APPLICATIONS OF ENZYMES IN PROCESSING CELLULOSIC TEXTILES – A REVIEW OF THE LATEST DEVELOPMENTS

MICHAELA DINA STANESCU

University Aurel Vlaicu, Elena Dragoi Str. 2,310130 Arad, Romania
✉ *Corresponding author: stanescu@uav.ro, stanescumichaeladina@gmail.com*

Received December 30, 2022

Dramatic climate changes impose the implementation of new non-polluting technologies to ensure a sustainable development. The textile industry is very polluting, with high energy and water footprints, as well as discharges of toxic emissions and high waste water amounts. Thus, new, less polluting processes have to be brought in to decrease the environmental impact of this industry. Cellulosic fibers play an important role among the raw materials of textile industry. Classical treatments of natural cellulosic fibers use many chemical reagents and a large quantity of water. The progress registered lately in enzymes' production – regarding their preparation reproducibility and their stability as well – offer a good alternative to chemical reagents. The paper discusses the latest achievements in the application of enzymes for natural cellulosic fibers processing. The state of the art and recommendations for the future are presented.

Keywords: bast fibers, cotton, preparation and finishing, enzymes

INTRODUCTION

The alarming facts in connection with climate changes have led to a responsible attitude toward pollution. The textile industry is generating a high degree of pollution. All along the production, starting with the preparation of natural or synthetic fibers to their finishing processes, a variety of pollutants are generated. The production of cellulosic materials leads to environmental issues, such as air and water pollution, high energy and water consumption, land degradation, soil contamination, noise pollution, *etc*.[1-4]

There are a number of solutions to introduce cleaner production practices,[5,6] among which, the use of enzymes instead of harsh chemicals during the processing of fibers and/or materials is becoming increasingly prominent.[7,8] According to literature data, the textile sector is one of those using enzymes for processing raw materials (8%), after drugs (41%), food (17%), paper and leather (17%) and detergents (17%) producers.[9]

Progress in studying enzymes (synthesis, analysis, *etc*.), as well as in protein engineering by genetic modifications of bacterial or fungal strains, enlarged the enzyme application area.[10] Another asset was the discovery of extremoenzymes that are usually active under harsh conditions and can also be adjusted to other needed conditions by genetic engineering.[11,12]

ENZYMES FOR PROCESSING CELLULOSIC TEXTILES

The enzymes used in the cellulosic textile processing belong to the following classes: oxidoreductases (class I), hydrolases (class III) and lyases (class IV).[13,14]

Oxidoreductases

As oxidoreductases, laccases, glucose-oxidase and catalase are often employed.

Laccases (EC 1.10.3.2) belong to metallo-enzymes having four copper atoms in the reaction center. The enzyme oxidizes different substrates using oxygen as oxidation agent, which is turned into water by the hydrogen of the substrate (see Fig. 1), the copper atoms being the electron transporters.[15,16] Unlike other enzymes, laccases are non-specific enzymes, interacting with a variety of substrates.

Glucose-oxidase (EC 1.1.3.4) is specific for β-glucose, which is oxidized with oxygen to glucono-δ-lactone, the secondary product being hydrogen peroxide. The active site contains a coenzyme, *Flavinadenine dinucleotide* (FAD), transformed into $FADH_2$ by the reaction with the substrate. $FADH_2$ transfers hydrogen to oxygen, providing hydrogen peroxide (see Fig. 2).[17]

Catalase (EC 1.11.1.6) is also a metallo-enzyme with an iron atom coordinated to a

porphyrin ring.[18] Iron reacts with the oxygen of hydrogen peroxide, transforming it finally into water and oxygen. The intermediate of the process is an oxoferryl porphyrin radical-cation.[19] The steps of the transformation are shown in Figure 3.

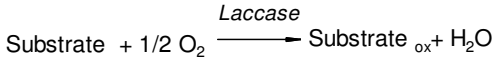

Figure 1: Reaction catalyzed by *Laccase*

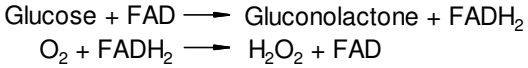

Figure 2: Reaction catalyzed by *Glucose oxidase*

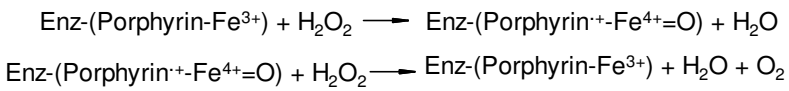

Figure 3: Decomposition of H_2O_2 catalyzed by *Catalase*

Hydrolases and lyases

The processing of cellulosic textile materials uses a number of hydrolases: amylases, cellulases, hemicellulases, pectinases, proteases, lipases *etc*.

Amylases are enzymes hydrolyzing starch and other related carbohydrates. Starch is formed by amylose, a linear 1-4 poly-α-glucose, and amylopectin, having beside 1-4 links, 1-6 branching links.[20]

Amylases are classified as α- (EC 3.2.1.1), *β*- (EC 3.2.1.2) and *γ*- (EC 3.2.1.3) amylases, according to their source and role in starch fragmentation.[21] α-Amylases break the starch [1,4] bonds randomly, producing different oligocarbohydrates. *β*-Amylases break the [1,4] bonds from the reducing end of the chain, producing maltose, while *γ*-amylases (amiloglicosidases) hydrolyze both [1,4] and [1,6] bonds. Pullanases are known as enzymes specific for hydrolyzing [1,6] bonds.[22] The mechanism for α-amylase transformation is presented in Figure 4.[23,24] The hydrolysis process is an acid-base catalysis, the dicarboxylic aspartic (Asp) and glutamic (Glu) aminoacids from the protein chain of the enzyme being involved as a *push-pull* driver during the fragmentation steps (see Fig. 4).

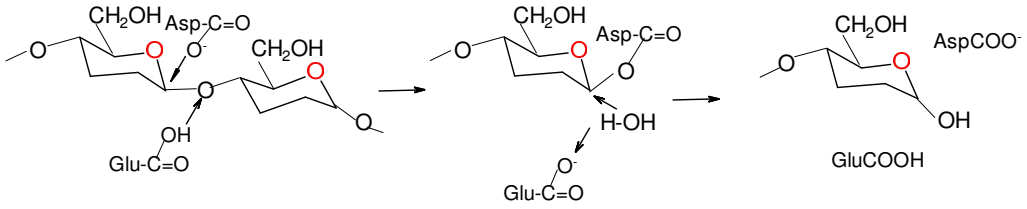

Figure 4: Acid-base catalysis in starch hydrolysis

Cellulases are enzymes specific for cellulose fragmentation. Cellulose is a poly-β-glucose having [1-4] links. It is a solid, with crystalline and amorphous regions. The strength of cellulosic fibers is due to their parallel arrangement, with both intra- and inter-molecular hydrogen bonds.[25]

An important source of cellulases for industrial applications are fungi.[26] There are different types of cellulases based on their way of action.[27,28] Endocellulases (glucanohydrolases) (EC 3.2.1.4) hydrolyze randomly the amorphous region of cellulose chain, producing oligocarbohydrates. Exocellulases (cellobiohydrolases) (EC 3.2.1.91) attack the chain ends, producing glucose and cellobiose (see Fig. 5). Finally, β-glucosidases (EC 3.2.1.21) hydrolyze the obtained cellobiose, producing two molecules of glucose.

The catalytic mechanism of cellulases involves the acid-base action of two dicarboxylic aminoacids in tandem, similarly to amylases. The transformation may be performed with inversion or retention of the substrate configuration at the

anomeric carbon atom attacked by the enzyme.[29,30]

Hemicellulases hydrolyze the hemicelluloses, polycarbohydrates formed by a variety of monomers, such as: manose, galactose, xylose, arabinose, glucose, *etc*., having complex branched structures.[31] Hemicelluloses are usually placed between lignin and cellulose or between cellulose microfibrils.[32] Depending on the specific substrate, there are different hemicellulases. Some examples are: endo-1,4-β-D-xylanases (EC 3.2.1.8), exo-1,4-β-D-xylosidases (EC 3.2.1.37), α-L-arabinofuranosidases (EC 3.2.1.55), α-D-glucuronidases (EC 3.2.1.139), α- (EC 3.2.1.22) and β- (EC 3.2.1.23) galactosidases *etc*.[33,34] These enzymes act similarly to amylases (see Fig. 4) by the ion pair catalytic mechanism.[34]

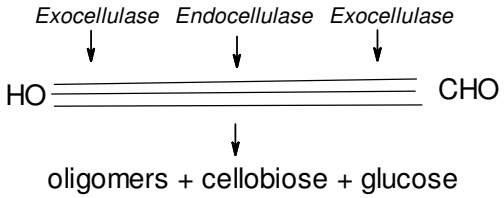

Figure 5: Action of cellulases on cellulose chain

Pectinases are enzymes hydrolyzing the pectin, another polycarbohydrate present in plants. Pectin contains as monomers mainly α-D-galacturonic acid and its methyl ester, but also small quantities of cross-linked L-rhamnose, L-arabinose and D-xylose.[35,36] According to their mode of action, pectinases may be endo- and exo-polygalacturonases (PG), pectinmethylhydrolases (PE), as well as pectinlyases (PL).[37,38] PGs hydrolyze the pectin chain at the link next to the free carboxylic groups, endo-enzymes randomly and exo at the non-reducing end of the pectin chain, forming monomers or dimers.[37] PE hydrolyze the methyl groups, leading to free carboxylic groups. Beside hydrolytic enzymes from group 3 (PG and PE), the pectin chain may be split by pectinlyases (PL) enzymes from group 4 (lyases). The PLs act by an elimination reaction, generating a smaller saturated pectin chain, together with an unsaturated oligomer. PLs also break the chain next to a free carboxylic group, either randomly inside the pectin chain (endo) or at the reducing end (exo).[39,40]

For processing cellulosic materials, small quantities of other hydrolytic enzymes, also found in detergents, may be added, such as lipases, proteases.

