Abdusalom Vakhitovich Umarov
Tashkent railway engineering institute
Doctor of technical sciences, professor

Asatullo Usubkhanovich Sulaymanov
Namangan State University
Scientific researcher (PhD) in the specialty
"02.00.07 - Chemistry and technology of
composite, varnish and rubber materials"

EXPERIMENTS OF WORLD SCIENTISTS WITH COTTON CELLULOSE

Abstract: *The article provides information on some of the experiments and results of world scientists who have been achieved in the field of cotton cellulose in modern scientific laboratories. The article also briefly describes the first Uzbek scientists and founders who conducted research in the field of cotton cellulose.*

Key words: *cellulose, cotton, polymer history, biopolymer, polymer, composite material, nanostructure, nano particle.*

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Introduction

Cellulose - the most common natural polymer on earth - is a very important object of research, since its field of use expands every year, and the available reserves with rational use may be inexhaustible.

Currently, cellulosic materials are actively used to create a variety of nanostructures: nanocrystals, nanofibers and nanocomposites. Nanocomposites can be completely formed from cellulose (with the matrix being longer fibers, and the filler is cellulose nanocrystals), may contain metal nanoparticles of semiconductors, have an organic matrix of bacterial or chemically modified cellulose. In composite materials, cellulose is also combined with synthetic polymers. [1, 238-240]

The first founders of cellulose

For the first time, the terms cellulose and lignin were introduced into science by the French chemist Ansel Payen. He published his article on this in 1838, and in 1839 the term cellulose appeared in the literature. A.Payen discovered the chemical composition of the stages of plant growth. According to the source, the cellulose content is carbon-43.85%, hydrogen-5.86% and oxygen-50.28%. After the invention of A.Payen, research on the processing of cellulose became active.

Alexlandr Pavlovich Zakoshchikov - a famous chemist who conducted research in the field of cellulose from 1920 to 1980. A.P. Zakoshchikov comes from Russia to Tashkent and since 1929 has been studying the structure, chemical composition, ripeness and other properties of cotton fiber. Also, he determines that well-ripened cotton contains 97-98% pure cellulose.

Until today, scientists from our republic have conducted many experiments related to cotton cellulose, and several scientific discoveries have been made in this field. In Uzbekistan, cotton cellulose was first studied by Academician Kh.U. Usmonova (1916-1994). Nowadays, students of Academician Kh.U. Usmonov continue to study cotton cellulose. Of them: Academician G.Rakhmonberdiev works on obtaining the necessary matter from medicine from cellulose,

Professor A.S. Turaev works on cellulose sulfite ethers, Professor K.Rozikov works on electro-microscopic structure of cotton fibers, Professor A.Sarimsakov is working on creating technology for producing cellulose microcrystal. [1,240 -2, 72]

Classification of experiments of world scientists on cotton cellulose

Zhenyun Zhao, Jing Zhou, Ming Lu, Hang Xiao & Yiping Liu, Cellulose micro-dissolution by *N*-methylmorpholine *N*-oxide as a facile route for magnetic functional cotton textiles.

In this work, an environmental micro-dissolution method to prepare Fe_3O_4 NPs@cotton composite fabrics without using binders is reported. The controlled *N*-methylmorpholine *N*-oxide (NMMO) treatment can micro-dissolve superficial layers of fibers through the strong hydrogen bonding force. The micro-dissolved superficial layers themselves can work like glue to physically adhere surrounding Fe_3O_4 NPs and then these Fe_3O_4 NPs can be embedded onto the layers. In the subsequent heating treatment, the micro-dissolved superficial layers would physically re-coagulate, immobilizing Fe_3O_4 NPs onto fibers' surface. The as-obtained Fe_3O_4 NPs@cotton composite fabrics were systematically characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Additionally, through vibrating sample magnetometry tests, the Fe_3O_4 NPs@cotton fabrics exhibit para-magnetism, and the saturation magnetization can remain up to 90% after 20 washing cycles. Thermal gravimetric analysis and moisture absorption tests show that there are no obvious influences on thermal stability and moisture absorption capability of cotton fabrics. Even noticeable enhancements in mechanical properties can be observed. [3, 3153-3165]

Zhe Ling, J.Vincent Edwards, Zongwei Guo, Nicolette T.Prevost, Sunghyun Nam, Qinglin Wu, Alfred D.French & Feng Xu, Structural variations of cotton cellulose nanocrystals from deep eutectic solvent treatment: micro and nano scale.

