Comparative Analysis Between Conventional Pretreatment and Bio-Preparation

Abstract -- The textile is a growing sector which traditionally requires huge amounts of water, energy, harsh chemicals, starting from pesticides for growing cotton to a variety of finishing chemicals, which results in high amounts of wash water in waste streams causing environmental burdens. Thus the desired textile processing procedures are those environmental friendly and economic ones that can save water, time and chemicals, yet preserve product qualities. Enzymes are known for their specificity, high efficiency and ability to work under milder conditions and thus inexorably provide a promising solution to those problems.

This research paper focuses on a comparative analysis between the conventional pre-treatment processes with bio-preparations using enzymes. Since use of the gentle enzyme process replaces the need for harsh processing with sodium hydroxide and other harmful chemicals, there is less contribution to the textile effluent and gives a softer textile product.

Index Term -- Pre-treatment, Conventional process, Bio-preparation, Enzyme.

1. INTRODUCTION

For perfect coloration of a substrate, it is necessary that all the impurities, either natural or acquired, be removed so that the colorants can perfectly sit on the surface or penetrate inside the substrate as required by the particular system. The colorant should also be clearly visible without interference by the color of impurities. Before cotton fabric or yarn can be dyed, it goes through a number of preparatory processes. One of the most negative environmental impacts from textile production is the traditional processes used to prepare cotton fibre, yarn or fabric. The conventional highly alkaline preparation of cotton can be an example. 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. By doing so the preparatory processes yields an adequately absorbent and appropriately white material with cellulose content of 99%, but the processes generates huge amounts of effluent. 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. 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. It is believed that the replacement of caustic scouring of cotton substrates by bio-preparation with selected enzymes will result in the following quantifiable improvements: lower BOD, COD, TDS and alkalinity, process time, cotton weight loss and harshness to handle.

2. GENERAL INFORMATION

Composition of cotton: Cotton fibre is a single biological cell. It is built up of four parts – lumen, secondary wall, primary wall and cuticle. Lumen is the nutrient transportation tube for the cell containing small amounts of bio-organic materials, which add a yellowish shade to the fibre. The secondary wall is built up of cellulose layers which contribute about 91.5% of fibre and a crystalinity index of 70%. The primary cell wall, which mainly consists of protein, pectic substances and glucans, is about 2.5% of fibre weight. It has a crystallinity index of about 30%. The protective cuticle is made of wax, mineral matters, pectins, fatty acids, high molecular weight alcohols and their esters.

Viscose Rayon: The regenerated cellulose fibres are simply regenerated from wood pulp or cotton linters, which are sources of pure natural cellulose, without any change in chemical constitution in polymer. But there is only a certain variation in degree of polymerization and as well as modified physical properties.

Since viscose is a regenerated fibre the raw material undergoes purification before it is spun into yarns and thus contains very little (acquired during spinning like spin finish etc.) or no impurities.

2.1 Pretreatment:

Textile materials possess a variety of impurities. Some are natural or inheriting, or may be added purposely for better spinnability or weavability. Materials are also occasionally contaminated by accidental impurities acquired while handling of materials. All such impurities are to be removed before actual dyeing or printing. Such processes which are used for the removal of these impurities are called preparatory processes and may be broadly classified into two categories:

1. Cleaning processes, where bulk of the foreign matters or impurities are removed by physical or chemical means.
2. Whitening processes, in which trace coloring matters are destroyed chemically or the whiteness of the material is improved optically.
2.2 Conventional Process:
The first step of wet pre-treatment is the removal of starch or other sizing materials, which are applied on yarn before weaving, for better weavability. The process is known as desizing. Enzymatic desizing of cellulosic fabrics is a long established standard process. Amylolitic enzymes are used to convert any type of starch size into water-soluble products without affecting the cellulosic fibres. Using enzymes in their natural or modified state products are available to allow desizing at 20-70°C, 70-90°C or at 85-115°C.

The most important preparatory step is known as scouring, by which complete or partial removal of the non-cellulosic components found in native cotton as well as impurities such as machinery and size lubricant takes place. Traditionally it is achieved through a series of chemical treatments and subsequently rinsing in water. The process essentially consists of a strong alkali like caustic soda and detergent. In non-continuous cotton processing, caustic soda is used within the range of 10-20g/L, that is about 3-6% of the weight of fabric. While in a continuous scouring process caustic concentration should be a minimum of 30g/L, with 100% pick-up. Scouring treatment generates large amounts of salts, acids and alkali and requires huge amount of water.