The enzymes may replace chemicals in textile material processing due to the following advantages:

- Specificity;
- Biodegradability;
- Mild conditions of the reaction, saving energy;
- Reduced water footprint of the process, not needing supplementary washings.

However, the implementation of enzymatic treatment in processing natural cellulosic fibers depends on a number of factors, such as:

- The enzyme cost;
- Needs to increase enzyme activity for reducing enzyme consumption;
- Needs to increase enzyme stability to work under reaction conditions.

A number of recently published papers are dedicated to this subject. The cost of an enzymatic treatment is the first reason why such a process has not been largely embraced by the textile industry yet.[41] The progress registered in the study of enzymes has led to solutions for this problem. Research has been performed for finding new, low cost enzymes, with higher thermal stability and increased activity. Thus, bacteria and fungi, some of the less expensive sources for enzymes, have been studied for their enzymatic activity. So, a number of new amylases, pectinases, hemicelulases, cellulases, laccases, *etc*. have been evidenced and their activity on textile fibers or materials was studied. A number of examples are presented below.

Sharma and Satyanarayana isolated and characterized a new thermostable exo-polygalacturonase, produced by *Bacillus pumilus*, which was successfully applied for degumming ramie.[42]

A detailed report of laccases production was presented by Chauhan and coworkers,[43] who remarked the fact that, by using different wastes

as sources of carbon and nitrogen in enzyme synthesis, the cost was substantially reduced.

A new amylase produced by *Trichoderma pseudokoningii* and developed on residual orange peel was isolated and characterized.[44] Using starch effluent from the textile industry, amylases with increased activity were produced in higher yields and used for cotton desizing.[45,46] Also, earthworms are a good source for obtaining enzymes, a quite thermo-stable amylase being isolated and characterized.[47] A more reactive α-amylase was obtained with a good yield, from the fungus *Aspergillus oryzae*, by plasma treatment.[48] A recent review presents the preparation of amylases using thermophlic bacteria, highlighting the advantages of protein engineering, as well as of enzyme immobilization.[49]

For producing microbial pectinases, agricultural and food waste are very good substrates.[50] The extract from tobacco leaves is rich in pectinases. These enzymes are low-cost and more stable than the commercial products.[51]

Studies for increasing the yield of cellulase production by *Bacillus licheniformis* TLW-3 strain have been performed, giving promising results.[52] An increase in cellulase production and activity by optimizing fermentation methods and using textile waste as carbon source was reported by Hu and coworkers.[53]

A cost reduction and activity increase may be obtained by the co-expression of multiple enzymes, as described by Chen and coworkers, by using a strain of *Escherichia coli*.[54]

Genetically modified enzymes are also efficient. New enzymes may be obtained by genetic engineering, having higher thermal stability and activity and, if possible, a low cost. The development of enzymes for industrial use requires expertise as well as the application of appropriate technologies.[55,56] Thus, new, recombinant bacterial glycohydrolases were successfully employed for degumming ramie.[57,58] Two truncated amylases were generated from *Bacillus subtilis* MTCC 121, having higher activity and thermostability, and they were efficient for cotton desizing.[59]

Different approaches for producing laccase at a larger scale by genetic engineering have been described in a review paper.[60]

Another way to stabilize enzymes and to reduce the cost by making possible their reuse is the immobilization. The progress in immobilization techniques made this alternative interesting for improving enzymatic treatments.[37,61] The immobilization process may be performed by adsorption, entrapment, encapsulation, cross-linking and covalent bonding.[62] One of the main advantages of using immobilized enzymes consists in the possibility to recover and recycle the catalyst. Progress has been recorded in synthesizing adequate carriers,[63,64] co-immobilization,[65-67] *etc*. According to literature, the first application of immobilized enzymes in the textile field was for the biodegradation of dyes from waste waters.[68]

A source for more stable enzymes are the extremophiles, microorganisms tolerating extreme environmental conditions.[69] Isolation and processing of the enzymes produced by such organisms are of great interest, as reflected by recent research in this field.[70]

NATURAL CELLULOSIC FIBRES

Natural fibers are interesting as raw materials for textiles due to their high wearing comfort level, as well as their biodegradability. The natural fibers used by the textile industry can be of vegetal or animal origin. Vegetal fibers are based on cellulose, being classified according to their source: bast, leaf, fruit or seeds.[71] The most common cellulosic fibers come from the bast or the seeds.

Bast fibers are plant fibers obtained from the bast (phloem) of the plant. The most common are: flax, hemp, kenaf, jute, and ramie, especially flax and hemp.[72]

Cotton is a fluffy material with a protection role, found around the seeds. It is the most spread of natural fibers, making about 90% of their production.[73] Cotton has the highest content of cellulose, followed by flax and hemp (see Table 1).[74] Due to the cellulose content and the easy way of separation from the plant, cotton accounts for 90% of all natural fibers.[75] Pectin binds the fibers, its removal determines the fineness of the fiber and the ease in spinning. Lignin is inlaid in the amorphous parts of cellulose and makes the fiber hard and rough, which imposes its removal.

Bast fibers

Bast fibers have been known since ancient times. For instance, evidence was found that flax was used for textile materials in year 6000 BC.[76] Plants producing bast fibers have been cultivated before cotton.[73] After the discovery of cotton, it replaced the bast fibers mainly due to the difficulty to extract them from the stem. Lately, the interest in bast fibers increased, because of the

pollution generated by the cultivation of cotton.[77,78] This interest is also due to their potential to improve the quality of the atmosphere (CO_2 adsorption) and soil, as well as to their potential application in composite materials.[79-81] Besides, the crop waste left on the field is biodegraded to nutritious organic compounds, reducing the necessary quantity of fertilizers.[82]

The cellulose of bast fibers has to be separated from lignin and hemicelluloses, which give stiffness and hydrophobicity, as well as from pectins, which link the fibers in bundles.[83] Fortunately, improvements have been recorded lately in the techniques used to obtain yarn and fabrics from bast plants.

The plant is harvested and the fibers extraction process starts. Fibers are extracted in bundles, being separated at first from other components.[84] Such separation is performed by a fermentation process called retting and may be achieved by different procedures. The process may be done on the field, by exposing the crop to light and water (rain and dew).[79] Bacteria developed during this time help the process. Figure 6 describes the stages for obtaining flax fibers, including field retting. Instead of field disposal, retting can be performed in ponds with water in the presence of specific microorganisms.[79]

The retting process may be made also by chemical or physical treatments, as well as by using enzymes.[77-79,81-85] Retting, which is a polluting process, may be avoided. By mechanical decortication, the bast fibers may be separated from the woody part. Unfortunately, as the resulted bundles of fibers are accompanied by many impurities and, consequently, are not suitable for producing textile materials, a degumming process needs to follow.[80]

As mentioned before the enzymatic treatment is less polluting, being also rapid, specific and needing mild conditions.[86,87] Also, the use of the resulted reaction residue for enzyme production makes the process more economic,[85] a low cost of enzymes supporting their applications.[86,87] Examples of enzymatic treatment for separating the bast fibers from the plant stem are presented below.

Table 1
Composition of some cellulosic fibers

Fiber	Cellulose (%)	Lignin (%)	Pectin and hemicelluloses (%)
Cotton	83-99	6	5
Flax	64-84	0.6-5	19
Hemp	67-78	3.5-5.5	17
Kenaf	44-57	15-19	-
Jute	51-78	10-15	37
Ramie	67-99	0.5-1	22
Sisal	60-80	6-14	13

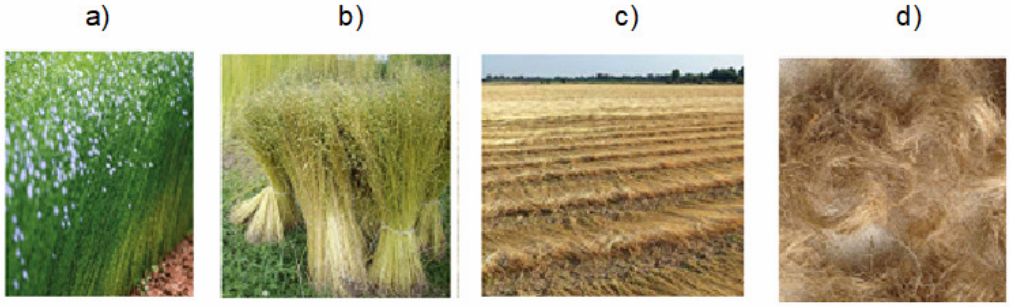

Figure 6: From flax to fibers: a) plant cultivation, b) harvesting, c) retting on field, d) resulted fibers

A review of enzymatic retting has been presented by a group of Belgian researchers.[79] Taking into account the chemical composition of the stem (see Table 1), the enzymes used for flax fiber extraction are: pectinases for the pectins, xylanases for hemicelluloses and laccases for wood degradation. Small quantities of cellulases may be added. A correct dosage of the enzyme mixture is essential for the resulting fiber quality. Due to the content of calcium in the pectin

composition,[88] the addition of chelators helps the retting process. Sometimes, pretreatments (mechanical, chemical) help the process of fiber extraction, facilitating the enzyme access to the matrix. The conclusion of the review paper mentioned above[79] underlined the important role of pectinases in this process. The same team of researchers studied the properties of flax fibers after enzymatic retting.[81] This paper revealed the high potential of enzymatic extraction of fibers to improve the quality of composite materials based on such flax fibers.

