

ENZYMATIC TREATMENTS FOR COTTON

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Abstract: *Textile processing is a growing industry that traditionally has used a lot of water, energy and harsh chemicals. Conventional chemical processes are generally severe and fibre damage may occur. Enzymes are characterized by their ability to operate under mild conditions and as a result processes can be carried out without further damaging the fibers. Enzymes are also readily biodegradable and therefore potentially harmless and environmentally friendly. Furthermore, the use of enzymes results in reduced process times, energy and water savings, improved product quality. This work represents a review of current research and future directions on the applications of enzymatic treatments for cotton. The enzymes used in the textile field are amylases for desizing of cotton and cellulases for denim finishing and biopolishing. The application of cellulases for denim finishing and laccases for decolourization of textile effluents and textile bleaching are the most recent commercial advances.*

Keywords: enzymes, cotton, application, eco-friendly characteristics.

ENZIMSKI TRETMANI ZA PAMUK

Apstrakt: *Prerada tekstila je rastuća industrija koja tradicionalno koristi puno vode, energije i štetnih hemikalija. Konvencionalni hemijski procesi su generalno teški i može doći do oštećenja vlakana. Enzimi se odlikuju njihovim sposobnostima da rade pod blagim uslovima i kao rezultat toga procesi mogu da se odvijaju bez dodatnog oštećenja vlakana. Enzimi su takođe lako biorazgradivi i stoga potencijalno bezopasni i ekološki. Pored toga, upotreba enzima rezultira skraćenim vremenom procesa, uštedom energije i vode, poboljšanim kvalitetom proizvoda. Ovaj rad predstavlja pregled trenutnih istraživanja i budućih pravaca primene enzimskih tretmana za pamuk. Enzimi koji se koriste u tekstilnom polju su amilaze za uklanjanje skroba i celulaze za završnu obradu teksasa i biopoliranje. Primena celulaza za završnu obradu teksasa i laka za dekolorizaciju tekstilnih otpadnih voda i beljenje tekstila najnoviji su komercijalni napredak.*

Ključne reči: enzimi, pamuk, primena, ekološke karakteristike.

1. INTRODUCTION

Enzymes are biocatalysts with selective and specific activity, accelerating distinct reactions and remaining unchanged after the reaction. All enzymes are made of protein and because they are sensitive to heat, pH and heavy metal ions. Today enzymes are produced by biotechnological processes in great amounts of constant quality, and are therefore applicable to large-scale processes. In the case of natural

fibre substrates, the enzyme designer needs a certain knowledge of cotton morphology, and of the effect of any particular enzyme on the fibre components. Currently, enzymes are becoming increasingly important in sustainable technology and green chemistry. This has led to the tremendous interest among textile research community to explore exciting opportunities in industrial biotechnology which can offer new and transformative alternatives to conventional textile processing methods [1].

The conventional highly alkaline preparation of cotton can be an example. The traditional pretreatment is carried out with caustic soda at high temperature, which not only wastes energy and water, causes pollution, but also damages fabrics. Bio-preparation may be a valuable and environmentally friendly alternative to harsh alkaline chemicals for preparing cotton.

Especially in textile manufacturing the use of enzymes has a long tradition. Starch is widely used as a sizing agent. Using amylase enzymes for the removal of starch sizes is one of the oldest enzyme applications [2]. Amylases are enzymes which hydrolyse starch molecules to give diverse products, including dextrans and smaller polymers composed of glucose units [3]. Moreover, cellulases, pectinases, hemicellulases, lipases and catalases are used in different cotton pre-treatment and finishing processes [4].

Recent advances in biofinishing of cellulosic fabrics have led to multiple improvements of surface properties. The main objective of biofinishing is to upgrade the fabric by removing the protruding fibers. Biopolishing is an important finishing treatment carried out on cellulosic fabrics using acid cellulases to achieve improvement in gloss, luminosity of colours and resistance to pilling, cooler feel and clear surface [5].