Solvents that produce cellulose nanocrystals (CNCs) and promote cellulose fibrillation are of current interest. In this work, CNCs were fabricated from cotton at 80 and 100 °C using deep eutectic solvents (DESs) having choline chloride/oxalic acid dehydrate (OA) ratios of 1:1, 1:2 and 1:3. To investigate the side effects of the fabrication, the crystal structure and morphology of micro-sized treated cellulose together with nano-sized CNCs were analyzed by X-ray diffraction, field emission scanning electron microscopy and atomic force microscopy. OA promoted the formation of carboxyl groups on the C6 positions of molecules on the hydrophilic (1–10) lattice planes, causing extensive fibrillation of cellulose and disruption of surface layers on (110) and (200) planes. Lower crystallinity and lamellar structures for CNCs with mild treatment were observed after mechanical disintegration and subsequent lyophilization, which was ascribed to van der Waals forces and hydrogen bonding between adjacent crystalline cellulose chains, accelerating the self-assembly into cellulose macrofibrils. This work is discussed in light of cellulose supramolecular structures that are modified from CNC fabrication via DES treatment, with a view to enhancing the efficacy of treatment by understanding the variations that arise in cellulose structure from a green solvent. [4, 861-876]
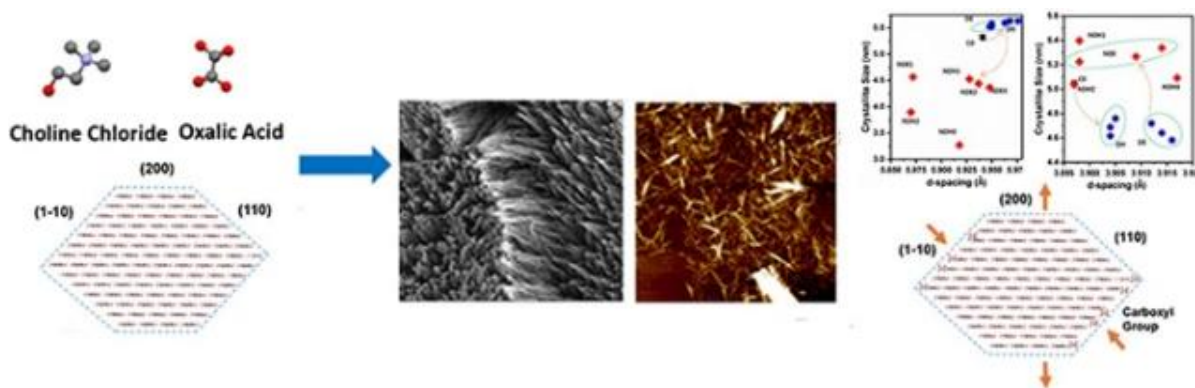

Figure 1 - Graphic abstract.

Anita Tarbuk, **Katia Grgić**, **Emilija Toshikj**, **Daniel Domović**, **Dejan Dimitrovski**, **Vesna Dimova** &

Igor Jordanov, Monitoring of cellulose oxidation level by electrokinetic phenomena and numeric prediction model.

Cellulose with a low level of oxidation is suitable for producing stable long-lasting materials with high added value, while extensively oxidized once is applicable for disposable products. In our previous comprehensive research, the fundamental behavior of the cotton under the action of different oxidants has been explored. Different levels of oxidation, as well as the type of functional groups, have been achieved by properly selected oxidants while controlling their concentration and treatment time. In this research, the electrokinetic ζ-potential of KIO_4 and TEMPO-oxidized cotton and the isoelectric point are measured by the streaming potential method, while the surface charge is calculated from the adsorbed cationic surfactant by the back-titration method. The results of electrokinetic phenomena are compared with the amount of created carboxyl groups determined by the calcium acetate method. The machine learning algorithms Waikato Environment for Knowledge Analysis for regression analysis is employed to develop models that make numeric predictions of the ζ-potential values based on the known number of carboxyl groups. The model with the correlation coefficient between the actual and the predicted value of ζ-potential is given for the first time. [5, 3107-3119]
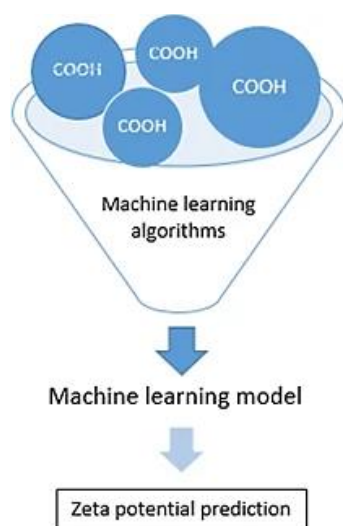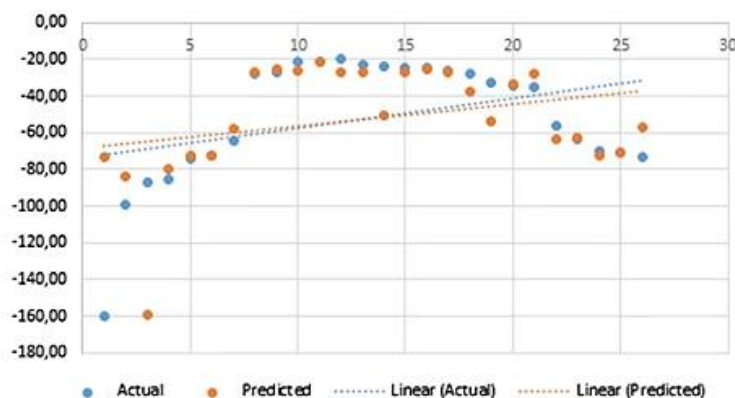

