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***From the Editor's Desk***

# Chemistry and Applications of Cellulase in Textile Wet Processing

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## Introduction

The term 'Enzyme' came from the Greek word 'Enzymos' means 'In the cells or Ferments'. These are naturally available, high molecular weight proteins, capable of catalyzing chemical reaction of biological process and therefore popular as 'Bio-catalyst'. Enzymes are soluble organic substance, produced by living organisms whose different amino acids form long poly peptide chains $(\text{-HN-R-CONH-R-CO-})_n$ by condensation polymerization. Enzyme, has unique three dimensional shape and presence of ionic groups, make the structure more complex[1-3].

During the last twenty years, the industrial use of enzymes has been expanded rapidly. Their application has been well established in various industries like detergent, textiles, food stuffs, medicines, animal feeds and others. The important significant of this bio reaction can be summarized as[4]. i. Enzymes are characterized by their ability to operate under very mild conditions and therefore, processes are safer in terms of degradation to fiber, ii. Enzymes are biodegradable and substitute the harmful chemicals and thus reduce the effluent load. iii. Enzymatic actions are specific and hence subtract quality will not be effected. iv. Enzymatic processes are economical as they utilize less steam energy and avoid use of costly chemical and/or auxiliaries. v. Enzymes are catalyst and after reaction it will obtain as it is and reused again.

## Chemistry of enzymatic reaction[5-8]

Enzyme does not proceed the reaction but accelerate it at substrate surface, which would otherwise occur at slower speed and lower the activation energy of reaction (Ea) as shown in figure-1. The polypeptide chain of enzyme is folded in such way that a small three dimensional pocket or cleft, called active site to form enzyme substrate complex (ES), which finally, breaks in to the product and regenerated enzyme through bio reaction mechanisms explained in formula-1. The effectiveness of enzyme is due to the specific binding and location of specific groups at the active site. Till date about 1200 different enzymes have been isolated and studied, and each one of them has been found to possess a range of specificities.

$$\underset{\text{(Enzyme)}}{\mathbf{E}} + \underset{\text{(Substrate)}}{\mathbf{S}} \rightarrow \underset{\text{(Enzyme-Substrate}}{\mathbf{ES}} \rightarrow \underset{\text{(Product)}}{\mathbf{E}} + \underset{\text{(Complex)}}{\mathbf{P}} \quad (1)$$

It is generally believed that the functional groups at the active site are fixed points of attachment with subtract. Emil Fischer postulates a 'Lock and Key' hypothesis to explain this interaction between enzyme molecules and subtract explained by Figure-1. Since enzymes are catalyst, they themselves are not changed by the reaction that the subtract undergoes. After the reaction has been completed, enzyme will reabsorbed on the other part of subtract. The process continues until the enzyme is 'poisoned' by a chemical bogie or inactivated by extreme conditions of temperature, pH or negative chemical reactions.

## Application of enzymes in textile processing[9]

Application of enzyme began around 1857 for splitting starch by amylase in desizing of cotton fabric. The enzyme uses, then steadily popularized in pretreatment and finishing processes of natural fibers. Recently, the new enzymes are developed for application in various wet processing for different fibers and constant researches are going on in the same line. The important classes of enzymes along with their applicability are reported in table-1.

## Cellulase enzyme[10]

Cellulase is multi component system commonly produced by soil-dwelling fungi and bacteria. This fungi and bacteria produce cellulase to reduce cellulose to glucose, which is then used as a nutrient. It is the most popular enzyme used in textile wet processing. Industrial cellulases are complexes of a number of cellulases, cellobiase and related enzymes in non-uniform composition, with molecular weight average ranging from 10,000 to 4,00,000. Cellulase comprises a multicomponent enzyme system, including endoglucalases (EGs) and cellobiohydrolase (CBHS) cellobiases.