Bleaching is a process which is designed to produce white goods and must be accomplished with a minimum of damage to the cotton being bleached. H₂O₂ bleaching is widely used for the natural cellulosic fibres, protein fibres and is also effective on regenerated cellulose fibre. Blends of synthetic fibre with natural fibres, like cotton/polyester, is also achieved with H₂O₂. With few exceptions bleaching with H₂O₂ is carried out under alkaline conditions. The maximum bleaching activity from H₂O₂ is obtained generally at about pH 11.5.

2.3 Bioprocess – the Green Alternative:
Like other applications of biotechnology, modern bioprocess technology is an extension of ancient techniques for developing useful products by taking advantage of natural biological activities. When our early ancestors made alcoholic beverages, they used a bioprocess: the combination of yeast cells and nutrients (cereal grains) formed a fermentation system in which the organisms consumed the nutrients for their own growth and produced by-products (alcohol and carbon dioxide gas) that helped to make the beverage. Although more sophisticated, today's bioprocess technology is based on the same principle: combining living matter (whole organisms or enzymes) with nutrients under the conditions necessary to make the desired end product.

In textile application, the knowledge of specific action of enzymes (amylase) for starch splitting began around 1857, when malt was used to remove gum from fabrics before printing. The enzymes have now been largely used for pretreatment processes of textile materials. Such processes include scouring and bleaching of cellulosic materials, degumming of silk, carbonizing, bleaching and shrink-resisting treatments of wool. In stone washing of denim fabrics, the color of indigo or sulphur dyed materials is faded at certain places with oxidizing agents. Enzymes are nowadays used for such coloration. Bio-stoning has achieved considerable importance for treating casual-wear garments to give them a washed-down or worn appearance. This is more environmentally acceptable and it replaces or decreases the amount of pumice stones that may damage machinery and causes harshness of the fabric.

Because bioprocesses use living material, they offer several advantages over conventional chemical methods of production: they usually require lower temperature, pressure, and pH (the measure of acidity); they can use renewable resources as raw materials; and greater quantities can be produced with less energy consumption.

2.4 Enzymes:
Enzymes are proteins that catalyze (i.e., increase the rates of) chemical reactions. In enzymatic reactions, the molecules at the beginning of the process are called substrates, and the enzyme converts them into different molecules, called the products. Almost all processes in a biological cell need enzymes to occur at significant rates. Since enzymes are selective for their substrates and speed up only a few reactions from among many possibilities, the set of enzymes made in a cell determines which metabolic pathways occur in that cell.

Like all catalysts, enzymes work by lowering the activation energy (E_a) for a reaction, thus dramatically increasing the rate of the reaction. Most enzyme reaction rates are millions of times faster than those of comparable un-catalyzed reactions. As with all catalysts, enzymes are not consumed by the reactions they catalyze, nor do they alter the equilibrium of these reactions. However, enzymes do differ from most other catalysts by being much more specific. Enzymes are known to catalyze about 4,000 biochemical reactions. Synthetic molecules called artificial enzymes also display enzyme-like catalysis.

2.5 Structure:
Enzymes are proteins, i.e. sequences of amino acids linked by peptide bonds. The sequence of amino acids within the polypeptide chain is characteristic of each enzyme. This leads to a specific three-dimensional conformation for each enzyme in which the molecular chains are folded in such a way that certain key amino acids are situated in specific strategic locations. This folded arrangement, together with the positioning of key amino acids, gives rise to the remarkable catalytic activity associated with enzymes. Enzymes are usually very specific as to which reactions they catalyze and the substrates that are involved in these reactions. Complementary shape, charge and hydrophilic/hydrophobic characteristics of enzymes and substrates are responsible for this specificity.
"Lock and key" model: Enzymes are very specific, and it was suggested by Emil Fischer in 1894 that this was because both the enzyme and the substrate possess specific complementary geometric shapes that fit exactly into one another. This is often referred to as "the lock and key" model. However, while this model explains enzyme specificity, it fails to explain the stabilization of the transition state that enzymes achieve. The "lock and key" model is therefore less accurate than the induced fit model.

