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Modern Biotechnological Pre-treatment Techniques

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Abstract
Sustainable processing is now becoming compliance for the Textile industries. Bio-processing is the one of the eco-label fields in the modern technologies. Therefore, this article mainly focuses on new research on biological treatments for pretreatment sector of cellulosic substrate for eco-friendly processes and eco balancing by using various enzymes, instead of harsh & hazardous chemicals. In addition, the future trends in the biotechnology are also discussed in the end of this paper. This paper presents also short introduction to the method of new bio-processes. Biotechnology can be used in new production processes that are themselves less polluting than the traditional processes and microbes or their enzymes are already being used to degrade toxic wastes. The use of enzymes in the textile chemical processing is rapidly gaining globally recognition because of their non-toxic and eco-friendly characteristics with the increasingly important requirements for textile manufactures to reduce pollution in textile production The reduction in pollution load represents a major option for potentially decreasing both the environmental impacts as well as the treatment costs.
Keywords: Biological Treatment, AMG-Amyloglucosidase/Pullanase Mixture.

INTRODUCTION

The impact of biotechnology in the production of textiles is increasingly significant. Enzyme technology has already proven to be advantageous in industrial textiles processing of natural fibres. The Novozymes Report 2009 discloses that the major share of the industrial enzyme market [10] is divided between Novozymes (47%), Danisco Genencor (21%), and DSM (6%), with the remaining 26% shared between other minor players. Sales of industrial enzymes have increased by 32% since 2005 and the worldwide value of the industrial enzyme markets in 2009 was estimated to be about 12000 million.

The textile wet processing sector is the one of the biggest production sectors of Asia which drain highest amount of hazardous effluent and directly involved to create ambient problem now it is became serious problem to major textile producing zones like Pakistan ,China, India ,Bangladesh, . It also creates negative impact on textile market of those countries who doesn't take serious action against environmental issues like zero drainage eco-friendly products [8].

Therefore, The researchers and scientists are working to solve economical, ecological, eco- friendly issues by troubleshooting converting the chemical treatments into biological treatments, recently successful working on biological treatments appeared in the field of wet processing specially in pretreatment sector and are in industrial practices biological evolution, textiles also have gone through a lot of metamorphosis to reach the present day level. It is surprising to note that from time immemorial biological processing of textiles have taken place in one way or the other to bleach, color and print.

ENZYMATIC DE-SIZING

Starch is a polysaccharide carbohydrate; a polymer of glucose joined together by glycosidic bonds. Starch consists mainly of amylose and amylopectin; amylose being a relatively linear polymer of glucose joined by α-1,4-glycosidic bond, and amylopectin being a branched polymer of glucose joined by both α-1,4-glycosidic bond (linear) and α-1,6-glycosidic bond (branching) (Caballero, 2003). *See Fig. 1*

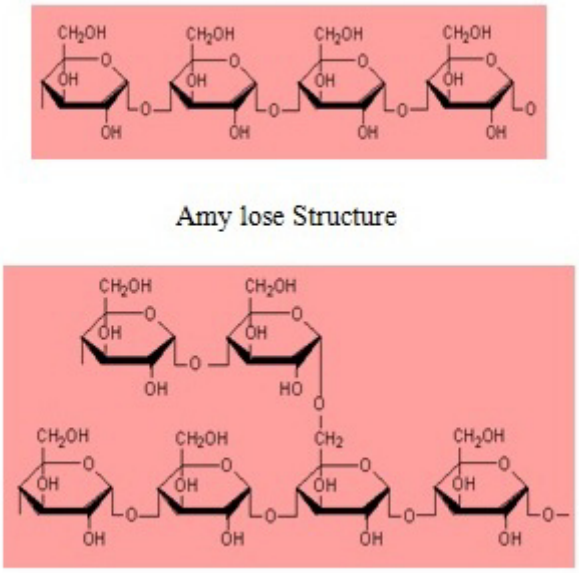

Fig. 1 Chemical Structure of Starch [2]

To convert this polymer into its monomer, the amylase enzyme is used. The amylase enzyme can be classified into three categories: α-amylase, β-amylase, and glucoamylase. α-amylase will break the α-1, 4-glycosidic bond randomly, giving molecules of dextrins. α-amylase can also break the α-1, 6-glycosidic bond, but at a much slower rate (usually the enzyme pullulanase is added to accelerate the breakage of α-1, 6-glycosidic bond). β-amylase breaks the α-1, 4-glycosidic bond from the non-reducing end, giving molecules of maltoses. And glucoamylase breaks the α-1, 4-glycosidic bond also from the non-reducing end, giving molecules of glucose (Wiseman, 1985).
The traditional enzyme α-amylase will break down the α-1, 4-glycosidic bond, but not the α-1, 6-glycosidic bond. Therefore, the reaction yields molecules of branched but short glucose. Branched molecules are soluble in water, whereas linear ones are insoluble. In other words, the branched molecule will make a less viscous solution that the linear ones. Hence the viscosity of the starch solution will decrease as the α-amylase works (Wiseman, 1985)
Using amylase enzymes for the removal of starch sizes is one of the oldest enzyme applications. [1, 3-4] Amylases are enzymes which hydrolyse starch molecules to give diverse products, including dextrins and progressively smaller polymers composed of glucose units [5]. These partly degraded oligosaccarides or cannot be reused [2] and are usually discharged, contributing large amounts of Chemical Oxygen Demand (COD) and Biological Chemical Oxygen Demand (BOD) to effluent streams [6, 7]. 50-80% of the COD in the effluents of textile finishing.