The application of enzymes has many advantages compared to conventional, non-enzymatic processes. Enzymes can be used in catalytic concentrations at low temperatures and at pH-values near to neutral. Today enzymes have become an integral part of the textile processing. There are two well established enzyme applications in the textile industry. Firstly, in the preparatory area amylases are commonly used for desizing process and secondly, in the finishing area cellulases are used for softening, bio-stoning and reducing of pilling propensity for cotton goods.

Biopolishing is an important finishing treatment carried out on cellulosic fabrics using acid cellulases to achieve improvement in gloss, luminosity of colors and resistance to pilling, cooler feel and clear surface. Biopolishing of cotton fabrics carried out, either before or after the dyeing process, has an influential role on dyeability of the fabrics [6]. The disadvantages of scouring with sodium hydroxide have motivated textile industry to introduce more enhanced biological agents which would be as effective in removing non-cellulose substances as sodium hydroxide but would not have damaging effects on cellulose and would be less water and energy consum-

ing. Favorable effects of scouring have been obtained with the enzymes pectinases [7].

Problems associated with textile industry are one of the major concerns of today's green chemistry community. Global textile research arena is eager to find sustainable alternatives for existing environmental and economic constraints. Researchers are trying to find most suitable enzymes for various textile processing steps [8, 9].

This paper discusses these aspects and surveys recent developments in the field of enzyme treatments for cotton.

2. COTTON FIBRE AND HIS STRUCTURE

Cotton, the seed hair of plants of the genus *Gossypium*, is the purest form of cellulose readily available in nature. It has many desirable fibre properties making it an important fibre for textile applications. Cotton is the most important of the raw materials for the textile industry. The cotton fibre is a single biological cell with a multilayer structure. The layers in the cell structure are, from the outside of the fiber to the inside, cuticle, primary wall, secondary wall, and lumen. These layers are different structurally and chemically [10].

Cotton consists of cellulosic and non-cellulosic material. Chemically, the cotton fibre is typically about 95% cellulose and the other roughly 5% is a complex mixture of pectic substances, hemicelluloses, waxes, proteins, amino acids, and various organic and inorganic salts [11]. The outer most layer of the cotton fibre is the cuticle, covered by waxes and pectins, and this surrounds a "primary wall", built of cellulose, pectins, waxes and proteinic material. The inner part of the cotton fibre comprises the "secondary wall", subdivided into several layers of parallel cellulose fibrils, and the lumen [12].

The primary and secondary walls have different degrees of crystallinity, as well as different molecular chain orientations. The cuticle, composed of wax, proteins, and pectins, is 2.5% of the fiber weight and is amorphous. The primary wall is 2.5% of the fiber weight, has a crystallinity index of 30%, and is composed of cellulose. The secondary wall is 91.5% of the fiber weight, has a crystallinity index of 70%, and is composed of cellulose. The lumen is composed of protoplasmic residues [13]. The chemical composition of cellulose is simple, consisting of anhydroglucose units joined by β -1,4-glucosidic bonds to form linear polymeric chains [14]. The details of the composition of the cotton fibre are given in Table 1 [15].

Table 1: Cellulosic and non-cellulosic material in whole cotton fibre and in primary wall

Compounds	Whole fibre	Primary wall
Cellulose	88-96	52
Pectins	0,7-1,2	12
Waxes	0,4-1,0	7
Proteins	1,1-1,9	12
Minerals	0,7-1,6	3
Other organic compounds	0,5-1,0	14

Enzymatic hydrolysis of cotton is performed by cellulase being composed of at least three enzymes systems working together synergistically. Endo- β -(1,4)-glucanases hydrolyse chains of native cellulose, degrading structures of low crystallinity and producing free chain endings. Exo- β -(1,4)-glucanases degrade cellulose from the chain end, liberating cellobiose, which is hydrolysed by β -(1,4)-glucosidase to form glucose units [16].

A number of enzyme preparations are available in today's market for different processing steps for cotton such as desizing, bio-scouring, bleaching, bio-stoning and bio-polishing.

In Table 2 are given some representative examples of commercial enzyme preparations for cotton processing.