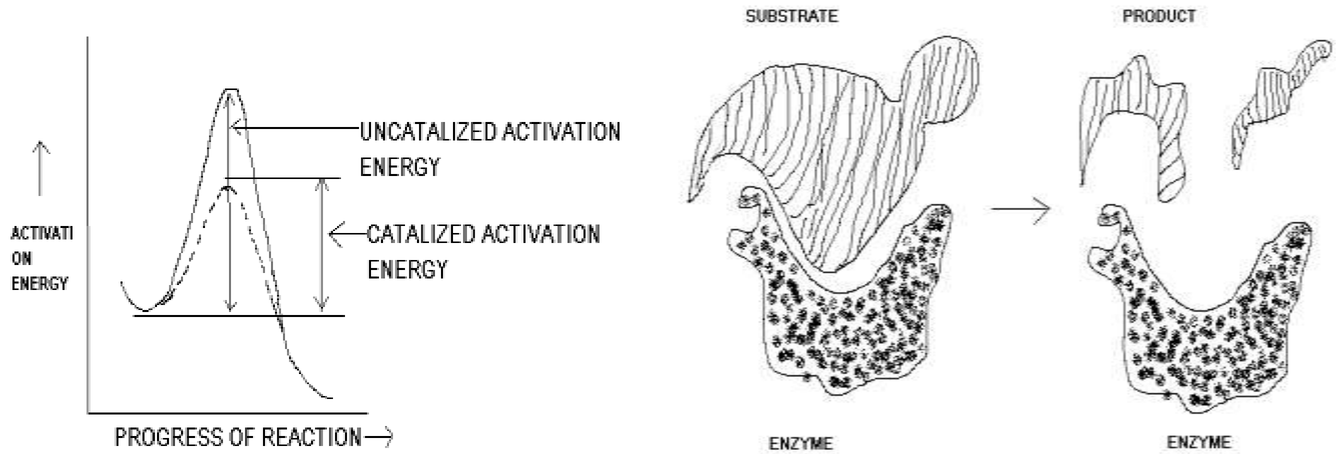



**Figure-1**
**Activation energy and Key-Lock mechanism of enzymatic reaction**

**Table–1**
**Important enzymes used in textile processing**

| Name of enzyme | Origin | Substrate | Reaction involved |
|---|---|---|---|
| Amylase | Bacillus Subtilis | Amylose and starch | Removal of size |
| Cellulase | Aspergillus Niger | Cellulose | Cellulose hydrolyses |
| Protease | Bacillius subtilis | Protein | Scouring of animal fibers and degumming of silk |
| Pectinase | Aspergillus Niger | Pectin | Degradation of pectin |
| Lipase | Plant, Gastric juice | Fats and waxes | Fats and waxes removal |
| Laccase | Aspergillus Niger penicilium | Indigo dye | Denim finishing |
| Hemicellulase | Rhizopous, Oruaze | Hemicellulose | Hydrolysis of hemicelluloses |
| Catalase | Aspergillus Niger penicilium | Peroxides | Insitu peroxide decomposition |

EG or EG-rich preparation are best for ageing and defibrillation of fiber surfaces while complete cellulase systems are best for cleaning and depilling effects. In general, there are two major commercial classifications of cellulase enzymes based on optimum ranges : 'acid cellulases' exhibit the most activity within pH range 4.5 – 5.5 at a temperature of 45 –55$^{o}$C, while 'neutral cellulases' are more effective in the 5.5–8 pH range at 50–60$^{o}$C. Currently, acid cellulases and neutral cellulases are more commonly used. With alkaline cellulases, there is a possibility of applying the enzymes in combination with reactive dye from the dye bath.

## Chemistry of cellulase enzyme[11-12]

The first postulates, concerning the nature of the mechanism of cellulase enzymatic hydrolysis was revealed by Reess, etal. It proposes two steps processes. A component termed as C1 was thought to initiate hydrolysis by preliminary activation or disaggregation of the cellulose chains. Subsequently, Cx the second component was responsible for the depolymeristion to soluble cello-oligo saccharides. The cellulase enzyme consists mainly three types of activity, namely,

**Endoglucanases or β-1,4-Glucanohydrolase:** It hydrolyses cellulose polymers randomly along the chains, preferentially attacking on amorphous region. It acts on the interior of the polymer to generate new ends.

