

## ENZYME APPLICATIONS IN TEXTILE PREPARATORY PROCESS: A REVIEW

Dr KiroMojsov\*

### **Abstract:**

Industrial use of biotechnology is bringing about new products and processes aimed at the use of renewable resources, as well as the application of green technologies with low energy consumption and environmentally healthy practices. Textile processing is a growing industry that traditionally has used a lot of water, energy and harsh chemicals. Due to the ever-growing costs for water and energy worldwide investigations are carried out to substitute conventional chemical textile processes by environment-friendly and economically attractive bioprocesses using enzymes. This work represents a review of enzyme applications in textile preparatory processes. After hot bleaching enzymatically pre-treated cotton exhibits similar or even better properties compared to conventionally desized, alkaline scoured and bleached cotton. The combined use of the enzymes allows to omit the alkaline scouring without a loss of quality in the finishing result. The described enzymatic procedure is accompanied by a significant lower demand of energy, water, chemicals, time and therefore costs. So it has advantages as well in terms of ecology as in economy.

**Key words:** Textile Preparatory Process, Bio-preparation, Eco-Friendly Characteristics, Enzymes.

\*Assistant Professor, Dept. of Textil Technology, University "Goce Delcev" Stip, Macedonia.

### 1.Introduction:

Caused of the evergrowingcosts for energy and polluted waste water, enzymatic technologies will stay inthe focus of science and technique, and their relevance will increase significantly in thefuture. Enzymes, biological catalysts with high selectivities, have been used in the foodindustry for hundreds of years, and play an important role in many other industries(washing agents, textile manufacturing, pharmaceuticals, pulp and paper). Currently,enzymes are becoming increasingly important in sustainable technology and greenchemistry. Modern wet processing industries are followed the enzymes in the preparatory process instead of using harmful chemical because enzyme are more convenient, effective and environment friendly.

Especially in textile manufacturing the use of enzymes has a long tradition. Starch is widely used as a sizing agent, being readily available, relatively cheap and based on natural, sustainable raw materials [Lange 1997]. About 75% of the sizing agents used worldwide are starch and its derivatives [Opwis et al. 1999]. Using *amylase* enzymes for the removal of starch sizes is one of the oldest enzyme applications [Ciechanska and Kazimierezak 2006; Marcher et al. 1993]. Amylases are enzymes which hydrolyse starch molecules to give diverse products, including dextrans and smaller polymers composed of glucose units [Gupta et al. 2003]. These partly degraded oligosaccharides can not be reused, and are usually discharged, contributing large amounts of Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) to effluent streams [Opwis et al.1999]. Moreover, cellulases, pectinases, hemicellulases, lipases and catalases are used indifferent cotton pre-treatment and finishing processes [Meyer-Stork 2002].Other natural fibers are alsotreated with enzymes. Examples are the enzymatic degumming of silk with sericinases[Gulrajani1992], the felt-free-finishing of wool with proteases [Fornelli 1994] or the softening of jute withcellulases and xylanases [Kundu et al. 1991].The application ofenzymes has many advantages compared to conventional, non-enzymatic processes.Enzymes can be used in catalytic concentrations at low temperatures and at pH-valuesnear to neutral. Their high substrate selectivity allows a very gentle treatment of thegoods. Moreover, enzymes are biologically degradable and can be handled without risk[Uhlig 1991;Ruttloff 1994].

Beforecotton fabric or yarn can be dyed, it goesthrough anumber of preparatory processes. One of the mostnegative environmental impacts from textile production isthe traditional processes used to prepare cotton fibre, yarnor fabric. The conventional highly alkaline preparation ofcotton 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 damage fabrics. About 75% of the organic pollutants arising from textile finishing are derived from preparation of cotton goods. In the conventional preparatory process concentrated sodium hydroxide solution and hydrogen peroxide or sodium hypochlorite solutions are applied for removing the impurities from raw cotton. On the fibre level oxidative damage may occur and be reflected in a lower degree of polymerization and decreased tensile strength. Bio-preparation may be a valuable and environmentally friendly alternative to harsh alkaline chemicals for preparing cotton. The relating properties of amylase, pectinase, and mixed-enzyme (amylase, pectinase, cellulase, xylanase and lipase) provides a theoretical support for developing enzymatic pretreatment for cotton fabrics. Different individual enzymes and their mixtures were studied on the efficiency of pretreatment by monitoring the treated cotton fabrics for residual starch and pectin content, whiteness, tearing strength and so on [Hsieh et al. 1996; Robner 1993; Hartzell-Lawson and Durrant 1998; Hossain and Uddin 2011]. Enzymes can be used to prepare cotton under very mild conditions. The environmental impact is reduced since there is less chemicals in the waste and a lower volume of water. The bio-preparation process decreases both effluent load and water usage to the extent that the new technology becomes an economically viable alternative. Instead of using hot sodium hydroxide to remove the impurities and damaging parts of the fibre, enzymes do the same job leaving the cotton fibre intact.

## 2. Literature Review:

### 2.1 Cotton fibre and his structure:

Cotton is the most important of the raw materials for the textile industry. Cotton grows as unicellular fibre on seeds. The mature cotton fibre forms a highly convoluted flat ribbon, varying in width between 12 and 20  $\mu\text{m}$ . Cotton fibres have a fibrillar structure. A mature cotton fibre is composed of several concentric layers and a central area called lumen. A cuticle, a primary cell wall, intermediary wall as well as secondary cell wall follow each other from the outer to the inner part of the fibre. The whole cotton fibre contains 88 to 96.5% of cellulose, the rest are uncellulosic substances, called in crusts (Karmakar, 1999). The primary wall in mature fibres is only 0.5-1  $\mu\text{m}$  thick and contains about 50% of cellulose. Noncellulosic constituents consist of pectins, fats and

waxes, proteins and natural colorants. The secondary wall, containing about 92-95% cellulose, is built of concentric layers with alternatic shaped twists. The layers consist of densely packed elementary fibrils, organized into microfibrils and macrofibrils. They are held together by strong hydrogen bonds. The lumen forms the centre of the fibres. Cotton is composed almost entirely of the polysaccharide cellulose. Chemical composition of cellulose is a linear (1→4)-linked polymer of β-D-glucopyranose. The degree of polymerization of cellulose varies with its source and the processing stage of the cellulosic material [Lewin and Pearce1998].

