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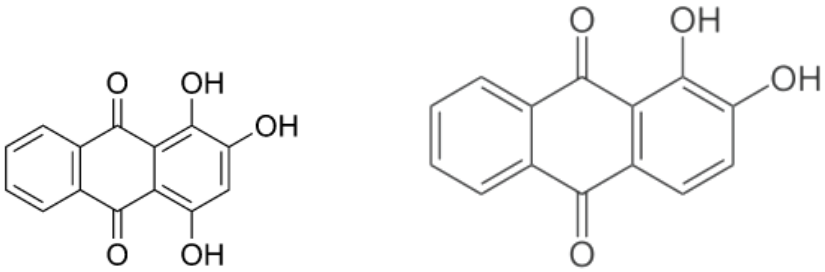
CONTINUOUS DYEING OF CELLULOSIC TEXTILE BY RUBIA TINCTORUM EXTRACT USING SOL-GEL METHOD

Abstract. In this article considers a new method of dyeing cotton fabrics using sol-gel method wiht natural plant origin dyes. The modified sol-gel method, allowing formation on the fiber a functional barrier coating of silicon oxide, which includes a plant dye. Application of this fixation method allows reducing the yield of the dye from the fiber significantly, as well as introduce additional agents for polyfunctional finishing of textile materials, therefore the method can be referred to the methods of functional depomaterials production. The effect of processing parameters on the intensity and color stability of the obtained materials was studied. The method scanning electron microscopy used for study the surface structure of the treated fibers and to obtain evidence of the presence silica coating. The existance of silicon oxide is also confirmed by the availability of its absorption peaks by Fourier-transform infrared spectroscopy (FTIR).

Key words: sodium silicate, sol-gel, coloring, natural dyes, filer.

Introduction. Developing the chemical industry allows of getting synthetic dyes with the properties and range of colors, which consumer needs for. The undeniable advantages of this dyes type are their low cost, availability of raw materials and, of course, a wide range of colors. However, despite their obvious advantages, they also have disadvantages as their harmful effects on the environment and on humans. The environmental risks of using this type dyes are high, because many of them have carcinogenic properties [1]. In addition, the traditional technology of dyeing with synthetic dyes requires high water resource costs. For example, dyeing one kilogram of cotton fabric carries a flow rate of 70-150 liters of water, about 40 g of active dyes and 0.6 kg of sodium chloride. At the same time, appearence of harmful effect of this type of dye on the environment due to its release into sewage is a known and proven fact [2]. For this reason, in order to create safer textile materials and develop harmless ways of coloring and finishing, it makes sense to return for using natural plant origin dyes particularly. The most complete information about the plants used for these purposes is well studied and presented in previous works [3-6].

The purpose of this work is to develop a technology of coloring cellulose-containing textile materials using a sol-gel method. In this study a water extract of the roots of the madder dye (lat.Rubiatinctorium) has been used, so the main coloring substances are porphyrins, namely, alizarin and purpurin (figure 1). The roots of this plant have been used since ancient times for coloring processes silk, cotton and wool. However, with the advent of the era of synthetic dyes, madder plant used for medical purposes as an anti-inflammatory drug mainly.



Purpurin
(1,2,4-Trihydroxyanthraquinone)

Alizarin
(1,2-Dihydroxyanthraquinone)

Figure 1 – Main colorants of Rubia tinctorum

The traditional technology of dyeing textile materials with plant dyes uses a periodic dyeing method, there is a long-term presence of the dyed materials in the dyeing solution. It is known that a periodic method of dyeing involves a large expenditure of resources compared to a continuous one. Therefore, using sol-gel dyeing at finishing technology will be better. The name "sol-gel technology" combines a group of methods for synthesizing materials from solutions, so the main result is the preparation of a gel at one stage of the process. Often this process is based on the reaction of controlled hydrolysis of compounds like alkoxides.

Several papers [7-9] about using of the sol-gel method in the coloring of textile materials are known. Most of the precursors of the sol process are alko-silanes (TEOS, GMPTS, APTES, TESP-A) and alcohol as solvent with acid, which is a hydrolysis catalyst. in this way the first step is to obtain the sol by reaction of hydrolysis and polycondensation. The second stage is the synthesis of a monolithic gel by the intensive formation of contacts between the particles and the production of a three-dimensional silicon oxide network by increasing the volume of the dispersed phase. The third stage is drying and heat treatment. Products with different levels of density and pore size (xerogels, ambigels, airgels and cryogels) can be obtained. It depends on the method of their implementation. At the textile finishing process there is a tendency of making silicon oxide coatings by sol-gel synthesis on the fiber, which includes a functional substance. In this way it is possible to obtain hydrophobic, fire-resistant, biocide and colored textile materials. The mechanism of functional agent fixation is similar to the technology of printing pigments using a polymer binder, but it has less harm to the environment. Existence of a silicon oxide coatings on the fiber also leads to a decrease photochemical degradation processes under UV radiation [10]. The coloring methods, mentioned above, present an alkoxide sol-gel method, which involves using of a large amount of organic solvents (mainly ethanol). Thus, the method, described in the literature [11, 12] and involves using an aqueous sodium silicate solutions, is most appropriate.

