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Application of Enzymes in the Textile Industry: A Review

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Abstract
Enzymes are currently being used in various textile processing and are gaining global recognition because of their non-toxic and eco-friendly characteristics. This review summarizes various enzyme-based textile processing and compares their performance with traditional chemical-based textile processing. The aim of this review is to provide textile technologist with a fundamental concept of enzymes and their applications in various textile processing.

Keywords: Enzymes, Textile Industry, Enzyme-Based Processing, Chemical-Based Processing.

1. Introduction
Textile industry is a recognized and growing industry in the world economy, where many chemical-based processes are accomplished. Some of the chemicals cause serious damage to the machines because of their corrosive nature. Conventionally, after completion of a chemical process, the remaining chemicals and dyes are drained in the effluents. The carcinogenic, recalcitrant, and geno toxic nature of the chemicals and dyes in the effluents can disturb the natural ecosystem, if they are discharged in the open stream without any proper treatment which is very costly. The chemical-based processes also deteriorate the natural properties of the processed fabric. Therefore, the textile industries are looking for a way to substitute the conventional process by environmentally friendly and economic alternative process [1].

In recent years, industrial use of enzyme has brought about environmentally friendly and economic process. Enzymes are used in various textile processing, such as amylases in de-sizing, cellulases in bio-polishing and proteases in wool and silk fibres processing [2, 3]. This review will briefly cover about some fundamental concepts of enzyme and their application in various textile processing.

2. Discussion
2.1 Enzymes
Enzymes are catalysts that accelerate the rate of a reaction. They are mainly made up of proteins. The molecule that an enzyme acts on is known as its substrate. The 3D shape of an enzyme has a small area which is known as the active side where the substrate binds to form an enzyme-substrate complex. Finally, products are obtained, and enzymes remain unchanged after the reaction. Enzymes have many special properties such as they accelerate the rate of a reaction by lowering the activation energy of the reaction, they operate under an optimum temperature and pH, they are very specific catalyst (a particular type of enzyme will catalyze a particular type of substrate or reaction) and they are biodegradable [4]. Enzymes typically have a trivial or common name. The name indicates the reaction that the enzyme catalyzes or the substrate on which the enzyme act, such as cellulase is an enzyme which catalyzes the hydrolysis of cellulose substrate. However, some trivial names do not give proper information about the substrate and reactions involved. Therefore, in the 1950s the Enzyme Commission (EC) developed a numerical system to specify each enzyme. For example, the enzyme with trivial name cellulase has the EC number 3.2.1.4 [5].

Commercial sources of enzymes are plants, animals, and microorganisms. However, as the fermentation technology developed, the microbial enzyme (obtained from microorganism) has become more popular in different industries. In fermentation technology, a microorganism (e.g., bacteria, yeast, fungus) that will produce the desired enzyme is isolated and an environment is optimised for its growth and finally commercial quantities of microbial enzymes are extracted. There are two fermentation methods which are used to produce the microbial enzymes industrially, namely submersed fermentation, and solid-state fermentation [6]. The produced enzymes which are called to the native or free enzymes which can be used directly for different reaction or substrate. There is also an alternative way to use enzymes is called immobilization where the native enzymes are fixed on a suitable carrier or substrate. The immobilized enzymes have higher stability to dyeing chemicals and temperature compared to native enzymes. Besides that, these immobilized enzymes offer easy separation and a possibility to reuse. Immobilization is performed by direct attachment of enzymes on substrate or carrier materials using different methods, such as physical adsorption, ionic binding, covalent binding, encapsulation, and cross-linking [7].

2.2. Application of enzymes in cotton textile processing

Enzymes are being used in various processes from preparatory to finishing in the textile industry. Enzymatic de-sizing by amylases was first successfully implemented in textile industries in 1912. The use of catalases enzymes were then introduced into the bleaching and scouring process in the early 1980s [1]. Nowadays various enzymatic processes have been extensively used in cotton textile processes. This review summarizes these enzyme-based processing and compares their performance with traditional chemical-based processing used in textile industry.

2.2.1. De-sizing

Historically, size materials are applied to the warp yarns to perform the weaving action smoothly. Starch-based materials are mostly used to size the warp yarns. The protective layers of size must be removed from the yarns before the bleaching and dyeing. The size materials from the warp yarns are removed by a process called de-sizing. Conventionally, de-sizing is performed by treating the woven fabric with chemicals (acid, alkali, oxidizing agents) at higher temperatures. However, these conventional processes cannot effectively remove the starch which makes the dyeing uneven. The chemicals used in the conventional process also cause degradation of the cotton fabric, as a result the cotton fabric loses its soft natural feel. After completion of the process, the waste chemicals are discharged into the environment which causes serious pollution [8, 9].