The primary wall is about 1 μm thick and comprises only about 1 % of the total thickness of cotton fibre. The major portion of the noncellulosic constituents of cotton fibre is present in or near the primary wall. Noncellulosic impurities, such as fats, waxes, proteins, pectins, natural colorants, minerals and water-soluble compounds found to a large extent in the cellulose matrix of the primary wall and to a lesser extent in the secondary wall strongly limit the water absorbency and whiteness of the cotton fiber [Yamamoto et al. 2001]. During the growth of the fibres uncellulosic substances, especially waxes, protect them against the loss of water, insects and other outside influences that might damage the fibres. Furthermore, they also protect them against mechanical damage that can occur as a result of processing.

Pectin is located mostly in the primary wall of the fibre. It is composed of a high proportion of D-galacturonic acid residues, joined together by α(1→4)-linkages. The carboxylic acid groups of some of the galacturonic acid residues are partly esterified with methanol. Pectic molecule can be called a block-copolymer with alternating the esterified and the non-esterified blocks. In the primary cell wall pectin is covalently linked to cellulose or in other plants to hemicellulose, or that is strongly hydrogen-bonded to other components. Pectin, there is 0.4 to 1.2% of pectin in cotton fibres, acts as an adhesive, a glue between the cellulose and uncellulosic substances. The mostly water-insoluble pectin salts serve to bind the waxes and proteins together to form the fiber's protective barrier.

Raw cotton fibres have to go through several chemical processes to obtain properties suitable for use. With scouring, non-cellulose substances (wax, pectin, proteins, hemicelluloses...) that surround the fibre cellulose core are removed, and as a result, fibres become hydrophilic and suitable for bleaching, dyeing and other processing.

By removing pectin, it is easier to remove all other uncellulosic substances. The processes of bioscouring that are in use today are based on the decomposition of pectin by the enzymes called *pectinases*.

## 2.2 Enzymes, classification, action and properties

Enzymes are biological catalysts that accelerate the rate of chemical reactions [Cavaco-Paulo & Gübitz 2003]. The reaction happens with lower activation energy which is reached by forming an intermediate enzyme – substrate. In the reaction itself the enzymes are not used up, they do not become a part of the final product of the reaction, but only change the chemical bonds of other compounds. After the reaction is complete, the enzyme is released again, ready to start another reaction. Usually most enzymes are used only once and discarded after their catalytic action.

All known enzymes are proteins. They therefore consist of one or more polypeptide chains and display properties that are typical of proteins. Some enzymes require small non-protein molecules, known as cofactors, in order to function as catalysts (Jenkins 2003).

Generally they are active at mild temperatures. Above certain temperature the enzyme is denatured. Enzymes have a characteristic pH at which their activity is maximal. Extreme pH values influence on the electrostatic interactions within the enzyme, leading to inactivation of enzyme. Other important factors that influence the effect of enzymatic processes are the concentration of enzyme, the time of treatment, additives like surfactants and chelators and mechanical stress [Tavčer 2011].

Enzymes are very specific in comparison to inorganic catalysts such as acids, bases, metals and metal oxides and they differ in several important characteristics. Enzyme catalysed reactions are several times faster than chemically catalysed ones [Cavaco-Paulo & Gübitz 2003]. Enzyme can break down particular compounds. The molecule that an enzyme acts on is known as its substrate, which is converted into a product or products. For each type of reaction in a cell there is a different enzyme and they are classified into six broad categories namely hydrolytic, oxidising and reducing, synthesising, transferring, lytic and isomerising. The essential characteristic of enzymes is catalytic function. Consequently, the original attempt to classify enzymes was done according to 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), to put some order to the hundreds of enzymes that had been discovered by that point and establish a standardized terminology that could be used to systematically name newly discovered enzymes. The EC classification system is divided into six categories of basic function:

- EC1 Oxidoreductases: catalyze oxidation/reduction reactions.
- EC2 Transferases: transfer a functional group.
- EC3 Hydrolases: catalyze the hydrolysis of various bonds.
- EC4 Lyases: cleave various bonds by means other than hydrolysis and oxidation.
- EC5 Isomerases: catalyze isomerization changes within a single molecule.
- EC6 Ligases: join two molecules with covalent bonds.

Each enzyme is described by a sequence of four numbers preceded by “EC”. The first number broadly classifies the enzyme based on its mechanism.

Enzymes can work at atmospheric pressure and in mild conditions with respect to temperature and acidity (pH). Most enzymes function optimally at a temperature of 30°C-70°C and at pH values, which are near the neutral point (pH 7). Enzyme processes are potentially energy saving and save investing in special equipment resistant to heat, pressure or corrosion. Due to their efficiency, specific action, the mild conditions in which they work and their high biodegradability, enzymes are very well suited for a wide range of industrial applications.

Enzymes work only on renewable raw materials. Fruit, cereals, milk, fats, cotton, leather and wood are some typical candidates for enzymatic conversion in industry. Enzymes are used in the textile industry because they accelerate reactions, act only on specific substrates, operate under mild conditions, are safe and easy to control, can replace harsh chemicals and enzymes are biologically degradable i.e. biodegradable [Uhlig 1991; Ruttloff 1994].

Properties of enzymes used in textiles:

### 1. Enzyme accelerates the reaction

- An enzyme accelerates the rate of particular reaction by lowering the activation energy of reaction.
- The enzyme remains intact at the end of reaction by acting as catalyst.