A comparison between different modes of retting was carried out by Goudar and coworkers.[89] Three types of flax retting were performed: with water, with water and urea, and with a microbial consortium. The authors concluded that chemical retting with urea gave a higher percent of fibers, while the enzymatic treatment provided longer fibers.

A microbial consortium was used by Mao and coworkers for retting ramie.[90] The authors present the 4 steps of retting, as follows: i) water absorption, ii) formation of calcium oxalate crystals, iii) removal of middle lamella and, finally, iv) removal of the gum from the fiber surface. The microbial consortium plays an important role in the degumming steps (iii) and (iiii) due to the pectinases produced in the process. By valorizing the obtained residue (microcrystalline cellulose, pectin, xylan and pectinase), the enzymatic ecologic process also became more economic.

Not only the pectinases are important for degumming, experiments confirm the importance of strains producing xylanases in the degumming process.[91] To the same results arrived another group of researchers, who produced an alkaline xylanase by the fermentation of *Bacillus halodurans* CM1, which proved its higher efficiency in ramie retting, compared to the chemical process (with NaOH).[92]

The role of different microbial strains in the ramie retting process was evidenced by Yang and coworkers.[93] The enzymatic activity of the strains was determined, as well as their synergetic compatibility. According to experimental data, the co-culture strategy gave good results.[93] The ramie extraction with a mixture of enzymes (pectinases, xylanases, laccase) has also been studied, the action of the enzymes being proven by the quality of the fibers evidenced with different types of microscopy.[94]

A combination of mild chemical (dinitrosalicylic acid and potassium sodium tartrate) and enzymatic retting of ramie was experimented. The enzymes were produced *in situ* from a mixture of *Bacillus subtilis* ABDR01 and *Bacillus thuringiensis* MCC2138, resulting in a joint activity of the combination of pectinases, xylanases, amylases and cellulases. The integrated treatments led to fibers of good quality.[95] A similar combination of chemical and enzymatic processes has been performed on a previously ultrasound pre-treated ramie, resulting in fibers with less than 3% residual gum. The enzymes were produced by *Bacillus subtilis* ABDR01 as a mixture of pectinases, xylanases and cellulases.[96]

To improve the pectinases content produced by *Bacillus* sp. Y1, the fermentation was optimized so that the PL activity was increased two-fold, and for PG – 3.44-fold.[97] Pectinolytic bacteria *Acidovorax temperans* and *Bacillus thuringiensis* are also efficient in ramie degumming based on their pectinase production.[98] A thermo-alkaline PL from *Bacillus* sp. RN1 was over expressed, proving to be efficient for ramie degumming.[99] The thermo-stability of a PL derived from *Dickeya dadantii* DCE-01 was improved by modifying its protein chain. Thus, its ability for degumming ramie was increased.[100,101] Similar mutations were performed on a PL (EC 4.2.2.2), resulting in three variants, with higher activity at 60 °C, compared with the wild one.[102] From *Bacillus paralicheniformis* CBS32, a PG was isolated, which proved to be efficient for ramie treatment.[103]

Fungi also developed highly active pectinases and laccases during flax retting.[104] A very efficient endo-xylanase for ramie degumming was produced by *Aspergillus terreus* HG 52.[105] A comparison of different modes of hemp retting showed better results when using an extract of a mutant of *Phlebia radiata* Cel 26 fungus.[106]

The reuse of retting water is also efficient for flax degumming, due to its high content of bacterial enzymes.[107] This procedure is also eco-friendly, reducing the water footprint of the retting process.

The extracted bast fibers contained other carbohydrates, besides cellulose (pectins, hemicelluloses) and lignin. It imposed treatments after retting for increasing the cellulose content and eliminating the other components. As for the retting process, this cleaning could be done by different methods, the enzymatic ones being ecological.

Ramie fibers may be scoured using xylano-pectinolytic enzymes for removing pectins and hemicelluloses. The treatment increased the hydrophilicy, whiteness and brightness of the ramie fibres.[108] Similar results for hemp, obtained with a commercial enzyme, were displayed by Sahi and coworkers.[109] Enzymatic scouring was efficient for obtaining good quality fibers from ramie, flax and jute.[110] In his review on bast fibers, Summerscales[111] discussed the use of fungal enzymes for reducing the hydrophobicity by removing lignin and the use of pectinases with chelators for pectin elimination. Commercial cellulase mixed with silicone softener were used for finishing linen terry clothes, a technological process being proposed.[112]

For achieving better results, the process may be accompanied by a variety of physical treatments. Thus, US assisted enzymatic degumming improved the cellulose content of ramie fibers.[113] A similar procedure was applied to jute, when an efficient elimination of impurities and improvement of hydrophobicity, without reducing the tensile strength, was observed.[114] Microwave (MW) or radiofrequency (RF) pretreatments also increased the degree of degumming, the MW procedure giving better results.[115,116]

The application of biotechnology for processing bast fibers may increase the interest in the use of these cellulosic fibers as raw materials for different products due to the reduction of water and energy footprints. To this, the reduced environmental burden for their cultivation, by comparison with cotton, has to be added.

Cotton

As presented above, cotton is the main natural fiber used for textile products (around 90%), based on the easy harvesting and the high content of cellulose.[73] After being harvested from the seeds, cotton is sent to the ginning plant for mechanical separation of the fibers from the seeds, other plant parts and dirt. Ginning is considered a part of the harvesting, being performed by the saw or roller.[117] After the ginning process, the fibers are spun, giving the yarn, and then woven to obtain the fabric. During the last process, some compounds are added, mostly starch. In order to obtain the suitable textile material, a number of operations have to be carried out on the obtained fabric. The processes that can be catalyzed by enzymes are presented in Scheme 1. The first stages of cotton processing comprise the preparation, consisting in: desizing, scouring and bleaching. The preparation is followed by the finishing operations.

Scheme 1: Treatments applied to cotton during processing

Desizing is the process that removes the material added during the weaving process, for increasing the resistance of cotton fibers. When starch is used for this purpose, it may be eliminated by chemical or enzymatic treatment. Amylases are the enzymes used for desizing, the expertise concerning their optimal work conditions (pH, temperature) being essential.[118] Introduced in 1919, the enzymatic desizing process has been subject to improvements. For instance, it was observed that the ratio of α- and β-amylases is of importance for an efficient desizing.[119] As mentioned before, research has been performed to find more efficient and low cost amylases. Commercial enzymes are too costly for industrial applications. Thus, a number of solutions were studied, such as: the inoculation of microorganisms for synthesizing new amylases and using waste as carbon source for enzyme synthesis, obtaining new enzymes by genetic engineering, combination of enzymatic treatment with plasma or ultrasounds (US) or even attempts to use immobilized enzymes.[120]

A new enzyme for starch hydrolysis, extracted from *Aspergillus tubingensis* SY 1, was successfully applied for gray-cotton fabric desizing.[121] Progress in enzymatic desizing was registered with high-temperature resistant amylases that reduce the operation time, facilitate the elimination of starch and are suitable for continuous processes.[122]

Combinations of enzymes led to better results. The addition of lipases seemed efficient for eliminating the hydrophobic part of the size.[123] Amylases may be used together with pullulanases, which act synergetically on starch, breaking the 1-4 and 1-6 bonds.[124]

After desizing, the preparation of cotton is performed by scouring and bleaching. The scouring process consists in the elimination of compounds, such as pectins, wax, fats and proteins, which make the surface of cotton fibers hydrophobic and look dirty. The enzymatic treatments seem efficient due to the large number of suitable enzymes acting under mild conditions.[125] The use of enzymatic scouring reduces the water and energy consumption, leading to a reduced cost of the process.[126] The bioscouring yields a softer cotton and does not affect the cellulose. The process is recommended also at an industrial level for fabrics dyed in medium and dark shades, when no previous bleaching is necessary.[127]

The efficiency of the enzymatic treatments depends on the material's thorough washing after the desizing procedure.[128]

The preparation of new pectinolytic enzymes from *Aspergillus tamari* using agro-industrial waste was beneficial due to the low cost, as well as the better quality of the cotton fibers obtained, compared with those resulting from classical NaOH scouring.[129] A cutinase produced by *Acinetobacter baumannii* AU10 was successfully used for cotton bioscouring, the scoured fabric being tested by the absorbency test.[130] A *Humicola insolens* cutinase was expressed in *Pichia pastoris*, being obtained in good yield and giving better cotton scouring results than the classical alkali procedure.[131]

Chelating agents help the process by extracting the calcium ions of the galacturonic acid salts from the pectin polymer. The substitution of the usual EDTA with citrate is a better solution in terms of the toxicity level.[132] It is worthwhile mentioning that the extent of pectin elimination after the scouring process is satisfactorily achieved by the determination of the Ca content of the textile material.[88]

A more efficient procedure for scouring used a recombinant PL from *Clostridium thermocellum*, immobilized on magnetic nanoparticles. The catalyst was active for 5 cycles, the time of the process was shorter, compared with the free enzyme treatment, and the bioscoured coarse cotton had good wettability.[133]

Improvements of the bioscouring procedure may be obtained by using enzymes and high frequency US (220 kHz), which also resulted in a reduction of the waste water effluents.[134,135]

The use of an enzyme mixture composed of PL from *Bacillus licheniformis* and a lipase from *Thermomyces lanuginosus* for the removal of pectins, wax and other impurities, together with a cellulase from *Aspergillus oryzae* for increasing brightness index and surface smoothness, improved the bioscouring performance, the enzymes acting synergically.[136] Another enzyme mixture composed of PL, lipase, protease and xylanase performed an efficient scouring, after the application of the Box–Behnken design method for finding the optimal working conditions.[137] A synergic effect for cotton scouring was observed using cutinase and PL.[138]

