RESOURCE-SAVING TECHNOLOGY OF PRODUCING TEXTILE MATERIALS WITH ANTIMICROBIAL PROPERTIES

MARTIROSYAN IRINA[1*], PAKHOLIUK OLENA[2], DZIUBYNSKYI ANDRII[2], NIKOLAICHUK LARISA[3], LUTSKOVA VIKTORIA[1], LUBENETS VIRA[4] AND PEREDRIY OKSANA[2]

1 Odessa National Academy of Food Technologies, Kanatna st, 112, Odessa, 65023, Ukraine
2 Lutsk National Technical University, S.Kovalevska ave., 29, Lutsk, 43008, Ukraine
3 Hetman Petro Sahaidachnyi National Ground Forces Academy, Heroiv Maidanu street, 32, Lviv, 79026, Ukraine
4 National University, Lviv Polytechnic, St. Yura Square, 2, Lviv, 79013, Ukraine

ABSTRACT

This work is devoted to the study of antimicrobial properties of cellulose-containing textile materials treated with new safe biocidal products of thiosulfonate structure. A resource-saving method of providing antimicrobial properties to cellulose-containing textile materials is presented. High antimicrobial activity of biocidal products after washing was established. The duration of action and expediency of their use in the textile industry are proved. It is shown that after 10 washes the treated tissues lose only 14-15% of antimicrobial properties.

KEYWORDS

Antimicrobial properties; Cotton; Biocidal treatment; Thiosulfonates.

INTRODUCTION

Today in the textile industry of Ukraine there is an active search for better ways to improve the quality and safety of cellulose-containing textile materials and products with the help of special treatments. Taking into account that one of the criteria for the wear of textiles is biodegradation, their biocidal treatment remains relevant today, as microorganisms not only degrade the appearance, reduce the reliability of textile materials, but also pose a threat to human health. Of course, the process of creating new technologies and decisions on how to provide antimicrobial properties to textiles continues, but this question remains open, as many of these treatments are unable to ensure the stability of the effect, and during a certain period of operation these properties are lost [1-3]. Therefore, the issue of search and development of new antimicrobial substances and technologies, including environmental and resource-saving ones, aimed at protecting textile materials from biodegradation remains very important. It is known that textile materials made of natural fibers provide excellent conditions for the development and growth of microorganisms due to their ability to retain moisture and microbial enzymes. Cellulose is known worldwide as the most common, renewable and almost inexhaustible raw material with an exciting chemical structure and properties. Given these facts, the provision of textile materials with antimicrobial properties is associated with the need to protect tissues from the action of microorganisms and protect the human body from the action of pathogenic microflora. Molds, yeasts and bacteria live and thrive where there are suitable conditions for them - moisture, nutrient medium, the required temperature. The process of decomposition of fiber of plant fibers occurs as a result of exoenzyme action secreted by microorganisms. Hyphae of mycelium of fungi penetrate into the fiber and destroy it from the inside and outside [2,4].

METHODS

Analysis of the literature [2-8] suggests that biocidal substances not only provide antimicrobial protection, but also help to improve the consumer properties of textile materials and increase their wear resistance. After all, antimicrobial textiles due to their properties become a protective barrier to the penetration of microorganisms into the human body. Under such conditions, the use of biocidal substances in the textile industry becomes practical importance.

* **Corresponding author:** Martirosyan I., e-mail: miaviva@ukr.net
Received October 3, 2022; accepted November 21, 2022