## 2. Enzymes operate under milder condition

- Each enzyme have optimum temperature and optimum pH i.e. activity of enzyme at that pH and temperature is on the peak.
- For most of the enzyme activity degrades on the both sides of optimum condition.

## 3. Alternative for polluting chemicals

- Enzymes can be used as best alternative to toxic, hazardous, pollution making chemicals.
- Also some pollutant chemicals are even carcinogenic. When we use enzymes there is no pollution.

## 4. Enzyme acts only on specific substrate

- Most enzymes have high degree of specificity and will catalyse the reaction with one or few substrates.
- One particular enzyme will only catalyse a specific type of reaction. Enzymes used in desizing do not affect cellulose hence there is no loss of strength of cotton.

## 5. Enzyme are easy to control

- Enzymes are easy to control because their activity depends upon optimum condition.

## 6. Enzymes are biodegradable

- At the end of reaction in which enzymes used we can simply drain the remaining solution because enzymes are biodegradable and do not produce toxic waste on degradation hence there is no pollution.

### 2.3 Production of enzymes from microorganisms

Commercial sources of enzymes are obtained from three primary sources, i.e., animal tissue, plants and microbes. These naturally occurring enzymes are quite often not readily available in sufficient quantities for food applications or industrial use. However, by 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. Most of the industrial enzymes are produced by a relatively few microbial hosts like *Aspergillus* and *Trichoderma* fungi, *Streptomyces* fungi imperfecti and *Bacillus* bacteria. Yeasts

are not good producers of extracellular enzymes and are rarely used for this purpose. There is a large number of microorganisms which produce a variety of enzymes [Boyer 1971; Fersht 2007]. Microorganisms producing enzymes of textile importance are listed in Table 1.

Table 1. Microorganisms producing enzymes of textile importance

Microorganisms	Enzymes
<b>1. Bacteria</b>	
<i>Bacillus subtilis</i>	<i>Amylase</i>
<i>B. coagulans</i>	<i>α-amylase</i>
<i>B. licheniformis</i>	<i>α-amylase, protease</i>
<b>2. Fungi</b>	
<i>A. niger</i>	<i>Amylases, protease, pectinase, glucose oxidase</i>
<i>A. oryzae</i>	<i>Amylases, lipase, protease</i>
<i>Candida lipolytica</i>	<i>Lipase</i>
<i>P. notatum</i>	<i>Glucose oxidase</i>
<i>Rhizopus sp.</i>	<i>Lipase</i>
<i>Trichoderma reesei</i>	<i>Cellulase</i>
<i>T. viride</i>	<i>Cellulase</i>
<i>Ascomycetes</i>	<i>α-amylase</i>
<i>Basidiomycetes</i>	<i>α-amylase</i>
<i>Aspergillus sp.</i>	<i>Pectinase, lipase</i>

The enzymes are inducible, i.e., produced only when needed, and they contribute to the natural carbon cycle. Several methods, such as submerged fermentation (SmF), solid-state fermentation (SSF) and whole cell immobilization have been successfully used for enzyme production from

various microorganisms [Cao et al. 1992; Kapoor et al. 2001]. Agro-industrial residues such as wheat bran, rice bran, sugarcane bagasse, corncobs, and apple pomace are generally considered the best substrates for processes [Blandino et al. 2002; Maldonado and Saad 1998; Pandey et al. 1999].

For practical applications, immobilization of microorganisms on solid materials offers several advantages, including repeated usage of enzyme, ease of product separation and improvement of enzyme stability [Kapoor et al. 2001].

#### 2.4 Enzyme applications in textile preparatory process

The fabric should be free from natural and added impurities before it goes colouration. Some of the chemicals like caustic soda, soda ash, hydrogen peroxide, hydrochloric acid, detergent and auxiliaries that are used at different stages preparatory process to remove such an impurities are found to be harmful to the environment. Modern wet processing industries are followed the enzymes in the preparatory process instead of using harmful chemical because enzyme are more convenient, effective and environment friendly. 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.

Especially in textile manufacturing the use of enzymes has a long tradition. Enzymes used in textile processing and their effects are shown in Table 2. Hydrolases type of enzyme is mostly used in textile processing and now to some extent is oxidoreductase, but their innovative applications are increasing and spreading rapidly into all areas of textile processing.

Table 2. Enzymes used in textile processing and their effects

Enzyme	Effect
Amylase	Desizing (to decompose starches applied in sizing)
Catalase	Act on H <sub>2</sub> O <sub>2</sub> to decompose it into water&oxygen
Protease, lipase and	When combined, act on proteins, pectins and natural waxes to effect

pectinase	scouring
Laccase	Decomposes indigo molecules for wash-down effect on denim
Cellulase	Break down cellulosic chains to remove protruding fibres by degrading & create wash-down effect by surface etching on denims etc.
Cellulases and Hemicellulases	Biostoning of jeans Desizing of CMC Stylish effect on cellulose fibres
Pectinase	Breaks down pectins in scouring
Proteases	Scouring of animal fibres, degumming of silk and modification of wool properties
Lipases	Elimination of natural triglycerides (in scouring) or present in desizing (tallow compounds)

The enzymatic desizing of cotton with  $\alpha$ -amylases is state-of-the-art since many decades (Marcher et al. 1993). The amylose is bioconverted to 100% by the  $\alpha$ -amylase into glucose whereas the amulpectin is converted to 50% into glucose and maltose. 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. Moreover, *cellulases*, *pectinases*, *hemicellulases*, *lipases* and *catalases* are used in different cotton pre-treatment and finishing processes (Meyer-Stork, 2002).