EXPERIMENT

Materials and methods. Samples of 100% bleached cotton fabric, article 1030, with size 200x200mm and surface density of 147 g/m^2, washed in distilled water at 40 °C, dried in a oven and kept in a desiccators for 24 hours. The precursor of the barrier silica coating is an aqueous solution of sodium silicate (liquid glass of Na_2SiO_3 in the mass ratio of water: Na_2SiO_3 equal to 9: 1) with a density of 1.36 g/m^3. As a catalyst of hydrolysis, citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) was chosen. The raw material for dye extract obtaining was the crushed roots of Rubia tinctorium. As a mordant, $AlK(SO_4)_2$ was chosen.

Extraction of the dye. Pre-dried and shredded roots of the madder dyeing (10 g/l) were poured with an aqueous solution containing NaOH (1-2%), received mixture was heated in a water bath to 80 °C and held for 30 minutes. After removal from the bath, the solution was filtered and held for 12 hours in a cool place. The solution storage process over a long period of time is required to precipitate poorly soluble colloidal impurities in the solution, which can be nuisance for uniform coloration.

Sample preparationg and dyeing. Pre-washed and dried samples of cotton cloth with a size of 200x200 mm were impregnated with a solution, containing 10 g/l of $AlK(SO_4)_2$, for a minute at a temperature of 60-65 °C which followed by 90% padding. At next, tissue samples were impregnated in a second bath with a dye solution, prepared on the basis of an aqueous extract with the addition of liquid glass (50-100 g/l). Impregnation was carried out at a temperature of 65-70 °C for one minute, followed by padding a laboratory padder. After this, the dyed samples were immersed in a third bath, containing an aqueous solution of citric acid (20-50 g/l). Impregnation was carried out at a temperature of 65-70 °C for one minute, followed by padding. Further, it was dried at a temperature of 70-80 °C for 5 minutes and heat treatment at temperatures of 120-160 °C. After heat treatment, the solution was washed with solution, which consists a surfactant containing 2 g/l at 50 °C, and rinsing in distilled water.

Research methods. For determine the color stability to dry and wet friction, the PT-4 device and the gray standards scale were used in accordance with GOST 9733.27-83 "Textile materials. Method of testing the color fastness to friction". For determine the color stability to wet-heat treatments, the stained samples were subjected to repeated washing according to the conditions given in ISO 105-C06-2011 "Textiles. Tests for colour fastness. Part C06: Colour fastness to domestic and commercial laundering". The color intensity K/S of samples were obtained from tabulated data by comparison with the reflection coefficient R%, which measured on a CarlZeiss spectrophotometer. The fact of the availability of coating is one of the reasons for the change in the strength and stiffness parameters in comparison with the original fabric. Determination of the tensile strength of the fabric was carried out on a tensile machine RT-250M in accordance with GOST 3813-72. "Textile materials. Fabrics and piece goods. Methods for determining tensile properties". Determination of the inflexibillity parameters of the

processed and untreated samples was carried out with the MT-376 device (Metrotex, Russia) according to the ring method according to GOST 10550-93 "Textile materials. Fabrics. Methods for determining rigidity in bending". For research of chemical compounds and bonds, FTIR method, using Nicolet 6700 spectrometer (USA), was applied. To study the structure of the surface of the processed samples the electron microscopy (SEM) method, using a JEOL JSM-6490LA scanning electron microscope with an energy dispersive analyzer (EDX), was applied.

RESULTS AND DISCUSSION

The results of measuring the intensity of the color of the obtained samples are shown in table 1.