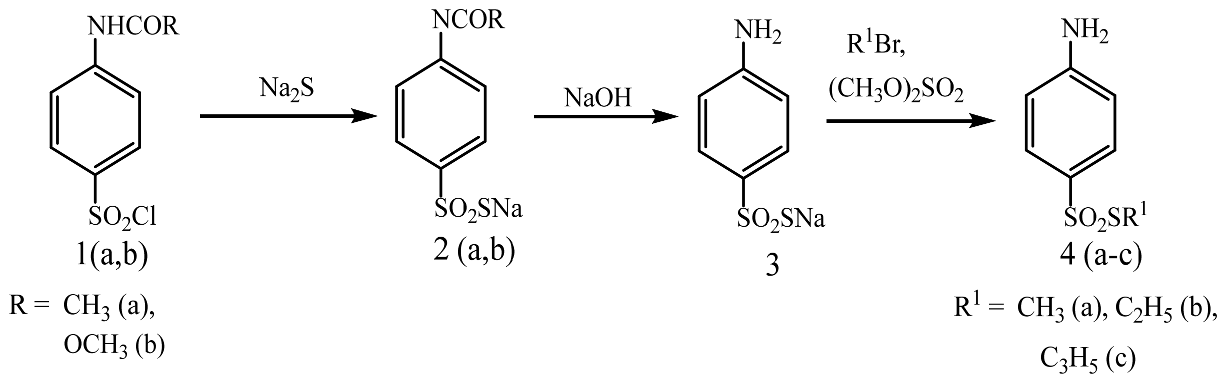

Figure 1. Scheme of obtaining biocidal products of thiosulfonate structure.

The global biocides market is expected to reach $ 11,787.3 million in 2022, according to a new study by Grand View Research, Inc[9]. Nanotechnology also plays an important role in the development of antibacterial textiles. As a promising tool for creating highly stable, effective and environmentally friendly antibacterial textile coatings, sonochemistry was first used by applying inorganic nanoparticles (CuO, ZnO, MgO) to tissues without damaging the structure of textile materials [10-12]. The bactericidal properties of such textile coatings have been preserved after repeated washing, making them an alternative to known bactericidal preparations such as triclosan, various Quaternary ammonium salts and other toxic compounds [13,14].

In recent years, the role of practical use of silver nanoparticles has increased, in particular, in the production of nonwovens for workers of the Ministry of Emergencies. Basic technologies for modification of sanitary and hygienic and disinfectants with silver nanoparticles have been developed. A significant segment of the market for protective products is also occupied by the American companies DSM Biomedical and Agion with their lines of antifungal solutions based on silver ions with bactericidal and fungicidal properties. The technology for the introduction of active ingredients in the form of microcapsules containing solid particles (microdroplets) of antimicrobial substances that are released under certain conditions (eg by friction, pressure, dissolving the capsule shell or their biodegradation) was patented by Earth Holding (USA) for the processing of nonwovens [15,16]. Another achievement in this direction are cyclodextrins [17], which are widely used for tissue treatment, because they due to their unique chemical structure show good absorption capacity, namely form complexes with various antimicrobial and other biologically active substances.

Kathon MW (USA) based on diazolines is considered to be a universal highly effective antimicrobial agent, which has been widely used in various industries. Methods for imparting antimicrobial properties to textile materials by introducing nitrofuran preparations into spinning solutions with their subsequent fixation in the fine structure of fibers during molding have also been developed. A significant place among them is occupied by guanidine compounds as physiologically active substances. Their bactericidal action is determined by their ability to bind to bacterial membranes, penetrate the cell nucleus and produce cellular enzymes [18]. But today it is classified as a toxic biocide. Considering the above, we face the task of finding new ecological biocidal preparations that would be not only safe, but also have a duration of action, would be economically expedient and resource-saving; simple in application, in particular, they did not require a change of equipment and the purchase of new devices when introduced into textile production.

METHODOLOGIES

Despite existing developments, and taking into account the changing general biological resistance of the human body, new species of microorganisms' resistant to most biocidal products are emerging, and ways, modes of transmission and duration of life are changing [11, 2, 19-21]. Therefore, scientists are faced with the task of finding new, more effective and environmentally friendly long-acting biocidal products.

The aim of our research is to obtain an effective resource-saving method of providing antimicrobial properties to textile materials. Given the above, we have a task to investigate the antimicrobial activity of new BPTS by determining their effective concentration and to develop effective conditions for prescription-technological regime of processing of cellulose-containing tissues. In this regard, we have selected new biocidal preparations of thiosulfonate structure (BPTS) [22-24], which have no analogues in the market of Ukraine and abroad. They have a wide range of antimicrobial action and are presented by developers as low-toxic, and can be used for antimicrobial protection in various industries, namely:

- ethylthiosulfanilate (ETS) - ethyl biocide;
- allylthiosulfanilate (ATS) - allyl biocide;
- methylthiosulfanilate (MTS) - methyl biocide.

These thiosulfonates were synthesized at the Department of Technology of Biologically Active Compounds, Pharmacy and Biotechnology of the National University "Lviv Polytechnic" according to the scheme (Fig. 1).