Figure 2 - Graphic abstract.

Wensheng Zou, **Xiaofei Ma** & **Pengwu Zheng**, Preparation and functional study of cellulose/carbon quantum dot composites.

Cotton was chosen as the carrier for carbon quantum dots. The primary hydroxyl groups in the cotton cellulose were oxidized to carboxyl groups, and the nitrogen-containing carbon quantum dots were bonded to the oxidized cellulose through silane coupling agent KH-560. The obtained cellulose/carbon quantum dot composites (CKHCs) were characterized by FTIR, SED-EDS, XRD and XPS. The results indicated that carbon quantum dots were grafted on cellulose. CKHCs were used as the probes for a fluorescent Hg^{2+} detection, because Hg^{2+} could induce fluorescence quenching of carbon quantum dots. The sensing system exhibits excellent sensitivity and selectivity for Hg^{2+}, with detection limits for mercury ions as low as 3 nM. The attachment of carbon quantum dots on cellulose makes the recycle of carbon quantum dots more convenient and improves the utilization of carbon quantum dots. The fit equations of the fluorescence intensity and Hg^{2+} concentrations for CKHC can test the unknown Hg^{2+} concentrations in the fluorescence quenching method, in which CKHC can be recycled to test the fluorescence quenching due to Hg^{2+} introduction. [6, 2099-2113]

Kanza Hina, Hantao Zou, Wu Qian, Danying Zuo, Changhai Yi, Preparation and performance comparison of cellulose-based activated carbon fibres.

Activated carbon fiber (ACF) is widely used sorbent material for wastewater treatment. Three natural cellulosic fibers (kapok, cotton, and ramie) and three regenerated cellulosic fibers (bamboo fiber, viscose, and Iyocell) are used to prepare ACFs using chemical activation. These ACFs are characterized using scanning electron microscope, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) testing, elemental analysis, adsorption property and nitrogen adsorption–desorption. XRD and FTIR spectrum of all six cellulosic ACFs are almost similar showing that ACFs have almost same

chemical and physical composition. All cellulosic ACFs are constituted of C, H, ash and O, but C content is higher in natural cellulosic fibers. Surface morphology and surface area of cellulosic ACFs play the basic role in adsorption. The 2nd order pseudo kinetic model is fitted for all cellulosic ACFs as $R^2 > 0.99$ and adsorption controlling process is chemical sorption. The adsorption capacity of the kapok-based ACFs is best, owing to their hollow structure, the micro pores on surface and high specific surface area. Bamboo, ramie and cotton based ACFs also have high adsorption but they need more time to adsorb impurities than kapok based ACFs. Viscose based ACFs shows moderate adsorption, while the least adsorption is shown by the Iyocell based ACFs because of their smooth and uniform structure. Adsorption analysis and other properties evaluation show that kapok fiber is the best precursor than other five cellulosic fibers. [7, 607-617]

Yasuko Saito, Shinichiro Iwamoto, Naoya Hontama, Yuki Tanaka & Takashi Endo, Dispersion of quinacridone pigments using cellulose nanofibers promoted by CH–π interactions and hydrogen bonds.