*Cellulase* enzymes were first introduced after decades of amylase usage as an industry standard for desizing processes. Today, efforts within the textile industry seem to focus on replacing traditional natural-fiber scouring processes with enzyme-based solutions. As the purpose of scouring is to remove natural impurities such as polymeric substances like pectins, waxes and xylomannans, among others from cotton or other natural fibers, there are plenty of enzyme that can act on such impurities. Alkaline *pectinases*, which loosens fiber structure by removing pectins between cellulose fibrils and eases the wash-off of waxy impurities, is the key enzyme for a

bioscouring process. Other enzymes including *cellulases*, *hemicellulases*, *proteases* and *lipases* have been tested, but at present, the only commercial bioscouring enzyme products are based on *pectinases*.

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  $\alpha$ -*amylases*. This inspecific alkaline scouring process has a high energy, water and alkali consumption and can also cause a damage of the cellulosic material.

The group of enzymes called *laccases*, or *phenol oxidases*, possesses the ability to catalyze the oxidation of a wide range of phenolic substances, including indigo. The first commercial use of *laccases* in the textile industry has been in the denim washing process, where *laccases* enhance abrasion levels and bleach indigo.

An efficient biopreparation process should be based on a combination, preferably simultaneously, of enzymes for desizing, scouring and bleaching in one bath. Success in developing such a process would result in a simple process, including savings in water, time and energy consumption.

#### 2.4.1 Enzymatic Desizing

During the weaving process the warp (chain) threads are exposed to considerable mechanical strain. In order to prevent breaking, they are usually reinforced by coating (sizing) with a gelatinous substance (size). Cotton fibres and cotton/synthetic fibre blends are sized, i.e. they are coated with a strengthening, adhesive like material (usually starch in native or modified form or a starch based material) to prevent damage during the weaving process. Small amounts of fats or oils may be also added to the size, with the aim of lubricating the warp coat surface. Sizing is the process where size is applied to warp yarns for weaving. The purpose of size is to protect the yarn from the abrasive action of the loom. The size must be removed (desizing) before a fabric can be bleached and dyed, since it affects the uniformity of wet processing. Desizing is the process of removing the size material from the warp yarns in woven fabrics. Sizing agents are selected on the basis of type of fabric, environmental friendliness, ease of removal, cost considerations, effluent treatment, etc. Desizing, irrespective of what the desizing agent is, involves impregnation of the

fabric with the desizing agent, allowing the desizing agent to degrade or solubilise the size material, and finally to wash out the degradation products. Various types of desizing methods are available. If the size is water soluble, an alkali wash with detergents may be used. Oxidative chemicals such as persulphate and alkali or bromide and alkali may also be used at high pH and temperature. Alternative eco-friendly desizing agents are available in the market in the form of enzymes. *Amylases* are used to remove starch. The major desizing processes are:

- Enzymatic desizing of starches on cotton fabrics
- Oxidative desizing
- Acid desizing
- Removal of water soluble sizes

Enzyme desizing is the most widely practiced method of desizing starch. In the textile industry *amylases* are used to remove starch-based size for improved and uniform wet processing. *Amylase* is a hydrolytic enzyme which catalyses the breakdown of dietary starch to short chain sugars, dextrin and maltose. The advantage of these enzymes is that they are specific for starch, removing it without damaging to the support fabric. An amylase enzyme can be used for desizing processes at low-temperature (30-60°C) and optimum pH is 5,5-6,5 [Cavaco-Paulo and Gübitz, 2003].

The enzymatic desizing process can be divided into three stages :

**Impregnation** : Enzyme solution is absorbed by the fabric. This stage involves thorough 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. Under these conditions there is sufficient enzyme stability (temperature, pH, calcium ion level govern the stability). During this stage gelatinization of the size (starch) 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 (with NaOH) at the highest possible temperature.

The use of the enzyme depends on the kind of size. If there are chemicals used in the size to which the enzyme is not resistant then it is impossible to use the enzyme.

#### 2.4.1.1 Environmental and Economic Benefits:

- Avoidance of chemical fiber damage
- Increased biodegradability of effluent
- Less handling of aggressive chemicals

#### 2.4.2 Enzymatic Scouring (Bioscouring)

Scouring is removal of non-cellulosic material present on the surface of the cotton. Raw cotton contains about 90 % of cellulose and various noncellulosics such as waxes, pectins, proteins, fats, lignin-containing impurities and colouring matter. The goal of the cotton preparatory process is to remove the hydrophobic and noncellulosic components and produce highly absorbent fibres that can be dyed and finished uniformly. In the conventional and chemical intensive process concentrated sodium hydroxide solution and additional hydrogen peroxide and sodium hypochlorite solutions are applied for removing the impurities from greige cotton. The mild reaction conditions offered by enzymatic treatment provide an environmentally friendly alternative. The starting studies of enzyme treatment for scouring that is, cleaning of cotton fibres, were carried out by German researchers [Schacht et al. 1995; Rößner 1995], and they included *pectinases*, *proteases* and *lipases* that act upon impurities and *cellulases* which hydrolyse the cellulose chain. Many other researchers followed in their path. They established that *cellulases* and *pectinases* are the most effective ones, *lipases* less with *proteases* being the least effective. On the basis of their studies they concluded that a simple procedure with *pectinases* in presence of non-ionic surfactant is sufficient to attain good absorbency [Li & Hardin 1998; Hartzell & Hsieh 1998; Buchert et al. 2000; Traore & Buschle-Diller 2000; Galante & Formantici 2003]. *Pectinases*, *cellulases*, *proteases* and *lipases* have been investigated most commonly and compared to alkaline scouring. Favourable effects of scouring have been obtained with the enzymes *pectinases* [Etters 1999; Hartzell & Hsieh 1998; Li & Hardin 1998; Csiszar et al. 2001; Anis & Eren 2002; Buchert et al. 2000], that catalyse the hydrolysis of pectin substances. Three main types of enzymes are used to break down pectin substances [Jayani 2005]:

*pectin esterases, polygalacturonases and pectin lyases*. In generally *cellulase* and *pectinase* are combined and used for Bioscouring. In this *pectinase* penetrate into the fibre through the cuticle in places where there are cracks and microscopes, and catalyse the reaction of hydrolysis of the pectin molecules, whereas *cellulase* can destroy cuticle structure by digesting the primary wall cellulose immediately under the cuticle of cotton [Li & Hardin 1998]. But at present, the only commercial bioscouring enzyme products are based on *pectinases*. Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) of enzymatic scouring process are 20-45 % as compared to alkaline scouring (100 %). Total Dissolved Solid (TDS) of enzymatic scouring process is 20-50% as compared to alkaline scouring (100%). Handle is very soft in enzymatic scouring compared to harsh feel in alkaline scouring process. Enzymatic scouring makes it possible to effectively scour fabric without negatively affecting the fabric or the environment. It also minimises health risks since operators are not exposed to aggressive chemicals. Bioscouring process provides many advantages, such as reduced water and wastewater costs, reduced treatment time and lower energy consumption because of lower treatment temperature (the optimal temperature is from 40 to 60°C) [Li & Hardin 1998]. Moreover, the weight loss in fabric is reduced, and fabric quality is improved with a superior hand and reduced strength loss [Pawar et al. 2002]. The potential advantages that make the enzyme scouring commercially appealing, are a higher quality of the fibres (softer to the touch and better strength), less waste waters, economy of energy and compatibility with other procedures, equipment and materials [Cavaco-Paulo & Gübitz 2003].

Beside the temperature, the pH of the environment is crucial for the activity and stability of the enzyme. The majority of enzymes are active in the pH range between 5 and 9. Alkaline or acidic environment depends on the type of pectinases. 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) are known, both types have similar effects on cotton [Aly et al. 2004, Tzanov et al. 2001; Yachmenev et al. 2001].

In the starting researches, longer times of treatment were pointed out as the main disadvantage of the enzyme scouring [Sawada et al. 1998]. By developing new *pectinases*, the times of treatment have shortened. Thus, the present forms of *pectinases* need 30 to 60 minutes for their functioning [Aly et al. 2004; Hartzell-Lawson & Durant 1998].

Added surfactants also have a big influence on removing noncellulose impurities. Anionic surfactants can form complexes with proteins and influence the structure. Cationic surfactants have a similar influence on proteins, however, with a lower affinity. Non-ionic surfactants are compatible with enzymes and do not break their three-dimensional structure. They accelerate the effects of scouring due to lowering the surface tension of the fibres and an easier penetration of the enzyme into micropores and cracks of the fibres. Surfactants take an active part in removing waxes and grease [Li & Hardin 1998; Tzanov et al. 2001; Durden et al. 2001].

Enzyme inhibitors such as heavy metals and ionic detergents as well as product on the basis of formaldehyde need to be avoided since they deactivate the enzyme [Cavaco-Paulo & Gübitz 2003; Li & Hardin 1998].

One of the possibilities of improving the degradation of pectin is also the addition of the chelating agent. It is well known that calcium ions play an important part in the structure of the pectin, the  $Ca^{2+}$  ions bond the nonestrified molecules of pectin. By removing the ion, the structure of the pectin is destabilised which enables the *pectinases* an easier access to the areas of attack. Therefore, the use of weaker chelating agents, such as phosphate, silicate and carbon chelating agents, is recommended [Durden et al. 2001; Preša & Tavčer 2008].

*Pectinase*, as the name suggests, hydrolysis pectins that are present in cotton as a non-cellulosic impurity. The best kinds of *pectinase* are those, which can function under slightly alkaline conditions even in the presence of chelating agents. Such enzymes are called "alkaline pectinases". Most conventional *pectinases* are usually inactive under these commercially useful conditions, their optimum activity lying in the slightly acidic region.

Bioscouring is a process by which alkaline stable *pectinase* is used to remove pectin and waxes selectively from the cotton fibre. Unlike the traditional alkaline scouring, this process is substrate-specific and does not alter the cellulose component. The treatment here is also rather lower than that of the high-temperature alkaline scouring. The bioscouring however does not swell or remove the seed coat fragments called motes. This can be beneficial when scouring for the "natural look", because of the mote and colour retention in the cotton fabrics scoured with this process, pastel or light shades need to be bleached prior to dyeing, but medium to dark shades can be dyed directly after bioscouring. During the *pectinase* treatment the pectin content of cotton fibre can be decreased by about 30 %. Removal of pectin results in lower amounts of waxes on the cotton

surface and subsequently in improved water absorbency of the fabric, which supports the hypothesis of chemical linkage between pectin and waxes. Pectin acts as a sort of cement or matrix that stabilizes the primary cell wall of the cotton fibres.

Waxes have a melting point about 70 °C, therefore during pretreatment they melt and disperse into the treatment bath or they are redistributed on the fibre surface and the thickness of the fabrics increases.

Novozymes, Bayer and Dexter Chemical Corporation have introduced an enzymatic alternative for scouring woven and knitted cotton fabrics in the textile industry on the basis of an alkaline *pectinase* (DextrolBioscour 3000) produced by a genetically modified *Bacillus* strain. For cotton knits, enzyme is added in this step. The temperature is brought to 57 °C and held for 10 minutes. This is the actual bioscour part of the procedure. The bath is then heated to 95 °C to melt and emulsify waxes and held for 5 minutes. The scour is followed by at least one 80 °C rinse before proceeding for dyeing. The later modifications include reducing the time used for rinsing by skipping the drain step and going directly to another flow wash. Among other modifications, at 50 °C rinse prior to the bioscour process has proved to be effective in helping remove knitting oils and reducing foam levels. For cotton woven fabrics, batch process, pad-batch bioscour as well as continuous bioscouring have also been suggested. The bioscouring process results in textiles being softer than those scoured in the conventional sodium hydroxide process [Nierstrasz and Warmoeskerken 2003].

After the bioscouring the cotton fibres are darker than after alkaline scouring [Preša&Tavčer 2009; Tavčer 2008].

Bioscouring can also be used for mixtures of cotton and silk, wool and cashmere.