Table 1 – Intensity and color stability

Sample	Concentration of liquid glass, g/l	Concentration of citric acid, g/l	Temperature of heat treatment, °C	K/S			Colour fastness for friction	
				Without washing	After 5 washing	After 10 washing	dry	wet
1	100	50	160	0.9618	0.7225	0.6108	5	5
2	100	50	120	0.7748	0.6255	0.5332	5	5
3	100	20	160	0.9742	0.7403	0.6368	5	5
4	100	20	120	0.8372	0.6843	0.5860	5	5
5	50	50	160	0.9376	0.7181	0.6218	5	5
6	50	50	120	0.8691	0.6640	0.5622	5	5
7	50	20	160	1.0394	0.7726	0.6561	5	5
8	50	20	120	0.8372	0.6561	0.5791	5	5
Untreated				0.009713			5	5

The stability of the stain to dry and wet friction for all samples was 5 points. According to the results of the K/S measurement, it can be seen that samples with a heat treatment at 160 °C have the highest color intensity compared to samples treated at 120 °C, this fact can be explained by the presence of a denser structure of the silica coating, which prevents the dye from desorption. And there is also seen that an increasing of the liquid glass concentration makes it possible to obtain the most stable coloration for wet-heat (laundering) treatments.

The durability of the paint to dry and wet friction for all samples was 5 points, which indicates a sufficient fixation of colorant on the fiber.

Along with the color strength index, the influence of the dyeing conditions on the physical and mechanical characteristics of the fabric was studied, and the inflexibility (toughness) data of the processed samples without the use of a dye was also given. The data obtained during testing of the samples are given in table 2.

Table 2 – Mechanical properties

Sample	Concentration of liquid glass, g/l	Concentration of citric acid, g/l	Temperature of heat treatment, °C	Inflexibility, cN		Tensile strength, N	
				Coloured by sol-gel	Treated by sol-gel, without colorant	Main	Weft
1	100	50	160	11.074	9.741	162	122
2	100	50	120	9.555	11.613	201	148
3	100	20	160	12.769	9.800	162	161
4	100	20	120	10.662	11.437	161	130
5	50	50	160	10.251	8.751	153	110
6	50	50	120	11.250	10.692	163	136
7	50	20	160	10.643	9.016	171	118
8	50	20	120	11.417	9.320	187	115
Clear	0	0	0	7.232	7.232	232	221
Non-coloured, treated by $AlK(SO_4)_2$	0	0	0	9.878	9.898	409	249

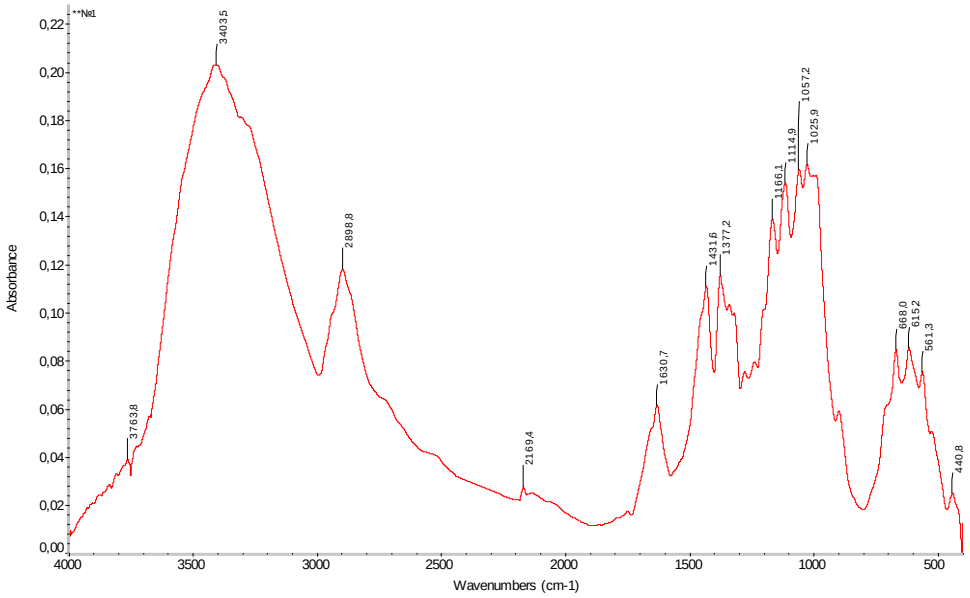


Figure 2 – FTIR absorption spectrum of a coloured sample

Data analysis shows that heat treatment at elevated temperature leads to a decrease in the strength characteristics of the fabric, which is caused both by the dehydration of the cellulose fiber and by decreasing elasticity of the coating and

leads to a decrease in the mobility of the fibers. It can be seen from the table that impregnation with alums before the dyeing process, also leads to strength increasing.