A new direction for making the process more efficient was proposed by Colombi and coworkers, who have succeeded in recycling the bioscouring bath, adding each time small quantities of fresh PL.[139]

Better results may be achieved by combining desizing and scouring in the same bath, reducing the time and the water consumption. The enzymes employed have optimal activity at similar pH and temperature values.[140,141]

The last step of preparation, the bleaching is usually performed with chemical reagents, mainly hydrogen peroxide.[142]

A combination of bleaching and scouring was performed on knitted cotton. For bioscouring, a mixture of commercial pectin lyase (EC 4.2.2.2), protease (EC 3.2.1.4) and lipase (EC 3.1.1.3) was used, while for bleaching – glucose oxidase (EC 1.1.3.4) and glucose for generating hydrogen peroxide – were used. The resulted cotton fabric had a satisfactory brightness index and hydrophilicity.[143]

An ecologic solution was the one-step desizing-scouring-bleaching with a mixture of amylase, amyloglucosidase generating glucose from starch, acid pectinase for bio-scouring and glucose oxidase (EC 1.1.3.4) for producing hydrogen peroxide.[144,145] The process was optimized in order to obtain enough glucose for the synthesis of H_2O_2 (see Fig. 2). The improvement of the thermal stability of the glucose oxidase by gene engineering improved the process.[146]

Cotton preparation is followed by the finishing processes. One of the most important steps in textile finishing is the dyeing operation. New procedures have been developed regarding the use of natural dyes, instead of the synthetic ones. In a review concerning sustainable finishing processes, the use of natural dyes is presented, emphasizing the advantage of these dyes based on their biodegradability, as well as their low

toxicity.[147] Some recent examples of cotton dyed with natural dyes follow. Thus, the dyeing of cotton fabrics with an extract of *Eucalyptus* leaves,[148] roots of madder (*Rubia tinctorum*) or turmeric (*Curcuma longa*) and fruits of harde (*Terminalia chebula*) (see Fig. 7),[149] anthocyanins from blueberries accompanied by a biomordant like tannic acid,[150] melanoidin from spent coffee ground, fixed with chitosan and citric acid,[151] was sucessfully achieved.

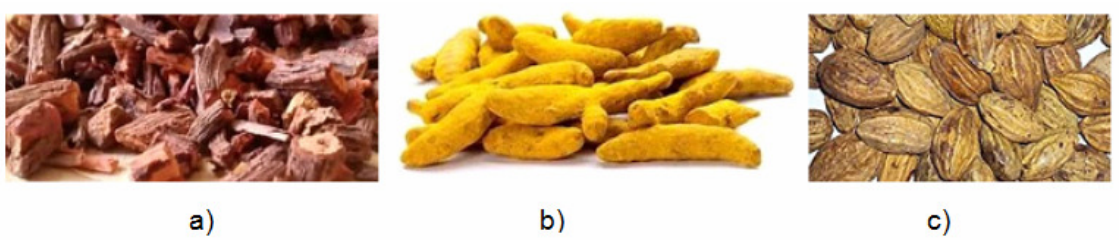

Figure 7: Roots of a) madder, b) turmeric and c) fruits of harde

Another source of natural dyes based on anthraquinone (moridone, alizarin, purpurin, *etc.*) are the plants from the *Rubiaceae* family. Mordants are needed for dye fixation, as well as pretreatment (US, plasma, oil, enzymes) for increasing dye adsorption. Cotton dyed with moridone proves to also have antibacterial properties.[152]

A review concerning the application of natural dyes, analyzing its advantages and disadvantages was published some years ago.[153] There are a number of problems related to the use of natural dyes. First of all, the quantity available is not in agreement with an industrial, large scale, application. Also, it is not so easy to obtain the expected shade, and for good fixation, mordants (mainly non-ecological metal salts) are needed. The reduced fastness to light of natural dyes is another inconvenience of their application.[154,155] An improvement of natural dye uptakes was achieved by the use of some eco-friendly treatments for modifying the material surface, including plasma, enzymes, US, UV-radiation.[156]

Another solution to avoid the usual synthetic dyes is to synthesize the dye *in situ*, on the fabric, from less toxic compounds like polyphenols, by enzymatic reaction using oxidases as catalyst.[157,158] The polymer dye obtained directly on the textile material presents higher fastness, compared with natural dyes. A large number of precursors for synthesizing dyes by oxidation with laccases as catalyst were tested by Atav and coworkers.[159] The conclusions of their experiments confirmed the environmental advantages of using precursor and enzyme, in comparison with the corresponding synthetic reactive dyes, but the authors evidenced the higher cost of the enzymatic process in comparison with classical dyeing. Also, 2-amino-3-methoxy-benzoic acid proved to be a good precursor for enzymatic dye synthesis using, as catalyst, free and immobilized laccase obtained from a *Pleurotus ostreatus* strain. The dye obtained was a phenazine derivative and had high color fastness.[160]

A recently published paper emphasized the advantages of enzyme utilization in textile finishing, including the dyeing process, such as improvements of the product quality, as well as lower energy and water consumption.[161] At the same time, the paper highlights the necessity to investigate the possibility to reduce the cost of the dye biosynthesis, for making the process compatible with a large scale application.

Another process of cotton finishing is the polishing – an operation that eliminates the fuzz and provides a smooth surface. In the last years, the process was performed with enzymes. The polishing is mainly recommended for Lyocell, a regenerated cellulosic fiber, for gaining a silky aspect.[162] Some new researches in this area are presented. Enzymes suitable for this process may be cellulases and laccases. A commercial *Aspergillus niger* cellulolytic enzyme was used to improve the surface and the hydrophobicity of cotton and Lyocell.[163] It turned out that cellulase biopolishing treatment improved the comfort properties and the smoothness of cotton fabrics.[164]

A successful attempt to bio-polish cotton was performed by using an immobilized cellulase. Compared with the results obtained when using the corresponding free enzyme, the cotton has a minimum reduction of weight and tensile strength, having also a better whiteness index.[165]

Similar results were reported using an immobilized laccase produced by *Madurella mycetomatis*.[166] The bio-polishing with laccase is a better solution, the weight and tensile strength losses being lower than in the case of the cellulase treatment.

Another finishing operation of cotton, where enzymes may replace classical reagents, is the so-called bio-stoning. It is used to give a distressed appearance to denim, a woven tilt fabric made from cotton. The classical procedure for this finishing process uses stones, which creates problems to the equipment, as well as to the environment. Similarly to polishing, laccases and cellulases are suitable for replacing stones. A new thermostable laccase was isolated from *Brevibacillus agri* and tried on indigo dyed denim fabric. The obtained results revealed the possibility to use this new enzyme at industrial scale.[167] Another promising laccase was obtained from bacteria *Pseudomonas* sp. HRJ16 developed on mandarin peels.[168] Recently, a mixture of laccase, cellulase and sodium hydrosulfite was used with good results for indigo-dyed denim discoloration.[169] A cellulase obtained by genetic engineering was successfully used for treating denim jeans.[170] Other oxidases may also be used for bio-stoning. Good results have been obtained with a fungal manganese peroxidase from *Cerrena unicolor* BBP6, even better than those with laccases.[171]

Unfortunately, the denim bio-stoning is frequently accompanied by back-staining, the re-deposition of indigo from the bath onto the garments. Studies on this subject have shown reduced back-staining on treatment with neutral cellulases (optimal pH 5-7), but a longer time for bio-stoning, compared with acid cellulases.[172] It generated interest in developing new, more efficient enzymes, as reported by Agrawal.[173] The progress registered in the identification of new cellulolytic enzymes was presented by a group of researchers from India.[174]

The enzymatic treatment for stoning cotton has a number of advantages: it is ecological, not producing pumice, developed under mild conditions, thus preserving the equipment, and reproducible.[175]

CONCLUDING REMARKS

The application of enzymatic treatment for processing cellulosic fibers is a valid solution for diminishing the pollution generated by the textile industry.

Newly developed techniques related to genetic engineering have led to the discovery of novel enzymes, with higher stability and lower cost. The progress in obtaining suitable low-cost enzymes encourages the application of biotechnological solutions at an industrial level. Besides, the development of small and medium enterprises (SME) in the textile field is an asset for applying biotechnological solutions, considering the reduced enzymes amount needed and the facility of processing smaller quantities of materials.

One of the advantages of the application of enzymes in cellulosic textile processing is the possibility of using enzymes prepared "*in situ*", not needing additional purification and consequently, reducing enzyme cost.

As a result of enzymatic treatments, the water, carbon and energy footprints of cellulosic materials processing decrease, the biodegradability of the enzymes reduces water consumption by avoiding extra washings necessary in chemical treatments, the enzyme specificity reduces the quantity of residue and the mild conditions needed reduce the consumption of energy for the processes.

In conclusion, the advantages brought by enzymes in processing cellulosic textile materials, together with the progress in obtaining stable enzymes, recommend bio-treatments for larger scale applications.

