ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 1, pp. 177–184. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.V. Cheshkova, A.E. Zavadskii, V.A. Loginova, 2011, published in Rossiiskii Khimicheskii Zhurnal, 2011, Vol. 55, No. 3, pp. 59–66.

New Biochemical Approaches to Fiber Modification in the Solution of the Problem of Unifying Cellulose Pretreatment Technologies

A. V. Cheshkova, A. E. Zavadskii, and V. A. Loginova

Ivanovo State University of Chemistry and Technology, pr. F. Engel'sa 7, Ivanovo, 153000 Russia
e-mail: cheshkova@isuct.ru

Received July 26, 2011

Abstract—New approaches to the development of a biochemical pretreatment process, leading to an improvement of the finishing technology through its unification, are formulated. Evidence is provided that the multidirectional selective action of enzymes in complex lignin-containing polysaccharides promotes efficient delignification processes. New simplified, uniform, two-stage production schemes for cotton, half-flax, flax cotton, and flax fabrics have been developed.

DOI: 10.1134/S1070363213010386

The development of textile chemistry as a scientific and practical basis of the finishing process is controlled by two inter-related factors: economics and environmental safety, since they are to great extent responsible for the cost and competitiveness of the production on the domestic and, especially, international market. The urgent demand for energy-saving and environmentally safe finishing technologies for especially popular cotton, flax, and blended fabrics is explained by the present raw material and energy disbalance in the manufacturing of these fabrics (strong growth of prices for cotton which is an imported raw material, persistently high cost of the long flax finishing technologies, and advent of multicomponent fabrics with a new texture). Of no less importance are environmental safety problems of the finishing process, especially of its pretreatment stages. The Western European standards for the consumption of water and energy for finishing 1 kg of textile materials are 100 l and 15–20 kWh, respectively. The real consumption of process water at Russian manufactures exceeds the Western European standard by a factor of 2–3 [1, 2]. As a consequence, over the past years the total mineral contents of many Russian rivers has increased from 250 to 1000–1500 mg l^{-1}, whereas the surfactant contents of wastewater at certain manufactures comprise 100–200 MAC (maximum allowable concentration).

The modern textile finishing technologies are based on the use of multicomponent textile auxiliary substances and chemical catalysts.

However, is it not excluded that during chemical treatment the composite textile auxiliaries enter reactions to form toxic products which are accumulated not only in wastewater, but also in the fiber material. No regulations for the contents of such pollutants in textile materials are still available. Complete solution of the problems of textile finishing technologies requires a lot of money and long time, and most Russian manufactories cannot presently manage these problems.

Biochemical catalysts offer an alternative approach to the development of rational textile manufacturing technologies. Biochemical technologies are a priory highly environmentally friendly, which is of no little importance for the Ivanovo Region, where most textile finishing factories are located in the centers of towns or in regions with low-water rivers and do not have wastewater treatment facilities. Unlike chemical catalysts, biochemical catalysts are 100% degradable, they are easily utilized, exhibit a high catalytic activity toward substrates (cellulose, associated substances, process contaminants) under fairly mild conditions, and, which is the most important, work highly selectively.

Over two decades the Ivanovo State University of Chemical Technology (ISUCE) has been developing biochemical fabric finishing technologies targeted on cotton and flax manufacturing, with account for the specific features of its instrumentation [2, 3]. These are two-stage processes for cotton fabrics, in which biochemical treatment has replaced the costly alkaline treatment, as well as three-stage chlorine-free bleaching technologies for flax and half-flax fabrics, adapted for Russian manufacturing conditions. The developed technologies have been successfully tested at more than 15 Russian manufactures and implemented, in particular, at the Teikovskie tkani OAO (Ivanovo) and Zvorykinskaya manufaktura OAO (Kostroma).

