



Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Intensification of dyeing of silk and cotton-silk fabrics with water-soluble dyes in the presence of chitosan

D.A. Khazratova^a, F.M. Nurutdinova^b, X.Q. Razzoqov^a^a Bukhara State University, Bukhara 200100, Uzbekistan^b Bukhara state medical institute named after Abu Ali ibn Sino, Bukhara 200100, Uzbekistan

ARTICLE INFO

Article history:
Available online xxxxx

Keywords:
Silk fabric
Active dyes
Dyeing
Chitosan
Degree of fixation

ABSTRACT

The results of the study of the effects of textile excipients are striking for the intensification of the processes of dyeing silk and mixed fabrics with active dyes. For the first time, a technique has been developed for using chitosan isolated from dead bees *Apis Mellifera* as an intensifier. It was found that treatment with chitosan leads to an increase in their sorption capacity and the appearance of centers of charge in silk and cellulose fibers. A certain nature of the bond and the chemical mechanism of action in the fiber-chitosan-dye system, as well as the effect of intensifiers on the degree and amount of fixation of active dyes on the fiber. The article uses modern physical and chemical research methods: IR and UV spectroscopy, scanning electron microscopy (SEM), standard methods for determining the physical and mechanical properties, as well as color indicators of the quality of dyed fabrics. The practical significance of the results of the study is explained by the fact that the dyeing of silk and cotton-silk fabrics in the presence of chitosan improves the color characteristics of the fabric, reduces the use of imported dyes and reduces the consumption of chemical reagents.

Copyright © 2023 Elsevier Ltd. All rights reserved.

Selection and peer-review under responsibility of the scientific committee of the Fourth International Conference on Recent Advances in Materials and Manufacturing 2022.

1. Introduction

At present, in the world in the field of the textile industry, there is a need to reduce the cost of energy resources and chemical reagents while improving the quality of textile products to ensure its competitiveness in the world market. Therefore, scientific and practical research on improving the process of coloring silk and mixed fabrics based on it with active dyes using organic intensifiers are considered relevant. In turn, the use of chitosan as an intensifier is important to achieve high economic efficiency with a minimum concentration of an expensive dye, as well as an increase in the quality of textile products. (See Table 1).

In the world of chemical finishing of textile materials based on silk and cotton-silk blended fabrics, research work is being carried out aimed at developing innovative techniques and technologies that provide for the effective application of modern achievements in science and technology, and the modernization of existing technologies. Also, determining the optimal parameters in the process of coloring textile materials based on cotton and silk fabrics, determining the degree of influence of reagents on the quality of the material, diffusion, sorption, the degree of binding of fabric dyes,

studying the laws of the effective use of expensive dyes is an urgent problem.

The main directions for improving the dyeing technology are: saving energy, water, fibers, dyes and AIT without compromising product quality. Reducing the technological cycle is possible by eliminating individual operations, combining several operations, reducing processing time by intensifying processes and introducing high technologies [1].

In [2] the effect of chitosan treatment on the dyeing process and color properties of fabrics made from polyester and polyamide fibers was studied. The effect of chitosan concentration on the color characteristics of the studied tissues was studied.

The works [3,4] on the use of chitosan to impart crease resistance, anti-shrink and antimicrobial properties to woolen fabrics. Woolen fabrics were treated with solutions containing 3.5% chitosan and 4% citric acid, then the fabric was thermally treated at 90–135 °C.

The film-forming properties of chitosan are the basis for its use in the textile industry for the preparation of sizing solutions [5], indelible dressings to increase the resistance of the fiber to physical and mechanical influences [6], anti-shrink agents that simulta-

<https://doi.org/10.1016/j.matpr.2023.06.020>

2214-7853/Copyright © 2023 Elsevier Ltd. All rights reserved.

Selection and peer-review under responsibility of the scientific committee of the Fourth International Conference on Recent Advances in Materials and Manufacturing 2022.

Table 1

The effect of chitosan and uzkhitan on the degree of fixation and color intensity when dyeing silk and cotton-silk fabrics.

Chitosan/uzkhitan concentration	Color Intensity	K/S Boosts	Covalent dye fixation g/kg	Degree of use of dye
Silk				
0	6	0	16	53,3
0,5	8	18	24	80
1	9	36	25	83,3
1,5	11	40	25,5	85
Silk-cotton 55/45				
0	6	0	16,2	54
10	7,5	37,5	24	80
15	8	48	24,3	81
20	9	55	25	83,3

neously improve the dyeing of fabrics, [7,8]. In addition, chitosan can be used as a thickener; in pastes for pigment printing of fabrics, as a reagent that prevents contamination of textile materials and improves the neck of fabrics, as well as for applying deodorizing and antibacterial additives to fabrics [9,10].

