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Chapter

Sustainable Textile Processing by Enzyme Applications

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Abstract

Enzymatic treatments have gained popularity in the textile industry because of environmental friendly and energy conserving alternatives. Advancement in biotechnology and modification of enzymes has been focused based on various textile process applications. All the manufacturing steps of textile chemical processing, enzymes are using for implementations of the green technology to meet up the challenge of fourth industrial revolution. In this category, amylases, peroxidase used for desizing and bleaching, cellulase activates for bio polishing and denim finishing. This chapter summarizes the current developments of enzyme technology and highlights the environment-friendly and sustainable enzymatic textile processing in the textile industry.

Keywords: enzyme, microorganisms, textile fibre, bio-processing, finishing

1. Introduction

Enzymes are biocatalysts obtained from living cells through biochemical reactions specifically metabolic process of the cells [1]. Enzymes obtained from the natural source since ancient times in the production of food products, such as cheese, sourdough, beer, wine, vinegar and indigo formation [2]. The development of fermentation processes has grown during the last century, specifically for the production of purified enzymes in a large scale [3]. The use of recombinant gene technology has improved enzyme-manufacturing processes. Most industrial enzymes occurred hydrolysis for degrading the natural substances [4]. Enzymes are used in not only food production but also pharmaceuticals, textiles, leather processing [5–7]. There are prominent enzyme manufacturer for textile processing are listed in **Table 1**.

2. Enzyme structure and its mechanism

Enzymes are amino acid based globular proteins that range in size from less than 100 to more than 2000 amino acid residues. One or more polypeptide chains can be arranged and folded to form a specific three-dimensional structure, called active site incorporate with substrate. The active site may involve a small number (less than 10) of the constituent amino acids [9] (**Figure 1**).

The hypothesis of an enzyme-substrate complex was first proposed by the German chemist Emil Fischer in 1894. The lock and key theory explained, as a key is the

Industrial enzymes	Manufacturer	Established	Applications
Protease, xylanase, glucoamylase	Novozymes, Denmark	1921	Household care, textiles, food and beverages, oil and fats
Amylase, protease, phytase, xylanase, β-mannanase	Genencor, Denmark	1982	Food and Beverages, Textiles, Detergents, Biofuels
Amylases, Proteases, Cellulases, Xylanase, Pectinase	AB Enzymes, Germany	1907	Feed additives, food, textile, detergent, pulp and paper, biofuels
Protease, Amylase, Laccase, Catalase, Cellulase, Lipases	Dyadic, USA	1979	Food, brewing and animal feed enzymes, pulp and paper, textile enzymes

Table 1.
Industrial enzyme for textile applications [8].

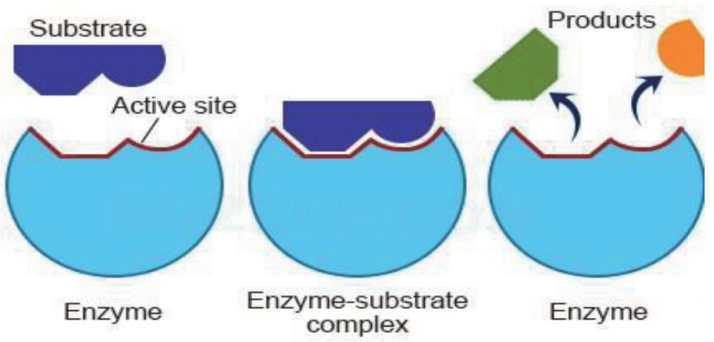


Figure 1.
Mechanism of enzyme-substrate complex [9].

substrate and lock is an enzyme. Enzyme are not shown rigid structures in a crystallographic x-ray but quite flexible in shape. In 1958, Daniel Koshland presented the 'induced-fit model' of substrate and enzyme binding, which is also known as 'hand-in-glove model' [10].

3. Enzyme classification for textile processing

Enzymes are biocatalysts, which can speed up the chemical processes [11]. Enzymes activates like other inorganic catalysts such as acids, bases, metals, and metal oxides. The molecule that an enzyme acts on is known as its substrate, which is converted into a product. The original attempt to classify enzymes was done according to different function. The International Commission on Enzymes (EC) was established in 1956 by the International Union of Biochemistry (IUB) in consultation with the International Union of Pure and Applied Chemistry (IUPAC) recommended hundreds of enzymes that had been discovered. The EC classification system is divided into six categories [12]:

- EC1 Oxidoreductases: catalyze oxidation/reduction reactions.
- EC 2 Transferases: transfer a functional group.
- EC 3 Hydrolases: catalyze the hydrolysis of various bonds.

- EC 4 Lyases: cleave various bonds by means other than hydrolysis and oxidation.
- EC 5 Isomerases: catalyze isomerization changes within a single molecule.
- EC 6 Ligases: Join two molecules with covalent bonds.

In textile industry mainly hydrolases and Oxidoreductases are engage for various enzymatic applications. Most of the enzyme applications in textiles are confined to cotton processing: removal of impurities (desizing, scouring, bleaching); biofinishing to improve appearance; bio-stoning or stone washing of denims to produce the fashionable aged look; bleaching cleanup to remove residual H_2O_2 before dyeing [13–17]. In addition to that there are efforts to substitute conventional processes of anti-shrinking, anti-pilling wool & degumming of silk with protease enzyme, retting of bast fibers with pectinase or hemicelluloses the several studies have been reported on modification of synthetics using hydrolases class of enzymes to impart hydrophilicity and antistatic properties [18, 19]. Moreover, detergent with the mixture of enzymes to remove varieties of stains in garments laundering [20]. Textile chemical processing is highly chemical intensive, and a variety of complex chemicals & auxiliaries are regularly used. So, mixed color to water causes toxicity for different form of life. It is essential to treat the effluent specially the residual colorants before discharging in environment. Hence, different enzymes employed for the textile effluent treatment containing synthetic dyes as colorants has been used. International Union of Biochemistry and Molecular Biology set up the Enzyme Commission for solving the complexity of and inconsistency in the naming of enzymes. They proposed almost 7000 enzymes; however, 75 are commonly used in the textile industry [21] According to the use of enzymes in textile industries, enzyme can be classified as shown in **Table 2**.

3.1 Hydrolases

The group of hydrolases enzyme includes amylases, cellulases, pectinases, proteases and lipases. In addition, hydrolases enzymes mainly act as hydrolysis. For isolating microbial strains that produce the desired enzyme and optimizing the conditions for growth, commercial quantities can be obtained. This technique, well known for more than 3,000 years is called fermentation [8].

EC digit	Enzyme groups	Enzyme class	Reaction type
a	Hydrolases	Amylases	Hydrolysis
		Cellulase	
		Proteases	
		Pectinase	
		Lipases/Esterase's	
b	Oxidoreductases	Catalases	Oxidation/reduction
		Peroxidase	
		Laccases	

Table 2.
Classification of enzyme based on textile applications.