For a more detailed study of the chemical composition and the existance of chemical bonds, an FTIR analysys was made. The results are shown in figure 2. The detailed description of the absorption peaks is presented in table 3.

Table 3 – Supposed availability of chemical bonds

Absorption peaks, cm^{-1}	Description	Possible cause
440	-S-S-	Use of alumina potassium alum
561	C-H	–
615	C-Cl or CH-O-N=O	–
668	Presence of benzole ring	Presence of dye
1025	Alkylcyclopropanes or benzole ring existence	Presence of dye
1057	Si-O	Presence of silicon oxide
1115	Acetals	–
1166	Alkylsulfones or disubstituted sulfomides	Due to the reaction of alumacalic alum with a dye, the formation of lacquers
1377	$-CH_3$	–
1431	Dimers of carboxylic acids	–
1630	Crystallization Water	Non-full dehydration of Cellulose and Gel Coating
2170	$-NH_3$	–
2899	$AlK(SO_4)_2$	Remains of unreduced alumina potassium alum
3403	-OH	Presence of cellulose

The absence of peaks in the region of 1870-1770 cm^{-1}, indicates the absence of sodium citrate salts, the peaks at 559 and 667 cm^{-1} indicate the availability of tetrapyroll, which confirms the presence of the dye.

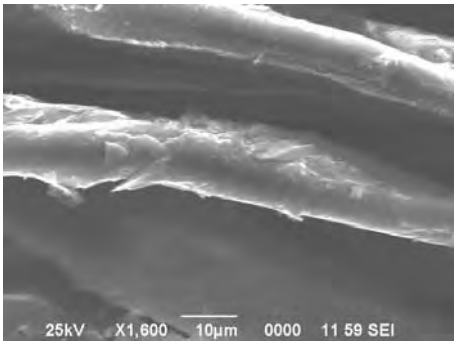
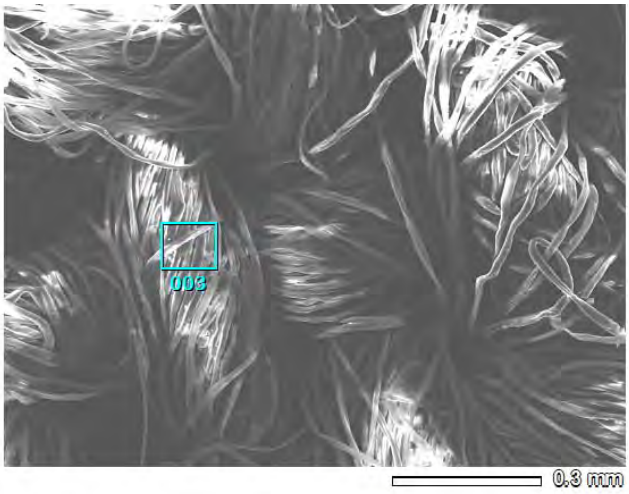


Figure 3 –
The SEM image of coloured sample



Memo	C	O	Si	Total(mass%)
3	46.17	48.52	5.32	100

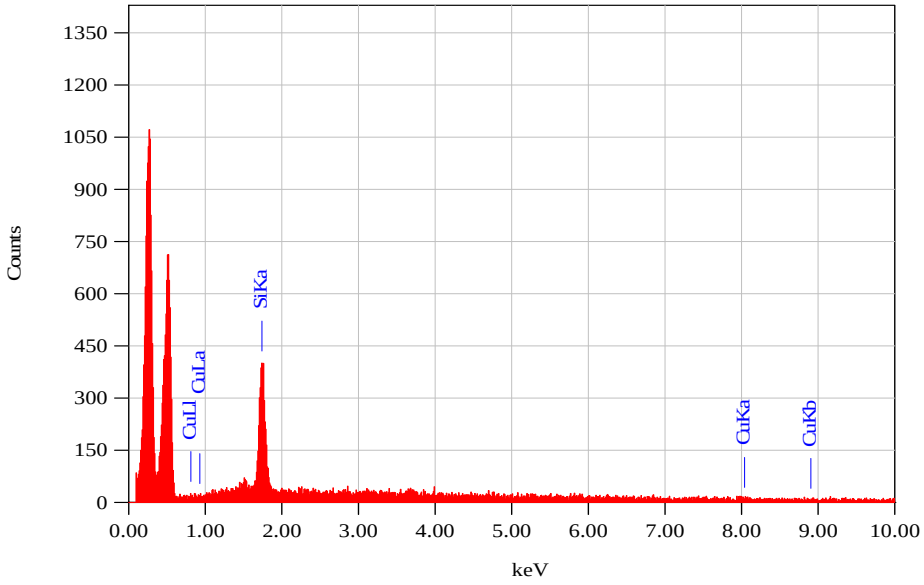


Figure 4 – EDX data of coloured sample

The microstructure and elemental composition of the obtained samples were studied using the scanning electron microscopy method and energy-dispersive elemental analysis. The results of a study of the morphology of the fiber surface are shown in figures 3 and 4.