The modern approach to the development of textile pretreatment technologies envisions not only minimization of chemicals consumption and of the number of process stages, but also unification of technologies [4, 5]. The problems of unification of different textile technologies have gained in importance not only because of the deficiency and high cost of cotton, as well as high cost of finishing of flax fabrics, but also in view of the advent of multicomponent fabrics and versatile equipment, specifically, ejector machines or small-scale bleaching plants, like Benninger or Goller machines. The unification of textile technologies will allow manufactures to adapt, on the competitive market, for changes in raw materials, as well as demand and fashion trends.

The problem of technology unification is quite urgent for textile factories in Russia. At present Russian factories are strictly divided in terms of types of fibers and even in terms of groups of fabrics. The erosion of frontiers between different technologies targeted on specific fibers in Russia is prevented by the fact that the differences in the order and number of stages, optimal oxidants, optimal temperature and time process parameters are associated with essential differences in the properties of natural fibers and their higher, compared with foreign analogs, contents of non-cellulose compounds. Modern textile pretreatment technologies are time-, water-, and energy-consuming and quite diverse. Thus, cotton pretreatment processes involve high-temperature alkaline treatment, acidification, and, sometimes, mercerization, whereas flax bleaching involves a multistage treatment in peroxide and hypochlorite solutions. For bleaching blended cotton–viscose, cotton–polyether, or multicomponent fabrics (flax cotton–cotton–polyether–viscose–elastane), a “super delicate” chemical treatment is required to avoid destruction of one or another component of the fiber. The above circumstances much complicate the development of a unified technology suitable for pretreatment of fabrics from different raw materials on the same equipment, and are responsible for crisis conditions which call for radical review of classical approaches to textile pretreatment processes.

As mentioned above, biochemical technologies are one of the stages of development of the textile production process in terms of its unification on a radically new level. However, their implementation occurs not as dynamically as expected, regardless of the availability of a broad spectrum of both domestic and foreign commercial textile auxiliaries.

The known enzyme-based short-term pretreatment processes for cotton and flax fabrics have not received wide acceptance in the Russian practice [6–17] by several reasons. First, the existing foreign technologies and enzyme preparations are not adapted to domestic finishing technologies and raw fabrics which feature high contents of cellulose-associated substances and process contaminants. No other technologies but amylase desizing of cotton fabrics have proved their worth in practice. However, efficient size removal alone cannot ensure high-quality pretreatment, and, therefore, the hydrogen peroxide concentration at the subsequent bleaching stage has to be increased from 5–6 to 8–10 g l^{-1}. Pectinases combined with amylases have found limited application only for bleaching of cotton fabrics before pigment printing and for three-stage pretreatment of flax and half-flax fabrics. Second, many existing solutions on the intensification of cellulose modification with the aim of enhancing their sorption capacity and reactivity with respect to dyes ignore the difficulties associated with bleaching of the lignin component. Thus, cellulases strongly intensify the cotton hydrophilization process. The high wicking capacity of fabrics allows the spectrum of dyes to be extended from pigments to active and vat dyes which provide high-quality coloration. However, to avoid profound destruction of cellulose in a cellulase-based process, high operation and process management standards (in terms of process control) should be maintained, which is not always feasible. Third, one of the factors hindering commercialization of research results is a narrow specialization of the proposed technical solutions which are targeted on finishing a limited range of fabrics with specific raw material compositions. There are seemingly promising

Table 1. Chemical composition of natural cellulose-containing biopolymers

Substrate	Cellulose, %	Component content, % (on an absolutely dry weight basis)			
		hemicelluloses	pectin substances	lignin	wax-like substances
Cotton husk	15.4–27.0	35.7–45.0	10.2–14.8	29.5–35.0	0.36–0.54
Cotton fiber	88.5–89.4	9.1–11.5	0.7–1.1	3.5–4.2 (“tick”)	0.6–0.8
Flax shive	26.0–34.4	18.0–22.8	–	33.0–38.5	7.4–8.0
Short flax fiber no. 2	65.0–69.2	22.1–25.5	2.1–2.4	7.2–9.8	4.0–4.5
Long flax fiber no. 10	71.1–72.2	18.5–21.6	2.8–4.9	4.2–7.2	1.4–1.7

solutions based on the selection of special compositions suitable for pretreatment of one-group fabrics and exclusively on a definite equipment [18]. High-purity enzymes are too costly to be used in finishing, and, moreover, switching from one process regime to another when changing from one type of fabric to another makes the process cycle too complicated and time-consuming.