### 2.4.3 Enzymatic Bleaching

Scouring is regularly followed by a bleaching process, which removes the natural pigments of cotton fibres. Mainly flavonoids are responsible for the colour of cotton [Hedin et al. 1992; Ardon et al., 1996]. The most common industrial bleaching agent is hydrogen peroxide. Cellulose fibres are most frequently bleached with hydrogen peroxide resulting in high and uniform degrees of whiteness. Namely, the bleaching process is conducted in an alkaline bath at pH 10 to 12 and at

temperatures up to 120°C. Due to high working temperature, a large amount of energy is consumed [Alaton et al. 2006].

Bleaching with peracetic acid (PAA) is an alternative to bleaching with hydrogen peroxide [Križman et al. 2005; Hickman 2002; Tavčer 2008]. It is a powerful oxidizing agent (redox potential: 1.81 eV) [Preša & Tavčer 2009] with excellent antimicrobial and bleaching properties. It is efficient at low concentrations, temperatures and in neutral to slightly alkaline medium. Its products of decomposition are biologically degradable. In the past, it was prepared in situ from acetic acid anhydride and hydrogen peroxide [Rucker 1989; Wurster 1992]. However, the risk of explosion during the synthesis reaction prevented affirmation of PAA as a bleaching agent in industry.

Conventional preparation of cotton requires high amounts of alkaline chemicals and consequently, huge quantities of rinse water are generated. However, radical reactions of bleaching agents with the fibre can lead to a decrease in the degree of polymerisation and, thus, to severe damage. Therefore, replacement of hydrogen peroxide by an enzymatic bleaching system would not only lead to better product quality due to less fibre damage but also to substantial savings on washing water needed for the removal of hydrogen peroxide. An alternative to this process is to use a combination of suitable enzyme systems. Amyloglucosidases, pectinases, and glucose oxidases are selected that are compatible concerning their active pH and temperature range.

Tzanov et al. (2001) reported for the first time the enhancement of the bleaching effect achieved on cotton fabrics using *laccases* in low concentrations. In addition, the short time of the enzymatic pre-treatment sufficient to enhance fabric whiteness makes this bio-process suitable for continuous operations. Also, Pereira et al. (2005) showed that a *laccase* from a newly isolated strain of *T. hirsuta* was responsible for whiteness improvement of cotton most likely due to oxidation of flavonoids. More recently, Basto et al. (2007) proposed a combined ultrasound-*laccase* treatment for cotton bleaching. They found that the supply of low ultrasound energy (7W) enhanced the bleaching efficiency of *laccase* on cotton fabrics. Natural fabrics such as cotton are normally bleached with hydrogen peroxide before dyeing. *Catalase* enzyme is used to break down hydrogen peroxide bleaching liquor into water molecules and less reactive gaseous oxygen.

Compared with the traditional clean-up methods, the enzymatic process results in cleaner waste water or reduced water consumption, a reduction of energy and time.

### 3. Future Directions:

The continued development of new enzymes through modern biotechnology may, for example, lead to enzyme products with improved cleaning effects at low temperatures. This could allow wash temperatures to be reduced, saving energy in countries where hot washes are still used. Today, white biotechnology is geared towards creating new materials and bio-based fuels from agricultural waste and providing alternative bio-based routes to chemical processes. These efforts could lead to the development of improved enzymes such as *amylases*, *hemicellulases* or *cellulases* that could be used in the textile industry. The possibility of leveraging innovations over industries could lead to new opportunities for bio-based textile processes. New enzymes with high specific activity, increased reaction speed, and tolerance to more extreme temperatures and pH could result in development of continuous processes for bioscouring or biofinishing of cellulosic fibres. Development of other processes in the future could also expand the use of enzymes on natural fibers into use on man-made fibers such as nylon and polyester.

Today, the application of biotechnology to industrial processes holds many promises for sustainable development. One of the first goals on white biotechnology's agenda has been the production of biodegradable plastics, and in textiles, DuPont has invested much in the production of textile fibers from corn sugar (Sorona®) while Cargill Dow has introduced NatureWorks™, a polymer made from lactic acid which is used in textiles under the brand name Ingeo®.

New and exciting enzyme applications are likely to bring benefits in other areas: less harm to the environment; greater efficiency; lower costs; lower energy consumption; and the enhancement of a product's properties. New enzyme molecules capable of achieving this will no doubt be developed through protein engineering and recombinant DNA techniques.

Enzymes are now widely used to prepare the fabrics that your clothing, furniture and other household items are made of. Increasing demands to reduce pollution caused by the textile industry has fueled biotechnological advances that have replaced harsh chemicals with enzymes in many textile manufacturing processes. The use of enzymes not only make the process less toxic

(by substituting enzymatic treatments for harmful chemical treatments) and eco-friendly, they reduce costs associated with the production process, and consumption of natural resources (water, electricity, fuels), while also improving the quality of the final textile product.

#### 4. Conclusion:

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 textile industry was identified as a key sector where opportunities available from adapting biotechnology are high but current awareness of biotechnology is low. In textile processing the enzyme can be successfully used for preparatory process like desizing, scouring and bleaching. These enzymatic processes are gives the similar results as that of conventional methods. Though this enzymatic processes we can reduce the water consumption, power energy, pollution, time, and increasing quality. These are just a few applications of Biotechnology, however many such potentials are yet to be explored.

Pollution free processes are gaining ground all over the world. In this scenario, enzymes emerging as the best alternative to the polluting textle processing methods. 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. It seems that in the future it will be possible to do every process using enzymes.

Enzyme producing companies constantly improve their products for more flexible application conditions and a more wide-spread use. The textile industry can greatly benefit from the expanded use of these enzymes as highly specific and efficient, non-toxic, environmenatally friendly compounds, work under mild conditions (pH, temperature) with low water consumption that results in reduced the use of harsh chemicals in the textile industry, process times, energy and water savings and improved product quality. The main hindrance in using enzymes is their high cost. Enzymes are emerging in a big way in the field of textile wet processing. If their cost can be managed, enzymes can be put to use in a much bigger way for textile processing applications.