Organic pigments are prone to aggregate, resulting in decreasing of their properties. Therefore, pigment dispersants are demanded to have both high adsorption capacity and aggregation inhibiting property for pigment particles. In the present study, the suitability of cellulose nanofibers (CNFs) as a dispersant for quinacridone, a common red–violet organic pigment, was investigated. Quinacridone particles were well adsorbed on the CNFs. Scanning electron microscopy images of the quinacridone–CNF mixtures showed that the quinacridone primary particles were stacked along the cellulose fibers, and the aggregations were inhibited. In addition, the size of the quinacridone particles had an effect on their color. The interactions of quinacridone and cellulose were investigated by Fourier transform infrared (FTIR) and solution-state nuclear magnetic resonance (NMR) spectroscopies. FTIR spectra of the quinacridone–CNF mixtures indicated the intermolecular interactions between quinacridone and cellulose. Because quinacridone and CNFs were insoluble in the NMR solvents, gel-state NMR spectroscopy, which has been used for the whole plant cell wall analysis, was conducted on them. Consequently, whole signals arising from quinacridone and cellulose were enabled to be assigned, and the coupling constant of quinacridone has reported for the first time. The nuclear Overhauser effect spectroscopy (NOESY)-NMR spectrum of the quinacridone–CNF mixture revealed both NH group and aromatic moiety of quinacridone were interacted with glucose unit. The former was considered to be related to hydrogen bonding, and the latter to CH–π interactions. These specific interactions might contribute to achieve the high adsorption capacity of CNFs for quinacridone. [8,3153-3165]

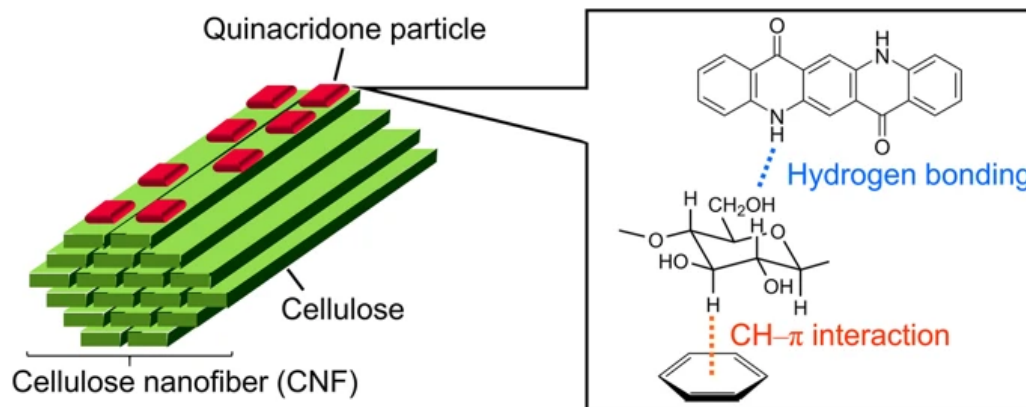**Figure 3 - Graphic abstract.**

Zhiming Jiang, Denghui Xu, Xingbo Ma, Jian Liu & Ping Zhu, Facile synthesis of novel reactive phosphoramidate siloxane and application to flame retardant cellulose fabrics.

A novel reactive phosphoramidate siloxane (DTSP) containing silica, phosphorus and nitrogen was successfully synthesized by the Atherton–Todd reaction and characterized by FT-IR and NMR. DTSP was bound onto cotton fabrics through the sol–gel method to improve flame retardancy. The combustion and thermal degradation properties of cotton fabrics before and after treatment were investigated with tests based on limiting oxygen index (LOI), vertical flammability, cone calorimetry and by thermogravimetric analysis. The phosphoramidate siloxane compound can significantly improve the flame retardant properties of cotton fabrics by promotion of char layer formation and release of noncombustible volatiles. The LOI of cotton with 16% of weight gain can reach 30.3%, which is significantly higher than control cotton and 27.0% of LOI value can be maintained after 20 washing cycles. In addition, this finishing method caused a slight decrease of tensile strength and breaking elongation

for cotton fabrics, which suggests that this kind of flame retardant material has a certain potential in practical applications. [9, 5783-5796]

Grunin Yu.B., Grunin L.Yu., Gal'braikh L.S., Sheveleva N.N., Masas D.S., Dispersion Peculiarities of Crystalline Cellulose Upon its Moistening.