The presence of a silica coating is seen on the surface images (figure 3) of the material, which is also proved by the presence of peaks for silicon on the energy-dispersion analysis diagram (figure 4).

Conclusion.

1. A new method of dyeing cotton fabrics with plant colourants applying modified sol-gel method, was developed, where a silica coating plays role as a binder and barier for the dye.

2. The present method makes it possible to increase the storage time of using solution up to several days by applying sequential treatment first in the precursor and then in the catalyst of hydrolysis, with avoiding the premature formation of the hydrogel in the impregnating baths, and being polycondensation reaction occurs at the fiber-solution interface.

3. The use of this method makes it possible to obtain a silica coating, as evidenced by the results of electron microscopy and energy dispersive analysis, as well as to increase the rigidity of the treated materials in comparison with the untreated ones. The study showed that the fixation of pigments by a new method without polymer binders is possible in principle.

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Резюме

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RUBIA TINCTORUM ЭКСТРАКТЫ МЕН
ЗОЛЬ-ГЕЛЬ ӘДІСІН ҚОЛДАНА ОТЫРЫП ЦЕЛЛЮЛОЗАЛЫ
ТЕКСТИЛЬ МАТЕРИАЛДАРЫН ҮЗДІКСІЗ ӘДІСПЕН БОЯУ

Мақалада целлюлозалы текстиль материалдарын табиғи текті боғыштармен золь-гель әдісі арқылы бояудың жаңа әдісі ұсынылған. Зерттеу жұмысының негізгі нәтижесі болып маталарды марена боғышы мен золь-гель әдісін пайдалана отырып экологиялық қауіпсіз бояу технологиясының құрастырылуы болып табылады. Ол текстиль материалының прекурсор мен гидролиз католизаторында сіңіріліп, одан кейін кептіру және термоөңдеу процестері арқылы жүзеге асады. Өңдеу параметрлерінің текстиль материалының физико-механикалық қасиеттері, бояу интенсивтілігі мен беріктілігі зерделенген. Нәтижесінде, 10 жуудан кейін бояу интенсивтілігінің жоғары деңгейі натрий силикатының 100 г/л мөлшеріндегі, 160 °С термоөңдеуден өткен үлгілер көрсетті. Сонымен қатар электронды микроскопия әдісін қолдана отырып функционалды жабын мен боғыштың бекітілгені зерделенген. Зерттеу нәтижесі целлюлозалы текстиль материалдарын өңдеу өндірісінде пайдалауға болады.

Түйін сөздер: натрий силикаты, золь-гель, колорлау, табиғи боғыштар.

Резюме

Ф. Р. Ташмухамедов, А. Ж. Кутжанова

НЕПРЕРЫВНЫЙ СПОСОБ ОКРАШИВАНИЯ ЦЕЛЛЮЛОЗНЫХ
ТЕКСТИЛЬНЫХ МАТЕРИАЛОВ ЭКСТРАКТОМ «RUBIA TINCTORUM»
С ИСПОЛЬЗОВАНИЕМ МЕТОДА ЗОЛЬ-ГЕЛЬ

В статье приведен новый способ окрашивания целлюлозных текстильных материалов золь-гель методом с применением красителей растительного происхождения. Основным результатом исследования является разработанная экологически безопасная технология колорирования тканей с применением золь-гель метода и экстракта марены красильной, которая состоит в последовательной пропитке текстильного материала в прекурсоре и катализаторе гидролиза с последующей сушкой и термообработкой. Исследовано влияние параметров обработки на физико-механические свойства ткани, интенсивность и прочность окраски. Выявлено, что наибольшей интенсивностью окраски после 10 стирок обладают образцы, обработанные при концентрации жидкого стекла, равной 100 г/л, и прошедшие термическую обработку при 160 °С. Так же применен метод электронной микроскопии, результаты которого доказывают наличие функционального покрытия и фиксации красителя в его объеме. Результаты исследования могут быть применены в отделочном производстве текстильных целлюлозосодержащих материалов.

Ключевые слова: силикат натрия, золь-гель, колорирование, растительные красители.