3.1.1 Amylases

Amylases hydrolyze starch molecules to give dextrins and maltose, which composed of glucose units [22]. The various starch-splitting enzymes are known as α-amylases and β-amylases [23] (**Figure 2**).

α-amylases are produced from different fungi, yeasts and bacteria. The different microorganisms from α-amylases are listed in **Table 3**.

α-amylases are quite stable over a wide range of pH from 4 to 11. Optimum temperature for the activity of α-amylases is usually applied for modified microorganism. Addition of Ca^{2+} cans enhances thermo stability [24].

Commercial desizing compound under name Rhozyme DX, Rhozyme GC, Diastafor LCD (Bacterial α-Amylases) is more suitable for desizing compared to β-amylase from crude Barley & amyloglucosidase from (*Rhiszopus genus mold*) [25]. Amylase obtained from cheap waste animal pancreas are efficient in desizing for exhaust and pad batch application [26]. Microbial α- Amylase obtained from *Bacillus amyloliquefaciens* performed 100% desizing efficiency with pH 6.5 & 60° C for 1 hour [27]. α- Amylase obtained from *Aspergillus niger* sp. MK 07concentration of 300 U/ml performed at 75° C, pH 6.5 with 0.3 M $CaCl_2$ [28]. Glucoamylase (Multifect GA 10 L) and α- Amylase (Optisize Next) enzymes mixed with chelating agent in citric acid perform simultaneous acid-demineralization and desizing [29]. Ultrasound assisted α-amylase save half desizing process time [30] and α-amylase in winch machine performs highest desizing quality [31]. Ca^{2+} ion independent α-Amylase (*Bacillus sp. KR8104*) activate at moderate temperature (30-70°) desizing with acid-demineralization possible under acidic condition, presence of salts could

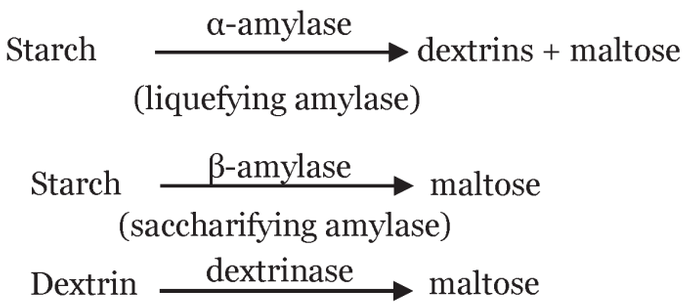


Figure 2.
Degradation of starch by α-amylases and β-amylases.

Microorganisms	Enzyme
1. Bacteria	
Bacillus subtilis	Amylase
B. coagulans	α-amylase
B. licheniformis	α-amylase
2. Fungi	
A. niger	Amylase
A. oryzae	Amylase
Ascomycetes	α-amylase
Basidomycetes	α-amylase

Table 3.
α-amylase from different microorganisms.

decrease enzyme dosage and process time [32]. Amylase obtained from *Aspergillus niger & Aspergillus flavus* shows higher desizing efficiency (*A. niger – 96%, A. flavus – 90%*) with significant improvement in absorbency & extractable impurities [33]. α- Amylase (*Bacillus sp. KR 8104*) shows simultaneous enzyme production and desizing optimized using inexpensive raw materials for α- Amylase [34]. Amylase assisted with other enzyme like *Aquazym* amylase & Lipase improve starch removal and shorten desizing time [35]. α-Amylase (*Aquazym*) incorporate of H_2O_2 or neutral cellulase improves desizing with whiteness and dye-ability presence of wetting agent governed extent of desizing [36]. Alkaline amylase (commercial enzyme Novozymes) performs both desizing & bio-scouring in single bath [37]. Polygalacturonase (*Trichoderma harzianum*) optimize combined pre-treatment in terms of weight loss, residual starch %, absorbency, strength loss and copper number [38]. Thermophile α-Amylase obtained from *Bacilluslicheniformis* optimizes cotton desizing using 3 g/l acidic with 6 pH at 85° C for 40 min [39]. α-Amylase obtained from *mesophilic* shows thermal stability in various additives for high temperature desizing, chitosan saves 2/3 enzyme dosage & improve desizing effect [40]. Amylase from *Aspergillus niger* immobilize with alkylamine glass beads are effective for removal of starch stains along with various detergents [41]. α-Amylase from soyabean seeds entrapped in agarose and agar matrices with 75% & 77% activity reused up to 5 cycles in starch stain removal [42].

3.1.2 Cellulases

Cellulases are hydrolytic enzymes that breakdown the cellulose to form oligosaccharides and finally glucose. Cellulase combining at least three types of enzyme for working synergistically on cotton (**Figure 3**).

The length of cellulose chains cleaves endogluconases or endocellulases in the middle of the amorphous region. However, exo-cellulases start their action from the crystalline ends of cellulose chains and convert to glucose by β-4-glucosidase [43]. These enzymes are commonly produced by soil-dwelling fungi and bacteria (**Table 4**).

A temperature range from 30 to 60° C is an active condition for cellulase. According to pH sensitivity, cellulase enzymes are classified in different categories

Figure 3.
Degradation of cellulose by cellulase enzyme

Microorganisms	Enzyme
1. Bacteria	
Pseudomonas fluorescents	Cellulase
E. coli	Cellulase
2. Fungi	
Trichodermareesei	Cellulase
Aspergillus niger	Cellulase

Table 4.
Cellulase enzyme from different microorganisms.

such as acid stable (pH 4.5–5.5), neutral (pH 6.6–7) or alkali stable (pH 9–10) [44]. Cellulase obtained from *Denimax L*& Pectinase (Pectinex USP) Novo Nordisk, V1–4 Xylanase (*Bacillus sp.*) optimized bio-polishing of jute-cotton blended fabrics for fuzz removal [45]. Cellulase, Endo-enriched cellulase, Exo-endo mixed cellulase are best suited for cotton and lyocell fabric especially for cotton, knits, linen and rayon [46]. Ecostone L883042 and Denimax L used for desorption the cellulase from cotton using ultra filtration for recovering and recycling [47]. Commercial cellulase like Gempil 4 L used for ring spun colored knitted fabrics for pill and fuzz removal [48]. G-ZYME VGB ST trade mark from Rossari are very useful for the action of cellulases on reactive dyed cotton and also show very good effect of bio-polishing on various spun yarn knitted fabrics [49, 50]. On the other hand, Acid cellulase from Genencor, USA performed better enzymatic hydrolysis on viscose, lyocell, modal &cotton fabrics were examined in-terms of degradation rate and weight loss [51]. Acid cellulase obtained from *Talaromyces emersonii* are thermostable cellulase obtained & applied for jute-based fabrics finishing to exhibit improved lusture, handle and durable softness [52]. Commercial cellulase Biopolish EC used for combined scouring-bleaching by cellulase treatment for knit fabrics [53]. Cellulase from *Trichoderma Vride G* optimizes cotton fabric for bio-polishing to improve its smoothness with minimum weight loss [54]. Indiage44L (Gencor) complex with mixed cellulase act as bio-scouring followed by bleaching either peroxide or peracetic acid is efficient for towels and endoglucanase is effective instead of cellulase as additive for terry towel washing [55]. Cellulase from *Trichoderma reesei* performed cotton bio-polishing & its effect on the morphologies [56]. Cellulase from *Chaetomium globosum* performed cotton bio-polishing in-terms of breaking strength, weight loss, thickness, drape and abrasion resistance [57]. Cellulase from *Aspergillus niger* immobilized on maleic anhydride modified PVA coated chitosan beads improves stability of acidic cellulase in neutral pH range [58]. Endoglucanase II (*Trichoderma reesei*) is effective for removing color from denim, producing a good stonewashing effect with lowest hydrolysis level [59].