A modernized scheme of the structure of native cotton cellulose micro fibrils is proposed, providing for the presence of slit-shaped pores in its structure and satisfying most of the results of modern studies of its supramolecular structure and sorption properties. It is shown that within the framework of this scheme it is possible to determine the content of elementary fibrils in micro fibrils and the degree of crystallinity of cellulose using 1H-NMR and sorption measurements. The mechanism and character of dispersion of micro fibrils, accompanied by supramolecular rearrangements of moistened cellulose, was investigated. [10, 321-326]

Mikhail A.T., Vasiliy I.M., Elena V.U., Lyudmila A.A., Andrey I.P., Nikolay V.T., Pavel V.K., Cellulose nanocrystals with different length-to-diameter ratios extracted from various plants using novel system acetic acid/ phosphotungstic acid/octanol-1.

The novel system [acetic acid/ phosphotungstic acid ($H_3PW_{12}O_{40}$)/octanol] was proposed for catalytic solvolysis of cellulose and for obtaining cellulose nanocrystals (CNC). Several alternative experiments involving mixtures with different compositions were carried out; reaction time was also varied. CNC particles from cotton, linen, softwood and hardwood cellulose were prepared in the experiments performed for 40 min in the presence of 0.25 mol% of the heteropolyacid. CNC samples were characterized by transmission electron microscopy and atomic force microscopy, X-ray diffraction analysis, and thermogravimetric analysis. It was established that the resulting nanoparticles had high crystallinity and rod-like shape; their length varied from 160 to 400 nm (cotton CNC had the shortest length, and linen CNC had the longest length), and CNC thickness ranged from 6 to 10 nm. Thermal stability of CNC was lower than that of initial celluloses and decreasing in the following sequence: *cotton > softwood > hardwood > linen cellulose*. [11, 1031-1046]

Ravindra D. Kale, [1]Prabhat Shobha Bansal, Vikrant G. Gorade, Extraction of Microcrystalline Cellulose from Cotton Sliver and its Comparison with Commercial Microcrystalline Cellulose.

The work was aimed at the extraction of microcrystalline cellulose (EMC) from raw cotton sliver (RCS) by acid hydrolysis using sulphuric acid. The EMC was characterized and compared with commercial grade microcrystalline cellulose (CMC).

Basic chemical pretreatments, bleaching and scouring were given to the RCS before extraction to remove natural colourants and hydrophobic impurities like oils, waxes, minerals, fats etc. The properties of EMC and CMC are considerably different from the RCS. Average particle size obtained was around 5–10 μm for EMC and CMC respectively. The EMC suspension was more stable than CMC suspension. The RCS, EMC and CMC were characterized by using X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy, scanning electronic microscopy and contact angle. EMC prepared from RCS has properties at par with CMC. Cotton being rich in cellulose content can be potentially used as the source for micro cellulose extraction, particularly in the production of hydrophilic micro composites. [12, 355-364]

Kim H.J., Liu. Y., Alfred D., Christopher M., Kim H., Comparison and validation of Fourier transform infrared spectroscopic methods for monitoring secondary cell wall cellulose from cotton fibers.

The amount of secondary cell wall (SCW) cellulose in the fiber affects the quality and commercial value of cotton. Accurate assessments of SCW cellulose are essential for improving cotton fibers. Fourier transform infrared (FT-IR) spectroscopy enables distinguishing SCW from other cell wall components in a rapid and non-invasive way. Thus it has been used for monitoring SCW development in model plants. Recently, several FT-IR methods have been proposed for monitoring cotton fiber development. However, they are rarely utilized for assessing SCW cellulose from cotton fiber due to limited validation with various cotton species grown in different conditions. Thus, we compared and validated three FT-IR methods including two previously proposed methods analyzing entire spectra or specific bands as well as a new method analyzing FT-IR spectral regions corresponding to cellulose with various cotton fibers grown in planta and in vitro. Comparisons of the FT-IR methods with reference methods showed that the two FT-IR methods analyzing the entire spectra or cellulose regions by principal component analysis monitored SCW qualitatively, whereas the FT-IR method analyzing specific bands (708, 730, and 800 cm^{-1}) by a simple algorithm allowed the monitoring of SCW cellulose levels quantitatively. The quantitative FT-IR method is a potential substitute for lengthy and laborious chemical assays for monitoring SCW cellulose levels from cotton fibers, and it can be used for a better understanding of cotton fiber SCW development and as a part of the quality assessment tools used to guide choices for improving fiber quality. [13, 49-64]

Jiaqi Pan, Xiufang Zhang, Jie Mei, Song Wang, Mingzhu You, Yingying Zheng, Can Cui,

Chaorong Li, The cotton cellulose nanofibers framework of Z-Scheme ZnO/Ag₃PO₄ heterojunction for visible-light photocatalysis.