REFERENCES

[1] M. Shabbir and M. Naim, in "Textiles and Clothing: Environmental Concerns and Solutions", edited by M. Shabbir, Scrivener Publishing LLC, 2019, pp. 1-9, https://doi.org/10.1002/9781119526599.ch1

[2] T. Gulzar, T. Farooq, S. Kiran, I. Ahmad and A. Hameed, in "The Impact and Prospects of Green Chemistry for Textile Technology", edited by Shahid-ul-Islam and B. S. Butola, The Textile Institute Book Series, Woodhead Publishing, 2019, pp. 1-20, https://doi.org/10.1016/B978-0-08-102491-1.00001-0

[3] R. Mia, M. Selim, A. M. Shamim, M. Chowdhury, S. Sultana *et al*., *J. Textile Eng. Fashion Technol*., **5**, 220 (2019), https://doi.org/10.15406/jteft.2019.05.00205

[4] M. Zubair, M. Farid, M. Danish and M. N. Zafar, *Environ. Eng. Manag. J*., **16**, 373 (2017), http://omicron.ch.tuiasi.ro/EEMJ

[5] P. Freire da Silva, G. C. de Oliveira Neto, J. M. Ferreira Correia and H. N. P. Tucci, *J. Clean. Prod*., **278**, 123855 (2021), https://doi.org/10.1016/j.jclepro.2020.123855

[6] M. T. Islam and S. Asaduzzaman, in "Textiles and Clothing: Environmental Concerns and Solutions", edited by M. Shabbir, Scrivener Publishing LLC, 2019,

pp. 101-129, https://doi.org/10.1002/9781119526599.ch6
[7] O. May, in "Industrial Enzyme Applications", edited by A. Vogel and O. May, Wiley-VCH, 2019, pp. 3-24, https://doi.org/10.1002/9783527813780.ch1_1
[8] R. S. Singh, T. Singh and A. Pandey, in "Biomass, Biofuels, Biochemicals, Advances in Enzyme Technology", edited by R. S. Singh, R. R. Singhania, A. Pandey and C. Larroche, Elsevier, 2019, pp. 1-40, https://doi.org/10.1016/B978-0-444-64114-4.00001-7
[9] N. Arabacı, T. Karaytuğ, A. Demirbas, I. Ocsoy and A. Katı, in "Green Synthesis of Nanomaterials for Bioenergy Applications", edited by N. Srivastava, M. Srivastava, P. K. Mishra and V. K. Gupta, John Wiley & Sons Ltd., 2021, pp. 165-190, https://doi.org/10.1002/9781119576785.ch7
[10] M. V. Arbige, J. K. Shetty and G. K. Chotani, *Trends Biotechnol.*, **37**, 1355 (2019), https://doi.org/10.1016/j.tibtech.2019.09.010
[11] H. El-Sayed, A. F. El-Fiky and S. Mowafi, *J. Nat. Fibers*, **19**, 15035 (2022), https://doi.org/10.1080/15440478.2022.2069634
[12] P. Kakkar and N. Wadhwa, *J. Text. Inst.*, **113**, 2007 (2022), https://doi.org/10.1080/00405000.2021.194825
[13] S. M. M. Kabir and J. Koh, in "Biodegradation Technology of Inorganic and Organic Pollutants", edited by K. Ferreira Mendes, R. Nogueira de Sousa and K. Cabral Mielke, Intechopen, 2022, pp. 134-154, http://dx.doi.org/10.5772/intechopen.97198
[14] L. Porto de Souza Vandenberghe, S. G. Karp, M. G. Binder Pagnoncelli, M. von Linsingen Tavares, N. Libardi Jr. *et al.*, in "Biomass, Biofuels, Biochemicals", edited by S. P. Singh, A. Pandey, R. R. Singhania, C. Larroche and Z. Li, Elsevier, 2020, pp. 11-13, https://doi.org/10.1016/B978-0-12-819820-9.00002-8
[15] S. Noreen, S. Perveen, M. Bilal and H. M. N. Iqbal, in "Micro and Nano Technologies, Nanomaterials for Biocatalysis", edited by G. R. Castro, A. K. Nadda, T. A. Nguyen, X. Qi and G. Yasin, Elsevier, 2022, pp. 567-594, https://doi.org/10.1016/B978-0-12-824436-4.00018-6
[16] S. M. Jones and E. I. Solomon, *Cell. Mol. Life Sci.*, **72**, 869 (2015), https://doi.org/10.1007/s00018-014-1826-6
[17] S. H. Khatami, O. Vakili, N. Ahmadi, E. Soltani Fard, P. Mousavi *et al.*, *Biotechnol. Appl. Biochem.*, **69**, 939 (2022), https://doi.org/10.1002/bab.2165
[18] A. L. Dounce, *J. Theor. Biol.*, **105**, 553 (1983), https://doi.org/10.1016/0022-5193(83)90219-9
[19] M. Alfonso-Prieto, P. Vidossich and C. Rovira, *Arch. Biochem. Biophys.*, **525**, 121 (2012), https://doi.org/10.1016/j.abb.2012.04.004
[20] J. Robyt, in "Glycoscience", edited by B. O. Fraser-Reid, K. Tatsuta and J. Thiem, Springer, 2008, pp. 1437-1472, https://doi.org/10.1007/978-3-540-30429-6_35
[21] M. A. Ahmad, U. Isah, I. A. Raubilu, S. I. Muhammad and D. Ibrahim, *Bayero J. Pure Appl. Sci.*, **12**, 352 (2019), https://doi.org/10.4314/bajopas.v12i1.53S
[22] R. Sindhu, P. Binod and A. Pandey, in "Current Developments in Biotechnology and Bioengineering", edited by A. Pandey, S. Negi and C. R. Soccol, Elsevier, 2017, pp. 3-24, https://doi.org/10.1016/B978-0-444-63662-1.00001-4
[23] M. J. E. C. van der Maarel, B. van der Veen, J. C. M. Uitdehaag, H. Leemhuis and L. Dijkhuizen, *J. Biotechnol.*, **94**, 137 (2002), https://doi.org/10.1016/s0168-1656(01)00407-2
[24] R. Das and A. M. Kayastha, in "Biocatalysis", edited by Q. Husain and M. Ullah, Springer, 2019, pp. 17-38, https://doi.org/10.1007/978-3-030-25023-2_2
[25] S. P. Gautam, P. S. Bundela, A. K. Pandey, M. K. Awasthi and S. Sarsaiya, *J. Appl. Nat. Sci.*, **2**, 330 (2010), https://doi.org/10.31018/jans.v2i2.143
[26] K. Sampathkumar, V. Kumar, S. Sivamani and N. Sivakumar, in "Approaches to Enhance Industrial Production of Fungal Cellulases", edited by M. Srivastava, N. Srivastava, P. W. Ramteke and P. K. Mishra, Springer Nature, 2019, pp. 19-36, https://doi.org/10.1007/978-3-030-14726-6_2
[27] A. Sharma, R. Tewari, S. S. Rana, R. Soni and S. K. Soni, *Appl. Biochem. Biotechnol.*, **179**, 1346 (2016), https://doi.org/10.1007/s12010-016-2070-3
[28] N. B. Shreya and A. K. Sharma, *J. Food Process Eng.*, **44**, e13623 (2021), https://doi.org/10.1111/jfpe.13623
[29] M. Schülein, *Biochim. Biophys. Acta - Protein Struct. Mol. Enzymol.*, **1543**, 239 (2000), https://doi.org/10.1016/s0167-4838(00)00247-8
[30] X. Li, S. H. Chang and R. Liu, in "Fungal Cellulolytic Enzymes", edited by X. Fang and Y. Qu, Springer Nature, 2018, pp. 267-282, https://doi.org/10.1007/978-981-13-0749-2_15
[31] H. V. Scheller and P. Ulvskov, *Annu. Rev. Plant. Biol.*, **61**, 263 (2010), https://doi.org/10.1146/annurev-arplant-042809-112315
[32] P. Maijala, N. Kango, N. Szijarto and L. Viikari, *Antonie van Leeuwenhoek*, **101**, 905 (2012), https://doi.org/10.1007/s10482-012-9706-2
[33] J. Puls, *Macromol. Symp.*, **120**, 183 (1997), https://doi.org/10.1002/masy.19971200119
[34] D. Shallom and Y. Shoham, *Curr. Opin. Microbiol.*, **6**, 219 (2003), https://doi.org/10.1016/s1369-5274(03)00056-0
[35] D. Ropartz and M. C. Ralet, in "Pectin: Technological and Physiological Properties", edited by V. Kontogiorgos, Springer, 2020, pp. 17-36, https://doi.org/10.1007/978-3-030-53421-9_2
[36] D. Mohnen, *Curr. Opin. Plant. Biol.*, **11**, 266 (2008), https://doi.org/10.1016/j.pbi.2008.03.006
[37] H. U. Rehman, A. H. Baloch and M. A. Nawaz, *Trends Pept. Protein Sci.*, **6**, 1 (2021), https://doi.org/10.22037/tpps.v6i.33871
[38] M. D. Stanescu and M. Fogorasi, *Chim. Oggi*, **36**, 38 (2018)