One more field which is presently being developed is based on an approach which allows reduction of the cost of enzyme-based textile pretreatment. Aleeva et al. [19] proposed a know-how to grow cultures directly in the finishing plant. However, it is hardly feasible in view of the high requirements to microbiological processes.

Analysis of the problems of textile manufacturing and practical tasks associated with the introduction of biotechnologies leads to a conclusion that the improvement of the finishing technology with the aim of its unification calls for an alternative approach. Such an approach can be provided by the use of a universal enzyme preparation (or enzyme composition) whose function is to catalyze hydrolysis of substances associated with cellulose and various contaminants in flux and cotton fibers, as well as delignification which does not damage the structure-forming biopolymer. A universal enzyme composition is quite difficult to find in view of a specific localization of lignin and substances to be hydrolyzed in cotton, flax, and blended fibers, and also because of a specific aggregation state of contaminants. These are just destruction, bleaching, and delignification, rather than cellulose modification, which are the limiting stages and define the pretreatment order and the result of chemical treatment (and the following peroxide bleaching) of the biopolymer as a whole.

In the development of unified technologies of pretreatment of cellulose-containing fabrics, in which delignification is the key target, one should take into account the properties of lignin, its content in cellulose-containing fibers, and its interaction with other associated components. Lignin is a 3D aromatic polymer. It is hydrophobic and hinders absorption of reagents from aqueous solutions and their penetration into the depth of the lignin-containing substrate. In cotton fabrics, lignin is represented by boll residues (so-called “speck”), whereas in flax materials, this is a structure-forming lignin whose fraction may reach 4–40% (Table 1). Thus, for instance, the lignin content of cotton husk is up to 35%.

Based on the modern view of the structure of complex fibers and biopolymer-forming cells, it is possible to define and restrict the choice of enzymes for a universal composition. Oxidoreductases are unsuitable candidates for oxidative degradation of lignin in textile production processes, because there enzymes are quite costly, and their biosynthesis is hardly controllable. As applied to the processes in focus, it is reasonable to choose commercial enzymes capable of catalyzing degradation of non-cellulose polysaccharides which are a connecting link between lignin and cellulose. When the problem is formulated in this way, the modification of cellulose and, first of all, delignification occurs due to disintegration of the intercellular substance of median platelets and cell walls composed primarily of a complex of cellulose, hemicelluloses, and pectic substances.

The new approach to degrading the lignocarbohydrate complex involves multiple selective attacks on polysaccharides mostly contained in biopolymers and retaining lignin in a “rigid” matrix, whereas cellulose remains virtually intact [4, 5]. The objects of enzymatic attack are the primary and secondary biopolymer walls rich in lignin–xylane and lignin–mannane complexes. Therewith, it is quite important to

Table 2. Modern classification and nomenclature of pectolytic enzymes

Code	Trivial name	Abbreviated name	Catalyzed reaction
3.1.1.11	Pectin esterase	PE	Pectin + H_2O = methanol + polygalacturonic acid
3.2.1.15	Endopolygalacturonase	EndoPG	Random hydrolysis of galacturonide bonds with cleavage of polygalacturonic acid into shorter fragments
3.2.1.40	Exopolygalacturonase	ExoPG	Hydrolysis of the same bonds in pectate and galacturonic acid
3.2.1.41	Endopolymethylgalacturonase	EndoPMG	Random hydrolysis of the same bonds in pectin
4.2.2.1	Endopectate transeliminase	EndoPCTE	Random cleavage of the same bonds in pectate and galacturinate with double-bond formation
4.2.2.2	Exopectate transeliminase	ExoPCTE	Cleavage of the same bonds to form 4,5-digalacturonic acid
4.2.2.3	Pectin transeliminase	EndoPTE	Random cleavage of the same bonds in pectin with double-bond formation

destroy, to a greatest possible extent, polysaccharides that directly retain lignin. These are glucuronoxylanes, whose complexes with lignin are formed by bonding with the side-chain carboxy groups of D-glucuronic acid, arabinoglucuronoxylanes, where lignin is bound with primary hydroxyl groups of the L-arabinofuranose residues, as well as galactoglucomannanes, where lignin forms bonds with primary hydroxyl groups of the D-galactopyranose residues.