Cx
|
G—G—G—G - - G - - - - - - - - - G—G—G—G—G

**Exoglucanases OR β -1,4 Glucan Cellobiohydrolase:** It acts on the non-reducing ends of the polymer chains to release cellobiose

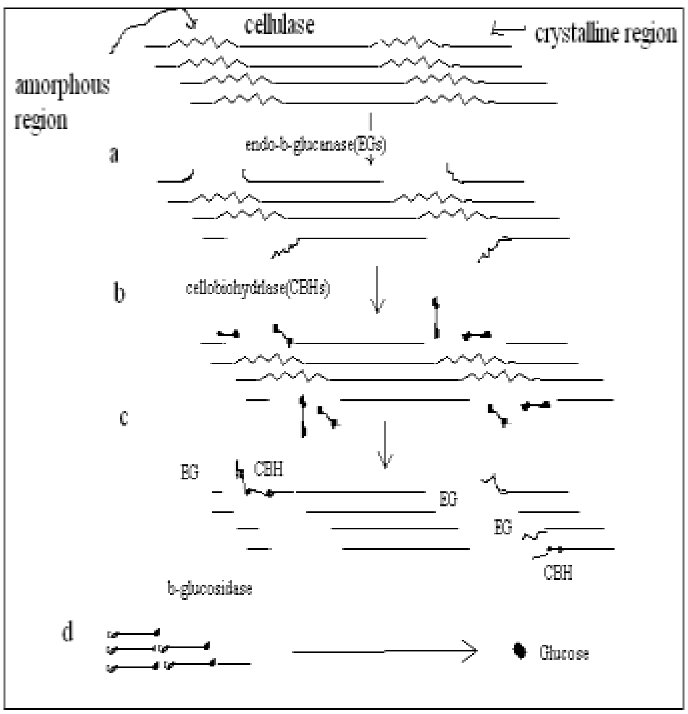
C1
|
G—G—G—G—G—G—G—G

**β -Glucosidase:** It hydrolyses cellobiose into glucose

B—G
|
B…….G

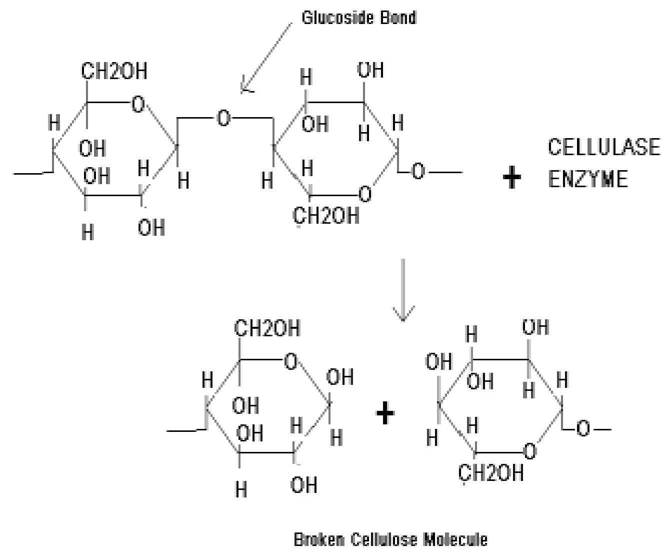
The three types of cellulase components act synergistically in degrading cellulose to glucose as shown in figure–2. A mechanism and rate analysis of the enzymatic hydrolysis of the cellulosic material shows that the rate of hydrolysis reaction depends on: i. Physical structure of the substrate, ii. The nature of the cellulase complex and iii. Inhibitory effects of both substrate and product.

The rate of enzyme catalyzed hydrolysis changes as the acidity of the reaction medium changes. If one plots the rate of hydrolysis against the pH of the solution, a bell shaped curve is obtained. The rate is fastest at about pH 7.4 and slowest in either acidic or more alkaline solution. The kinetics of enzymatic hydrolysis of cellulose has received relatively little attentions probably due to the difficulties arising from dealing with an insoluble substrate, complex enzyme systems etc. Mandels and Reese state that the enzymatic hydrolysis of disordered or crystalline cellulose does not follow zero or first order kinetics, but does confirm to the so called Schutz law. The latter states that viscosity (V) of reaction is proportional to the square root of the enzyme concentration and may be tested by linearity of plots of log V Vs. square root of time or log V Vs log time. However, the data of this mechanism are not matching in some courses.