[39] N. Martin, R. S. de Souza, R. da Silva and E. Gomes, Braz. Arch. Biol. Technol., 47, 813 (2004), https://doi.org/10.1590/S1516-89132004000500018
[40] P. Wu, S. Yang, Z. Zhan and G. Zhang, Appl. Microbiol. Biotechnol., 104, 7247 (2020), https://doi.org/10.1007/s00253-020-10769-8
[41] M. Rahman, M. M. Billah and D. Hack-Polay, Bus. Strateg. Dev., 2, 137 (2019), https://doi.org/10.1002/bsd2.58
[42] D. C. Sharma and T. Satyanarayana, Int. J. Biol. Macromol., 164, 3340 (2020), https://doi.org/10.1016/j.ijbiomac.2020.08.204
[43] P. S. Chauhan, B. Goradia and A. Saxena, *3 Biotech*., **7**, 323 (2017), https://doi.org/10.1007/s13205-017-0955-7
[44] W. H. Abdulaal, *BMC Biochem*., **19**, 4 (2018), https://doi.org/10.1186/s12858-018-0094-8
[45] S. Kalia, A. Bhattacharya, S. K. Prajapati and A. Malik, *Chemosphere*, **279**, 130554 (2021), https://doi.org/10.1016/j.chemosphere.2021.130554
[46] R. Aggarwal, T. Dutta and J. Sheikh, *Sustain. Chem. Pharm*., **14**, 100178 (2019), https://doi.org/10.1016/j.scp.2019.100178
[47] M. Nasiri, M. Arabi, R. Hemmati and G. Rigi, *Biomacromol. J*., **6**, 114 (2020)
[48] M. Veerana, S. Mitra, S. H. Ki, S. M. Kim, E. H. Choi *et al*., *Microb. Biotechnol*., **14**, 262 (2021), https://doi.org/10.1111/1751-7915.13696
[49] B. A. Kikani and S. P. Singh, *Crit. Rev. Biotechnol*., **42**, 325 (2022), https://doi.org/10.1080/07388551.2021.1940089
[50] A. R. Shet, S. V. Desai and S. Achappa, *RJLBPCS*, **4**, 337 (2018), https://doi.org/10.26479/2018.0403.30
[51] H. Daniell, T. Ribeiro, S. Lin, P. Saha, C. McMichael *et al*., *Plant Biotechnol. J*., **17**, 1154 (2019), https://doi.org/10.1111/pbi.13119
[52] T. Kiran, W. Asad, M. Ajaz, M. Hanif and S. A. Rasool, *Pak. J. Pharm. Sci*., **31**, 2333 (2018), https://pubmed.ncbi.nlm.nih.gov/30473501
[53] Y. Hu, C. Du, N. Pensupa and C. S. K. Lin, *Process Saf. Env. Prot*., **118**, 133 (2018), https://doi.org/10.1016/j.psep.2018.06.009
[54] H. Chen, R. Huang and Y. H. P. Zhang, Appl. Microbiol. Biotechnol., 101, 4481 (2017), https://doi.org/10.1007/s00253-017-8206-8
[55] A. M. Vogel, in "Industrial Enzyme Applications", edited by A. Vogel and O. May, Wiley-VCH, 2019, pp. 25-45, https://doi.org/10.1002/978352781380.ch1_2
[56] D. Ghosh and P. Talukdar, in "Microbial Fermentation and Enzyme Technology", edited by H. Thatoi, P. K. Das Mohapatra, S. Mohapatra and K. C. Mondal, CRC Press Taylor and Francis Group, 2020, pp. 195-206
[57] Y. Wang, Y. Bai, T. Shu, P. Fan, H. Zhang *et al*., *Text. Res. J*., **90**, 1602 (2020), https://doi.org/10.1177/0040517519894748
[58] R. Wang, Z. Liu, L. Cheng, S. Duan, X. Feng *et al*., *Text. Res. J*., **89**, 463 (2019), https://doi.org/10.1177/0040517517748511
[59] P. Saha, M. F. Khan and S. Patra, *Prep. Biochem. Biotechnol*., **48**, 635 (2018), https://doi.org/10.1080/10826068.2018.1479863
[60] T. Brugnari, D. M. Braga, C. S. A. dos Santos, B. H. Torres, T. A. Modkovski *et al*., *Bioresour. Bioprocess*., **8**, 131 (2021), https://doi.org/10.1186/s40643-021-00484-1
[61] B. M. Eid and N. A. Ibrahim, *J. Clean. Prod*., **284**, 124701 (2021), https://doi.org/10.1016/j.jclepro.2020.124701
[62] M. Bilal, T. Rasheed, Y. Zhao, H. M. N. Iqbal and J. Cui, *Int. J. Biol. Macromol*., **119**, 278 (2018), https://doi.org/10.1016/j.ijbiomac.2018.07.134
[63] D.-H. Zhang, L.-X. Yuwen and L.-J. Peng, *J. Chem*., **2013**, ID 946248 (2013), https://doi.org/10.1155/2013/946248
[64] A. Sharma, K. S. Thatai, T. Kuthiala, G. Singh and S. K. Arya, *React. Funct. Polym*., **167**, 105005 (2021), https://doi.org/10.1016/j.reactfunctpolym.2021.105005
[65] Y. Gu, L. Yuan, L. Jia, P. Xue and H. Yao, *RSC Adv*., **11**, 29498 (2021), https://doi.org/10.1039/d1ra05104k
[66] L. Betancor and H. R. Luckarift, *Biotechnol. Genet. Eng. Rev*., **27**, 95 (2010), https://doi.org/10.1080/02648725.2010.10648146
[67] R. Ahmad, J. Shanahan, S. Rizaldo, D. S. Kissel and K. L. Stone, *Catalysts*, **10**, 499 (2020), https://doi.org/10.3390/catal10050499
[68] J. Zdarta, K. Jankowska, K. Bachosz, O. Degorska, K. Kazmierezak *et al*., *Curr. Pollut. Rep*., **7**, 167 (2021), https://doi.org/10.1007/s40726-021-00183-7
[69] S. Vashist and R. Sharma, in "Extremophiles in Eurasian Ecosystems: Ecology, Diversity, and Applications. Microorganisms for Sustainability", edited by D. Egamberdieva, N. K. Birkeland, H. Panosyan and W. J. Li, Springer, 2018, vol. 8. pp. 345-351, https://doi.org/10.1007/978-981-13-0329-6_16
[70] C. Silva, M. Martins, S. Jing, J. Fu and A. Cavaco-Paulo, *Crit. Rev. Biotechnol*., **38**, 335 (2018), https://doi.org/10.1080/07388551.2017.1355294
[71] R. M. Kozłowski and M. Mackiewicz-Talarczyk, in "Handbook of Natural Fibres", edited by. R. M. Kozłowski and M. Mackiewicz-Talarczyk, Woodhead Publishing Series in Textiles, Elsevier, 2nd ed., 2020, vol. 1, pp. 1-13, https://doi.org/10.1016/b978-0-12-818398-4.00001-3
[72] M. R. L. Horne, in "Handbook of Natural Fibres", edited by. R. M. Kozłowski and M. Mackiewicz-Talarczyk, Woodhead Publishing Series in Textiles, Elsevier, 2nd ed., 2020, vol. 1, pp. 163-196, https://doi.org/10.1016/B978-0-12-818398-4.00007-4
[73] C. Felgueiras, N. G. Azoia, C. Gonçalves, M. Gama and F. Dourado, *Front. Bioeng. Biotechnol*., **9**, 608826 (2021), https://doi.org/10.3389/fbioe.2021.608826
[74] R. M. Kozłowski, M. Mackiewicz-Talarczyk, K. Wielgusz, M. Praczyk and A. M. Allam, in "Handbook of Natural Fibres", edited by R. M. Kozłowski and M.