Nowadays, enzymes are preferred for de-sizing. Enzymatic de-sizing is considered as the first commercial application of biotechnology in textile sector. The woven fabric is treated with amylases enzyme to destroy the starch which subsequently clean the warp yarn. Amylases can be classified into three types: α-amylases, β-amylases and Amyloglucosidase. Among these three amylases, α-amylases is more suitable for starch hydrolysis. These enzymes break the linkage between the glucoses of starch polymer and produce dextrin which can be simply washed away by water. The optimum temperature range of α-amylases is 30-60 °C and pH range is 5.5-6.5. The lower application temperature will save energy and milder pH condition will reduce the excessive use of chemicals. A variety of fungi, yeasts and bacteria are used to produce α-amylases, but bacterial sources are most used in industry [8, 10]. It is reported that use of ultrasonic waves helps to improve the effectiveness of amylase enzymes in the de-sizing operation [11]. Amylase can be used together with H_2O_2 or cellulase that improves their wet ability, dye-uptake, and stiffness of the treated fabric [12]. Alkali stable amylase enzymes are also reported for simultaneous de-sizing and scouring action [13]. A commercial alkali stable enzyme was introduced by Novozyme that can be used in wide pH (5-10) and temperature (20-85 °C) range [14]. Immobilized amylase which is less sensitive to pH, temperature, and chemicals, is also reported to remove the size materials. Talekar at al. used the magnetic cross-linked enzyme aggregation process to produce immobilized amylase enzyme which have potential application in industry. This immobilized enzyme can be easily separated under magnetic field for repeated uses [15].

2.2.2 Scouring

A raw cotton fibre contains natural impurities or non-cellulosic substance (oil, waxes, pectin, proteins, fats) in its cuticle and primary wall. Scouring is the process by which non-cellulosic materials are removed to make highly absorbent cotton fibres. Traditionally, the grey cotton fabric is boiled in 2% alkaline solution to perform the scouring process. This traditional process has many disadvantages, such as consuming excessive alkali chemicals, requiring heavy rising after scouring to make the fabric neutral, reducing 5-7% weight in fabric, reducing the strength of cotton fabric due to oxycellulose formation in the presence of oxygen and using higher energy owing to boiling temperature [16, 17].In this context, enzymatic scouring has been investigated to replace the traditional alkaline-based scouring. Bio-scouring offers a lot of advantages over the traditional process, such as reduced water consumption, lowered treatment temperature which saves energy. The enzymatic scouring also improves cotton fibres softness. Unlike traditional scouring, the function of enzymes is specific (does not attack the cellulose) thus there is no weight and strength loss [8].

Pectinases are commonly used in cotton scouring. It functions by degrading the pectin in the primary cell wall of cotton. Pectin keeps the non-cellulosic substance connected with the cellulose. Therefore, if the pectin is removed, the other impurities can be removed very easily [8]. Pectinases are divided into three classes: pectin esterases, polygalacturonases and polygalacturonate lyases. Pectin esterases catalyse hydrolysis of pectin methyl esters and form pectin acid at temperature ranges 40-60 °C and pH ranges 4.0-7.0. Polygalacturonases hydrolyse α (1→4) glycosidiclinkages in pectinat temperature range 30-50 °C and acidic pH ranges of 2.5-6.0. Polygalacturonate lyases causes degradation of pectin by chain cleaves at temperature range typically 30-40 °C and pH ranges of 8.0-10.0 [2].It is reported that in addition of surfactants increased the efficiency of pectinases[18]. In general, bio-scouring is done in combination with pectinases and cellulase. In this combination, the pectinases degrade the pectin and the cellulase destroy cuticle by breaking down the primary wall[19]. Pectinases have also been immobilized by using various support materials. Sawada and Ueda have used immobilized pectinase in scouring and have compared its effectiveness with native enzyme scouring. The results showed that the immobilized enzymes had equivalent or better effectiveness than that of aqueous bio-scouring [20].

2.2.3. Bleaching and bleach clean-up

Cotton possesses natural pigment, mainly flavonoids which is responsible for its natural greyness. Bleaching is the process which is used to remove the natural pigments from the cotton fibres. Traditionally, H_2O_2 is commonly used as industrial bleaching agent which performs the bleaching operation at pH 10-12 and temperatures up to 120 °C. Conventional bleaching process have some disadvantages. Such as, large amount of energy is required owing to the higher treatment temperature. The bleaching agents can decrease the degree of polymerization (DP) of cotton, therefore severe damage of cotton takes place. Besides that, after bleaching higher amount of water is required to neutralize the fabric and to remove excess H_2O_2 [16, 21]. The problems in the conventional process can be overcome by using enzymes.