Thus, unlike what takes place in chemical delignification and in delignification in the presence of redox enzymes, biochemical treatment causes no modification or destruction of lignin. In the latter case, lignin is removed due to destruction of the lignin–hemicellulose matrix which is formed by mutually superimposed network structures which include the lignin network, the network formed by lignin–hemicellulose covalent bonds, and the network formed by intermolecular hydrogen bonds and physical interaction in lignin and hemocelluloses, as well as between them.

The easiest enzyme-induced degradation is characteristic of pectic substances which represent a colloid carbohydrate complex containing mainly D-galacturonic acid residues in the pyranose form, linked by α-1→4 bonds. There is a wide range of enzymes and commercial preparations [14–17] capable of selectively catalyzing pectin destruction in annual plants, including flax and cotton (Table 2). Controlled pectin hydrolysis during treatment of textile materials, aimed, in particular, at preventing complete destruction of pectic substances and cottonization of complex flax fibers, is provided by a proper choice of enzymes, specifically those which selectively act on unbranched chains of different lengths or unesterified polymer chains containing no methoxycarbonyl groups. In view of the fact that flax and cotton pectins have different structures, the result of the action of an enzyme complex, too, is different. The esterification degree of flax pectin acids is more than 50–70%, and, therewith, the hydroxy groups (at C2 and C3) of certain pectic acid chain members are esterified by acetic acid. As in the case of flax fabrics, deed modification of pectins is not required, then, to avoid cottonization of the complex flax fiber, the enzyme complex should exhibit activity primarily to non-methylated polymer chains of pectin.

Previously we showed [2, 3] that pectinases are not quite efficient both in the delignification of flax and in the destruction of cotton husk. For deep destruction of such components of natural lignin-containing substrates as cotton seed hulls (boll residues), flax fiber, or chaff residues got into flax fabrics, the composition for enzymatic treatment should include biochemical catalysts active with respect to rhamnose substituents formed by galactan and araban residues linked to the galacturonic acid chain by physical forces or by covalent bonds. Of particular interest in terms of the efficiency of hydrolysis of the lignocarbohydrate components of cotton husk and flax fiber are enzymes which act not only on readily water-soluble arabinogalactoses and arabinoxylanes, but also on poorly water-soluble glucomannanes and glucuronoxylanes.

The enzymatic hydrolysis of xylanes involves a number of stages, each involving different enzymes, such as arabinosidases, endoxylanases, exoxylanases, and xylobiases, and results in formation of dextrins and water-soluble monomers. In the enzymatic

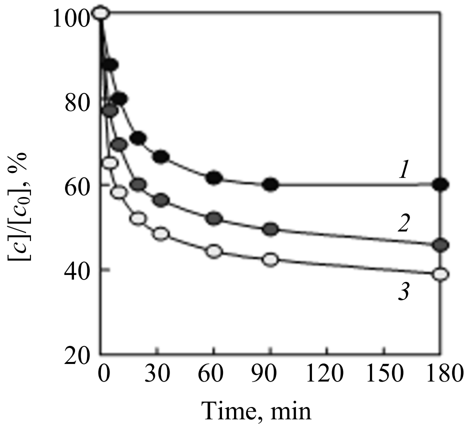

Fig. 1. Kinetic curves of the change of the lignin fraction in flax fibers under the action of enzyme preparations: (*1*) endopolygalacturonase, activity 100000 units/g; (*2*) pectofoetidine P10x (endopolygalacturonase, 1500 units/g, pectin esterase 80 units/g; pectolytic activity 100 units/g), (*3*) xyloglucanofoetidine P10x (endopolygalacturonase, 1500 units/g, pectin esterase, 80 units/g, xylanase activity, 2000 units/g, endo-1,4-glucanase, 100 units/g).