Alkali Cellulase (*Alkalothermophilic Thermomonospora sp.*) are first time alkali stable endoglucanase used for bio-polishing denims, provide abrasive effect and softness with lower backstaning& negligible weight loss [60]. Cellulase from *Hypocrea jecorina* with nonionic surfactant and dispersing agents provide double benefits of reduction in backstaning and increased cellulase activity [61].

Suhong 89 from Acid cellulase efficiently removes indigo from denim surface with minimum hydrolysis & possibility of cellulase reuse [62].

3.1.3 Pectinases

Pectinase are complex enzymatic group that degrade the pectic substances. They are produced from saprophytes and plant pathogens which can degrade the plant cell walls. There are three major classes of pectin degrading enzymes are pectin esterases, polygalacturonases and polygalacturonate lyases [63].

Pectin Esterases: Pectin esterases liberate pectin and methanol by de-esterifying the methyl ester. Their activity is highest on 65–75% methylated pectin, is to act on methoxy group adjacent to free carboxyl group. Its action has very little effect on the molecular weight of the pectin (**Figure 4**).

Pectin esterases active in the pH range of 4–8 and optimal temperature range for maximum activity is 40-50° C.

Polygalacturonases: Polygalacturonases reduce the molecular weight of the pectins. They catalyze the hydrolytic cleavage with the introduction of water across the oxygen. They are classified further as endo-galacturonases and exo-galacturonases (**Figure 5**).

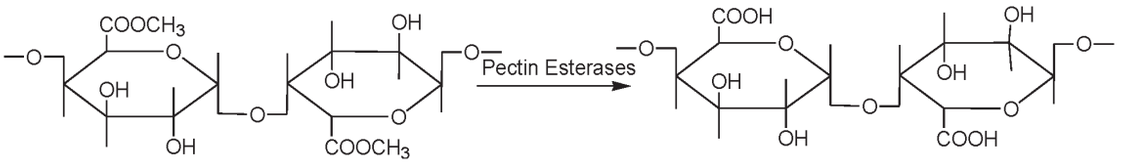


Figure 4.
Degradation of pectin by pectin esterases.

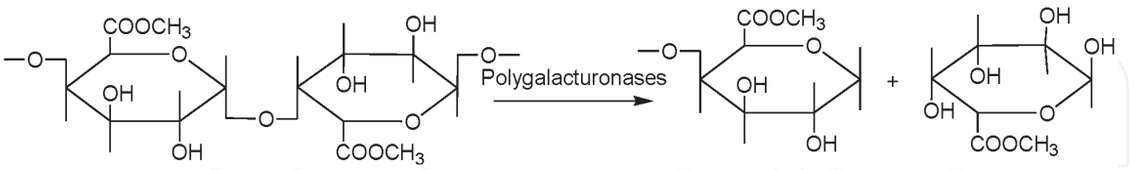


Figure 5.
Degradation of pectin by polygalacturonases.

Polygalacturonases obtained from different natural sources with respect to physiochemical and biological properties as well as their mode of actions.

Pectin Lyases: Pectin lyases depolymerise the pectin. These catalyse the trans-eliminative cleavage of the galacturonic acid polymer. It can break down the glycosidic linkages at C-4 and eliminate H from C-5 position (**Figure 6**).

Pectin esterases, polygalacturonases and pectin lyases are mainly produced in plants such as banana, citrus fruits and tomato, but also by bacteria and fungi (**Table 5**).

Bioprep 3000 L, Novozyme acts as alkaline pectinase are efficiently remove impurities formed uniform dyeing consistency & equivalent color depth with different direct dyes [64]. Pectinase from *Aspergillus niger* named as Bioprep 3000 L agitate improve efficiency and optimize enzymatic scouring provide less damage & superior fabric quality [65, 66]. Bioprep 3000 L Pect062L, Biocatalyst (Acid Pectinase) performs both acid and alkali pectinase are equally efficient but acid pectinase works with lower concentration [67]. Bioprep 3000 L scoured cotton knit fabric at 80° C for removing wax and higher dye uptake optimize bio-scouring for

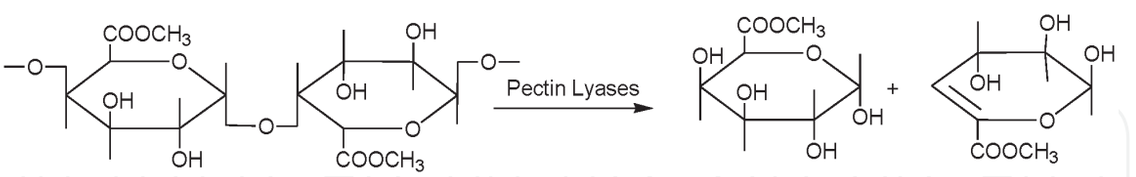


Figure 6.
Degradation of pectin-by-pectin lyases.