Biocidal products are close to structural analogues of natural volatiles - garlic Allium sativum, onion Allium cepa, various types of cabbage, especially cauliflower. It is known that synthetic esters of thiosulfonic acids exhibit a wide range of biological activity, which often exceeds the effectiveness of natural analogues. They are effective sulfenylating agents in organic synthesis, water-insoluble, and have valuable properties for solving complex problems of molecular biology and biochemistry [22].

These biocides are tested, patented and effectively used to protect paints and varnishes, as additives to protect against bio-damage to lubricants and coolants, biocidal component of anticorrosive composition for pipelines of circulating water supply systems, petroleum products, building materials and structures, algaecides for surface protection sterilization of culture fluid in biotechnological productions. But these biocides have not yet been tested in light industry, and we decided for the first time to experimentally investigate the protective properties of these drugs for textiles. This is dictated not only by the wide range of action of these drugs, but also by the attempt to solve the problem of finding ecological biocides [24].

ETS, MTS, and ATS, in our opinion, may be ideal for the term "environmental biocides", as they are also active substances for the treatment of various skin mycoses and onychomycosis of the nail, competitive with nizoral and clotrimazole. Environmental friendliness and safety of these drugs have also been confirmed by developers in tests on rats [25,26]. Given the above, we can assume that these preparations are completely harmless to the human body and the environment and their use is appropriate in the textile industry, where the human body is in direct contact with tissues.

The object of research is a fabric for making overalls. Pure cotton (100%) fabric of Toctals Fabrics TM (Netherlands) with a surface density of 245 g / m2, twill weave, porosity – 41,2%, fabric thickness is 1.37 mm, linear density is 58 tex, linear density, the number of threads per 10 cm - by warp - 307, by weft - 292. The choice of fibrous composition of the fabric is due to the fact that natural fabrics are more susceptible to destruction and for sewing overalls pure cotton fabric is popular due to its natural properties, taking into account the operating conditions.

The following fungi cultures were used for testing *Trihoderma viride Pers. ex S.F. Gray, Aspergillus niger van Tieghem, Penicillium funiculosum Thom, Paecilomyces variotii Bainier, Chaetomium globosum Kunze*, which have a devastating effect on textiles.

The study of fungicidal and fungistatic activity of biocidal substances of thiosulfonate structure was carried out in accordance with GOST 9.802-84. The studies used fungal cultures deposited at the National Center for Microorganism Strains of State Research and Control Institute of Biotechnology and Strain of Microorganisms: *Trihoderma viride Pers. ex S.F. Gray, Aspergillus niger van Tieghem, Penicillium funiculosum Thom, Paecilomyces variotii Bainier, Chaetomium globosum Kunze*. The activity of the compounds was determined by suspension method. Fungal cultures were grown in Saburo medium for 2 days and kept for 3-5 days in a dark place, then made a suspension of spores in saline with cell load 2 · 109 CFU / ml according to the optical standard of turbidity (Densilameter, Czech Republic, Brno) 0.05% solutions of test compounds were prepared, which were added to tubes with Saburo medium, followed by three serial dilutions up to 0.0002%. a test tube of test fungus suspension, with a cell load in a medium of 106 CFU / ml, mixed the contents, beveled on a tripod to increase the area.

Studies of bacterial resistance and fungal resistance of tissue samples were performed according to standard methods. Tissue samples (20 x 20 mm) were pre-treated with thiosulfonates (control tissue samples did not contain thiosulfonates). Sterile meat-peptone agar (MPA) for bacteria and wort agar (CA) for fungi were used for the experiment. The following types of microorganisms were used in the tests: bacteria Escherichia coli, Staphylococcus aureus, Mycobacterium luteum and fungi Candida tenuis, Aspergillus niger, which mostly destroy textile fibers. Sterile agar medium cooled to 40-450C was poured into Petri dishes, in which a suspension of microorganisms had been previously inoculated (microbial load: bacteria 109 CFU / ml; fungal spores 107 CFU / ml). The prepared samples were immersed in agar medium, cups with experimental and control samples were incubated in a thermostat for 24-48 hours. at a temperature of 37 ° C for germination of bacteria and 48-72 hours at a temperature of 28-30 ° C for fungi.

Tensile strength characteristics of tissue samples with working dimensions of the elementary sample of 25 × 50 mm were measured on a tensioner RT-250M-2 by standard methods (GOST 3813-72 (ISO 5082-82. Textile materials. Textile fabrics and piece-articles. Methods for determination of breaking under tension), the lowering speed of the lower clamp of the tensile testing machine is 100 mm/min, clamped length is 50 mm/ Guarantee error of variation coefficient (mc) was within 0,5 - 1.5%.