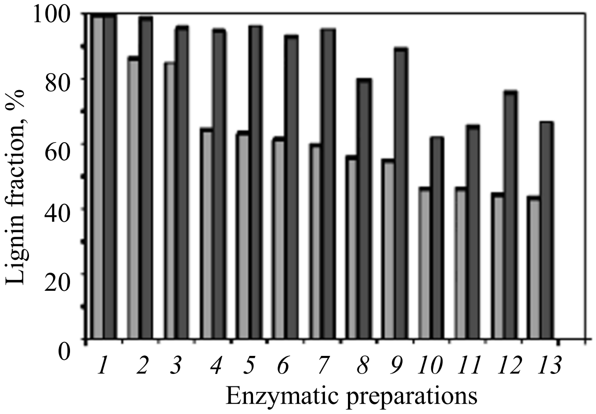

Fig. 2. Diagram of the results of enzymatic delignification of (light columns) scutched long flax no. 10 and (dark columns) cotton husk: (*1*) β-glucanase; (*2*) β-mannase G10x; (*3*) cellobranin G3x; (*4*) celloviridine G10x; (*5*) macerobacilline G3x; (*6*) endopolygalacturonase G10x; (*7*) pectofoetidine P10x; (*8*) pectavamorin P10x; (*9*) cellolignorin P10x; (10) MEC-1; (*11*) cellolignorin P10x and b-mannase G10x; (*12*) cellulase-100; and (*13*) xyloglucanofoetidine P10x.

hydrolysis of hemicellulose components, for example, xyloglucan, the limiting stage is cleavage of side chains from the glucan chain. Hydrolysis of the β-1→6 bond that links the xylose residues with glucan is catalyzed by xylosidase. After complete cleavage of the side chains xyloglucan is converted into β-1,4-glucan. Xylosidase is included into the cellulase enzyme complexes as an auxiliary enzyme, but xylodase preparations are not produced specially.

Of particular interest are modern enzyme preparations containing mannanase. This enzyme catalyzes hydrolysis of mannanes and complex polysaccharides composed of mannose and galactose, for example, galactomannanes. The latter are components of the lignocarbohydrate complex of cotton boll. In bast fiber cultures (jute, bastard jute, hemp, ramie), galactomannanes are components of the intercellular space and cell shells, and, therewith, in flax fiber, hexosanes (galactans and mannans) 85% of all hemicelluloses, pentosanes (araban and xylan) comprise 9%, and polyuronic acids, as little as 6%.

Analysis of the kinetic and correlation dependences of lignin and polysaccharides removal (Figs. 1 and 2, Table 3) showed that the depth of enzymatic degradation of polysaccharides strongly affects the degree of fiber delignification. It was found that the efficiency of delignification is more dependent on the composition of the enzyme composition than on the activity of the enzyme. Treatment with a composition of enzymes with different substrate activities makes possible gradual degradation of the polysaccharide complex through depectinization, hemicelluloses hydrolysis, and cleavage of bonds between hemicelluloses and cellulose. The results of the enzymatic treatment depend not only on the rates of component hydrolysis, but also on the physical structure and morphology of the substrate (density, presence of microcapillaries, number of covalent bonds between polymers of different natures, etc.).

The diagram in Fig. 2 shows the results of comparative assessment of the efficiency of bacterial and fungal hydrolytic enzymes as delignifying reagents. In a unified technology which would allow delignification both of long flax fiber or flax cotton and of cotton husk, the use of multienzyme preparations with prevailing hemicellulase activity is a more rational approach. Owing to their specificity, such enzyme preparations act both on arabinogalacton not linked to lignin, thereby destabilizing the matrix and facilitating access of other enzymes inside the biopolymer, and on the lignin–xylane and lignin–mannane substrate complexes, whereas cellulose remains almost intact.