Microorganisms	Enzyme
1. Bacteria	
Erwinia	Pectin esterases
Bacteroides	Pectin lyase
Pseudoalteromonas	Polygalacturonase
2. Fungi	
Aspergillus niger	Polygalacturonases

Table 5.
Pectinase enzyme from different microorganisms.

physical, chemical & low stress mechanical properties [68]. Pectinase obtained from *B.macerans* strain V-2692 contains cellulose & hemi-cellulase remove pectin but improve fabric capillary much greater which can substitute cotton boil-off [69]. Multifect cellulose GC obtained from *Trichoderma longibrachiatum* and Multifect pectinase PL from *Aspergillus niger* synergism of cellulose efficiency removes pectin and protein, mechanical agitation and compatible surfactants also play important role [70]. Viscozyme 120 L (Pectinase + hemicellulose) treatment prior to alkaline scouring along with chelating agent at acidic pH, efficiently lightens the seed-coat fragments to improve whiteness and gives better results of wet ability, pectin removal and dyeing with 60 min treatment time [71]. Pectinase, lipase and cellulase enzyme combinedly perform successful scouring, dye and water absorbency with some fiber damage [72]. Alkaline Pectinase (*Bacilus*), Acidic pectinase (Microorganism) along with neutral cellulose (*Apergillus aculeatus*) performs best in wax removal & high absorbency [73]. Alkali Pectinase & Cellulase combinedly scoured knitted fabrics in two step one bath process [74]. Bioprep 3000 L Alkali Pectinase (*Bacillus sp.*) & Lipolase 100 L (*T. lanuginosus*) combined lipase in one-step reduce time required & fabrics with superior properties and excellent dyeing performance obtained [75]. Xylanase from *Bacillus pumilus* are thermostable enzyme provide simultaneous desizing and scouring, addition of chelating & wetting agent increases hydrolysis and allowed reduction of H_2O_2 consumption in consecutive bleaching [76]. Bioprep 3000 L and Forylase KP. Cognis (Acidic Pectinase) simultaneous scouring & bleaching using Pectinase & PAA sufficiently remove pectin and wax to achieve excellent absorbance with medium degree whiteness without damaging fiber and good dye-ability with less energy & water use in enzymatic and/or PAA treatments because of 60° C & pH 6–8 [77–79].

3.1.3.1 Proteases

Proteolytic enzymes produced by microorganisms are mixtures of endopeptidases and exopeptidases. The simplified form the action of the proteases are (**Figure 7**).

Microbial proteases obtained from the plant source such as papain, ficin, and the animal proteases obtained from pepsin and trypsin. Microbial proteolytic enzymes obtained from different fungi and bacteria. Most fungal proteases activate in a pH range (about 4 to 8), and bacterial proteases generally work best over a range of about pH 7 to 8 [80] (**Table 6**).

Proteases with cellulase (Commercial Enzyme) mixture perform for bioscouring and optimized using ANN technique to achieve desired absorbency and pectin removal [81]. Proteases (*Bacillus*) and cellulase provide successful scouring, dye, and water absorbency with some fiber damage in presence of cellulase [82].

3.1.4 Lipases/Esterases

Esterases represent a group of hydrolases that catalyse the cleavage of fats, oils and formed ester bonds. They are widely obtained from animals, plants and microorganisms. These enzymes make attractive biocatalysts for the production of

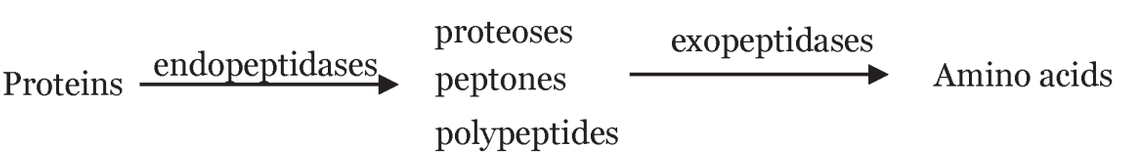


Figure 7.
Degradation of protein by proteases.

Microorganisms	Enzyme
1. Bacteria	
Bacillus clausii	Proteases
Pseudoalteromonas sp.	Proteases
2. Fungi	
Aspergillus flavus-oryzae	Proteases
Aspergillus tamarii	Proteases

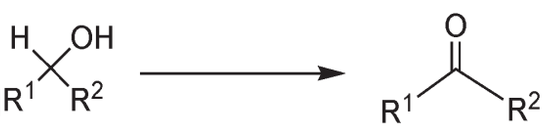
Table 6.
Protease enzyme from different microorganisms.

optically pure compounds in fine-chemicals synthesis. Lipases have three-dimensional structure with the characteristic α/β-hydrolase fold [83]. The phenomenon of interfacial activation can be distinguished by lipases and esterases. The interfacial activation is due to hydrophobic domain covering the lipase active site and the presence of a substrate concentration will lid open, making the active site accessible. It can be used for elimination of natural triglycerides in scouring and tallow compounds in desizing process [84]. The phytopahthogenic fungus is the best examples of lipases are shown in **Table 7**.

Arylesterase obtained from Bio-bleach system HUNTSMAN and H_2O_2 in situ generate peracetic acid for mild temperature at 65° C, neutral bleaching of cotton [85]. Lipase enzymes perform both bio-scouring and bio-bleaching, which provide high degree of whiteness [86].

3.2 Oxidoreductases

The enzymes catalyze oxido reduction reactions, transfer electrons through substrates like cellulose. In the majority of cases, the substrate that is oxidized is regarded as a hydrogen donor. The systematic name of oxidoreductases is based on donor acceptor groups. The enzymes named oxidase, which contains molecular oxygen (O_2) is the acceptor.



R^1 = hydrogen, organic residue

R^2 = hydrogen, organic residue, alcoxy residue

Microorganisms	Enzyme
1. Bacteria	
Pseudomonas	Lipases
Burkholderia	Lipases
2. Fungi	
Fusarium solani pisi	Lipases
Cunninghamella verticillata	Lipases

Table 7.
Lipase enzyme from different microorganisms.

Oxidoreductases enzymes categorize two nonhydrolytic enzymes such as peroxidase and catalase.

3.2.1 Peroxidase/glucose oxidase

Glucose oxidase or peroxidase acts in the presence of oxygen to convert glucose to gluconic acid and hydrogen peroxide. It can oxidize only β-D-glucose (**Figure 8**).

The galactose oxidase (GO) from *Dactylium deudroides* the oxidation of D-galactose at the C-6 position in the presence of oxygen to give D-galactohexodialdose and hydrogen peroxide. The enzyme contains one atom of Cu^{2+} per molecule as co-factor. Recent investigations indicate that the enzyme catalyses the stereo specific oxidation of glycerol, 3-halogenopropane-1-2-diols and polyols to the corresponding aldehydes (**Figure 9**).

Peroxidase is synthesized in several species of fungi and bacteria are illustrated in **Table 8**.

Glucose-Oxidase desize cotton fabric and enzymatically produce peroxide for bleaching at elevated temperature with high pH [87]. Combined glucose, glucose-oxidase & peroxidase for cotton bleaching [88]. Glucose-oxidase (Commercial Novo Nordisk- Denmark) optimized bio-bleaching of cotton, linen and their blends with 25 U/ml GOE, 10 g/l D-glucose at 85° C & pH 10 for 90 min [89]. Glucose-

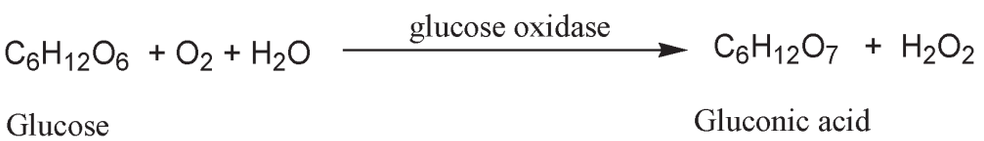


Figure 8.
Degradation of glucose-by-glucose oxidase.