EXPERIMENTAL AND RESEARCH RESULTS

As a result of tests on the sensitivity of fungi to ETS, MTS and ATS, it was determined that the minimum effective concentration of all three preparations is 0.05% (Table 1). As can be seen from table 1, all three drugs at a concentration of 0.05% are resistant to molds and can be used for fungicidal and fungistatic treatment of textile materials [27].

Table 1. Minimum effective concentration of thiosulfonate preparations for fungicidal (A) and fungistatic (B) treatment.

Type of microorganisms	Minimum effective concentration, [%]					
	ETS		MTS		ATS	
	A	B	A	B	A	B
Trichoderma viride	0,006	0,055	0,0185	0,055	0,015	0,006
Aspergillus niger	0,0185	0,055	0,0185	0,055	0,015	0,006
Penicillium funiculosum	0,006	0,0185	0,006	0,0185	0,015	0,006
Paecilomyces variotii	0,006	0,0185	0,002	0,055	0,015	0,006
Chaetomium globosum	0,006	0,055	0,006	0,055	0,008	0,006

Table 2. Optimal modes of antimicrobial treatment of tissue with biocidal products of thiosulfonate structure.

Biocide	Operation	The composition of the solution [%]	Processing mode
ethylthiosulfanilate (ETS)	Seepage (immersion) to full wet growth Squeezing Drying (Duration)	The minimum effective concentration is 0.05%, 0.5% was used Alcohol solution	T: 70°C t: 5-7 min.
allylthiosulfanilate (ATS)	Seepage (immersion) to full wet growth Squeezing Drying (Duration)	The minimum effective concentration is 0.05%, 0.5% was used Alcohol solution	T: 50°C t: 5-7 min.
methylthiosulfanilate (MTS)	Seepage (immersion) to full wet growth Squeezing Drying (Duration)	The minimum effective concentration is 0.05%, 0.5% was used Alcohol solution	T: 60°C t: 5-7 min.

Table 3. Influence of temperature and concentration on the breaking load of 100% cotton treated with ETS, MTS and ATS.

Processing temperature [°C]	Before treatment	The breaking load [N]					
	The breaking load [N]	ETS		MTS		ATS	
		Concentration of preparations [%]					
		0,1	0,5	0,1	0,5	0,1	0,5
50	745	757	759	755	760	759	763
60		761	761	760	763	757	759
70		764	767	757	759	755	757

Note: The guarantee error of the coefficient of variation (mc) was within 0.5%.

Among the effective ways to provide antimicrobial properties to textile materials, the simplest and most economical is impregnation. Therefore, this method was chosen for processing. Heat treatment was carried out at a temperature of from 50 to 70 ° C, because such parameters of the temperature regime do not destroy the microstructure of the fibers, and the biocides themselves do not lose their properties.

Antimicrobial treatment of the studied samples of textile materials was carried out in the Analytical Research Laboratory "Textile-TEST", Kyiv (Kyiv National University of Technology and Design). Tissue samples were impregnated with a prepared alcohol-water (60% / 40%) solution of biocidal products with a concentration of 0.5% at room temperature (18-20 ° C) and relative humidity of 63-65% for 1-2 minutes [28]. Then the samples were squeezed on a plate and dried at a temperature of 50-70 ° C for 5-7 minutes (Table 2). The results of tests for the selection of effective tissue treatment regimens for each biocidal product are presented in Table 2. In order to obtain longer-acting antimicrobial textile materials, we decided to increase the concentration of drugs in the next experiment. Table 3 shows the results of the treatment of pure cotton fabric ETS, MTS and ATS at a concentration of 0.1% and 0.5%.

It is known that microbiological destruction of tissues occurs due to the action of bacteria and fungi, which also leads to a decrease in physical and mechanical properties and functionality of clothing. Therefore, improving the tensile strength of textile products is one of the priorities before us, given the working conditions of workers, so when developing technology to provide antimicrobial properties, one of the determinants was mechanical properties, in particular tensile load, which is directly related to wear factors. The research results are shown in Table 3. On the basis of the received data (Tab. 3) mathematical modelling by a method of full factorial experiment was carried out (Fig. 2-4).