We obtained chitosan from dead bees by a chemical method. The chemical method is based on deproteinization, demineralization and depigmentation using chemical reagents - acids, alkalis, peroxides, etc. [11].

It is gratifying that chitosan is actively used even in the textile industry for dyeing, printing, and finishing various natural fabrics, such as wool, cotton, and silk [12,13]. In turn, the use of intensifiers provides for high economic efficiency and minimum concentration in the dye bath. Despite the widespread use of chitosan for printing as a thickener [14,15], its introduction into the processes of dyeing silk fabrics is hindered due to the lack of technology.

2. Methodical part

2.1. Materials and research methods

The study used chitosan synthesized from dead bees *Apis Mellifera* in the scientific laboratory of the Bux SU, cotton, silk and cotton-silk fabric (silk warp, silk cotton 55/45) produced at the joint venture Bukhara-China JSC "Bukhara Brilliant Silk", as well as anionic dye "Reactive blue K".

The dye solution in the alkaline method consists of g / l:

- active dye – 2% of the mass of the fabric,
 - electrolyte (sodium sulfate) – 10 g/l,
- in the second stage of the methods enter:
- alkaline agent sodium carbonate (Na_2CO_3) – 10 g/l.

When dyeing, we used chitosan synthesized from dead bees and the process was carried out according to a periodic method.

Active bright blue K was chosen as dyes. Chitosan concentration varied from 0 to 1.5 g/l. A solution of chitosan in acetic acid (2%) was applied to the fabric before dyeing and dried at a temperature of 100–110 °C until completely dry.

Study of the microstructure of textile materials on a scanning electron microscope. Morphological studies of the surface of the textile material were carried out using a scanning electron microscope SEM - EVO MA 10 (Zeiss, Germany).

The IR spectroscopic study of the samples was carried out on a Jacko 5300 and IR-Prestige 21 Fourier spectrometer (Shimadzu Corporation, Japan) in the wavenumber range from 400 to 4000 cm^{-1} .

3. Results and discussion

The study of the processes occurring between water-soluble dyes and the chitosan film, as well as the possibility of interaction between the chitosan film and the tissue, is of great importance,

since it allows one to judge the nature of the bonds that arise in the "tissue - chitosan - dye" system, which can largely determine the quality of coloring. when coloring textile materials.

Active and acid dyes are fixed in the amorphous film of chitosan, to which the dyes have a greater affinity. The chitosan film, in turn, is fixed on the fiber due to adhesive and intermolecular bonds. The adhesive strength of the bonds formed is 1.99 N/cm. The amorphous nature of the chitosan film was proved by X-ray diffraction analysis (Fig. 1).

To test the assumption about the interaction of chitosan with the dye, the absorption spectra of solutions of dyes, chitosan, and their mixtures were recorded at pH from 3 to 11 in the visible and UV regions of the spectrum using a UV-1900 i spectrophotometer (Shimadzu). For the study, a solution of chitosan from dead bees was used. Prepared by dissolving the dry preparation in 2% acetic acid with a concentration of 0.1 g/l, as well as active dyes: active bright blue K with a solution concentration of 0.1 g/l.

Fig. 2 shows that Fig. 2.c differs significantly from the additive sum of Fig. 2.a and 3.b. There is a sharp increase in optical density at a wavelength of 290–370 nm, which corresponds to the visible region of the spectrum and a large increase in the range of 590–700 nm, i.e. in the ultraviolet part of the spectrum. This indicates that a chemical interaction occurs between the dye and chitosan in solution under these conditions.

Studies of silk and cotton-silk fabrics in the presence of chitosan, both treated and unwrapped with chitosan, were carried out according to the method described in the methodological part. The obtained photographs are shown in Fig. 3. Comparison of the original fiber (Fig. 3.a) with that treated with chitosan (Fig. 3.b) shows that the polymer causes noticeable changes in the fiber surface. 4. it can be seen that the original fabric (Fig. 3. a) has a loose structure of the surface layer, while the fabric treated with chitosan (Fig. 3. b) has a different appearance, i.e. the surface of the fabric is smoothed, adhesions are formed, and a film is formed on the surface of the fiber.