Comparison of the UV spectra of the dioxane extracts of the residual lignin of cotton husk, flax fiber, and chaff, obtained under varied treatment conditions, gave evidence for the efficiency of the chosen

Table 3. Assessment of the modifying ability of the composition of hydrolytic enzymes with respect to cotton husk lignin and scutched long flax lignin

Treatment time, h	Polysaccharide fraction, %		Lignin removal degree, %	Reflectivity (λ 540 nm), %	Material weight loss, %
	easily hydrolyzed	hardly hydrolyzed			
Cotton husk					
–	26.5	40.4	–	7.8	–
1	20.9	45.5	46.0	5.5	16.7
3	19.5	49.7	63.6	5.0	17.2
24	5.2	55.1	71.8	1.8	19.8
Long flax					
–	45.3	27.9	–	12.9	–
1	10.1	39.1	25.0	19.8	8.5
3	5.9	39.7	40.5	25.5	10.2
24	5.3	40.2	56 .8	29.9	25.8

Table 4. Cellulose fraction, crystallinity, and normalized intensity of the 002 reflex for native and modified flax fibers

Sample	Cellulose fraction, %	Crystallinity, %	I^N_S(002), pulse/s
Native fiber	71.6	50.1	605
After enzymatic modification	75.9	58.0	657
After alkaline peroxide bleaching	82.6	66.3	725
Coefficient of variation, %	12.7	1.5	1.5

approach based on the use a complex of enzymes with a high activity toward polygalactourinides and hemicelluloses and a low cellulase activity. After the subsequent peroxide bleaching, the characteristic absorption maxima (at 280 and 320 nm) of aromatic lignin amines disappear almost completely.

As to modification of cellulose in itself, correlations showing that the depth of hydrolysis of the cellulose of native biopolymers is largely determined by the destruction of components shielding active centers of the substrate, whereas in the case of flax fiber, an additional factor is the destruction of median platelet substances. Thus, the highest modifying activity with respect to flax fiber cellulose is characteristic of compositions of cellulases and pectinases (polygalactouronase activity > 900 units/g).

Enzymes with pectate–transeliminase activity (commercial preparations with the commercial names macerobacillin G3x, macerin G10x, xylacom) enhance the destructive effect of cellulases on cotton fiber cellulose. Possibly, the destruction of the hydrophobic barrier formed by wax substances shielding cellulose and preventing attack of cellulase, facilitates access of the latter to active centers of the substrate. These results have to be taken into account in choosing enzyme compositions so that they allow exclusively a topolithic modification of fibers but prevent a deep destruction of cellulose.

X-ray diffraction analysis showed that the crystallinity of flax fibers regularly increases in going from native flax cellulose to the fiber modified by means of optimal enzyme compositions (MEK-1 or P10x+β-mannose G10x) and to the fiber subjected to enzymatic peroxide bleaching (Table 4 and 5). Therewith, the transverse dimensions of crystallites, which characterize the lateral order in a multicomponent polymer, tend to increase already in going from native to enzymatically modified fibers. This fact provides

Table 5. Dimensions and orientation factors of crystallite formation in native and modified flax fibers

Sample	Crystalline dimensions, nm [20]		Orientation factor [20]
	transverse	longitudinal	
Native fiber	4.35	20.70	0.913
After enzymatic modification	4.62	20.65	0.914
After alkaline peroxide bleaching (Ist stage)	4.67	20.68	0.912
Coefficient of variation, %	2.0		1.0

indirect evidence to show that the fibers undergo additional crystallization already at the first stage of enzyme treatment. Analysis of the resulting data gives grounds to suggest that the observed change of structural parameters is associated with hydrolysis of celluloses, in particular, xylanes which are chemically bound with cellulose and affect the X-ray diffraction pattern. Consequently, the increase of flax crystallinity on bleaching is explained not only by that the segmentary mobility of cellulose macromolecules is enhanced after associated substances have been removed from the polymer matrix, but also by partial removal of the amorphous phase.