From the analysis of graphic dependence, we see that for all 3 biocides increase in concentration leads to increase in indicators of breaking load. Based on the results of table 3, it can be stated that for ETS the optimal processing temperature is 70 ° C, for MTS - 60 ° C, for PBX - 50 ° C, at which the breaking load of pure cotton fabric is maximum: when treated with ethyl biocide - increases at 22 N (2.95%); methyl and allyl - by 18 N (2.4%).

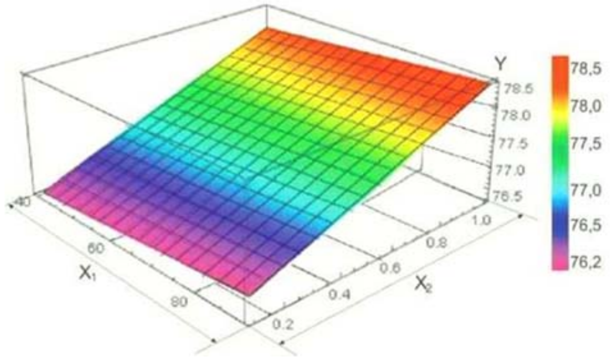

Figure 2. Dependence of breaking load Y on the concentration of ETS (X1) and heat treatment parameters (X2); Y = 75.8 + 0.0075 * X1 + 2 * X2 (three-dimensional graph).

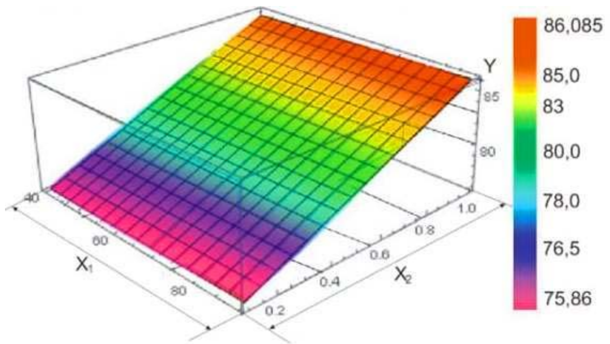

Figure 3. Dependence of breaking load Y on the concentration of MTS (X1) and heat treatment parameters (X2); Y = 74.5 + 0.0065 * X1 + 11 * X2 (three-dimensional graph).

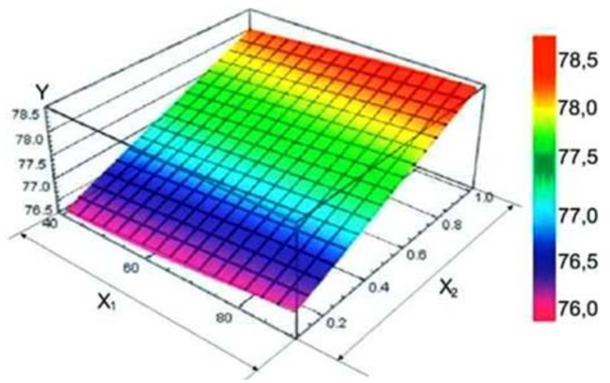

Figure 4. Dependence of breaking load Y on the concentration of ATS (X1) and heat treatment parameters (X2); Y = 75.8 - 0.0025 * X1-0.02 * X2 (three-dimensional graph).

However, given the importance of the regression coefficient, it can also be argued that the temperature of the treatment in the range of 50 - 70 °C does not significantly affect the strength of cotton fabric, so heat treatment of all 3 biocides can be carried out at 50 °C, which is more economical and resource efficient.

To determine the antimicrobial activity of textile materials treated with ETS, MTS and PBX according to the developed method, we investigated the effect of biocides on inhibiting the growth of microorganisms that are more common in the environment and have destructive effects, including Escherichia coli, Staphylococcus aureus, Mycobacter and Aspergillus niger. The test results are given in table. 4.To determine the antimicrobial activity of textile materials treated with ETS, MTS and PBX according to the developed method, we investigated the effect of biocides on inhibiting the growth of microorganisms that are more common in the environment and have destructive effects, including Escherichia coli, Staphylococcus aureus, Mycobacter and Aspergillus niger. The test results are given in Table. 4.

The results of Table. 4 confirm that the concentration of 0.5% has a better fungi-bactericidal effect, which can simultaneously increase not only the rupture characteristics, but also prolong the duration of antimicrobial action. Therefore, further studies will be conducted based on the concentration of preparations - 0.5%. However, it can also be seen that at concentrations of 0.05% and 0.1% the antimicrobial activity of textile materials remains high enough for all three biocides.