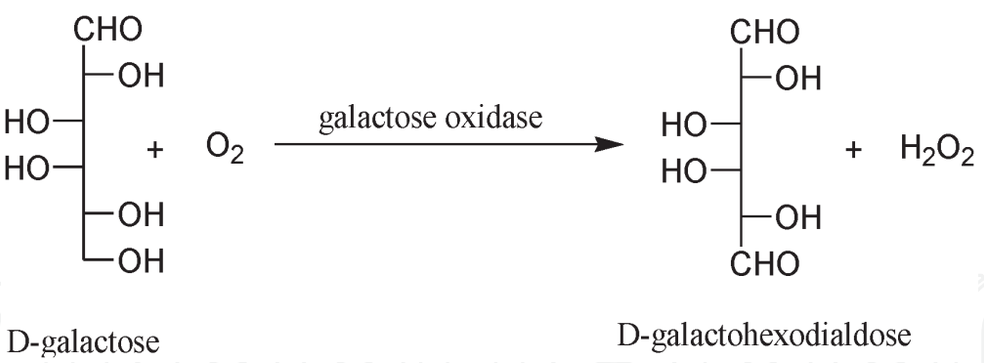


Figure 9.
Degradation of D-galactose by galactose oxidase.

Microorganisms	Enzyme
1. Bacteria	
Penicillium notatum	Peroxidase
Staphylococcus aureus	Peroxidase
2. Fungi	
Botrytis cinerea	Peroxidase
Aspergillus oryzae	Peroxidase

Table 8.
Peroxidase enzyme from different microorganisms.

Oxidase (*Aspergillus niger*) Biozyme with pullanase mixture used for sufficient (800 mg/l) H_2O_2 for bleaching and maximum whiteness obtained in alkaline pH compared to neutral and acidic pH [90]. Glucose-oxidase from (*Aspergillus niger*) with external oxygen supply and mechanical agitation essential for H_2O_2 generation cotton bleached at room temperature & acidic pH with high enzyme concentration [91].6% increase in whiteness index with comparable mechanical properties using peroxide produced by glucose oxidase [92]. One bath low temperature of cotton pretreatment by glucose oxidase where liberated H_2O_2 converted to peracetic acid using TAED as activator [93]. Glucose-Oxidase GC 199 combine desizing, scouring with enzymes followed by bleaching with in-situ generated peracetic acid using different activators [94]. Assistance of ultrasound with glucose-oxidase improves whiteness due to increase enzyme reaction at 90° C with pH 11 [95]. Multifect GO 5000 L, Genecor performed desizing, bleaching and reactive dyeing for cotton towel [96]. Glucose-oxidase from *Aspergillus niger* immobilized on porous carriers-glass & alumina, low enzyme concentration provides sufficient H_2O_2 release which further activated for textile bleaching [97].

3.2.2 Catalases

Catalases (CATs) also known as hydroperoxidases, catalyse the degradation of H_2O_2 to H_2O and O_2. Catalase, which is also found in commercial fungal glucose oxidase preparations [98] (**Figure 10**).

Catalases are ubiquitous oxidoreductases enzymes present in archaea, bacteria, fungi, plants and most have optimum temperatures (20-50° C) and neutral pH. Catalases obtained from animal sources (bovine liver) are generally cheap; therefore, the production of microbial catalase will be economically advantageous when recombinant technology is used. Catalases have special properties such as thermosatbility and operate both in alkaline or acidic pH. The chloroperoxidase from *Caldariomyces fumago* also catalyses the oxidation of halide ions except fluoride (**Table 9**).

Glucose-oxidase (multifect GO 5000 L, Genecor), Catalase (Terminox Ultra 10 L) integrated desizing, bleaching and reactive dyeing of cotton towel was performed [96].

Figure 10.
Degradation of hydrogen peroxide by catalase.

Microorganisms	Enzyme
1. Bacteria	
Pseudomonas putida	Catalase
Neurospora crassa	Catalase
2. Fungi	
Aspergillus terreus	Catalase
Aspergillus niger	Catalase

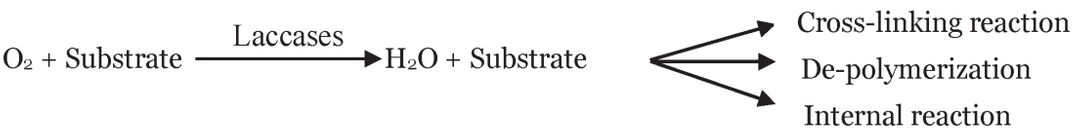
Table 9.
Catalases enzyme from different microorganisms.

Microorganisms	Enzyme
1. Bacteria	
S.lavendulae	Laccases
Theiophora terrestris	Laccases
2. Fungi	
Trametes villosa	Laccases
Botrytis cinerea	Laccases

Table 10.
Laccases enzyme from different microorganisms.

3.2.3 Laccases

Laccase originated from blue-multicopper oxidase family. It oxidizes a variety of aromatic and non-aromatic phenolic compound also depolymerizes the substrate by a radical-catalyze reaction mechanism.



Laccases have been found in plants, fungi, insect and bacteria. However, more than 60 fungal strains have found laccase activity. Fungal laccase is a protein approximately 60–70 KDa, which activate in the acidic pH range and optimal temperature between 50 and 70° C. Few laccases enzymes activate with optimum temperature below 35° C (**Table 10**).

Combined laccase/peroxide bleaching applied in batch & pad dry method [99]. Laccase from *Trametes hirsute* with mediator improve whiteness of cotton due to oxidation of flavonoids [100]. Complex enzyme Laccase & Peroxidase (*Ph Chrysoporium & Trichosporon cutaneum R57)* efficiently degrade & remove lignin from flax fiber to provide whiteness [101]. Laccase, Novozyme obtained from *Trametes villosa* assistance with ultrasound and PVA addition stabilize laccase and improve bleaching [102]. Ecolite II (Commercial Laccase, Jeans are company) and H_2O_2 performed bleaching of linen allows better dye uptake for both reactive and cationic dyes [103].

4. Textile applications

The enzymatic textile processing has started in the middle of nineteenth century. The enzymes were introduced in de-sizing purposes for the first time in 1857; however, enzymatic de-sizing process was successfully introduced in 1912 [104]. In addition, cellulases were introduced in 1980s for de-pilling and de-fuzzing of cellulose-based fabrics [105]. In the early 1990s, catalases were entered into the bleaching and pectin-degrading enzymes to replace traditional alkaline scouring [106]. In biotechnological research is underway, around the globe, introduce environmental friendlier strategies for textile processing is extensively to the modern industry. The potential of enzymatic textile processing is illustrated in **Figure 11**.