Laccases performs the bleaching of cotton by oxidizing the flavonoids. These enzymes are used at acidic pH and temperature 50-70 ℃ [2]. Basto et al. has found that use of ultrassound energy (7W) could intensify the bleaching action of laccases [22]. Besides that, glucose oxidasescan produce H_2O_2 and gluconic acid in aqueous solution by oxidizing glucose at pH acidic to neutral and at lower temperature. The produced H_2O_2 then perform bleaching action at 80-90 ℃ and at pH 11. This enzymatic system offers combined de-sizing and bleaching because reusing of de-sizing bath as glucose source is possible [23]. However, bleaching with native enzymes have some problems, such as denaturation of enzymes at higher temperature that causes the proteins to deposit on the fabric surface. This problem can be overcome by using immobilized glucose oxidases. Tzanov et al. immobilized the glucose oxidases covalently on alumina and glass. The semi mobilized enzymes performed the bleaching action successfully by higher rate of H_2O_2 generation [24].

Historically, after bleaching the cotton fabric with H_2O_2, the excess H_2O_2 is removed by using a reducing agent or by rinsing out with water. This process is called bleach clean-up which consumes a lot of water and pollute the open water streams [21]. This tradition process can be replaced by using catalases enzymes. These enzymes degrade H_2O_2 to H_2O and O_2. The optimum temperature for application of catalyses is 20-50 ℃ and the optimum pH is 7.0 [2, 25].

2.2.4. Bio-polishing or bio-blasting

It is a process by which floating fibres are removed from the surface of the cotton fabrics. After bio-polishing the fabric surface becomes smooth. Cellulases are mainly used for performing this operation. These enzymes catalyse the hydrolysis of cellulose by breaking the β (1→4) glycosidic linkages. This hydrolysis is performed by combined action of three types of cellulases: endo-cellulases, exo-cellulases and β-4-glucosidases. Endo-cellulases produce glucose and cello-oligosaccharides by breaking the cellulose chains randomly. Exo-cellulases break microcrystalline cellulose and produce cellobiose. Cellobiose and oligosaccharides are then transformed into soluble glucose by β-4-glucosidases. All enzymes work synergistically to produce glucose as final product. Fungi and bacteria are commonly used to produce these enzymes. The optimum temperature range for the application of cellulases is between 30-60 ℃. Their application pH can be acidic, neutral, and alkaline [2, 26]. However, bio-polishing by cellulases on cottonfibres has some problems to be solved. Cellulase can cause the weight and strength loss of the treated fabric by easily moving beyond the peripheral structure of the cotton cellulose. These problems can be solved by using immobilized enzymes which limits the action of enzyme only on the fibre surface [27].

2.2.5. Dyeing

Conventionally, the cotton fabric is first pre-treated (de-sizing, scouring, bleaching, bio-polishing) and then dyed [28]. Each step is done separately resulting in the consumption of enormous amount of water, energy, and chemicals. But use of enzyme can combine some pre-treatments processes with dyeing in a single bath which is good from both ecological and economic point of view. H A Eren et al. used glucose oxidases to combine the pre-treatment (de-sizing and scouring) and dyeing of cotton fabric in a single bath. The dyeing properties (colour yield, fastness etc) of enzymatically treated, and conventionally treated fabric were comparable. The tensile properties of enzymatically treated sample were higher than its conventional counterpart [29].

Natural dyeing of cotton always suffers from two problems, namely dyeing difficulty, and poor fastness properties. To overcome these two problems, the cotton fabrics first pre-treated with tannic acid and metal salts and then dyed. However, this approach of dyeing poses serious ecological constraint. Enzymes have recently been applied to replace the chemical pre-treatment of cotton fabric. Enzymes are used along with different natural colorants to enhance the dyeing properties [3]. In another study, cotton fabrics are pre-treated with the enzymes cellulase, amylase and trypsin and dyed with chlorophyl and carmine. The results showed that enzymatic pre-treatment increased the pigment uptake in all cases [30].