CONCLUSION

The developed technology of obtaining textile materials with antimicrobial properties has low advantages:

- this technology of obtaining antimicrobial properties does not require additional costs and efforts on the part of enterprises in the textile industry, as all the necessary equipment is available in the production line of any enterprise specializing in the production of textile materials;
- there is no need to change the technological line and stages of production, as the fabric is processed in the finished form, it is possible both in the final process and after sewing the finished product;
- low temperature regime and duration of heat treatment are energy saving;
- biocidal products of thiosulfonate structure have a high bactericidal and bacteriostatic effect. conditions and modes of processing do not affect the aesthetic properties, also do not impair the microstructure of the fibers, moreover, allow to increase the breaking load, in particular, ETS is the most effective.

It was found that all 3 biocides are effective at a minimum concentration of 0.05%, but when increasing the concentration to 0.5% has a better effect of antimicrobial activity, where the breaking load increases by 2.95%, for MTS and ATS - by 2.4%.

Thus, the presented technology of textiles with antibacterial properties can be considered promising and resource-saving.

Table 4. Fungicbactericidal activity of the test compounds (method A) on pure cotton tissue treated with BPTS.

Preparation	Concentration, [%]	Diameter of zones of suppression of growth of microorganisms, [mm]				
		E. coli	**S.aureus**	**M. luteum**	**C. tenuis**	**A. niger**
ETS	0,05	6,5	7,7	7,0	12,1	10,5
	0,1	11,0	12,0	20,0	36,0	18,0
	0,5	28,0	34,7	49,0	69,0	40,0
MTS	0,05	5,0	8,3	6,1	10,2	9,6
	0,1	9,0	15,0	12,4	25,7	15,7
	0,5	35,0	32,0	67,5	56,0	44,0
ATS	0,05	4,3	5,0	6,0	9,5	9,0
	0,1	8,5	11,0	12,7	15,4	13,7
	0,5	25,0	33,7	43,0	50,0	20,0