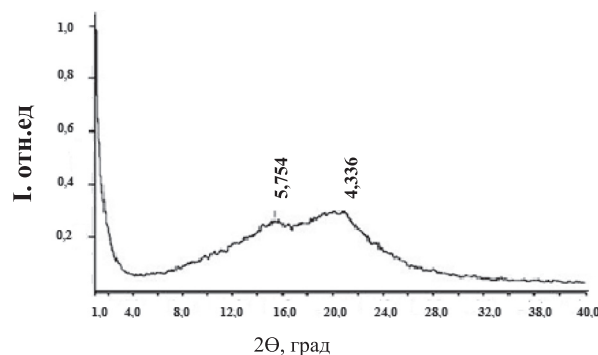


Fig. 1. X-ray pattern of a chitosan film.

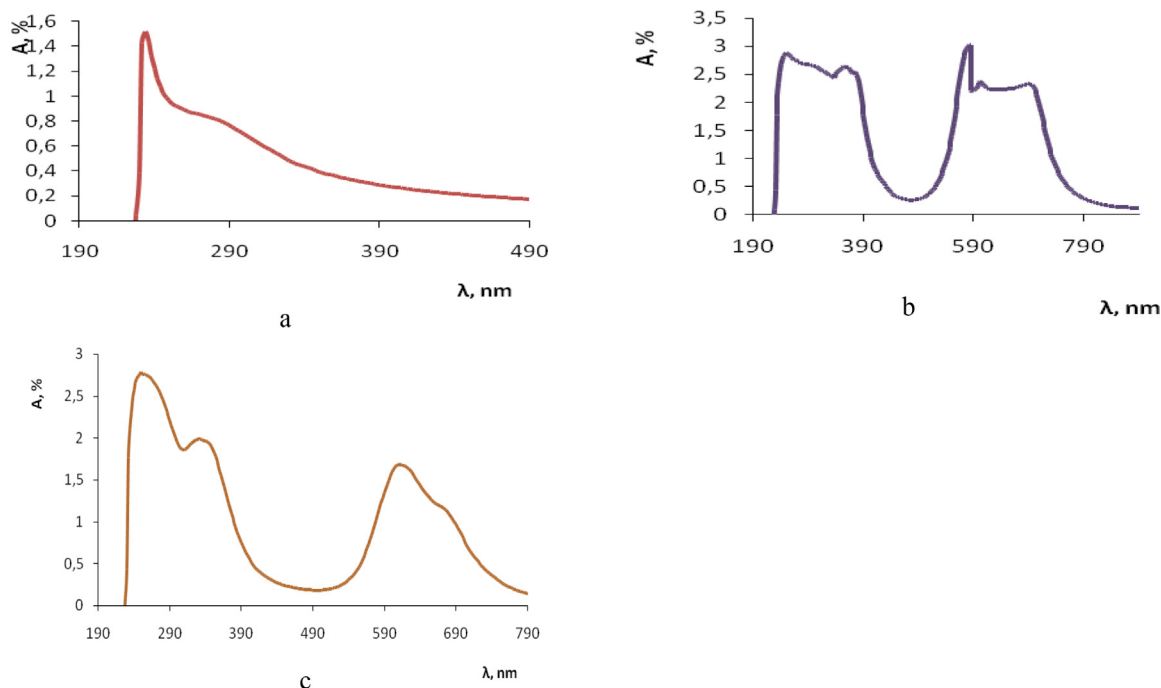


Fig. 2. a) absorption spectra of chitosan solutions b) absorption spectra of solutions of active bright blue k dye. c) absorption spectra of solutions of mixtures of active bright blue dye k and chitosan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

