

Study of chemical properties combination chemical method of wastewater treatment by methods IR-spectroscopy and X-ray diffraction

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Abstract. Complex formation processes of sericin compounds with Ni²⁺, Cu²⁺, Zn²⁺, Co²⁺ salts were studied. The possibility of maximum extraction of sericin was determined when wastewater is purified by the proposed method, and the developed purification method is recommended for amino acid purification of wastewater. By using the coagulants Al₂(SO₄)₃•18H₂O and FeCl₃•6H₂O and flocculant PAA together with the proposed sorbent, the concentration of coagulants in wastewater is 0.75 mg/l, 0.5 mg/l, 0.5 mg/l, and the amount of kaolin bentonite, respectively. An acceptable content of 2.0 g/l has been suggested. When the composition of the dry residue obtained after treatment with a composition consisting of bentonite, kaolin and aluminum sulfate was analyzed using X-ray structural analysis, it was found that the residue contained crystal spheres. The obtained results proved that the diffractograms of dry residue and bentonite samples are almost identical. It was found out in the research that these crystal spheres belong to the mineral contained in bentonite.

1 Introduction

Environmental protection and purposeful use of natural resources are becoming important in order to eliminate the pollution of water bodies by industrial wastewater at the world level. The composition, properties and consumption of industrial wastewater require the development and application of new methods of wastewater treatment.

Currently, the world's chemical and textile industry production volume is increasing dramatically, therefore, great attention is paid to research aimed at the development of its chemicalization, as a result of which they lead to an increase in water consumption, its consumption and composition of various industrial wastewaters. One of the main methods of wastewater treatment of cocoon enterprises is physical and chemical treatment. This is because this method can be used independently, and in this case in combination with other methods. Its relevance has increased in recent years, because one of the main principles of protection of water bodies requires a radical improvement of the water management system in industrial enterprises aimed at discharging wastewater into water bodies without or with a minimal amount [1-3].

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2 Materials and Methods

The purpose was formed by studying the scientific information on the field published in the Republic and abroad, the main scientific conditions, the level of accuracy and reliability of the conclusions were confirmed by modern physico-chemical methods such as IR spectroscopy, optical microscopy, X-ray diffraction.

3 Results and Discussion

In order to create a technology for cleaning the wastewater of cocoon enterprises using a highly efficient method, we based on the principle of conditionally dividing the wastewater into two main streams according to the nature of pollution: Stream 1 - silk glue (sericin) and natural dyes, as well as boiling of cocoons to clean them from silk components. wastewater generated during the washing process to make fabrics free of sericin using a soap solution; Stream 2 - effluents produced during dyeing, flower pressing and washing processes of silk fabrics.

The degree of pollution of the 1st stream wastewater is 1.5-2 times less than that of the 2nd stream, therefore the consumption of chemical reagents used in the treatment of the 1st stream is also less than that of the 2nd stream. In this context, it was proposed to conditionally separate the wastewater of cocooning enterprises into two streams.

Table 1 below shows the composition and concentrations of pollutants in the wastewater of "BBS Cluster" LLC.

Table 1. The composition of the 1st and 2nd streams of the cocooning enterprise's wastewater.

Indicators	Concentration. mg/l	
	Stream 1	Stream 2
pH	8.0	9.6
Suspended substances. mg/l	75-100	350-400
Dyes. mg/l: natural.	1.7	-
synthetic	-	11.6
CFM. mg/l	20	40
General alkalinity. mg-eq/l	9.1	8.0
Dry residue	110	400
Chlorides. mg/l	17	48
Sulfates. mg/l	50	170
KBC _{complete} . mg O ₂ /l	126	247
KKC _{complete} . mg O ₂ /l	160	210
Phosphorus (at the expense of P ₂ O ₅)	2.5	6.7
Ammonium ion	1.6	5.7
Transparency by font	2	3

The first stream of wastewater contains mainly sericin. Sericin (silk glue) belongs to the class of albuminoid proteins and is present together with fibroin in raw silk. It differs from fibroin in its composition. The chains of sericin macromolecules do not have an ordered and fibrous structure. By boiling raw silk with water, sericin is isolated, in which fibroin does not dissolve and only sericin passes into the solution. By boiling with dilute sulfuric acid, hydration occurs, yielding leucine, tyrosine, and serine, among many other products; glycolol is not formed, and thus sericin differs markedly from sericoin, which is formed from fibroin by the action of concentrated hydrochloric acid in the cold. In this process, 1% nitrogen (in the form of ammonia) is released from the fibroin and a solution is formed, when copious amounts of alcohol are added to the solution, sericoin is precipitated in the form of

a white powder. When boiled with dilute sulfuric acid, glycolol, tyrosine, and alanine are formed among the degradation products of sericoic, while leucine is not formed.