**Induced fit model**

Fig. 1. Diagrams to show the induced fit hypothesis of enzyme action

In 1958, Daniel Koshland suggested a modification to the lock and key model: since enzymes are rather flexible structures, the active site is continually reshaped by interactions with the substrate as the substrate interacts with the enzyme. As a result, the substrate does not simply bind to a rigid active site; the amino acid side chains which make up the active site are molded into the precise positions that enable the enzyme to perform its catalytic function. In some cases, such as glycosidases, the substrate molecule also changes shape slightly as it enters the active site. The active site continues to change until the substrate is completely bound, at which point the final shape and charge is determined.

2.6 Mechanisms:

Enzymes can act in several ways, all of which lower ΔG:

- Lowering the activation energy by creating an environment in which the transition state is stabilized (e.g. strain) and the shape of a substrate—by binding the transition-state conformation of the substrate/product molecules, the enzyme distorts the bond substrate(s) into their transition state form, thereby reducing the amount of energy required to complete the transition.
- Lowering the energy of the transition state, but without distorting the substrate, by creating an environment with the opposite charge distribution to that of the transition state.
- Providing an alternative pathway. For example, temporarily reacting with the substrate to form an intermediate ES complex which would be impossible in the absence of the enzyme.
- Reducing the reaction entropy change by bringing substrates together in the correct orientation to react. Considering AHlg, alone overlooks this effect.
- Increases in temperatures speed up reactions. Thus, temperature increase help the enzyme function and develop the end product even faster. However, if heated too much, the enzyme’s shape deteriorates and only when the temperature comes back to normal does the enzyme regain its shape. Some enzymes like thermo labile enzymes work best at low temperatures.

Based on the medium of their preparation enzymes are classified as bacterial, pancreatic (blood, lever etc) malt (germinated barely) etc. According to their major functions enzymes are grouped under the following groups—

Oxido-reductases: Catalyze oxidation reduction reactions.

Such as dehydrogenases, reductases

Transferases: Catalyze functional group transfer. Such as kinases, aminotransferases, thiolases.

Hydrolases: Catalyze hydrolysis reactions. Such as peptidases, glycosidases, lipases, phosphatases

Lyases: Catalyze elimination/addition of groups to form/break double bonds. Such as synthases, decarboxylases, dehydratases.

Isomerasis: Catalyze reactions that alter structure, not composition (optical, geometric, or structural isomers).

Such as isomerasis, mutases

Ligases: Catalyze coupling of two compounds along with hydrolysis of a phosphoanhydride bond. Such as synthetases, carboxylases, polymerases

HYDROLASES type of enzyme is mostly used in textile processing.

2.7 Enzymatic scouring and bleaching:

Compared to conventional alkaline boiling off, the advantages of bioscouring are obvious that it can save water and time by reducing one rinsing cycle: save energy by lowering the treatment temperature from boiling to around 50-60°C; and permit less fibre weight loss and less COD and BOD in the effluent. In addition the super soft handle, probably due to the retention of the beneficial wax, is unattainable by alkaline pre-treatment. Major companies involved in the preparation and marketing of enzymes useful for textile industries are Dystar, Clariant, Genencor and Novozenzymes (formerly Novo Nordisk), etc. In our research we worked with the Gentle Power Bleach™, a joint-venture product from Huntsman and Genencor. The novel enzyme
allows for the system to perform at much lower temperatures for bleaching and at neutral pH levels. Historically, the textile bleaching process requires temperatures of 95°C. Genencor’s unique enzyme allows this to be lowered to 65°C. By lowering the treatment and rinsing temperature considerably, savings in water and energy consumption of up to 40% are possible.