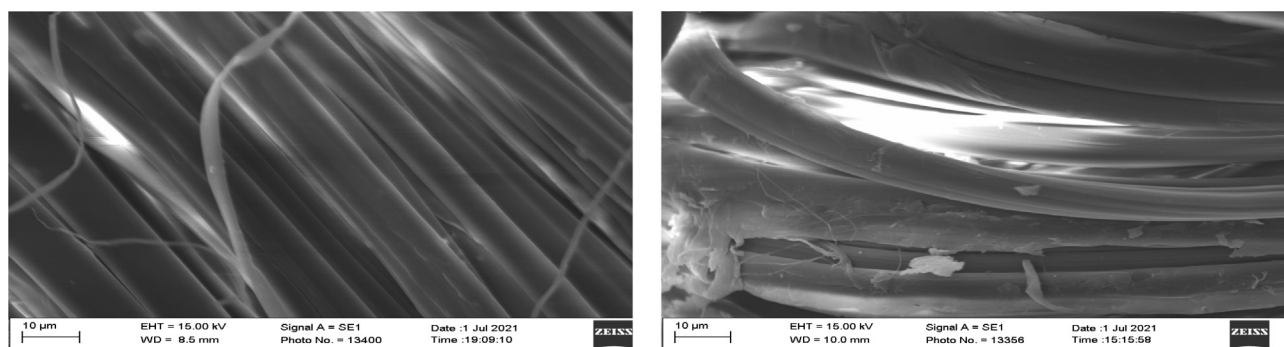


Fig. 3. Micrographs of silk fabric, untreated (a) and treated with chitosan (b).

A 2% solution of acetic acid was used to dissolve chitosan. In this work, a chitosan solution was used to treat tissues before the coloring process [16]. Next, IR spectroscopic studies of the samples were carried out according to the generally accepted method. The infrared spectra of the samples were recorded on a «Jacko 5300» and «IR-Prestige 21» Fourier spectrometer (Shimadzu Corporation, Japan) in the wavenumber range from 400 to 4000 cm^{-1} .

As can be seen in Fig. 4, the OH and NH absorption band is observed in the IR spectrum of chitosan, which is included in the hydrogen bond in the form of an intense wide band in the region of 3600–3100 cm^{-1} . The absorption spectra of fibroin are characterized by the presence of bands of Amide I (C = O), Amide II (N–H, C–H), Amide III (C–N, N–H bound, CH₃–C) at 1620 cm^{-1} , 1228.66 cm^{-1} , 1514, 12 cm^{-1} respectively. Dyeing of a chitosan film with an active dye also leads to an increase in the intensity of the absorption band in the range of 3500–3100 cm^{-1} of stretching vibrations and OH groups, and a narrowing of the band is observed, apparently associated with the disappearance of vibrations of the stretching NH₃⁺ groups.

In this scientific work, we solve the issue of saving an expensive dye when using chitosan obtained from bee submarine. The unique

structure of the chitosan macromolecule and the presence of a positive charge expand the areas of its application [17]. It is known that it is possible to intensify the dyeing process when fixing dyes by introducing organic compounds so that the substance is easily removed and biodegradable. In turn, the use of intensifiers provides for high economic efficiency and a minimum concentration in the dye bath. For the first time in the history of the plant, we used the preparation uzkhitan (mixture of carboxymethylcellulose and chitosan), we used the basis of sodium salts of carboxymethylcellulose and chitosan synthesized from the submarine bee *Apis Mellifera* [15] (Table 2).

Dyeing of cotton-silk fabrics was carried out using an anionic dye «Reactive red X-3B». To obtain even, bright, stable colors, it is necessary to choose dyes and optimal conditions in which both fiber components are equally fixed dye. The use of uzkhitan, containing a positive charge of NH₃⁺, as an intensifier eliminates these shortcomings.