Based on this, experiments were conducted on the extraction of sericin from wastewater, in which the processes of complex formation with Ni^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} ions were studied [5,6].

The conducted studies allowed to estimate the equilibrium schemes in the copper sulfate-methionine system at different pH and with the corresponding K_i constants. Copper (II) cations and methionine form mono- and biligand complex compounds in aqueous solution.

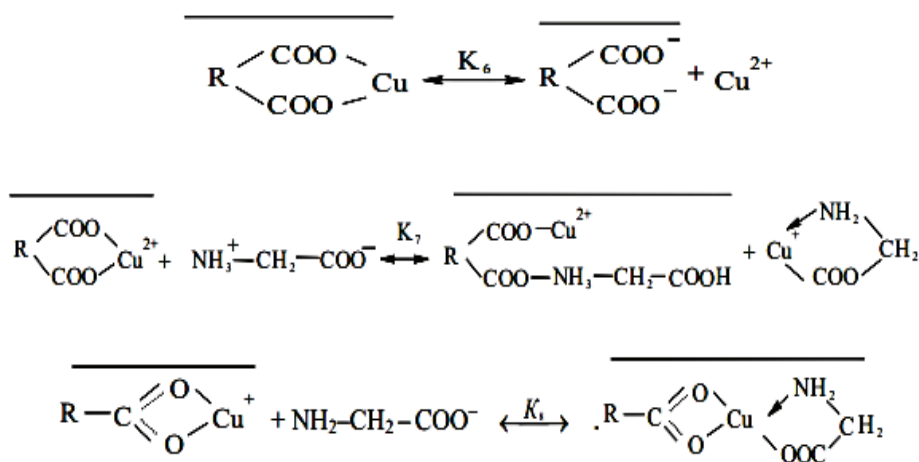


Fig. 1. Copper (II) cations and methionine form mono- and biligand complex compounds in aqueous solution.

Amino acids form chelate complexes with heavy metal ions, among which the dark-blue, easily crystallized $\text{Cu}(\text{II})$ compounds are well known. The formation of a chelate in the CuA_2 form is widely used in the complexometric titration of a number of amino acids. Titration is carried out with copper(II) sulfate solution at $\text{pH}=9$ in the presence of murekend indicator.