The cotton cellulose nanofibers framework of Z-Scheme ZnO/Ag₃PO₄ heterojunction has been successfully fabricated by a simple route of the electrospun-hydrothermal method. The photocatalytic activity of the as-prepared cotton cellulose nanofibers framework of Z-Scheme ZnO/Ag₃PO₄ heterojunction exhibits significant enhancement after the Ag₃PO₄ being introduced by the degradation of methylene blue (MB) under visible light irradiation. Furthermore, the high dispersibility of the CCNFs, high visible light absorption and photon-generated carriers separation of Z-Scheme ZnO/Ag₃PO₄ heterostructure are considered as the main reasons for the enhancement. [14, 57-65]

References:

1. Aleshina, L.A., Vlasova, Ye.N., Grunin, L.Yu., & Grunin, Yu.B. (2014). *Structure and physicochemical properties of celluloses and nano composites based on them:* Monograph [Text]: in 1 v. / Malekh. (p.240). Petrozavodsk: Publishing house PetrSU.

2. Pirimqulov, M. (2017). *Cellulose production technology* [Text] / M.Primqulov, G.Rakhmonberdiyev, G.Akmalov. MHSE of Rep.Uzb. (p.72). Tashkent: "Niso" Polygraph.

3. Zhenyun Zhao, Jing Zhou, Ming Lu, Hang Xiao, & Yiping Liu (2020). Cellulose micro-dissolution by *N*-methylmorpholine *N*-oxide as a facile route for magnetic functional cotton textiles. *Cellulose* 27, 3153–3165.

4. Zhe Ling, J.Vincent Edwards, Zongwei Guo, Nicolette T. Prevost, Sunghyun Nam, Qinglin Wu, Alfred D. French, & Feng Xu (2019). Structural variations of cotton cellulose nanocrystals from deep eutectic solvent treatment: micro and nano scale. *Cellulose* 26, 861–876.

5. Anita Tarbuk, Katia Grgić, Emilija Toshikj, Daniel Domović, Dejan Dimitrovski, Vesna Dimova, & Igor Jordanov (2020). Monitoring of cellulose oxidation level by electrokinetic phenomena and numeric prediction model. *Cellulose* 27, 3107–3119.

6. Wensheng Zou, Xiaofei Ma, & Pengwu Zheng (2020). Preparation and functional study of cellulose/carbon quantum dot composites. *Cellulose* 27, 2099–2113.

7. Kanza Hina, Hantao Zou, Wu Qian, Danying Zuo, & Changhai Yi (2018). Preparation and performance comparison of cellulose-based activated carbon fibres, pp. 607–617.

8. Yasuko Saito, Shinichiro Iwamoto, Naoya Hontama, Yuki Tanaka, & Takashi Endo, Dispersion of quinacridone pigments using cellulose nanofibers promoted by CH–π interactions and hydrogen bonds, pp. 3153–3165.

9. Zhiming Jiang, Denghui Xu, Xingbo Ma, Jian Liu, & Ping Zhu (2019). Facile synthesis of novel reactive phosphoramidate siloxane and application to flame retardant cellulose fabrics, pp. 5783–5796.

10. Grunin, Yu.B., Grunin, L.Yu., Gal'braikh, L.S., Sheveleva, N.N., & Masas, D.S. (2018). Dispersion Peculiarities of Crystalline Cellulose Upon its Moistening. *Fibre Chem,* 49, 321–326.

11. Mikhail, A.T., et al. (2018). Cellulose nanocrystals with different length-to-diameter ratios extracted from various plants using novel system acetic acid/ phosphotungstic acid/octanol-1. *Cellulose* 25, 1031–1046.

12. Kale, R.D., Bansal, P.S., & Gorade, V. G. (2018). Extraction of Microcrystalline Cellulose from Cotton Sliver and its Comparison with Commercial Microcrystalline Cellulose. *Journal of Polymers and the Environment* volume 26, pp. 355–364.

13. Kim, H.J., Liu, Y., Alfred, D., Christopher, M., & Kim, H. (2018). Comparison and validation of Fourier transform infrared spectroscopic methods for monitoring secondary cell wall cellulose from cotton fibers. *Cellulose,* 25, 49–64.

14. Pan, J., et al. (2017). The cotton cellulose nanofibers framework of Z-Scheme ZnO/Ag₃PO₄ heterojunction for visible-light photocatalysis. Journal of Materials Science Materials in Electronics, 28(23). August 2017.