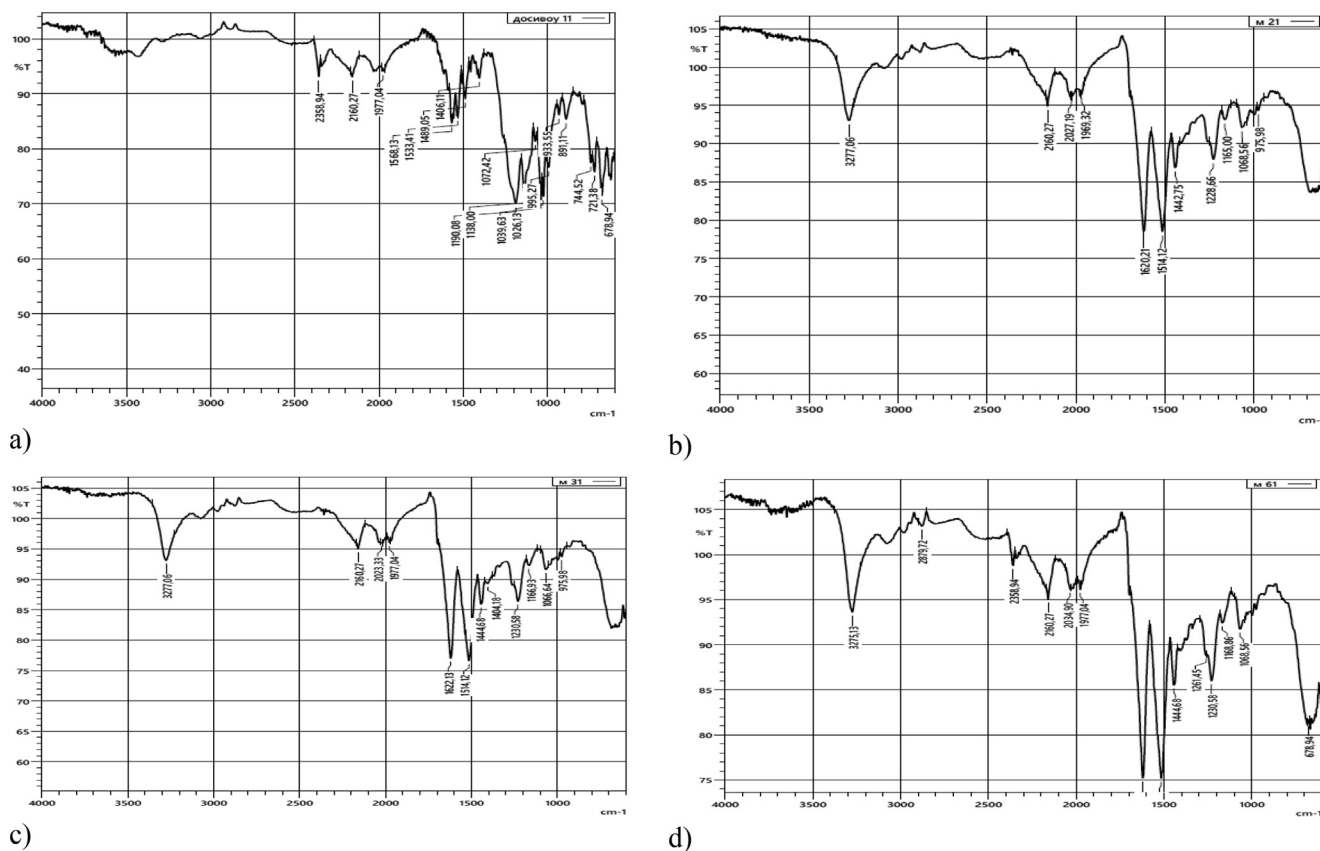


Fig. 4. IR Fourier spectra a) dye “Reactive blue K”; b) undyed silk fabric; c) dye-dyed fabric; d) dyed fabric using chitosan.

Table 2

Data of the drug UZKHITAN and its indicators $MM \times 10^3 (X3) = 162\ 000$; $C/A (X3) = 86,5\%$.

№	Name of indicator	Actually
1.	Appearance	Sediment is not present
2.	Color	Light beige
3.	Density, g/cm^3 , not less than	1,09
4.	Mass fraction of dry matter, %, not less than	0,92
5.	Hydrogen index, pH	5,5

4. Conclusions

It was found that at a concentration of chitosan 1–1.5 g/l, and uzkhitan 15 g/l at a temperature of 80 °C, the best indicators of the degree of fixation, penetration of dyes and color intensity are simultaneously provided. Thus, to obtain a single result, using uzkhitan in a dye bath at concentrations of 15–20 g/l, it is possible to reduce the dye concentration by 2% of the fabric weight (instead of 5% of the fabric weight, use 3% and lower, i.e., for 100 kg of dyed cotton-silk fabric, the savings amount to 2 kg of dye. Based on the results of a comprehensive study conducted, it can be concluded that the dyeing of silk and cotton-silk fabrics with active dyes in the presence of uzkhitan has improved physic-mechanical and coloristic indicators with high strength of the dyes, which ensures high performance properties of the finished product.