Mackiewicz-Talarczyk, Woodhead Publishing Series in Textiles, Elsevier, 2nd ed., 2020, vol. 1, pp. 93-162, https://doi.org/10.1016/b978-0-12-818398-4.00006-2
[75] C Yu, in "Textiles and Fashion", edited by Elsevier, 2015, pp. 29-56, http://dx.doi.org/10.1016/B978-1-84569-931-4.00002-7
[76] J. H. Taylor, "Unwrapping a Mummy: The Life, Death and Embalming of Horemkenesi", University of Texas Press, 1995
[77] C. Altenbuchner, S. Vogel and M. Larcher, *Renew. Agr. Food Syst.*, **33**, 373 (2017), http://dx.doi.org/10.1017/s174217051700014x
[78] M. Bevilacqua, F. E. Ciarapica, G. Mazzuto and C. Paciarotti, *J. Clean. Prod.*, **82**, 154 (2014), http://dx.doi.org/10.1016/j.jclepro.2014.06.082
[79] J. De Prez, A. W. Van Vuure, J. Ivens, G. Aerts and I. Van de Voorde, *Biotechnol. Rep.* (*Amst*), **20**, e00294, (2018). https://doi.org/10.1016/j.btre.2018.e00294
[80] M. Zimniewska, *Materials*, **15**, 1901 (2022), https://doi.org/10.3390/ma15051901
[81] J. De Prez, A. W. Van Vuure, J. Ivens, G. Aerts and I. Van de Voorde, *Compos. Part A Appl. Sci. Manuf.*, **123**, 190 (2019), https://doi.org/10.1016/j.compositesa.2019.05.007
[82] S. Roy and L. Binte Lutfar, in "Handbook of Natural Fibres", edited by R. M. Kozłowski and M. Mackiewicz-Talarczyk, Woodhead Publishing Series in Textiles, Elsevier, 2nd ed., 2020, vol. 1, pp. 30-59, https://doi.org/10.1016/B978-0-12-818398-4.00003-7
[83] I. I. Shuvo, *Bioresour. Bioprocess.*, **7**, 51 (2020), https://doi.org/10.1186/s40643-020-00339-1
[84] R. Rowell and H. Stout, in "Handbook of Fiber Chemistry", edited by M. Lewis, CRC Press, 3rd ed., 2006, pp. 405-452, https://doi.org/10.1201/9781420015270.ch7
[85] M. Subash and P. Muthiah, *Clean. Eng. Technol.*, **5**, 100304 (2021), https://doi.org/10.1016/j.clet.2021.100304
[86] R. M. Kozłowski and W. Rozanska, in "Handbook of Natural Fibres", edited by. R. M. Kozłowski and M. Mackiewicz-Talarczyk, Woodhead Publishing Series in Textiles, Elsevier, 2nd ed., 2020, vol. 2, pp. 227-244, https://doi.org/10.1016/B978-0-12-818782-1.00007-9
[87] L. Cheng, S. Duan, X. Feng, K. Zheng, Q. Yang *et al.*, *J. Eng. Fibers Fabr.*, **15**, 1 (2020), https://doi.org/10.1177/1558925020940105
[88] M. Dochia, M. D. Stanescu and C. Constantin, *Fibers Tex. East. Eur.*, **3**, 21 (2013), http://www.fibtex.lodz.pl/article922.html
[89] I. V. Goudar, S. D. Kulloli, J. V. Vastrad and S. C. Mogali, *J. Pharmacogn. Phytochem.*, **10**, 269 (2021), www.phytojournal.com
[90] K. Mao, H. Chen, H. Qi, Z. Qiu, L. Zhang *et al.*, *Cellulose*, **26**, 3513 (2019), https://doi.org/10.1007/s10570-019-02288-1
[91] H. Wang, T. Shu, P. Li, Y. Bai, M. Xiang *et al.*, *Text. Res. J.*, **92**, 1026 (2022), https://doi.org/10.1177/00405175211044913
[92] D. Nandyawati, D. I. Astuti, N. Nurhayati, A. Riswoko and I. Helianti, *Microbiol. Indones.*, **15**, 91 (2021), https://doi.org/10.5454/mi.15.3.3
[93] Q. Yang, S. Duan, L. Cheng, X. Feng, K. Zheng *et al.*, *J. Nat. Fibers*, **19**, 1555 (2020), https://doi.org/10.1080/15440478.2020.1784819
[94] H. Qi, H. Chen, K. Mao, Z. Qiu, L. Zhang *et al.*, *Cellulose*, **26**, 2955 (2019), https://doi.org/10.1007/s10570-019-02309-z
[95] S. R. Chaudhuri, M. Gogoi, T. Biswas, S. Chatterjee, C. Chanda *et al.*, *Biotechnol. Rep.* (*Amst*), **28**, e00532 (2020), https://doi.org/10.1016/j.btre.2020.e00532
[96] A. Yadav, P. Simha, P. Sathe, L. M. Gantayet and A. Pandit, *Environ. Technol. Innov.*, **28**, 102666 (2022), https://doi.org/10.1016/j.eti.2022.102666
[97] F. Guo, X. Li, J. Zhao, L. Guanxi, P. Gao *et al.*, *Biomed. Res. Int.*, **2019**, 8146948 (2019), https://doi.org/10.1155/2019/8146948
[98] L. Cheng, S. Duan, X. Feng, K. Zheng, Q. Yang *et al.*, *Text. Res. J.*, **91**, 1056 (2021), https://doi.org/10.1177/0040517520968280
[99] X. Zheng, Y. Zhang, X. Liu, C. Li, Y. Lin *et al.*, *Front. Bioeng. Biotechnol.*, **8**, 850 (2020), https://doi.org/10.3389/fbioe.2020.00850
[100] H. Xu, X. Feng, Q. Yang, K. Zheng L. Yi *et al.*, *Polymers*, **14**, 2878 (2022), https://doi.org/10.3390/polym14142878
[101] H. Xu, S. Duan, X. Feng, Q. Yang, K. Zheng *et al.*, *Processes*, **9**, 2106 (2021), https://doi.org/10.3390/pr9122106
[102] Z. Zhou and X. Wang, *BMC Biotechnol.*, **21**, 322021 (2021), https://doi.org/10.1186/s12896-021-00693-8
[103] M. S Rahman, Y. S. Choi, Y. K. Kim, C. Park and J. C. Yoo, *Polymers* (*Basel*), **11**, 1525 (2019), https://doi.org/10.3390/polym11091525
[104] W. M. A. El-Rahim, H. Moawad, M. M. Hashem, G. M. M. Gebreil and M. Zakaria, *Biocatal. Agric. Biotechnol.*, **25**, 101570 (2020), https://doi.org/10.1016/j.bcab.2020.101570
[105] Y. Wu, T. Shu, P. Li, Z. Wang, H. Wang *et al.*, *J. Nat. Fibers*, **19**, 13890 (2022), https://doi.org/10.1080/15440478.2022.2111390
[106] M. Liu, M. T. Ale, B. Kolaczkowski, D. Fernando, G. Daniel *et al.*, *AMB Expr.*, **7**, 58 (2017), https://doi.org/10.1186/s13568-017-0355-8
[107] H. Moawad, W. M. Abd El-Rahim, M. M. Hashem, G. M. Gebreil, A. T. Sabbor *et al.*, *Egypt. J. Chem.*, **62**, 2033 (2019), https://doi.org/110.21608/ejchem.2019.9571.1641
[108] A. Yadav, P. Simha, P. Sathe, L. M Gantayet and A. Pandit, *Environ. Technol. Innov.*, **28**, 102666 (2022), https://doi.org/10.1016/j.eti.2022.102666
[109] A. K. Sahi, M. K. Singh and A. Das, *Indian J. Fibre Text. Res.*, **47**, 281 (2022), https://doi.org/10.56042/ijftr.v47i3.54131
[110] N. Kumar, S. N. Chattopadhyay and A. Khan,

Indian J. Eng. Mater. Sci., **29**, 630 (2022), https://doi.org/10.56042/ijems.v29i5.48219
[111] J. Summerscales, *Compos. Part A: Appl. Sci. Manuf.*, **140**, 106149 (2021), https://doi.org/10.1016/j.compositesa.2020.106149
[112] N. Yasinskaya, K. Lenko, N. Skobova and D. Lisovsky, *AIP Conference Proceedings of International Conference on Textile and Apparel Innovations*, Vitebsk, 8-10 June 2021, edited by A. Vankevich, 070004 (2022), https://doi.org/10.1063/5.0077289
[113] H. Patil, S. Mudaliar and A. Athalye, *Color. Technol.*, accepted (2022), https://doi.org/10.1111/cote.12638
[114] P. Ruan, V. Raghavan, J. Du, Y. Gariepy, D. Lyew *et al.*, *Ind. Crop. Prod.*, **146**, 112204 (2020), https://doi.org/10.1016/j.indcrop.2020.112204
[115] P. Ruan, J. Du, V. Raghavan, D. Lyew, Y. Gariepy and H. Yang, *Ind. Crop. Prod.*, **151**, 112312 (2020), https://doi.org/10.1016/j.indcrop.2020.112312
[116] A. Singh, L. M. Varghese, B. Battan, A. K. Patra, R. P. Mandhan *et al.*, *Environ. Sci. Pollut. Res.*, **27**, 6701 (2020), https://doi.org/10.1007/s11356-019-07424-9
[117] C. Yu, in "Textiles and Fashion: Materials, Design and Technology", edited by R. Sinclair, Woodhead Publishing, 2014, pp. 25-56, https://doi.org/10.1016/B978-1-84569-931-4.00002-7
[118] H. Taniguchi and Y. Honnda, in "Encyclopedia of Microbiology" 3rd ed., edited by M. Schaechter, Academic Press, 2009, pp. 159-173, https://doi.org/10.1016/B978-012373944-5.00130-9
[119] S. V. Besegatto, F. Nunes Costa, M. S. Pascoal Dumas, B. L. Colombi and A. C. De Rossi, *Ind. Biotechnol.* (*New Rochelle NY*), **14**, 298 (2018), https://doi.org/10.1089/ind.2018.0018
[120] G. A. Tochetto, A. M. I. Aragão, D. de Oliveira and A. P. S. Immich, Process Biochem., 123, 27 (2022), https://doi.org/10.1016/j.procbio.2022.10.030
[121] S. Yahya, M. Sohail and S. A. Khan, J. Text. Inst., 113, 993 (2022), https://doi.org/10.1080/00405000.2021.1914393
[122] M. Rahman, D. Hack-Polay, M. Billah and N. Nabi, Int. J. Technol. Manag. Sustain. Devel., 19, 87 (2020), https://doi.org/10.1386/tmsd_00017_1
[123] M. Rahman, M. Billah, D. Hack-Polay and A. Alam, Technol. Forecast. Soc. Change, 159, 120204 (2020), https://doi.org/10.1016/j.techfore.2020.120204
[124] S. Rebello, E. M. Aneesh, R. Sindu, P. Binod, A. Pandey *et al.*, in "High Value Fermentation Products: Human Welfare", edited by S. Saran, V. Babu and A. Chaubey, Scrivener Publishing LLC, 2019, vol 2, pp. 49-64, https://doi.org/10.1002/9781119555384.ch3
[125] A. Madhu and J. N. Chakraborty, *J. Clean. Prod.*, **145**, 114 (2017), https://doi.org/10.1016/j.jclepro.2017.01.013
[126] U. Bristi, A. K. Pias and F. H. Lavlu, *J. Text. Eng. Fashion Technol.*, **5**, 41 (2019), https://doi.org/10.15406/jteft.2019.05.00179
[127] J. Sheikh and I. Bramhecha, in "The Impact and Prospects of Green Chemistry for Textile Technology", edited by Shahid-ul-Islam and B. S. Butola, Woodhead Publishing, 2019, pp. 135-160, https://doi.org/10.1016/B978-0-08-102491-1.00006-X
[128] B. L. Colombi, R. De Cássia Siqueira Curto Valle, J. A. Borges Valle and J. Andreaus, *Clean. Eng. Technol.*, **4**, 100160 (2021), https://doi.org/10.1016/j.clet.2021.100160
[129] M. Shanmugavel, S. Vasantharaj, A. Yazhmozhi, P. Bhavsar, P. Aswin *et al.*, *Biocat. Agric. Biotechnol.*, **15**, 295 (2018), https://doi.org/10.1016/j.bcab.2018.06.013
[130] P. Gururaj, S. Khushbu, B. Monisha, N. Selvakumar, M. Chakravarthy *et al.*, *Prep. Biochem. Biotechnol.*, **51**, 550 (2021), https://doi.org/10.1080/10826068.2020.1836655
[131] R. Hong, Y. Sun, L. Su, L. Gu, F. Wang *et al.*, *J. Biotechnol.*, **304**, 10 (2019), https://doi.org/10.1016/j.jbiotec.2019.07.011
[132] M. D. Stanescu, M. Dochia, D. Radu and C. Sirghie, *Fibres Text. East. Eur.*, **3**, 109 (2010), http://www.fibtex.lodz.pl/article366.html
[133] S. Chakraborty, T. Jagan Mohan Rao and A. Goyal, *Biotechnol. Prog.*, **33**, 236 (2017), https://doi.org/10.1002/btpr.2379
[134] M. Easson, B. Condon, A. Villalpando and S. Chang, *Ultrasonics*, **84**, 223 (2018), https://doi.org/10.1016/j.ultras.2017.11.007
[135] A. Erdem and M. İ. Bahtiyari, *J. Clean. Prod.*, **188**, 670 (2018), https://doi.org/10.1016/j.jclepro.2018.03.166
[136] L. G. de Melo da Silva, D. de Oliveira, A. A. Ulson de Souza and S. M. Guelli Ulson de Souza, *Can. J. Chem. Eng.*, **95**, 1253 (2017), https://doi.org/10.1002/cjce.22780
[137] S. Kalantzi, D. Kekos and D. Mamma, *Cellulose*, **26**, 2771 (2019), https://doi.org/10.1007/s10570-019-02272-9
[138] O. Degani, *Catalysts*, **11**, 84 (2021), https://doi.org/10.3390/catal11010084
[139] B. L. Colombi, M. D. Palozi, R. de Cássia Siqueira Curto Valle, J. Andreaus, M. J. L. Arias *et al.*, *Bioprocess. Biosyst. Eng.*, **45**, 1391 (2022), https://doi.org/10.1007/s00449-022-02753-5
[140] A. K. Patraa, S. Gupta and A. Ali, *Indian J. Fibre Text. Res.*, **47**, 242 (2022), https://doi.org/10.56042/ijftr.v1i2.50215
[141] M. D. Teli and T. T. Adere, *Int. J. Eng. Trends Technol.*, **35**, 257 (2016), https://doi.org/10.14445/22315381/IJETT-V35P255
[142] S. M. F. Kabir, S. Chakraborty, S. M. A. Hoque and K. Mathur, *Clean Technol.*, **1**, 232 (2019), https://doi.org/10.3390/cleantechnol1010016
[143] C. Zotis Reis, O. Fogolari, D. Oliveira, S. M. de Arruda Guelli Ulson de Souza and A. A. U. de Souza, *Can. J. Chem. Eng.*, **95**, 2048 (2017), https://doi.org/10.1002/cjce.22891
[144] K. Mojsov, *J. Text. Inst.*, **110**, 1032 (2019),