Thus, the enzymatic treatment with hydrolase compositions produces specific changes in the structure and composition of flax fiber and cotton husk, which allow efficient delignification and bleaching of cellulose materials under milder conditions. The obtained results create prerequisites for the development of unified (two-stage) schemes for pretreatment of fabrics of different brands and raw material compositions before ground printing and dyeing with active dyes.

Optimal parameters of the unified pretreatment regime involving biochemical treatment at the first stage and peroxide bleaching at the second stage, were determined for the first time. In view of the structural and chemical changes of fibers, as well as the technical characteristics of fabrics, formulations of enzyme and bleaching compositions were developed, which allow the whiteness of cotton, flax cotton-containing (20–50% flax cotton), and half-flax fabrics to be brought to 79–82% and of flax fabrics, to 72–79% (depending on the sort of the flax and its pretreatment technology). We obtained evidence to show that enzymatic modification and removal of hemicelluloses which form a water-repellent film on drying are quite efficient in terms of enhancing the capillary properties of fabrics. Thus, the wicking capacity of cotton fabrics (calico, coarse calico) after full-cycle bleaching reaches 90–120 mm h^{-1}; the respective values for flax cotton-containing fabrics (cotton 45%, flax cotton 35%, polyether 15%, elastane 5%) and straight flax fabrics are 110–135 and 150 mm h^{-1}, respectively. The specificity of enzymatic catalysis of the modification of components of plant fibers and cellulose in itself, as well as the "softness" of the subsequent peroxide bleaching make it possible to preserve the degree of cellulose polymerization and the fastness parameters of the textile material as a whole at a high level.

The new unified technologies of pretreatment of textiles of different raw-material compositions offer the advantage of less process stages. The pretreatment technologies of cotton, flax cotton, and blended fabrics exclude high-temperature alkaline treatment and acidification, and the pretreatment technologies of flax and half-flax fabrics exclude hypochlorite bleaching. Enzyme treatment at the first stage of the chlorine-free bleaching process by the unified technology reduces the total pretreatment time of flax and half-flax fabrics from 7.5–8 to 5–6 h and of blended fabrics to 2.5–4 h, which much increases the efficiency of the equipment.

New unified biochemical pretreatment technologies for a wide range of fabrics (flax, half-flax, flax cotton, blended) are adapted to the up-to-date active equipment (Beninger-220, Goller-220, Wakayama, LOB-280, LKhO-220) and can be implemented both at textile and at flax manufactures.

The economic effect of the implementation of the unified biochemical technology at cotton finishing enterprises of the Ivanovo Region was (calculations for 2008) from 130 to 160 rub/1000 m fabric. Provided an enterprise produces 250–300 thsd. m/day of fabrics, the economic effect only due to saving chemical reagents and process water and steam will comprise more than 40000 rub/day, whereas at enterprises with higher production capacities, say 450 thsd. m/day, more than 50000 rub/day. At flax manufactures which feature a lower performance, involving many pretreatment stages and low rates of open-width bleaching (as low as 35–50 m/min), the implementation of two-stage technologies provides a way to enhance performance from 40–70 to 100–150 thsd. m/day. The universalization of pretreatment technologies at flax manufactures can considerably facilitate production work due to the variability of the concentration and time-and-temperature process parameters in switching from one fabric brand to another, and also facilitate management of chemical reagent supply and maintaining process conditions. The exclusion of treatment with chlorine-containing reagents from the pretreatment technology excludes the necessity to supply liquefied chlorine gas. The high environmental safety of the proposed chlorine-free bleaching process was confirmed by the results of wastewater analysis. Thus, the biological and chemical oxygen uptakes were found to be decreased from 200 to 133.2 mg l^{-1} and from 129.5 to 58 mg l^{-1} O_2, respectively, and the dry residue decreased from 1720 to 799 mg l^{-1}.