**Figure–2**
**Synergestic action of cellulase component**

The oxygen bridge between β - glucose residues, known as 1,4 – glucoside linkage, is formed by glucose condensation with the elimination of water molecule in cellulosic fiber. Cellulase enzyme, which is capable of degrading cellulose, perform specific catalytic action on the 1,4 – linkage of the glucose residues of the cellulose molecules. The hydrolysis of this linkage breaks the long cellulose chains into smaller ones, which may further reduced to glucose. The chemical reaction can be represented as in figure-3.




**Figure–3**
**Degradation of cellulose by cellulase enzyme**

## Application of cellulase enzyme[13-18]

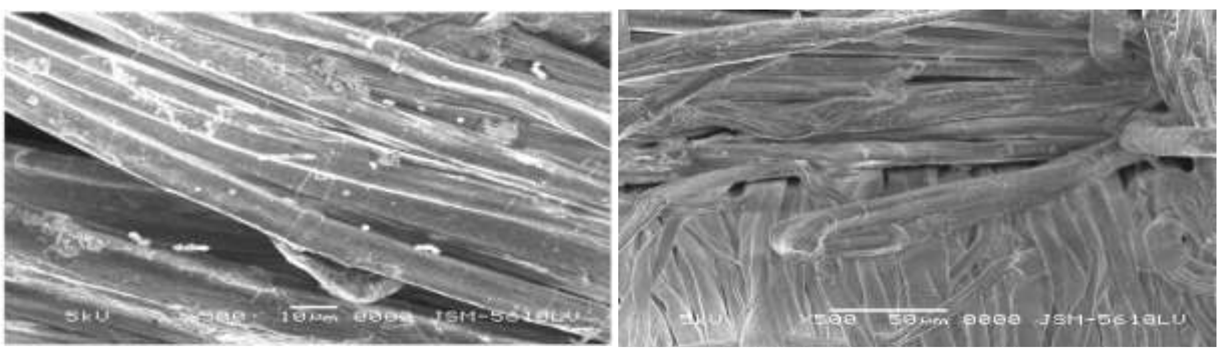
**In mercerization:** The effect of cellulase enzyme in mercerization seems to be very limited because of the stronger conditions of alkali of the said process. Enzymatic hydrolysis is accelerated when mercerization is carried out without tension. Mercerised cotton is generally more prone to enzymatic modification than unmercerised cotton.

**In scouring:** Enzymatic scouring of cotton fabric can be carried out using different enzymes as an alone or in combination namely, pectinase, cellulase, protease, lipase and others. Many researchers have worked on the said areas and results obtained are quite compatible with that obtained with conventional scouring. Further, many enzyme manufacturing companies have commercialized the scouring enzymes. Cellulase enzyme is especially used in scouring of cotton fabrics. The main function of is it penetrates the outer layer (cuticle) of the fiber strand and make contact with primary wall. The part of the primary wall at the contact point is hydrolysed and open up the space for pectinase and other enzymes to react. Cellulases break the linkage from the cellulase side and the pectinase break the linkage from the cuticle side. The result of the synergism is a more effective scouring in terms of speed and evenness. The degree of whiteness of a cotton sample treated with celluases only is lower by 8 – 10 % than the degree of whiteness of alkaline boiled – off treatment. The main advantages of enzymatic scouring are, the waste water is easily biodegradable, do not effect on other component of the blend and greener pretreatment.