3. CHEMICAL BACKGROUND

**Mechanism of hydrogen peroxide bleaching:**

Hydrogen peroxide is a very weak acid. It could be ionized to form perhydroxyl ions (HOO⁻)

\[ \text{H}_2\text{O}_2 \xrightarrow{\text{OH}^-} \text{HOO}^- + \text{H}^+ \]

The formation of the active perhydroxyl ions is favoured by alkaline conditions and these anions are the source of the active oxygen that has the bleaching effect.

\[ \text{H}_2\text{O}_2 + \text{OH}^- \leftrightarrow \text{H}_2\text{O} + \text{HOO}^- \]

\[ \text{HOO}^- \leftrightarrow \text{OH}^- + [\text{O}] \]

The mechanism of bleaching is very complicated and not completely understood. One opinion is that the color producing agents in natural fibers are often organic compounds containing conjugated double bonds. It is known in dye chemistry that conjugation is necessary for an organic molecule to perform as a dyestuff. Discoloration can occur by breaking up the chromophore, most likely destroying one or more of the double bonds within the conjugated system. Oxidative bleaches oxidize color bodies into colorless compounds. For example, double bonds are known to be oxidizing into epoxides which easily hydrolyze into diols.

\[-\text{C=C-C=C-} + [\text{O}] \rightarrow -\text{C=C-C - C=C} - \]

\[ \text{OH} \]

\[-\text{C=C-C=C-C=C-} \quad \text{OH} \]

In enzymatic bleaching the following reactions takes place:

**Activated, enzymatic peroxide bleach:**

**Perhydrolysis:**

\[ \text{R-C-X} \xrightarrow{\text{Hydrolase}} \text{R-C-OH} + \text{HX} \] (I)

**Bleaching reactions:**

\[ \text{R-C-OH} \xrightarrow{\text{Peracid}} [\text{O}] + \text{R-C-C} + \text{OH} \] (II)

\[ [\text{O}] + \text{Fiber} \xrightarrow{\text{Active oxygen}} \text{Bleached fiber} \] (III)

**Product Overview:**

- Invatex LTA: Agent to assist and boost the peroxide reaction in the Gentle Power Bleach.
- Invatex LTE: Enzyme for the Gentle Power Bleach to catalyze the peroxide bleach in combination with Invatex LTA.

4. TECHNICAL PART

**Materials used:** Grey woven fabric – cotton (plain weave) and grey knit fabric – viscose. The different pre-treatment chemicals and desizing enzyme was collected from BASF while the gentle power bleach was taken from Huntsman. At first the woven grey cotton fabric was desized using amylase enzymes at 70°C for 20 minutes in an automatic laboratory dyeing m/c. Then this fabric along with the viscose was subjected to single bath scouring-bleaching processes using, strong alkali and H₂O₂ at boiling temperature as in conventional method, and gentle power bleach in a neutral pH and at a temperature of 65°C as in the Bio-process. The amount of H₂O₂ used in both cases was 6g/l and 9g/l. To assess the amount of dye absorbed by the fabrics processed by conventional and bio-process, they were dyed at depths of 0.5%, 2.5% and 6% shade with Drimarine Dark Red HF-CD, reactive dye from Clariant. Dyeing was also performed in the automatic laboratory dyeing m/c according to the manufacturer’s recommended process.

4.1 Tests carried out:

1. **Absorbency test** – The absorbency of the pre-treated fabrics were assessed by the drop test method using 0.1% direct dye solution.

2. **% Weight loss** – The weights of un-scoured and scoured samples were taken separately and the weight loss was determined. The standard range of weight loss of fabric due to scouring is 4-8%.

3. **Strength testing** – **Tensile strength:** Machine - Titan Universal Strength tester, Origin - James H. Heal and Co. Ltd, Test method - ASTM D5034. **Bursting strength:** Machine - Bursting Strength tester, Origin - Mesdan Lab, Germany, Measuring range - 0-20kg/cm²

4. **Whiteness index** – it was evaluated using a Dual-beam spectrophotometer from Data color.

5. **Assessment of the amount of dye absorbed** – Color was evaluated in terms of k/s values, ΔE and CIE Lab coordinates (Illuminant D65/10° observer) with a Data color 650 spectrophotometer.

6. **RESULTS AND DISCUSSIONS**

**Absorbency result** –

- In case of cotton, best absorbency was obtained with conventional process using 9g/l H₂O₂.
- Bio 6 on cotton shows good absorbency relative to conventional 6, but is somewhat uneven.
- In case of viscose, absorbency of fabric treated conventionally and with bio-process is same.
Weight loss %: From the results we see that the weight loss % is higher in conventional process compared to the bio-process. So we can assume that more impurities have been removed from the fabric treated by conventional alkaline process and are more effective in this case than the bio-process (particularly in removing motes).