Table 2: Some examples of commercial enzyme preparations for cotton processing

Commercial preparation	Enzymes	Enzyme producer
Desizing		
Aquazyme	Amylases	Novozymes (Denmark)
Optisize	Amylases	Dupont (USA)
BEISOL	Amylases	CHT/BEZEMA Group (Germany)
Ecostone A400	Amylases	AB Enzymes (Germany)
Amylazyme	Amylases	Megazyme (Ireland)
Bioscouring		
Scourzyme	Pectinase	Novozymes (Denmark)
PrimaGreen EcoScour	Pectate lyase	Pectate lyase Dupont (USA)
Palkoscour	Multi-component enzyme	Maps Enzymes Limited (India)
Bleach clean-up		
Biotouch CAT200	Catalase	AB Enzymes (Germany)
Palkoperox	Catalase	Maps Enzymes Limited (India)
PrimaGreen Oxy	Catalase	Dupont (USA)
Denim washing		
DeniMax	Cellulases	Novozymes (Denmark)
BEIZYM	Cellulases	CHT/BEZEMA Group (Germany)
ROCKSOFT	Cellulases	Dyadic International, Inc. (USA)
ECOSTONE	Cellulases	AB Enzymes (Germany)
Palkowash	Cellulases	Maps Enzymes Limited (India)
Denistone	Cellulases	Denimist Chem. Company (Turkey)
Cellazyme C	Cellulases	Megazyme (Ireland)
Biopolishing		
Cellusoft	Cellulases	Novozymes (Denmark)
Primafast	Cellulases	Dupont (USA)
ROCKSOFT	Cellulases	International, Inc. (USA.)

3. ENZYMATIC COTTON PROCESSING

3.1. Desizing

For woven cotton fabrics sizing is a complementary process that is performed on warp yarns for additional strength, resistance to abrasion and better weaving efficiency during the weaving process. As the sizing agent, starch and its derivatives are the most common because of easy availability and relatively low cost. However, the presence of these sizing agents in cotton causes several problems and hence the sizes have to be removed. Desizing is the process of removing the sizing agent from woven cotton fabrics in order to prepare the fabric for further processing. Starch hydrolysing enzymes, particularly α -amylases, are often used in the desizing of cotton fabrics. The best pH value for the α -amylase is between 5.5 and 7.5. Desizing is usually carried out at temperatures at least 70°C, and higher temperatures are preferred. Availability of amylase preparations active at these temperatures has opened up the possibility of performing bio-desizing at temperatures higher than 70°C. Enzymatic desizing of cotton by the use of α -amylases is state of art since several decades [17]. Bio-desizing is preferred due to their high efficiency and specific action. Amylases bring about complete removal of the size without any harmful effects on the fabric besides eco friendly behavior.

3.2. Biostoning

Microbial cellulases find applications in textile industries as biostoning of jeans, biopolishing of textile fibers, improved fabrics quality, improved absorbance property of fibers, softening of garments, improved stability of cellulosic fabrics, removal of excess dye from fabrics etc. [5, 18]. Bio-stoning and biopolishing are the best-known current textile applications of cellulases. The second application of enzymes to cotton finishing is the replacement of the stone-wash process of denim material by the use of cellulases. However, denim washing with natural pumice stones has some unavoidable disadvantages. By using this enzyme treatment, the amount of stone material required can be reduced or even completely replaced. A well-known example is the stone-washing of denim jeans. The blue denim is faded by the abrasive action of pumice stones. The commercially available cellulases are a mixture of enzymes: endoglucanases, exoglucanases and cellobiases. The application of cellulases in textile processing started in the late 1980s with denim finishing. Currently, in addition to biostoning, cellulases are also used to process cotton and other

cellulose-based fibres. Cellulases are usually classified by the pH range in which they are more effective and, accordingly, acid cellulase, neutral cellulase and alkaline cellulase. In the biostoning process, cellulases (neutral or acidic) are used to accelerate the abrasion by loosening the indigo dye on the denim [19]. Today, a variety of cellulase preparation is available for denim washing and more than 80% of denim finishers use cellulases either alone or in combination with other enzymes and pumice stones in order to obtain a specific look [20]. The advantages in the replacement of pumice stones by a cellulase-based treatment include less damage of fibers, increased productivity of the machines, and less work-intensive and environment benign [21].