2.2.6. Bio-washing

Bio-washing by cellulase enzymes are mainly used for denims to create a faded and aged look. Conventionally, the denims are washed with a stone named pumice to get the desired faded and aged look. However, this traditional process has many demerits: damage to the garments and machines and dust in the laundry environment and difficulty in removal of residual pumice from the denim garments. The application of cellulases in denim industry has reduced or even eliminated the use of pumice stone. In textile industry, the denims are usually dyed with indigo dyes. The cellulase causes surface hydrolysis of the fibres which in turn removes some of the indigo dyes from the surface of the dyed fabric creating a faded and aged look [2, 10] However, the bio-washing shows back-staining problem in the treated fabric. It is reported that by using neutral and endo-cellulases, the back-staining problems can be minimised [31]. Alternatively, use of immobilized enzymes is an excellent way to reduce the back-staining problem. Since the enzymes are strongly bound on the carrier materials, staining was detected at lower level. [32].

2.2.7. Colour stripping

Colour stripping is a dye removal process from the dyed fabric. Traditionally, the colour stripping is performed by using harsh chemicals. For example, the colour stripping of reactive dyed fabric is performed by using hydros at alkaline condition followed by hypochlorite bleaching [33]. Hydros and hypochlorite are very toxic chemical causes ecological problems. On the other hand, enzymatic color strippingis is an economical and environmentally friendly process. Chatha et al. has used enzymes obtained from White-rot fungi (WRF) for stripping a reactive black B dye from cotton fabric [34].

2.3 Some other application of enzymes in textile processing

2.3.1 Treatment of wool fibres

Raw wool contains natural impurities such as wax and grease. Conventionally, these impurities are removed by using milder alkali such as sodium carbonate and ammonia or ammonium carbonate. Besides that, wool fibers show felting and shrinkage problems on wet treatment. Chlorine-Hercosett process is commercially used to make shrink resistant wool. Even though these chemical processes give satisfactory results but have some disadvantages: yellowing of fibers, poor quality, release of toxic organic halogens in environment and dyeing difficulty [35]. Proteases (Esperase) can be used as a substitute for the chemical pre-treatment of wool fibers. It has been found that treatment of wool with proteases removed all impurities resulting in increased dyeing affinity and improved anti-shrinkage properties of wool. Alkaline proteases which are used commonly, can be obtained from variety of Bacillus organism. This enzyme catalyzes the peptide and ester bond hydrolysis at 50-70 °C temperature ranges [2]. However, enzymatic treatment of wool cause damages to the wool fiber. This can be attributed to the small size of the enzyme which can easily penetrate the cortex of the fibers. This problem can be overcome by increasing the size of the enzymes. The increased size of the enzymes by glutaraldehyde could reduce the penetration of enzyme into the fibers cortex which subsequently reduces fiber damage [36]. Alternatively, the immobilization of enzyme can also increase the size of the enzymes which limit the action of the enzyme on the surface of the cuticle layer of wool. Immobilized protease has been successfully produced by linking the protease to Eudragit S-100.The immobilized protease has commercially replaced the chlorine treatments [37]. Besides, proteases, transglutaminases can also be used for treatment of wool goods. The transglutaminases are applied at pH 5.00-8.00 and temperature 55 °C [2, 38].

Wool fibers are usually dyed with acid dye at boiling temperature for good penetration, levelness, and fastness properties. However, under these conditions wool damage occurs. Conventionally, different dyeing auxiliaries are used for low temperature dyeing of wool. Nowadays, enzymatic treatment has become a possible alternative to the conventional methods. E K Karanikas et al. used proteases enzymes instead of dyeing auxiliaries and found improved dyeing properties [39].

2.3.2 Treatment of silk fibres

Raw silk is usually degummed or boiled off for about 2 hours or more if necessary, at about 95 °C in a 0.5 to 0.75 % solution of soap to remove sericin which covers the fibers.This is a harsh chemical treatment that damage the fiber structures and causes environmental pollution. Alkaline proteases are used to remove the sericin and improve the fiber handle, shine, and smoothness [17, 40].
Silk fibres can by dyed successfully with natural colorants in presence of enzymes which gives the best dyeing properties in the silk fabric [3].

2.3.3 Surface modification of synthetic fibres

Synthetic fibres such as polyethylene terephthalate (PET), polyamide (PA) and polyacrylonitrile (PAN) usually suffer from hydrophobicity which makes their dyeing and finishing operation difficult. Traditionally, chemicals such as NaOH is used to reduce their hydrophobicity. However, the treatment of fibres with NaOH causes undesirable weight and strength loss of the fibres and creates yellowing effect in PAN and PA fibres. Besides that, it is quite difficult to control the chemical process which has adverse effect to the environment. The alternative way is to replace the traditional chemical-based process with enzyme [2, 10].