Table II

<table>
<thead>
<tr>
<th>Process</th>
<th>Substrate</th>
<th>Weight before (g)</th>
<th>Weight after (g)</th>
<th>Weight loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Con 6</td>
<td>Cotton</td>
<td>37.10</td>
<td>36.17</td>
<td>2.51</td>
</tr>
<tr>
<td>Bio 6</td>
<td>Cotton</td>
<td>36.30</td>
<td>35.56</td>
<td>2.14</td>
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<tr>
<td>Con 9</td>
<td>Cotton</td>
<td>37.70</td>
<td>36.20</td>
<td>3.98</td>
</tr>
<tr>
<td>Bio 9</td>
<td>Cotton</td>
<td>35.45</td>
<td>34.21</td>
<td>3.50</td>
</tr>
</tbody>
</table>

Strength loss: Compared to the conventional process, loss of strength in both the fibres is found to be very low in the respective bio-processes. This means that very little damage occurs when the fibre are treated with bio-process.

Table III

<table>
<thead>
<tr>
<th>Process</th>
<th>Substrate</th>
<th>Strength before bleaching</th>
<th>Strength after bleaching</th>
<th>Strength loss %</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cotton (N)</td>
<td>Viscose (KPa)</td>
<td>Cotton (N)</td>
</tr>
<tr>
<td>Con 6</td>
<td>388</td>
<td>3.84</td>
<td>373.1</td>
<td>3.667</td>
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<tr>
<td>Bio 6</td>
<td>388</td>
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<tr>
<td>Con 9</td>
<td>388</td>
<td>3.84</td>
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<tr>
<td>Bio 9</td>
<td>388</td>
<td>3.84</td>
<td>384.8</td>
<td>3.567</td>
</tr>
</tbody>
</table>

Dye uptake %: It was found that cotton treated by bio-process absorbed more dyes than those treated conventionally, irrespective of the shade %. In case of viscose the reversed occurred, that is conventionally treated fabric absorbed more dyes. A probable answer can be while treating cotton enzymes might have reduced crystallinity and increased the amorphous region; as a result the fabric absorbed more dyes. But the structure of viscose is already more amorphous than cotton and thus the enzymes had no effect in changing the structure.

Graphical representation of dye uptake:

Whiteness index: It can be seen from the graph that, in case of cotton, the whiteness index is highest for the fabric processed with 9g/l H₂O₂ in the conventional way and the others are almost same. While for viscose, the whiteness achieved with all the processes are almost same. So we can conclude that bio-process can give excellent whiteness to regenerated fibers.
Table IV

<table>
<thead>
<tr>
<th>Process</th>
<th>Substrate</th>
<th>Whiteness index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional 9</td>
<td>Cotton</td>
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<td>Viscose</td>
<td>66.38</td>
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7. LIMITATIONS

Scouring is a process that specifically targets non-cellulosic impurities with pectinases. Technical feasibility of bio-scouring has been recognized. Yet it is not clear why bio-scouring has not yet been widely accepted by dye houses. Some probable limitations are discussed - Undoubtedly, the primary limitation is that bio-process has little effect on mote removal. Although bioprocess positions itself as a pretreatment only for the dark shades, it sometimes cannot prevent the appearance of motes even in the dark shaded fabrics. Another factor limiting the wide use of bio-scouring is its inability to give any whiteness improvement to treated fabrics. The process thus cannot be used to pre-treat full white, pale and medium shade fabrics. Finally, inability to remove wax impurity has greatly restricted bio-scouring from being accepted.

8. CONCLUSION

Enzymatic process is definitely a break-through and the path for a greener technology. Such pretreatment will sooner or later prevail, but in order for this to happen, more research needs to be done to resolve those technical problems. The necessity for the development of enzymatic solutions to pretreatment has never been as overwhelming as it is today. The elevated price of crude oil makes petrochemical based textile auxiliaries expensive and once again reminds people of the importance of sustainable development. The electricity shortage, in our country drove people to use energy saving technology and the water pollution caused by textile effluents, particularly from pretreatment, leaves dye houses no alter native but to choose an environmentally friendly process. It is not clear why bioprocess has not yet been widely accepted by industries. But we can say that, it is only a matter of time that the drawbacks will be conquered and it will be the future of textile processing. It remains to be seen when and how this technology becomes a reality.

REFERENCES


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