Advances in enzymology, molecular biology and screening techniques provide possibilities for the development of new enzyme-based processes for a more environmentally friendly approach in textile industry. It seems that in the future it will be possible to do every process using enzymes.

## 5. REFERENCES:

- Alaton, I. A., Insel, G., Eremektar, G., Babuna, F. G., & Orhon, D. (2006). Effect of textile auxiliaries on biodegradation of dyehouse effluent in activated sludge. *Chemosphere*, 62 (9), 1549–1557, ISSN 0045 – 6535.
- Aly, A. S., Moustafa, A. B., Hebeish, A. (2004). Bio-technological treatment of cellulose textiles. *Journal of Cleaner Production*, 12 (7), 697–705, ISSN 0959 – 6526.
- Anis, P., & Eren, H. A. (2002). Comparison of alkaline scouring of cotton vs. Alkaline pectinase preparation. *AATCC Review*, 2 (12), 22–26, ISSN 1532-8813.
- Ardon, O., Kerem, Z., Hadar, Y., (1996). Enhancement of laccase activity in liquid cultures of the ligninolytic fungus *Pleurotus ostreatus* by cotton stalk extract, *J. Biotechnol.*, 51, 201-207
- Basto, C., Tzanov, T., Cavaco-Paulo, A., (2007). Combined ultrasound-laccase assisted bleaching of cotton. *Ultrason Sonochem*, In Press, 14, 350-354.
- Blandino, A., Iqbalsyah, T., Pandiella, S.S., Cantero, D., Webb, C., (2002). Polygalacturonase production by *Aspergillus awamori* on wheat in solid-state fermentation, *Applied Microbiology and Biotechnology*, 58, 164-169.
- Boyer, P.D., (1971). *The enzymes*, 3<sup>rd</sup> ed., Academic Press, Inc., New York, Vol.5.
- Buchert, J., Pere, J., Puolakka, A., & Pertti, N. (2000). Scouring of cotton with pectinases, proteases, and lipases. *Textile Chemist and Colorist*, 32 (5), 48–52, ISSN 0040-490X.
- Cao, J., Zheng, L., Chen, S., (1992). Screening of pectinase producer from alkalophilic bacteria and study on its potential application in degumming of ramie, *Enzyme and Microbial Technology*, 14, 1013-1016.
- Cavaco-Paulo A. & Gübitz G. M. (2003). Cambridge: Woodhead Publishing, *Textile processing with enzyme*. 17–18, 30–34, 51–52, 90–95, 110, 124–125, 129–131, 158–169, ISBN 18557366101.

- Ciechańska D., Kazimierczak J.; (2006). *Fibres 4. & Textiles in Eastern Europe*, 14, No 1(55), 92-95.
- Csiszar, E., Losonczy, A., Szakacs, G., Rusznak, I., Bezur, L. & Reichar, J. (2001). Enzymes and chelating agent in cotton pretreatment. *Journal of Biotechnology*, 89 (2–3), 271–279, ISSN 0168 – 1656.
- Durden, D. K., Eters, J. N., Sarkar, A. K., Henderson, L. A. & Hill, J. E. (2001). Advances in commercial biopreparation of cotton with alkaline pectinase. *AATCC Review*, 1 (8), 28–31, ISSN 1532-8813.
- Eters, J.N., (1999). Cotton Preparation with Alkaline Pectinase: An Environmental Advance. *Textile Chemist and Colorist & American Dyestuff Reporter*, 1(3), 33-36.
- Fersht, A., (2007). Enzyme structure and mechanism, San Francisco: Brenda, W.H., The comprehensive enzyme information system, 50 (2), ISBN 0-7167-1615-1.
- Fornelli, S., (1994). *Melliand Textilber*. 75, 120.
- Galante, Y. M., & Formantici, C. (2003). Enzyme applications in detergency and in manufacturing industries. *Current Organic Chemistry*, 7(13), 1399–1422, ISSN 1385 – 2728.
- Gulrajani, M.L., (1992). *Rev. Prog. Coloration*, 22, 79.
- Gupta R., Gigras P., Mohapatra H., 5. Goswami V.K., Chauhan B.; (2003). *Process Biochemistry*, 38, 1599-1616.
- Hartzell, M. M. & Hsieh, Y. (1998). Enzymatic scouring to improve cotton fabric wettability. *Textile Research Journal*, 68(4), 233–241, ISSN 0040 – 5175.
- Hartzell-Lawson M, Durrant S. (1998). Improving the Efficiency of Pectinase Scouring With Agitation to Improve Cotton Fabric Wettability, Book of Papers, International AATCC Conference, Philadelphia, US 310–318.
- Hedin, P.A., Jenkis, J.N., Parrot, W.L., (1992). Evaluation of flavonoids in *Gossypium arboreum* (L.) cottons as potential source of resistance to tobacco budworm, *J. Chem. Ecol.*, 18, 105-114
- Hickman, W. S. (2002). Peracetic acid and its use in fiber bleaching. *Review of Progress in Coloration*, 32 (13–27), ISSN 0557-9325.