https://doi.org/10.1080/00405000.2018.1535240
[145] K. Mojsov, A. Janevski, D. Andronikov, S. Jordeva, S. Golomeova *et al*., *Tekstilna Industria*, **69**, 21 (2021), https://doi.org/10.5937/tekstind2101021M
[146] Q. Mu, Y. Cui, Y. Tian, M. Hu, Y. Tao *et al*., *J. Biol. Macromol*., **136**, 1060 (2019), https://doi.org/10.1016/j.ijbiomac.2019.06.094
[147] B. M. Eid and N. A. Ibrahim, *J. Clean. Prod*., **284**, 124701 (2021), https://doi.org/10.1016/j.jclepro.2020.124701
[148] M. Gomes da Silva, M. A. S. D. de Barros, R. Takato Ribeira de Almeida, E. J. Pilau, E. Pinto *et al*., *J. Clean. Prod.*, **199**, 807 (2018), https://doi.org/10.1016/j.jclepro.2018.07.221
[149] G. C. H. Derksen, F. L. van Holthoon, H. M. Willemen, C. A. M. Krul, M. C.R. Franssen *et al*., *Ind. Crop. Prod*., **164**, 113344 (2021), https://doi.org/10.1016/j.indcrop.2021.113344
[150] K. Phan, E. Van Den Broeck, V. Van Speybroeck, K. De Clerck, K. Raes *et al*., *Dyes Pigments*, **176**, 108180 (2020), https://doi.org/10.1016/j.dyepig.2019.108180
[151] R. Mongkholrattanasit, M. Nakpathom and N. Vuthiganond, *Sustain. Chem. Pharm.*, **20**, 100389 (2021), https://doi.org/10.1016/j.scp.2021.100389
[152] K. L. Do, M. Su and F. Zhao, *Dyes Pigments*, **205**, 110482 (2022), https://doi.org/10.1016/j.dyepig.2022.110482
[153] Shahid-ul-Islam and M. Faqeer, *ACS Sustain. Chem. Eng*., **3**, 2361 (2015), https://doi.org/10.1021/acssuschemeng.5b00537
[154] A. Fröse, K. Schmidtke, T. Sukmann, I. Juhász Junger and A. Ehrmann, *Optik*, **181**, 215 (2019), https://doi.org/10.1016/j.ijleo.2018.12.099
[155] S. Li, A. B. Cunningham, Y. Shi, Z. Qiu, A. Hartl *et al*., *Ind. Crop. Prod*., **188**, 115706 (2022), https://doi.org/10.1016/j.indcrop.2022.115706
[156] M. Singh, M. Vajpayee and L. Ledwani, *Mater. Today*: *Proc*., **43**, 2868 (2021), https://doi.org/10.1016/j.matpr.2021.01.078
[157] J. Su, J. Noro, J. Fu, Q. Wang, C. Silva *et al*., *J. Clean. Prod*., **202**, 792 (2018), https://doi.org/10.1016/j.jclepro.2018.08.205
[158] J. Su, J. Noro, J. Fu, Q. Wang, C. Silva *et al*., *Process Biochem*., **77**, 77 (2019), https://doi.org/10.1016/j.procbio.2018.11.007
[159] R. Atav, B. Buğdaycı and İ. Yakın, *J. Text. Inst*., **113**, 628 (2022), https://doi.org/10.1080/0405000.2021.1896159
[160] K. Wlizło, J. Polak, A. Jarosz-Wilkołazka, R. Pogni and E. Petricci, *Enzyme Microb. Technol*., **132**, 109398 (2020), https://doi.org/10.1016/j.enzmictec.2019.109398
[161] H. El-hennawi, *Egypt. J. Chem*., **64**, 1075 (2021), https://doi.org/10.21608/ejchem.2020.34098.2714
[162] M. Shabbir and F. Mohammad, in "Sustainable Fibres and Textiles", edited by S. S. Muthu, Woodhead Publishing, 2017, pp. 171-189, https://doi.org/10.1016/B978-0-08-102041-8.00007-X
[163] M. A. Rahman, C. Yun and C. H. Park, *Text. Res. J*., **91**, 40 (2021), https://doi.org/10.1177/0040517520932232
[164] M. Kumar, S. R. Shukla, A. Arputharaj, S. Saxena, S. Patil *et al*., *Fibers Polym*., **22**, 2803 (2021), https://doi.org/10.1007/s12221-021-0356-8
[165] N. Sankarraj and G. Nallathambi, *Carbohyd. Polym*., **191**, 95 (2018), https://doi.org/10.1016/j.carbpol.2018.02.067
[166] A. Tülek, D. Yıldırım, D. Aydın and B. Binay, *Colloids Surf. B*, **202**, 111672 (2021), https://doi.org/10.1016/j.colsurfb.2021.111672
[167] V. Panwar, J. N. Sheikh and T. Dutta, *Appl. Biochem. Biotechnol*., **192**, 1238 (2020), https://doi.org/10.1007/s12010-020-03390-y
[168] J. O. Unuofin, K. M. Moloantoa and Z. P. Khetsha, *Arab. J. Chem*., **15**, 104305 (2022), https://doi.org/10.1016/j.arabjc.2022.104305
[169] M. Sarafpour, F. Alihosseini and M. Bayat, *Appl. Biochem. Biotechnol*., **194**, 5848 (2022), https://doi.org/10.1007/s12010-022-04066-5
[170] L. Bussler, D. Jacomini, J. M. Corrêa, M. K. Kadowaki, A. Maller *et al*., *Cellulose*, **28**, 2813 (2021), https://doi.org/10.1007/s10570-021-03700-5
[171] H. Zhang, J. Zhang, X. Zhang and A. Geng, *Process Biochem*., **66**, 222 (2018), https://doi.org/10.1016/j.procbio.2017.12.011
[172] L. Rios de Souza Moreira, D. L. Sciuto and E. X. F. Filho, in "New and Future Developments in Microbial Biotechnology and Bioengineering. Microbial Cellulase System Properties and Applications", edited by V. K. Gupta, Elsevier, 2016, pp. 165-175, https://doi.org/10.1016/B978-0-444-63507-5.00014-9
[173] B. J. Agrawal, *Curr. Trends Biomed. Eng. Biosci*., **3**, 555612 (2017), https://doi.org/10.19080/CTBEB.2017.03.555612
[174] A. Sharma, R. Tewari, S. S. Rana, R. Soni and S. K. Soni, *Appl. Biochem. Biotechnol*., **179**, 1346 (2016), https://doi.org/10.1007/s12010-016-2070-3
[175] S. Adeel, S. Kamal, T. Ahmad, I. Bibi and A. Kamal, in "Advances in Functional Finishing of Textiles. Textile Science and Clothing Technology", edited by M. Shahid and R. Adivarekar, Springer, 2020, pp. 85-114, https://doi.org/10.1007/978-981-15-3669-4_4