After pigment printing and active dye dyeing, the cotton and flax cotton fabrics prepared by the new technology acquire medium dark and dark colors resistant to physical mechanical damage. Half-flax and flax fabrics, too, are successfully dyed by active dyes.

Thus, the unified pretreatment technology of cellulose materials makes it possible to organize textile production at a radically new level. The new technology offers a number of essential advantages, namely increased environmental safety of finishing operations, decreased energy/output ratio (by a factor of 1.5–2), decreased consumption of chemical materials (by a factor of 2–2.5), and flexible extension and change of the range of fabrics which can be treated, in response to changes in the availability or price of one or another raw material.

REFERENCES

1. Ostrovskaya, A.V., Bashilova, T.G., et al., *Materialy II Kongressa khimikov-tekstil'shchikov* (Proc. II Congress of Textile Chemists), Ivanovo, 1996, pp. 32–110.
2. Cheshkova, A.V., Kuz'min, A.P., and Piskareva, I.V., *Izv. Vyssh. Uchebn. Zaved. Tekhnol. Tekstil. Prom-sti*, 2004, no. 1, pp. 52–56.
3. Cheshkova, A.V. and Mel'nikov, B.N., *Tekstil. Khim.*, 2000, vol. 18, no. 2, pp. 112–117.
4. Cheshkova, A.V. and Blinov, M.E., *Izv. Vyssh. Uchebn. Zaved. Tekhnol. Legk. Prom-sti*, 2009 , vol. 6, no. 4, pp. 68–71.
5. Cheshkova, A.V. Belyakova, T.N., and Blinov, M.E., Abstracts of Papers, *2 Nauchno-prakt. konf. "Nanotekhnologii v tekstil'noi promyshlennosti"* (2 Sci. and Practical Conf. "Nanotechnologies in Textile Industry"), 2011, pp. 35–37.
6. Safonov, V.V., et al., *Biotekhnologiya*, 1991, no. 2, pp. 61–64.
7. Waddel, R.B., *AATCC Rev.*, 2000, p. 13.
8. Grishutin, S.G., Gusakov, A.B., etc., *Tekstil. Prom-st*, 2000, no. 4, pp. 19–25.
9. Canal, J.M., Navarro, A., Calafell, M., Vega, B., Caballero, G., and Rodriguez, C., *Proc. 19 IFATCC Int. Congress*, Paris, 2002, p. 102.
10. Sinitsyn, A.P. and Krichevskii, G.E., *Tekstil. Prom-st*, 2000, no. 6, pp. 22–28.
11. Csiszár, E., Szakács, G., Rusznák, I., Eriksson, K., and Cavaco-Paulo, A., *ACS Symp. Ser.*, 1998, vol. 687, p. 204.
12. Perel, J., Miettinen, A., et al., *Proc. 19 IFATCC Int. Congress*, Paris, 2002, p. 57.
13. Sojka-Leolahowicz, W., *Proc. 17 IFATCC Int. Congress*, Vienna, 1996, p. 277.
14. Nikolov, A., *Tekstil. Khim.*, 1998, vol. 14, no. 2, pp. 65–67.
15. Novoradovskii, A., *Ibid.*, 1998, no. 2, pp. 73–84.
16. Sinitsyn, A.P., Abstracts of Papers, *Mezhdunarodnyi nauchno-tekhnicheskaya konferentsiya "Dostizheniya tekstil'noi khimii v proizvodstvo"* (Tekstil'naya khimiya-2000) (Int. Scientific and Practical Conf. "Advances of Textile Chemistry to Industry" (Textile Chemistry 2000), Ivanovo, 2000, p. 116.
17. Nikolov, A. and Sychev, Kh. Kh., Ibid., pp. 33–151.
18. Koksharov, S.A., et al., *Tekstil. Khim.*, 2000, vol. 17, no. 1, p. 78.
19. Aleeva, C.B., Kulikova, I.V., and Koksharov, C.A., *Ibid.*, 2001, vol. 19, no. 1, pp. 62–68.
20. Zavadskii, A.E., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 2010, vol. 53, no. 3, pp. 90–92.