Lipases and esterases are mostly used for the surface modification of PET fibres resulting in increased hydrophilicity, wettability, and dyeing properties [41]. These enzymes catalyse the hydrolysis of ester and release acid as final product[42]. The maximum enzymatic activity of lipases and esterase is observed at pH 8 and pH 6, respectively. Several authors have performed the surface modification of PET fibres by using these two enzymes and confirmed the formation of terephthalic acid after the modification at 240 nm [2, 43]. Lipases and esterases can also remove oligomers formed during polycondensation reaction of PET production. These cyclic oligomers leech out the polyester fiber during high temperature dyeing. On cooling the dye bath, oligomers which is water insoluble can deposit on the fiber and machine surface resulting in dusty fabric appearance and damage of the dyeing machine. Traditionally, exhausted dyebath is drained to minimize the problem of oligomers [44]. Nechwatal et al. reported that lipases/ esterases could be adsorbed the oligomers and remove 80% weight of oligomers from the dye bath liquor [45]. Cutinases are other enzymes used for surface hydrolysis of PET. Hydrolysis by cutinases will cleave the ester bond and release the terephthalic acid and generate -OH and -COOH groups on the surface of the fibres. O'Neill and Cavaco-Paulo did coloration of the hydrolysed PET with reactive dye. The optimum pH for the application of cutinases is around 8 [2, 46].

Proteases, amidases, cutinases, laccases, lipase and peroxidases have the ability for bio modification of PA fibres which subsequently improved the dye ability of the fibres with acid and disperse dyes[10, 47].

Nitrilases, nitrile hydratases/amidases are used for biomodification of polyacrylonitrile (PAN) fibres. These enzymes catalyse the hydrolysis of the nitrile group on the surface of PAN fibres. Acrylic fibres are hydrophobic which makes its dyeing and finishing process difficult. Modification of PAN fibres with nitrile hydratases/ amidases increase the hydrophilicity and dye absorption prsopeoties of the fibres [2, 48]. Matama et al. reported the surface modification of PAN fibres with nitrilase in combination with sorbitol and N, N-dimethylacetamide resulting in enhanced catalytic efficiency in the treatment media [49].

2.3.4 Functionalization of textile fibres

Some enzymes confer antimicrobial activity on textile fibres. Lysozyme is one of such enzymes which can be immobilized on cotton fibres [50]. The antimicrobial wool fabrics are also produced by immobilization of lysozyme using glutaraldehyde [51]. Transglutaminase can be immobilized on wool fabric by using lactoferrin resulting in increased antimicrobial properties on wool fabric [52]. Kinases enzymes can be used to improve the flame retardant properties of natural fibres [53]. The enzymatic functionalization of textile fibres has opened a new opportunity in the textile fibre processing.

2.3.5 Treatment of textile effluents

The textile waste water is usually coloured and contains recalcitrant synthetic dyes and chemical. If the effluents are discharged into the open water without treatment, it can pollute the water and kill the aquatic life. The treatment of textile effluents can be done by using physical, chemical, and biological (eco-friendly) methods. Physical and chemical processes can remove the dyes and chemicals from industrial effluents but produce huge sludge that creates disposal problems. Biological methods can also remove dyes and chemicals from the effluents by using different microorganism such as bacteria or fungi [54]. White-rot fungi (WRF) is the example of an organism which have the ability for dye degradation and decolouration of the effluents. The ligninolytic enzymes obtained from the WRF are non-specific in nature and can remove various dyes and chemical compounds [55]. Laccases are also used for degradation of synthetic dyes and discoloration of the textile effluents [56].

3. Gap Analysis and Recommendations

There are only few commercially successful enzymes in textiles. Application of enzyme in textile processing suffers from some limitation, such as price and reusability[8].In addition, enzymes are very sensitivity to pH, temperature, and processing chemicals used during textile wet processing. The sensitivity of enzymes can be overcome by using immobilization techniques. But there are still some problems in the immobilization techniques to be solved, such as loss of specific activity of the native enzymes and larger size of the immobilized enzymes which limits its diffusion into the substrate [10]. Further research could be directed towards the immobilization techniques, commercialization of the enzymes with reduced price and reusability,and identification of new enzymes from different micro-organism which might find new application in future textiles processing.

4. Conclusion

This review discusses few applications of biotechnology or enzymes in textiles processing which will give the textile technologists a basic understanding of current enzymatic processes and research in this field. Enzyme-based processes are environmentally friendly alternative to the existing chemical processes. Interestingly, enzymatic process can be performed at mild pH and temperature that might solve the energy crisis and environmental issues in textile industry. It can also reduce water and energy consumption, pollution and process time as well as increase the quality of the treated fabric. Current awareness of biotechnology in textile industry is low. Therefore, more research should be conducted in enzymatic process, to expand their horizon in textile industry.

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