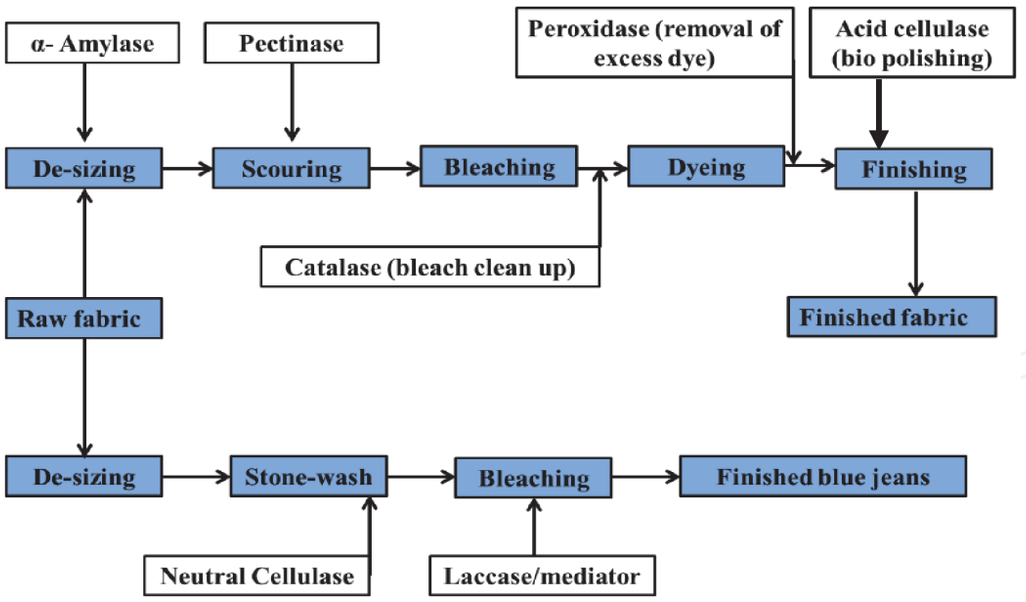


Figure 11.
Enzymes used in various operations in textile wet processing [107].

5. Enzyme used in textile wet processing

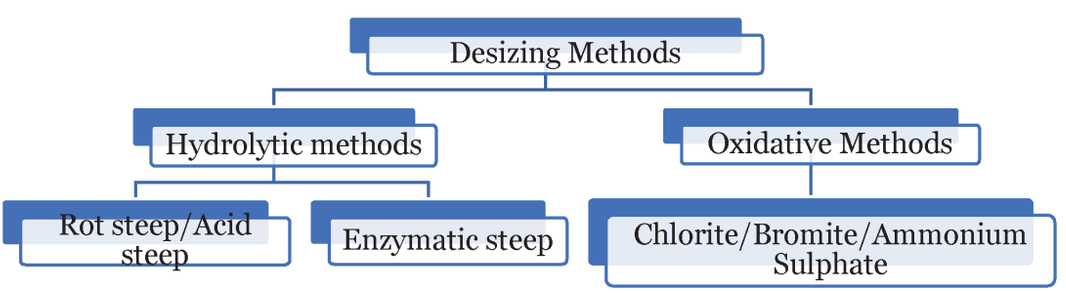
5.1 De-sizing

The cotton warp yarns are sized to improve the yarn strength. Besides help in the interweaving during the procedure, it protects yarn against abrasion and snagging. Mostly starch-based products are used to apply sizes, synthetic and semi-synthetic sizes are polyvinyl alcohol (PVA) and carboxymethylcellulose (CMC) used [104–106]. The purpose of size is to protect the yarn from the abrasive action of weaving loom.

Desizing is the first step for wet processing in textile finishing technology employed to remove sizing material from the fabric. The size must be removed before bleaching and dyeing, for uniformity of wet processing. Chemically, starch is poly-α-glucopyranose in which amylase and amylopectin are present. However, they are insoluble in water. They can be solubilized by hydrolyzing them to shorter chain compounds. The object of desizing is to convert starch to soluble dextrin. The stages of hydrolyzing are mentioned below:

Starch (insoluble) → dextrin (insoluble) → dextrin (soluble) → maltose (soluble) → α-glucose (soluble)

Types of desizing methods



Enzyme desizing is the most widely practiced method of desizing starch. *Amylase* can catalyses the breakdown of starch form sugars, dextrin and maltose. The advantage of these enzymes is specific for starch, removing it without damaging to

the support fabric. An enzymatic desizing process at low-temperature (30-60°C) and optimum pH is 5.5–6.5 is required for amylase [108]. Rising the temperature desizing facilities starch removal as well reduces process duration therefore the thermophile amylases have gained wider acceptance. Thermophile *Bacillus licheniformis* α-amylase can provide high temperature efficient starch removal efficiency with improved absorbency [109]. The enzymatic desizing process can be divided into three steps:

Impregnation: Enzyme solution is absorbed by the fabric. This stage involves through wetting of fabric with enzyme solution at a temperature of 70° C or higher with a liquid pick up of 1 liter per kg fabric. During this stage, gelatinization of the size is to the highest possible extent.

Incubation: The size is broken down by the enzyme. Long incubation time allows a low enzyme concentration.

After-wash: The breakdown products from the size are removed from the fabric. The desizing process is not finished until the size breakdown products have been removed from the fabric. This is best obtained by a subsequent detergent wash at the highest possible temperature.

5.2 Scouring

In textile terminology "scouring" applies to the impurities removal process. Raw cotton contains about 90% of cellulose and various non-fibrous impurities such as dirt, oils, waxes, gums and seed fragments. Pectins are complex polysaccharides comprised of α-(1, 4) linked D-galacturonic acid backbone. Pectin is non-cellulosic substance in cotton acts as cementing/adhesive material; therefore, removing pectin, will enhance to remove other non-cellulosic substances. In scouring process, the target fabric is usually boiled in the presence of alkali solution using large iron-made vessels called kiers. Classic alkaline scouring using sodium hydroxide removes most of such contaminations, essential to achieve satisfactory wet-ability. In textile processing, the process based on extensive alkali consumption requires heavy rinsing which ultimately leads several by-products in the wastewater effluent and poses severe damage to the cellulose contents of the fabric [110, 111].

The process of bio scouring is based on the concept of decomposition of pectin using enzyme. Bio scouring is ecofriendly, energy conserving alternative based on the idea of specially targeting the non-cellulosic impurities with appropriate enzymes without adversely affecting the substrate. Natural properties of the cotton fiber are preserved; the fabric is softer to the touch than after classic scouring. Pectinases enzyme activate in two medium acidic and alkaline. Acidic pectinases that function in a slightly acidic medium (pH between 4 and 6), as well as alkaline pectinases that function in a slightly alkaline medium (pH between 7 and 9) [112]. Optimum enzyme concentration varies from pectinase to pectinase but in general, pectinases are effective in low concentrations 0.005–2% range. In addition, the optimum temperature of pectinases application is form 40-60° C beyond which enzyme reduces its activity [113]. A high temperature rinsing after bio scouring is required for the removal of waxes (**Figure 12**).

