ions penetrate into the inner parts of "HF" and chemical with their polyfunctional group's bonds considered. IR spectroscopic analysis was performed to determine if the sorbed Cu^{2+} ions formed a chemical bond with the polyfunctional groups in the "HF".

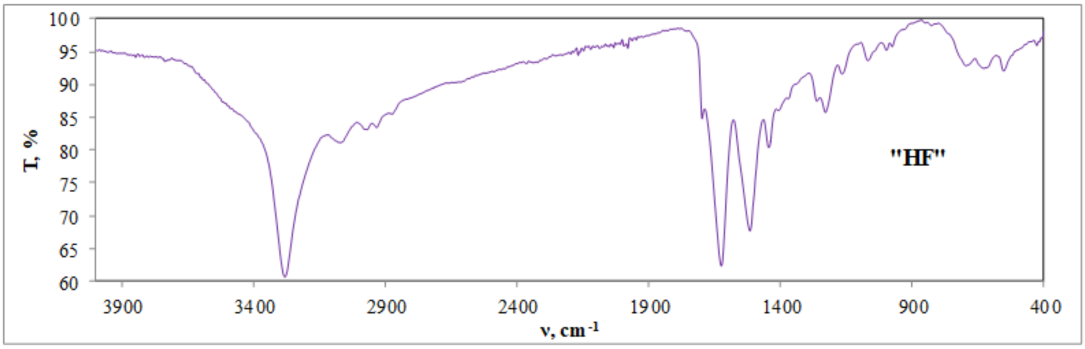

Fig. 5: IR spectrum of "HF".

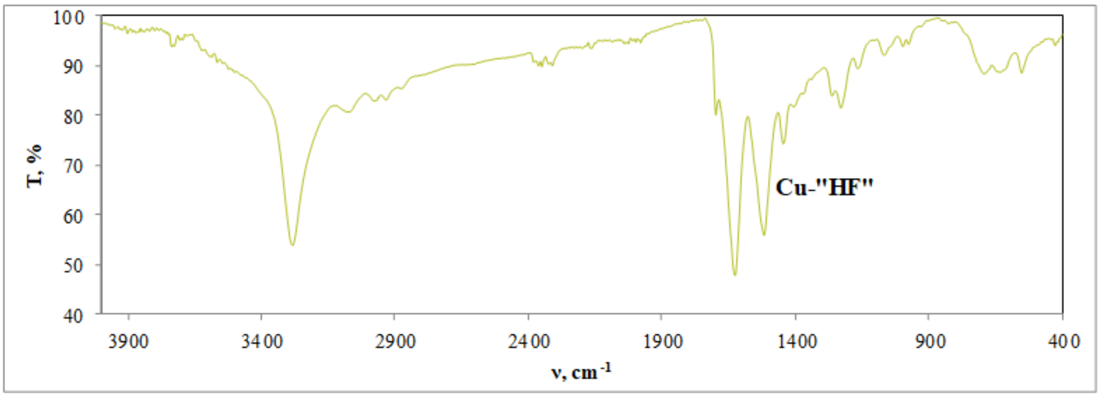

Fig. 6: IR spectrum of "HF" bound to Cu^{2+} ion.

Comparing the IR spectra of "HF" bound to "HF" and Cu^{2+} ions, a partial increase in peak intensity in the region of 426.191 cm^{-1} was observed. It is known from the literature (Nakamoto, 2008; Kazntsyna & Kupletskaya, 1971) that in the IR spectra of proteins bound by copper coordination bonds, vibrations related to Cu-N, Cu-O bonds at the absorption of 470-350 cm^{-1} areas can be observed. The absorption in the region of 426,191 cm^{-1} of the IR spectrum indicates the formation of a Cu-N and a Cu-O bond. An increase in intensity in the range of 1625.7 cm^{-1} indicates the binding of amide-I groups in the β-structure of fibroin to copper ions.

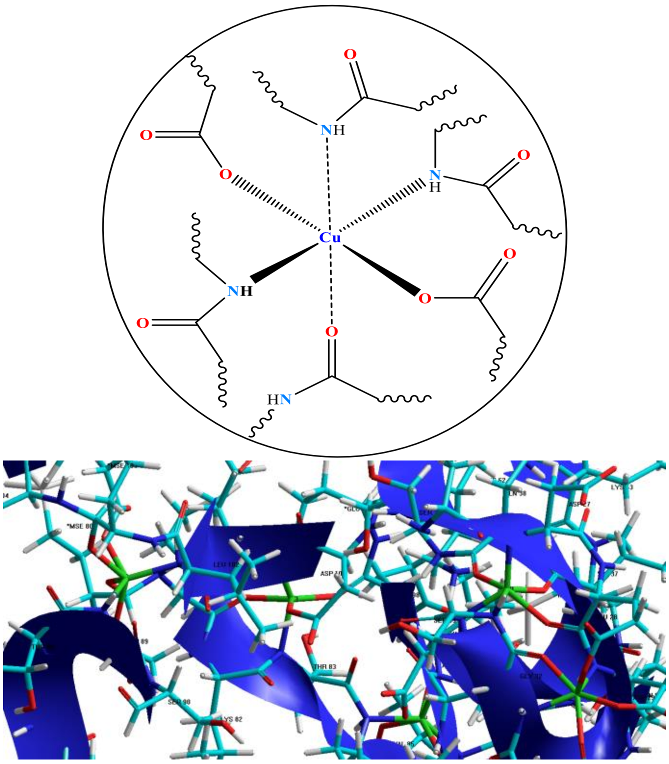

Fig. 7: The structure of the “HF” linked by a copper coordination bond.

4. Conclusion

According to the Dubinin-Radushkevich isotherm, the mechanism of physical sorption of copper ions on “HF” was found to predominate. However, over time it has been shown that copper ions interact with polyfunctional groups in “HF” to form coordinate bonds. It has been hypothesized that copper ions interact to form a coordinate bond when they reach the affected functional groups of “HF”.

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