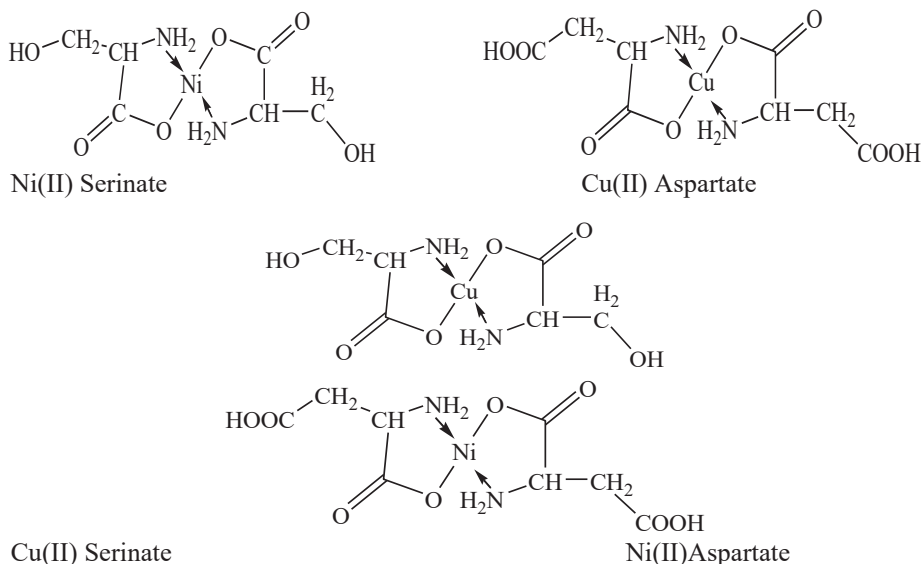
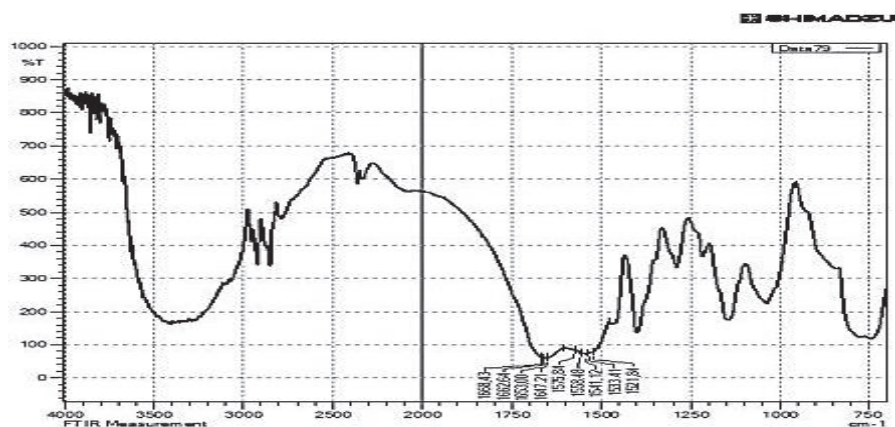
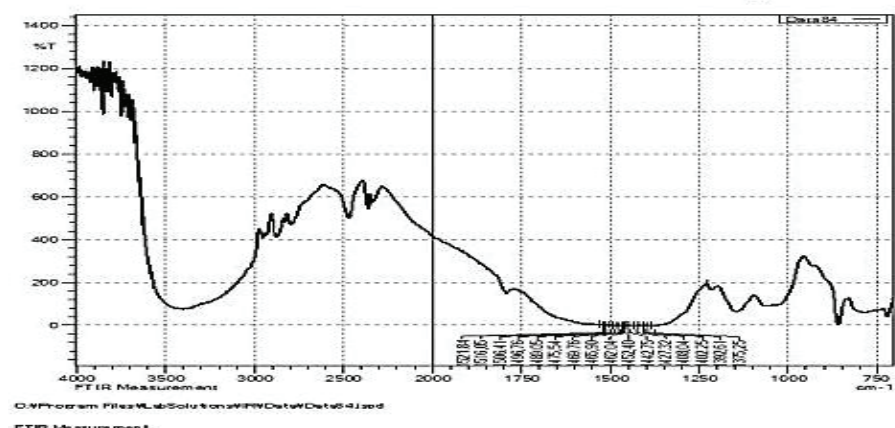


Fig. 2. Titration is carried out with copper(II) sulfate solution at $\text{pH}=9$ in the presence of murekend indicator.



a)



b)

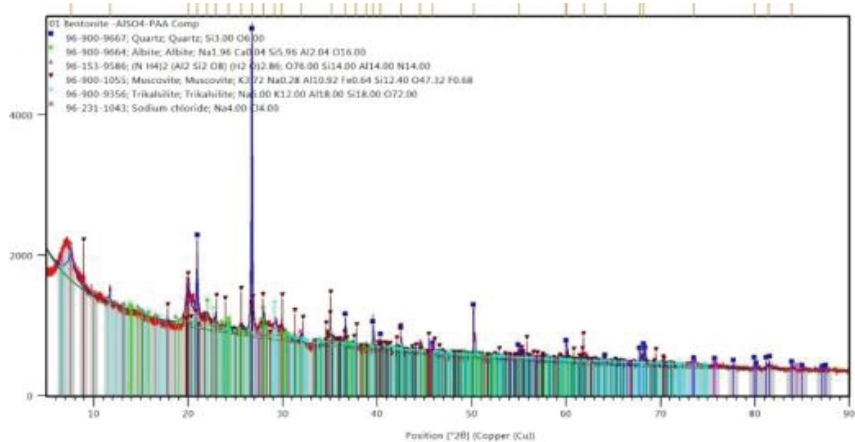
Fig. 3. IR spectrum of complexes of Cu^{2+} (a) and Ni^{2+} (b) cations with sericin and asparagine.

After purification, the precipitate formed during the treatment of wastewater with zinc and copper acetates was studied using the IR spectroscopy method (Fig. 3. IR spectrum of Cu-II.(a), IR spectrum of Ni-II.(b)). The results of the IR spectroscopic study also showed that nickel and copper metals formed a complex with amino acids in the wastewater. In the IR spectra of the residue obtained with nickel acetate (Fig. 3. IR spectrum (b) Ni-II.) absorptions in the region of $3200\text{--}3400\text{ cm}^{-1}$ correspond to valence vibrations of O–H and N–H bonds. Absorptions in the $1700\text{--}1300\text{ cm}^{-1}$ region of the spectra are characteristic for valence vibrations of C=O bonds and C–NH₂ (amide I) bonds in carboxylate ions. Absorptions in the $1300\text{--}1400\text{ cm}^{-1}$ range of spectra are specific for valence vibrations of C–O bonds in carboxylate ions. Absorptions in the $1000\text{--}1100\text{ cm}^{-1}$ region of the spectra are characteristic for valence vibrations of C–OH (carbinol) bonds held by hydroxyl groups.