The use of chitosan as an intensifier for coloring silk fabrics at the “Bukhara Brilliant silk” enterprise “Bukhara Cotton” made it possible to significantly reduce the amount of active dye by 30% while increasing the quality of textile materials and saving chemical reagents. As a result of the introduction of chitosan obtained from local raw materials, the color of the finished product has

improved and the cost has decreased. Dyed silk and cotton-silk fabrics can be used for sewing women’s clothing.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] Мельников Б.Н. Теория и практика интенсификации процесса крашения / Б.Н. Мельников М.: Легкая индустрия, 1969.-271с.
- [2] Манокова И.И. Влияние хитозана на процесс крашения химических волокон / И.И. Манокова, В.В. Сафонов // Химические волокна. - 2009. - №3. - С. 20-23.
- [3] Na, Lu . Перспективы использования хитозана для отделки шерстяных тканей / Lu Na, D. Bing-yao, Y. Jing, G. Wei-dong // Wool Text. J. - 2005. - №11. - С.18-21.
- [4] Hsieh S.H. Antimicrobial and-physical properties of woolen fabrics ured with citric acid1 and chitosan / S.-H. Hsieh, Z.K. Huang, Z.S. Huang, Z.S. Tseng // J. Appl. Polym. Sci. - 2004. -vol. 94. - №5. - С 1999-2007.
- [5] Stegmaier T. Neues aus der Schlichtereiforschung am ITV Denkendorf / T. Stegmaier, W. Wunderlich, H. Abele, T. Hager, S. A. Bakar, M.-U. Witt, H. Planck // Melliand Textilber. - 2005. - vol. 86. - №4. - С 240, 242-244.
- [6] Ключкова И.И., Сафонов В.В. Крашение и печатание тканей из природных, волокон, ацетирированных хитозаном вологорастворимыми, красителями // Изв. вузов. Технология текстил. пром-сти. -2006. - №4. - С. 50-53-.
- [7] Julia M.R. Influence of the molecular mass of chitosan on shrink-resistance and dyeing properties of chitosan - treatd wool / M.R. Julia, E. Pascual, P. Erra // Journal of the society of dyers and colourists. - 2000. - vol. 116. - №2. - P. 62-67.
- [8] Hudson S.M. Applications of chitin and chitosan as fiber and textile chemicals / S.M. Hudson // J. Macromol. Sci. C - 2003. - vol. 43. - №2. - P. 590-599.

- [9] Wang C.C. Anti-bacterial and swelling properties of acrylic acid grafted-and collagen/chitosamobilized polypropylene non-woven fabrics / C.-C. Wang, C.C. Chen//J. Appl. Polym. Sci. - 2005. -vol. 98. - №1. - С 391-400.
- [10] Chi-Hsiung J. Biocompatibility and antibacterial activity of chitosan and hyaluronic acid immobilized polyester fibers / J. Chi-Hsiung, Y. Ling, L. Shang-Ming, H. Mou-Chuan, C Wen-Li, Y. Da-Guang, Y. Ming-Chien // J. Appl. Polym. Sci. - 2007. - vol. 104. - №1. - С 220-225.
- [11] Ixtiyarova G.A., Hazratova D.A., Umarov B.N., Seytnazarova O.M. Extraction of chitozan from died honey bee *Apis mellifera* // International scientific and technical journal Chemical technology control and management. -Vol. 2020: Iss.2, Article 3.-P.15-20.
- [12] Вахитова Н.А. Применение хитозана в крашении текстильных материалов /Н.А. Вахитова, В.В. Сафонов // Мат. VII междунар. конф. «Современные перспективы в исследовании хитина и хитозана».- Санкт-Петербург - Репино. - М.: ВНИРО, 2003. - С. 286-288.
- [13] Ихтиyarova Г.А., Менлиев А.С., Хазратова Д.А., Аюпова М.Б. Применение комплексных загусток на основе узхитана для набивки хлопкошелковых тканей // Технология текстильной промышленности . -2021. -№ 4(394) . -С. 129-133.
- [14] Нурутдинова Ф., Хазратова Д., Жахонкулова З. Study of antimicrobial and rheological properties of chitosan-based apismellifera // EurasianUnionScientists. – 2021. – Т. 3. – №. 3 (84). – С. 48-52.
- [15] Ихтиyarova Г. А., Хазратова Д. А., Сафарова М. А. Разработка состава смешанных загусток на основе карбоксиметилкрахмала и узхитана для печатания хлопково-шелковых тканей //Universum: технические науки. – 2020. – №. 6-2 (75). – С. 33-35.
- [16] Хазратова Д. А., Ихтиyarova Г. А. Интенсификация процесса крашения шелковых тканей активными красителями с хитозаном //Universum: технические науки. – 2021. – №. 4-3 (85). – С. 17-20.
- [17] Ихтиyarova Г., Хазратова Д. Муталипова Д.«Интенсификация процесса крашения шелковых тканей активными красителями». InterConf, вып. 45, март 2021 г.