Mixed enzymatic treatments of unscoured cotton fabric conducted by German scientists involved pectinase, cellulase, protease, and lipase. Beside the temperature, the pH of the environment is crucial for the activity and stability of the enzyme. An assistance of lipases removes natural fats & lubricants for better absorbency and levelness in dyeing. Bio-scouring for mutations containing lipase are more effective in attaining good hydrophilicity for cellulosic textiles [114]. In recent years, pectinases have been immobilized by ion exchange resins, aminated silica gel and macroporuos polyacrylamide for cotton scouring.

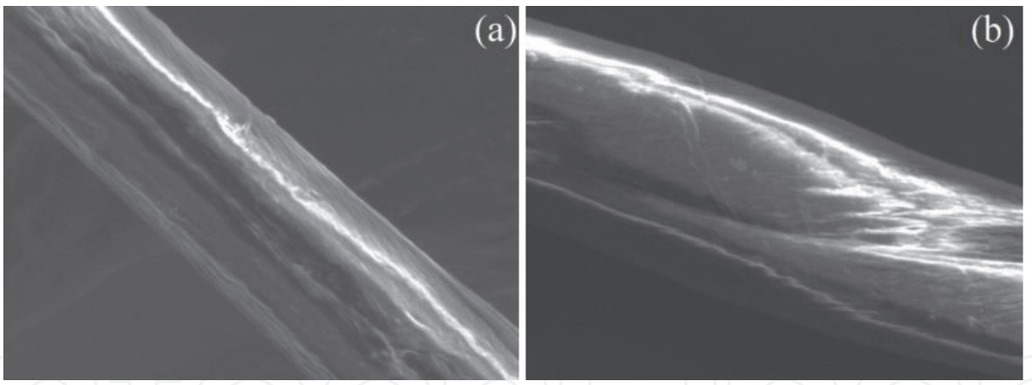


Figure 12.
SEM images of a Bio-scoured cotton fabric (a) Bio-scoured with pectinase enzyme, (b) Bio-scoured with cellulase and pectinase mixed enzyme.

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

Figure 13.
Dissociation of hydrogen peroxide.

5.3 Bleaching

Bleaching is a process for improving the whiteness of textile materials with or without removing the natural coloring matter or extraneous substances. Bleaching produces permanent and basic white effect on fabric, which is required for level dyeing and sharp printing. Among the different oxidizing and reducing bleaching agent, H_2O_2 is mostly used as a universal bleaching agent from last two decades. The dissociation of hydrogen peroxide increased with rising temperature and form perhydroxyl anion shown in **Figure 2**. Perhydroxyl ions (HO_2^-) demobilize the mobile electrons of conjugated double bonds in chromophores and caused decolorization. However, hydrogen peroxide bleaching process required high temperature and long processing time, which leads to higher energy consumption and increased fiber damage, which would cause problems in dyeing [115] (**Figure 13**).

Many researchers explored the alternative eco-friendly bleaching method for cotton processing, such as laccase/mediator or glucose-oxidase/peroxidase and bleaching with enzymatically in situ generated per acids. Lacasses with copper containing oxidoreductases enzymes used for bio bleaching to bleach textiles, modify fabric surfaces and coloration of cotton [116]. Another important bio-bleaching method for producing H_2O_2 is glucose oxidase. Generation of peroxidase with glucose oxidase requires slightly acidic to neutral conditions at low temperatures, however these conditions is insignificant. In addition, at the temperature 80-90° C and alkaline pH 11, glucose oxidase provides efficient results for improving the whiteness of the cotton fabric [117]. On the other hand, in addition of bleach activators such as Tetraacetylethylenediamine (TAED), nanoyloxybenzene sulphonate (NOBS), N-[4-(triethyl ammoniomethyl) benzoyl] caprolactum chloride (TBCC) enhances the bleaching performance. Combined laccase and glucose oxidase can perform better bleaching effect on linen fabric (**Table 11**).

5.4 Bleach clean up

In textile industry, bleaching is carried out by H_2O_2 after scouring and before dyeing. However, 10–15% of H_2O_2 retains on fabric, which can degrade the cellulose and formed pinhole on the fabric surface, it can reduce the strength of fiber.

Condition of Cotton Fabric		Whiteness (stensby degree)
Grey Fabric		52 ± 0.5
H_2O_2 bleached		80.0 ± 0.5
Enzymatic bleach		71.0 ± 1.2

Table 11.
Whiteness of different bleaching process.

Different reducing agent is used to destroy the hydrogen peroxide, or water to rinse out the hydrogen peroxide bleach. However, catalase enzyme can now be used to decompose excess H_2O_2 [118]. This eliminates the use of strong reducing agent and minimizes the water consumption. The cost of enzyme for degradation of hydrogen peroxide in bleaching effluents could be reduced by the immobilized catalase enzymes [119]. The process of bleach clean-up is very straightforward. A summary of the methodology is- 1) Drain the bleach liquor after bleaching 2) Fresh cold water filled 3) Maintain the pH is in the range 6.5–7 and the temperature 45° C 4) Add catalase (*Terminox Ultra*) enzyme 5) After 10–20 minutes checking the H_2O_2 removed by using Merck peroxide test strips 6) Start the dyeing process. Dyeing without and with bleach clean-up has shown in **Table 12**.

5.5 Removal of excess dye

The dye removal process from over dyed fabric is called as "back stripping" or "destructive stripping". Bio-enzymes used for decolorization is lignin peroxidase, manganese peroxidase and laccase. Previous studies have been investigated for color stripping from dyed textile fabric by microbial strains and their non-specific enzymatic system. The catalase enzymes from *G. lucidum* showed the ability for color stripping from the reactive black B dyed cotton fabric (**Table 13**) [120, 121].

The enzymes used for textile ETP are laccase, manganese peroxidase, lignin peroxidase and tyrosinase. These enzymes can catalyze the chlorinated phenolic compounds and halogenated organic compounds [122].

Dyeing without bleach clean-up	Dyeing with bleach clean-up
	

Table 12.
Bleach clean-up process on cotton fabric and dyeing effect.

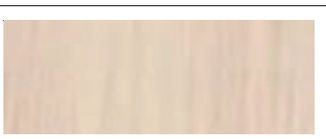
Dyed Fabric	Bio-stripping
	

Table 13.
Bio-stripping process on dyed cotton fabric.