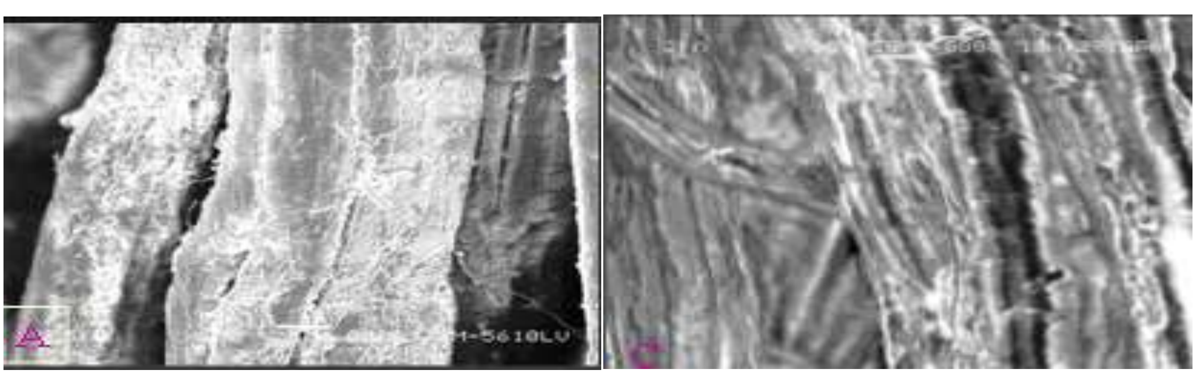
**In bio-polishing:** Surface modification of cellulosic fabrics to improve their cleaner surface conferring cooler feel, brighter luminosity of colors, softer feel and more resistance to pilling using cellulases is often known as bio-polishing. This treatment can be applied to knit and woven cellulosic fabrics such as cotton, viscose and linen. The elimination of superficial microfibrils of the cotton fiber through the action of cellulase enzyme is obtained by the controlled hydrolysis of cellulose leaving the surface of the fibers free and conferring a more even look. Enzymatic hydrolysis weakens the fiber ends and subsequent mechanical action removes the loose fiber ends. These improvements in fabric softness and smoothness are absolute safe, permanent and do not hamper the water permeability compared to chemical treatment. A number of patterns have been obtained for bio-polishing of cotton fabrics. This treatment can be carried out at any stage of wet processing, but the most conveniently performed after bleaching. Bio-finishing can be carried out either continuously or batch wise and either for piece or garment form of fabric often along with other process provided the compatibility must be present. Batch processes using, washers, jets, becks, and winches are extremely suitable as pH and temperature can be controlled easily. In case of lyocell spun yarn the tendency to form fibrillation on surface when treated with water. In the said fiber bio-finishing with cellulase enzymes are more preferred then chemical treatment.

**In washing:** There are three methods to remove surface fibers from cotton materials to improve aesthetic values, namely, singeing, bio-polishing and laundering using detergent contains cellulase enzyme. Laundering of knit fabrics with detergent containing cellulase enzymes help to maintain a clean surface appearance and look. Cellulase assists in the removal of particular soils by removing microfibril from the cotton fibers, which initially form the pills and scatter incident light. Today's detergents contain a sophisticated cocktail of enzymes.

**In stone finishing:** Denim, heavy grade cotton twill, dyed with indigo colors and well – worn look has gained much popular in recent trade market. The said effect is obtained by eroding action of pumice stone with or without oxidizing agent (potassium permanganate). Now days, bio-stone finishing with cellulase enzyme at optimal level has been used widely to obtain controlled superficial attack on fiber surface, leading to uneven discoloration without excessive loss of fabric strength. Cellulase removes the color by partial hydrolysis of the surface at fabric contains dye particles. This property has been exploited to produce garment with varying attractive and novel appearance. The treatment is mainly given after the denim has been prepared and more effectively with neutral cellulase enzyme. The acidic cellulose enzyme causes back staining of cotton garment and very little used with proper washing treatment. The important advantages of cellulase enzyme over conventional treatments are : i. Superior garment quality, ii. Environmental friendly process, iii. Less damage to ends of garments, iv. Extra softness does not need, v. Less equipement wear, vi. Garment load can be increased in machine



**Figure–4**
**Grey and enzymetic pretreated flax**



**Figure–5**
**Grey and enzymetic pretreated ramie**

**In pretreatment of bast fibers:** The natural bast fibers, namely jute, flax and ramie consist high amount of non cellulosic impurities (15–30 % owf). The said impurities are removed through pretreatment process and conventionally alkalis are used. Individual enzymes like pectinase, protease, hemicellulase can be used to remove single component. However, in combination of enzymatic treatment when cellulase enzyme is also added, the pretreatment process becomes fast and more efficient. In the mix enzymetic system, the role of cellulase enzyme is to remove the surface cellulosic components as shown in figure 4 and figure-5 and to facilitate the other enzymes to react on the specific components which are present in the inner layer of the fiber strands.