- Hossain, S., Uddin K., (2011). Comparative Analysis between Conventional Pre-treatment and Biopreparation, *International Journal of Engineering & Technology IJET-IJENS*, 11(3).
- Hsieh YL, Thompson J, Miller A., (1996). Water Wetting and Retention Properties of Cotton Assemblies as Affected by Alkaline and Bleaching Treatments. *Textile Res J* 66, 456–464.
- Jayani, R. S., Saxena, S., & Gupta, R. (2005). Microbial pectinolytic enzymes: a review. *Process Biochemistry*, 40 (9), 2931–2944, ISSN 1359 – 5113.
- Jenkins R. O. (2003). in: *Textile Processing with Enzymes*, Edited by Cavaco-Paulo A. & Gübitz GM, Woodhead publishing Ltd., CRC Press, Boca Raton, ISBN 18557366101.
- Kapoor, M., Beg, QK., Bhushan B., Singh, K., Dadhich, K.S., Hoondal, G.S., (2001). Production and partial purification and characterization of a thermo-alkali stable polygalacturonase from *Bacillus sp.* MG-cp-2, *Process Biochemistry*, 36, 467-473.
- Karmakar, S. R. (1999). *Textile Science and Technology* 12, Chemical Technology in the Pretreatment processes of textiles. Elsevier, Amsterdam, 3–8, 72–75, 86–89, 160, 168–173, 188–190, ISBN 0-444-50060-X.
- Kundu, A.B., B.S. Ghosh, S.K. Chakrabarti and B.L. Ghosh, (1991). *Textile Res. J.* 61, 720.
- Lange, N.K. (1997). *Textile Chemist and Colorist*, 29, 23-26.
- Lewin, M., Pearce, E.M., (1998). *Handbook of Fibre Chemistry*, Marcell Dekker Inc., New York.
- Li, Y., & Hardin, I. R. (1998). Enzymatic scouring of cotton – surfactants, agitation and selection of enzymes. *Textile Chemist and Colorist*, 30(9), 23–29, ISSN 0040-490X.
- Maldonado, M.C., Saad, A.M.S., (1998). Production of pectin esterase and polygalacturonase by *Aspergillus niger* in submerged and solid state systems, *Journal of Industrial Microbiology and Biotechnology*, 20, 34-38.
- Marcher, D., H.A. Hagen and S. Castelli, (1993). *ITB Veredlung*, 39, 20.
- Meyer-Stork, L.S., (2002). *Maschen-Industrie*, 52, 32.
- Nierstrasz, V.A., Warmoeskerken, M.M.C.G., (2003). Process Engineering and Industrial Enzyme Applications. In *Textile Processing with Enzymes* ( eds. Cavaco-Paulo, A., Gübitz), Woodhead Publishing Ltd, Cambridge, England, 129-131.
- Opwis, K., Knittel, D., Kele, A., Schollmeyer, E., (1999). *Starch/Starke*, 51, 348-353.

- Pandey, A., Selvakumar, P., Soocol, C.R., Nigam, P., (1999). Solid state fermentation for production of industrial enzymes, *Current Science*, 77, 149-162.
- Pawar, S.B., Shah, H.D., Andhorika, G.R., (2002). *Man-Made Textiles in India*, 45(4), 133. Eppers, J. N. (1999). Cotton preparation with alkaline pectinase: an environmental advance. *Textile Chemist and Colorist*, 1(3), 33–36, ISSN 0040-490X.
- Preša, P, Tavčer, P. F. (2008). Bioscouring and bleaching of cotton with pectinase enzyme and peracetic acid in one bath. *Coloration Technology*, 124 (1), 36-42, ISSN 1472 – 3581.
- Preša, P, Tavčer, P. F. (2009). Low water and energy saving process for cotton pretreatment. *Textile Research Journal*, 79 (1), 76-88, ISSN 0040 – 5175.
- Robner U., (1993). Enzymatic Degradation of Impurities in Cotton. *Melliand Textilberichte* 74, 63.
- Rößner, U. (1995). Enzyme in der Baumwollvorbehandlung. *Textilveredlung*, 30 (3-4), 82–88, ISSN 0040 – 5310.
- Rucker, J. W. (1989). Low temperature bleaching of cotton with peracetic acid, *Text. Chem. Color.*, 21 (5), 19–25, ISSN 0040-490X.
- Ruttloff, H., (1994). Industrielle Enzyme, Behr's Verlag, Hamburg.
- Sawada, K., Tokino, S., Ueda, M., & Wang, X. Y. (1998). Bioscouring of cotton with pectinase enzyme. *Journal of the Society of Dyers and Colourists*, 114 (11), 333–336, ISSN 0037-9859.
- Schacht, H., Kesting, W. & Schollmeyer, E. (1995). Perspektiven Enzymatischer Prozesse in der Textilveredlung. *Textilveredlung*, 30, 237–243, ISSN 0040 – 5310.
- Tavčer, P. F. (2008) The influence of different pretreatments on the quantity of seed-coat fragments in cotton fibres. *Fibres & Textiles in Eastern Europe*, 16 (1), (66), 19-23, ISSN 1230 – 3666.
- Tavčer, P.F., (2011). Biotechnology in Textiles – an Opportunity of Saving Water, *Waste Water - Treatment and Reutilization*, ISBN: 978-953-307-249-4.
- Traore, M.K. & Buschle-Diller, G. (2000). Environmentally friendly scouring processes. *Textile Chemist and Colorist*, 32 (12), 40–43, ISSN 0040-490X.
- Tzanov, T., Calafell, M., Guebitz, G. M., & Cavaco-Paulo, A. (2001). Bio-preparation of cotton fabrics. *Enzyme Microb. Technol.*, 29 (6–7), 357–362, ISSN 0141 – 0229.

- Uhlig, H., (1991). Enzyme arbeiten für uns, C. Hanser Verlag, München.
- Wurster, P. (1992). Peracetic Acid bleach an alternative to bleaching processes using halogenated oxidizers. *Textil praxis int. Sonderdruck*, 10, 960–965, ISSN 0340-5028.
- Yachmenev, V.G., Bertoniere, N.R. and Blanchard, E.J., (2001). Effect of Sonication on cotton Preparation with Alkaline Pectinase. *Textile Res. J.*, 71(6), 527-533.
- Yamamoto, R., Buschle-Diller, G., Takagishi, T., (2001). Eco-friendly processing of cotton: application to industrial manufacturing. In: *Proceedings of the American Chemical Society National Meeting*, April 2001, San Diego, Calif. ACS, Washington D.C.