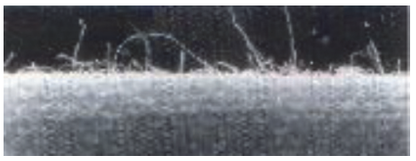
Before cellulase treatment	After cellulase treatment
	

Table 14.
Bio-polishing process on cotton fabric.

5.6 Bio-polishing

The process of removal of micro, fuzzy fibrils from the fabric surfaces through the action of cellulase enzyme is called bio polishing. It enhances the color brightness, hand feel, water absorbance property of fibers; strongly reduce the tendency for pill formation [123]. Cellulase enzymes are widely used for bio polishing.

Cellulases enzymes hydrolyze the cellulose structure by degrading β-(1-4) glycosidic linkages. Endocellulases cleave bonds along the length of cellulose chains in the middle of the amorphous region, exoglucanases act from the crystalline ends of cellulose chains and convert soluble oligosaccharides to glucose. Commercially available cellulases enzyme for bio polishing are a mixture of endogluconases, exoglucanases & cellobioses (**Table 14**).

Bio polishing is done before or after dyeing to the cotton, fabrics influence dyeability, besides improving the appearance and handle properties. Cellulase enzyme treatment enhances the post dyeing effect and resin finishing with increases softness. Endoglucanases with acid cellulase are suited for bio polishing of cellulosic fabrics [124]. The enzymatic hydrolysis of cotton also enhanced by mechanical action with the addition of surfactant. For bio polishing acid and neutral cellulases bath is maintained at 4.5–5.5 and 7 respectively, the process is heated at 55° C. Finally, the process is terminated at the temperature 85° C. The immobilization of cellulase can restrict its action to fiber surface. Various immobilization of cellulases enzyme methods improve thermal stability and reusability [125].

6. Denim manufacturing

Due to special fading effect and aging process, denims became the most popular fashion trends in recent times. For increasing softness of denim garments usually pumice stones washing are using. However, the use of natural pumice stones has many disadvantages; it can cause severe physical damage to garments, machine and stone dust can clog the machine drainage lines and large amount of back staining on the fabric. In addition, the complete rid of pumice stones; several wash is required for denim fabrics. It causes high water consumptions [126, 127].

6.1 Denim wash using neutral cellulase

Cellulase enzyme application on denim finishing has started in the late 1980s. Cellulase enzyme can remove trapped indigo dye from the denim fabric, which causes non uniform shade fading & worn looking. Bio washing with cellulase enzyme is an ecofriendly and superior quality for denim fabric. Application of neutral cellulases enzyme is active in a wide temperature range from 30° to 60° C and based upon their application pH 6.6–7 cellulase [128, 129].

6.2 Denim bleaching using laccase/mediator

Eco friendly denim bleaching has been originated in the late 1980s due to adverse effect of the conventional chemical bleaching process. By oxidizing the flavonoids of denim fabric, laccase enzyme can enhance the whiteness of the fabric. Enzymatic bleaching system leads not only damage of the denim fabric but also save water consumption. There are some successful industrial laccase enzymes for denim bleaching are used as DenLite®from Novozyme (Novo Nordisk, Denmark) and Zylite from the company Zytex (Zytex Pvt. Ltd., Mumbai, India) [130].

7. Modification of synthetic fiber by enzyme

Even though synthetic fibers are mostly hydrophobic, however improving the hydrophilicity along with some properties such as weaving comfort, anti- pilling, dyeability, antistatic charge generation by Enzymes are used. Different classes of enzymes such as cutinases, lipases and esterases are suitable for polyester modification. Less potential for surface hydrolysis of polyester modification were esterases. Esterases from *Thermobifida halotolearans* have performed for both PET and PLA surface hydrolysis [131]. Hydrolyzing the polyester has been carried out by cutinases obtained from *Aspergillus oryzae*, *Penicillium citrinum, Fusarium solani, Thermobifida fusca. Thermobifida fusca, Thermobifida celluloysitica* [132, 133]. Lipases obtained from *Humicola sp., Candida Antarctica, Thermomyces lanuginosus, Triticum aestivum. And Rhizopus delemar* considered as a suitable for polyester hydrolysis [132]. Digital printed polyester fabric was treated by lipases for improving the color fastness [133].

Laccases with a mediator have been performed to increase the hydrophilicity of nylon 66 fabrics [134]. For improving dye bath exhaustion with reactive and acid dyes on Nylon 66 fabrics were treated by proteases from *Beauveria sp.,* an amidase from *Nocardia sp.* and a cutinase from *F. solani pisi* [135]. It was confirmed that acid and disperse dyes showed higher exhaustion on the protease & lipase treated Nylon 6 [136]. Proteases from a novel *Bacillus* isolate improve hydrophilicity and cationic dye affinity of nylon fabric without affecting the mechanical properties [137]. The vinyl acetate moieties in PAN can be hydrolyzed by cutinases and lipases [138].

8. Enzymatic treatments of ETP in textile industry

Textile effluents are usually highly colored, presenting different chemical substances when discharged into waters after finishing processes. Textile effluents can be discolored through physical, chemical and biological technologies. Several researches have been carried out for the removal of dyes from industrial effluents by chemical, physical and biological techniques. The decoloration dyestuffs and recalcitrant compounds using some biological techniques such as anaerobic, aerobic and combined process [139]. WRF are the principal organisms which have been investigated for dye degradation and decolorization purposes. The major lignin mineralizing enzymes of WRF are LiP, MnP and laccase that are involved in dye degradation [140]. Other than these enzymes many oxidase including versatile peroxidase, glyoxal oxidase, aryl alcohol oxidase and oxalate decarboxylase can perform dye degradation [141]. Toxic organic compounds can be detoxified through oxidative coupling is mediated with oxidoreductases. The detoxification of toxic organic compounds through oxidative coupling is mediated with oxidoreductases [142]. Enzymes like laccase, manganese peroxidase and lignin peroxidase

catalyze the removal of chlorinated phenolic compounds [143]. Microbial oxygenases, such as monooxygenases and dioxygenases are active against a wide range of compounds [144].

9. Conclusion

Enzymes have tremendous progress in textile chemical processing to meet up the green and sustainable demand in 21st century. There are several commercially successful enzymes are amylases, cellulases, pectinases and catalase for textile wet processing. Enzyme immobilization is another important technique for highly efficient textile processes. This chapter highlights the integration of enzyme based biotreatments in textile processing. In this context, different enzymatic processes have already been developed or in the process of development for textile processing. In this regard, this chapter summarizes current developments and highlights the environment-friendly enzymatic applications. So, extensive research is required for the implementation of enzyme-based processes for both synthetic and natural fibers. Due to wide variations in the properties of individual enzymes and their reaction mechanism, there are still considerable and reliable tools for potential applications in different textile processing.

Conflict of interest

The authors have declared no conflicts of interest.

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