3.3. Bleaching

Bleaching is one of the fundamental wet processing steps prior to cotton dyeing. The purpose of cotton bleaching is to decolourise natural pigments and to confer a pure white appearance. Currently, the most common industrial bleaching agent for cotton is hydrogen peroxide, which is usually applied at alkaline pH and temperatures close to boiling. A huge amount of water is needed to remove residual peroxide from fabrics which would cause problems in dyeing. After bleaching cotton with hydrogen peroxide, the bleaching liquor cannot be used for the next treatment step-dyeing, because of the oxidative effect of the residual peroxide. The degradation of this residual peroxide in the bleaching bath by the enzyme catalase makes replacing of the treatment liquor, or the washing of the goods, unnecessary. Thus, the same liquor can be used for the next processing step, leading to a saving of time, waste water and energy.

Several authors have successfully demonstrated the use of laccases in cotton bleaching based on the assumption that these enzymes could also decolorize or eliminate colored flavonoids of cotton by attacking phenolic hydroxyl groups [22, 23].

Glucose oxidase (GOD) is another enzyme with great potential in cotton bleaching due to its highly specific catalytic action on β -D-glucose to produce hydrogen peroxide. The reuse of the desizing and scouring treatment baths containing glucose generated during these processes as a substrate for hydrogen peroxide generation by action of glucose oxidase for cotton bleaching seems an interesting prospect. Hydrogen peroxide produced by glucose oxidase may be a good alternative of commercially available hydrogen peroxide that is currently the most exten-

sively used bleaching agent in conventional bleaching process [24].

3.4. Bioscouring

The cuticle layer of a cotton fibre has a complicated composition containing cutin, wax, pectin and protein. In conventional pre-treatment these substances are removed by a strong alkaline treatment at high temperatures after the enzymatic desizing of raw cotton fabrics with α -amylases. This inspecific alkaline scouring process has a high energy, water and alkali consumption and can also cause a damage of the cellulosic material. Enzymatic scouring promotes the efficient interruption removal of non-cellulosic impurities without negatively affecting the fabric or the environment. Generally, bio-scouring is carried out either in acidic or alkaline media depending on the type of pectinases at 50–60°C [25].

Cotton bioscouring could be as much efficient as the conventional alkaline treatment in terms of physicochemical properties such as, wettability, whiteness index, polymerization degree, crystallinity index, color depth, brightness, softness, absorbency, weight loss as well as low-stress mechanical properties [26, 27, 28].

3.5. Biopolishing

Biopolishing (de-pilling enzymes) is a biological process in which the cellulose acts on the surface of the fabric. The enzyme molecule is more than a thousand times larger than a water molecule and is therefore too large to penetrate the interior of a cotton fiber.

The objective of the process is elimination of micro fibrils of cotton through the action of cellulase enzyme. The acidic cellulases, when used in biopolishing, offers a number of benefits such as improve softness and water absorbance property of fibres, strongly reduce the tendency for pill formation, and provide a cleaner surface structure with less fuzz [29].

4. CONCLUSIONS

Biotechnology offers a wide range of alternative environmentally-friendly processes for the textile industry to complement or improve the conventional technologies. The use of various enzyme is in the early stages of development but their innovative applications are increasing and spreading rapidly into all areas of textile processing.

The progress of the enzymatic technologies in textile processing is attracting worldwide attention. Enzymatic processes are already well established in the cotton industry. Enzymes have become an indispensable part of the textile processing and are utilized for a wide variety of applications in modern textile industry.

New enzymes with high specific activity, increased reaction speed, and tolerance to more extreme temperatures and pH could result in development of continuous processes. The textile industry can greatly benefit from the expanded use of these enzymes as non-toxic, environmentally friendly compounds. Textile processing industry is characterized by high consumption of energy and resources and time consuming processes. Enzymes are not only beneficial from ecological point of view but they are also saving lot of money by reducing water and energy consumption which ultimately reduce the cost of production.

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