**In carbonization process:** Polyester-cotton blend of varying proportion are dyed with disperse-reactive or disperse vat system and then treated with strong sulphuric acid solution to remove cellulosic component. This effect makes the material finer and altering the $\lambda_{max}$ towards disperse dye sides. The cellulase enzyme treatment is the best alternative because it hydrolysed the cotton component. In case of cotton rich blends, the traces of cellulosic part remain on material and therefore more severe enzymatic treatments are required. The acidic cellulase enzyme is the best suitable in this application. The same principle is used in brasso style of printing in which cellulosic portion is removed from the polyester – cotton blend material after printing. The advantages of carbonization using cellulase enzymes are: i. The process is non-corrosive and non-hazardous. ii. Less wear and tear to machines, iii. Eco-friendly process, iv. No separate curing is required as in conventional brasso printing, v. No adverse effects on print color and feel of fabric

**In wool scouring:** Raw wool consists, natural impurities along with vegetable impurities. The natural vegetable impurities are cellulosic in nature and can be removed by cellulase enzyme treatment. However, the process can partially remove the natural impurities the subsequent chemical treatment may be necessary to complete the pretreatment of wool fiber.

## Conclusion

Cellulse enzyme is the versatile enzyme can be used in textile processing effectively to substitute the non eco-friendly chemical treatments. Recently, it is used in many processes and still the high potential is present. The researchers, technocrats and industrialists are required to constant developments and exploration of the new eco - friendly process. The said application is the best alternative for conventional environmental affecting wet processing.

## References

**1.** Kosaric N., Carius W. L. and Gray C.C., Biosurfactants and Bio-technology, Marve Dekker Pub., 2 **(1987)**

**2.** Marcher D., *International Text. Bull., Dyg/ Ptg/ Fing.,* **36,** 30 **(1993 )**

**3.** Etters J.N. and Annis P.A., *Ame. Dye. Rep.,* **87,** 18 **(1998)**

**4.** Horridge P. and Khan S., *Ame. Dye. Rep.,* **83,** 38**( 1994 )**

**5.** Gacen J., Cagera J. and Caro M., *J. Soc. Dyers Color.,* **113,** 218 **(1997 )**

**6.** Well J.H., General Biochemistry, 6th Edn., Wiley Eastern Ltd. Pub., 64 **(1990)**

**7.** Deb A.C., Fundamental of Biochemistry, 3rd Edn., Books and Allied Pvt. Ltd., Calcutta, 124 **(1989)**

**8.** Das, Biochemistry, 8th Edn., Academic Pub. Calcutta, 96 **(1995)**

**9.** Carr C.M., Chemistry of Textile Industry, 1st Edn., Blackie Acad. Pub., 28 **(1996)**

**10.** Lentz J., *J. Appl. Poly. Sci.,* **41,** 315**(1990)**

**11.** Kumar A., Purtell C. and Yoon M., *International Dyer,* 19**(1996)**

**12.** Tyndall M. R., *Text. Chem. Color.,* **24,** 23**(1992)**

**13.** Shirish kumar G V N, *J of Text Asso.,* **67,** 263 **(2007)**

**14.** Bokylston E. K. and Hebert J. J., *Text Res J.,* **65,** 429 **(1995)**

**15.** Jeffries R., *Cellul. Chem Tech.,* **3,** 225 **(1969)**

**16.** Li Y. and Hardin L, *Text Chem and Color.,* **29(8),** 71 **(1997)**

**17.** Kan C. W., Yuen C. W. M. and Jiang S.Q., *J. Text Inst.,*363 **(2008)**

**18.** Guha S. B.and Shah S. R., *J. Text Asso Jou.,215* **(2001)**