REFERENCES

1. Martirosyan I., Pakholiuk E.: Modern assortment and actuality of the use biocidal preporesions in the textile industry, Integration of education, science and business in the modern environment: summer disputes, International scientific-practical conference, Dnipro, 2019, pp. 433-437.
2. Emam H. E.: Antimicrobial cellulosic textiles based on organic compounds, 3 Biotech 9(29), 2019, pp. 1152-1163. https://doi.org/10.1007/s13205-018-1562-y
3. Nikolaichuk L. G., Galyk I. S., Semak B. D., et al.: The role of nanotextile si the formation of the domestic market of special clothing and application in logistic provision of military units, Herald of Lviv University of Trade and Economics. Technical Sciences. 23, 2020, pp. 49-57. https://doi.org/10.36477/2522-1221-2020-23-06
4. Martirosyan I., Pakholiuk E.: Investigation of the resistance of textile materials to the action of sea fungi. Innovations in the management of the range, quality and safety of goods and services. In: 4th International scientific-practical conference, Lviv, 2018, pp. 87-90.
5. Gutarowska B., Pietrzak K., Machnowski W., et al.: Historical textiles–a review of microbial deterioration analysis and disinfection methods, Textile Research Journal, 87(19), 2017, pp. 2388-2406. https://doi.org/10.1177/0040517516669076
6. Borkow G., Gabbay J.: Biocidal textiles can help fight nosocomial infections, Medical Hypotheses, 70(5), 2018, pp. 990-994. https://doi: 10.1016/j.mehy.2007.08.025
7. Black S.: Fashion and function: factors affecting the design and use of protective clothing, Textiles for Protection, 1(16), 2015, pp. 60-89.
8. Agarwal Ch., Csoka L.: Functionalization of wood/plant-based natural cellulose fibers with nanomaterials, TAPPI Journal, 17(02), 2018, pp. 92-111. https://doi.org/10.32964/TJ17.02.92
9. Biocides in textile global report. 2018. Available from: https://www.researchandmarkets.com/reports/4662348/biocides-in-textiles-global-report-2018/
10. Ahamed M., Akhtar M. J., Raja M, et al.: ZnO nanorod-induced apoptosis in human alycolar adenocarcinoma cells via p53, surviving and bax/bel-2 pathways: role of oxidative stress, Nanomedicine, 7(6), 2011, pp. 904-913. https://doi.org/10.1016/j.nano.2011.04.011
11. Lin J., Chen X. Y., Chen Ch. Y., et al.: Durably antibacterial and bacterially antiadhesive cotton fabrics coated by cationic fluorinated polymers, ACS Applied Materials & Interfaces, 10(7), 2018, pp. 6124-6136. https://doi.org/10.1021/acsami.7b16235
12. Martirosyan I., Pakholiuk E.: Ecological safety of textile materials for the production of overalls. Materials of the international scientific and practical conference of the applicants of higher education and young scientists "Youth - Science and Production", Innovative Technologies of Light Industry", Kherson, 2018, pp. 107-109.
13. Zhang C., Cui F., Zeng G., et al.: Quaternary ammonium compounds (QACs): A review on occurrence, fate and toxicity in the environment, Science of The Total Environment, 2(518), 2015, pp. 352-362. https://doi.org/10.1016/j.scitotenv.2015.03.007
14. Galik I. S., Semak B. D.: Problems of formation and evaluation of ecological safety of textiles, Herald of Khmelnytskyi National University, 4(239), 2016, pp. 71-76.
15. Industries LNC. Cotton-Products, Available from: http://www.lnchemicals.com/cotton-products2.html
16. Sciessent. Agion antimicrobial-technology, Available from: http://www.sciessent.com/agion
17. Singh N., Sahu O: Sustainable cyclodextrin in textile applications, The Impact and Prospects of Green Chemistry for Textile Technology, 11, 2018, pp. 83-105. https://doi.org/10.1016/B978-0-08-102491-1.00004-6
18. Morais D. S., Guedes R. M., Lopes M. A. Antimicrobial approaches for textiles: From research to market, Materials, 9, 2016, pp. 498-512. https://doi.org/10.3390/ma9060498
19. Hanczvikkel A., Vig A., Toth A.: Survival capability of healthcare-associated, multidrug-resistant bacteria on untreated and on antimicrobial textiles. Journal of Industrial Textiles, 48(7), 2019, pp. 1113-1135. https://doi.org/10.1177/1528083718754901
20. Salieri B., Turner D.A., Nowack B., et al.: Life cycle assessment of manufactured nanomaterials: Where are we? NanoImpact, 1, 2018, pp. 108-120. https://doi.org/10.1016/j.impact.2017.12.003
21. Xu Q., Ke X., Ge N., et al.: Preparation of copper nanoparticles coated cotton fabrics with durable antibacterial properties, Fibers and Polymers, 19(5), 2018, pp.1004-1013. https://doi.org/10.1007/s12221-018-8067-5
22. Lubenets V., Karpenko O., Ponomarenko M., et al.: Development of new antimicrobial compositions of thiosulfonate structure, Chemistry & Chemical Technology, 7(2), 2013, pp.119-124.
23. Pakholiuk O. V., Martirosyan I. A., Lubenets V. I.: The influence of biocidal treatment of cellulose textiles to replace its properties, Herald of Khmelnytskyi National University 6, 2018, pp. 94-98. https://doi:10.31891/2307-5732-2018-267-6(2)-94-95
24. Lubenets V. I.: Thiosulphonic acids derivatives: synthesis and properties, Ukrainian Chemistry Journal 69(3), 2003, 109-117.
25. Lubenets V.I., Havryliak V.V., Pylypets A.Z., et al.: Changes in the spectrum of proteins and phospholipids in tissues of rats exposed to thiosulfanilates, Regulatory Mechanisms in Biosystems, 9(4), 2018, pp. 295-500. https://doi.org/10.15421/021874
26. Pylypets A.Z., Iskra R.Ya., Havryliak V.V., et al.: Effects of thiosulfonates on the lipid composition of tissues, The Ukrainian Biochemical Journal, 89(6), 2017, pp. 56-62. https://doi.org/10.15407/ubj89.06.056
27. Martirosyan I., Pakholiuk E., Lubenets V., et al.: Investigation on stability of textile materials for overalls processed by new biocidal preparation, Technological Complexes, 1(15), 2018, pp. 52-59.
28. Martirosyan I., Pakholiuk O., Semak B., et al.: Investigation of wear resistance of cotton-polyester fabric with antimicrobial treatment, Lecture Notes in Mechanical Engineering. Springer International Publishing, 2020, pp.433-441. https://doi.org/10.1007/978-3-030-40724-7_44