In the IR spectra of the residue obtained with copper acetate (IR spectrum Cu-II). Absorption characteristic of valence vibrations of O–H and N–H bonds was determined in the region of $3200\text{--}3400\text{ cm}^{-1}$ of the spectrum. Also, valence vibrations of C=O bonds in carboxylate ions and signals characteristic of C–N (amide I) bonds were observed in the $1700\text{--}1500\text{ cm}^{-1}$ regions of the spectra. Absorptions in the $1300\text{--}1400\text{ cm}^{-1}$ region of the spectra correspond to valence vibrations of C–O bonds in carboxylate ions. Absorptions in

the 1000-1100 cm^{-1} region of the spectra are characteristic for valence vibrations of C–OH (carbinol) bonds held by hydroxyl groups.

a)



b)

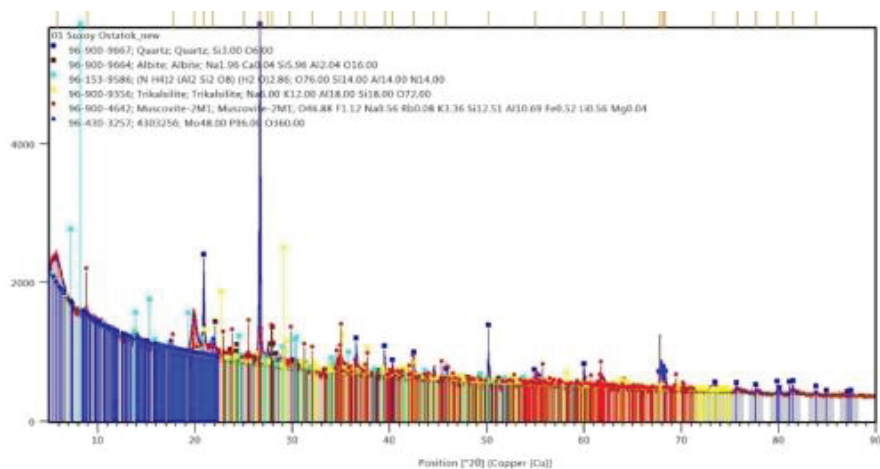


Fig. 4. X-ray structural analysis of bentonite (a) and dry residue (b).

X-ray structure analysis of the dry residue obtained after treatment with bentonite, kaolin and aluminum sulfate compositing showed the presence of crystal spheres in the residue (Fig. 4). The obtained results showed that the diffractograms of dry residue and bentonite (Fig. 4.) samples are almost the same. This indicates that these crystal spheres identified in the research belong to the mineral content of bentonite.

The analysis of the crystal structure of complexes of metals with proteins showed that the complexes of amino acids with metals have an octahedral structure, in which two residues of the amino acid are connected to the central metal atom by amino- and carboxy-groups, and the empty coordination positions are occupied by water molecules. Complexes formed by amino acids such as histidine with functional side chains, for example, are characterized by high stability, because the imidazole nitrogen forms an additional bond with the central atom [7,8].

The method of chemical cleaning with only coagulants is associated with a large consumption of chemicals and gives a lot of slurry, which dries poorly due to its ointment-like consistency. Therefore, a comprehensive approach to the chemical treatment of

wastewater by coagulation or sorption-coagulation method is proposed. The advantage of the proposed method, that is, coagulation purification, is the simplicity of the process implementation and the absence of several purification steps. For this, iron sulfate is used as a coagulant. It reacts to form iron hydroxide and iron salts, forming a light viscous slurry that separates on the surface as a layer. It is extracted and treated with sulfuric acid. The resulting fatty acids are turned into soap, and the acidic solution of iron sulfate is repeatedly used as a coagulant.

4 Conclusion

Thus, by forming complexes with Ni^{+2} , Cu^{+2} , Zn^{+2} and Co^{+2} salts of sericin compounds in wastewater, the maximum extraction of sericin has been achieved when wastewater has been purified. The optimal amount of reagents for the removal of dyes, suspended particles and the reduction of KKS content in wastewater has been determined.

The current cleaner and the proposed combined method: a high level of wastewater treatment was achieved by using a sorbent with coagulants $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and flocculant PAA. When the combined technology of wastewater treatment of the developed content was introduced into production, high economic efficiency has been achieved.

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