NEW ENZYME (MIXTURE) FOR DE-SIZING:
New desizing process of Cotton pretreatment chemicals with enzymes known as (amyloglucosidase/pullanase) to create an environmentally friendly process for water and energy savings. In this enzyme selection and process optimization was made in order to increase the glucose content of the de-sizing liquor of a starch-sized cotton fabric

PRACTICAL APPROACH:
Desizing trials were performed on The fabric of plain weave 100% raw cotton fabric with a mass per square meter of 175 g/m2 with equal weft and warp counts of 62.5 tex and densities of 14 ends/cm. The fabric was sized with a 100% starch sizing agent and 4% (owf: over the weight of the fabric) starch was present in the sized fabric. According to the recipes listed in Table 1 with fabric specimens of 20 grams (approximately 30 × 30 cm^2) at a liquor ratio of 1:10 using distilled water. The process time for the commercial de-sizing enzymes was prolonged to 90 minutes (30-60-90 minutes) in order to investigate any further increase in the glucose content. Optimization trials were performed for the amyloglucosidase/pullanase mixture.

Table 1.

Enzyme types and desizing recipes recommended by manufacturers; CD: Commercial Desizing enzyme, a - Amyloglucosidase 186 Units/g, pullanase 395 Units/g. b - Commercial enzyme for food industry, no data available for desizing process.

Enzyme Type	pH	Dosage	Temp. °C	Time, min.	Supplier
CD1- α-amylase	6 - 7	0.25-1.3 g/l	70	30	Novozymes, Bagsvaerd, Denmark.
CD2- α-amylase	6 - 7	0.06-0.3 g/l	70 - 110	30	
CD3- α-amylase	6 - 7	0.5-2 g/l	90 - 98	30	R-Duraner, Bursa, Turkey.
CD4- α-amylase	6 - 7	0.2-0.4 g/l	90 - 98	30	
CD5- α-amylase	6.5	0.02-0.05 g/l	80 - 90	30	AB Chem., Bursa, Turkey.
CD6- α-amylase	7 - 7.5	0.05-0.2 %	90 - 95	10 - 20	Gemsan, Istanbul, Turkey.
CD7- α-amylase	6.5 - 7	0.05-0.2 %	50 - 70	20 - 30	
CD8- α-amylase	5.4 - 8	1.2 g/l	30 - 60	30	CHT, Istanbul, Turkey.
CD8- α-amylase	5.4 - 8	0.5-2 g/l	60 -100	30	
AMG- Amylo-glucosidase/ pullanase mixturea	4.1 - 4.3b	- b	60 -63b	- b	Novozymes, Bagsvaerd, Denmark.

Table 2.

Glucose generated in desizing liquor during the desizing process; CD: Commercial Desizing enzyme, AMG: Amyloglucosidase/pullanase enzyme mixture.

Enzyme	pH	Dosage	Temp., °C	Generated glucose, mg/l			Iodine test
				30 min.	60 min.	90 min.	
CD1	6.5	1.3 g/l	70	200	210	205	7-8
CD2	6.5	0.3 g/l	90	210	205	210	7-8
CD3	6.5	2.0 g/l	90	180	200	190	7-8
CD4	6.5	0.4 g/l	100	213	200	208	7-8
CD5	6.5	0.05 g/l	85	180	200	190	7-8
CD6	7.0	0.2%	90	180	190	185	7-8
CD7	6.5	0.2%	60	190	185	200	6-7
CD8	6.5	2.0 g/l	50	205	220	208	6-7
AMG	4.1	0.25%	62	3116	3920	3606	6-7

The absorbance of the solution was measured using a spectrophotometer with a 460 - 560 nm interval; the darker the color, the greater the glucose amount. The absorbance of the desizing liquor was compared to the absorbance of standard glucose solution (5.55 mmol/l). The Glucose content of the desizing liquor was calculated by with formula Gd = (Ad/As).Gs, where Gd and Ad are the glucose amount (mg) and absorbance of the desizing liquor, and Gs and As are those of standard glucose solution.

The performance of a commercial enzyme (an amyloglucosidase/ pullanase mixture) produce optimum circumstances obtained were: 0.75% (o.w.f.) enzyme, PH 4.1, 62 °c and a process time of 45 minutes.

The results indicated that commercial desizing enzyme formulations of α-amylase enzymes were not appropriate to produce a large quantity of glucose in the desizing bath; the glucose amounts obtained were about 200 mg/l. however, the food market enzyme used, an amyloglucodidase/pullanase mixture (amyloglucosidase 186 units/g, pullanase 395 units/g), produced approximately 4000 mg/l glucose in the desizing bath after process optimization

In the table 2: compares the glucose generation and de-sizing effect of the enzymes used. Results indicate an acceptable desizing effect but very low glucose generation for α-amylases. The amount of hydrogen peroxide required to obtain a satisfactory whiteness is reported to be 400 - 600 mg/l, requiring a glucose amount of

approximately 4,000 mg/l in the desizing bath for hydrogen peroxide generation of gox [10]. The amounts of glucose reported in table 2 for α-amylases were not enough even for prolonged processing times. The low glucose generation can be attributed to the reaction mechanism of α-amylases, which are endoamylase enzymes and do not involve the degradation of starch until single glucose units exists, despite their well-known and satisfactory desizing effect .

amyloglucosidases, exoamylases and pullanases are debranching enzymes that produce starch degradation until single glucose units, as described before [8, 10]. The results reported in table-2 for amyloglucosidase (amg) enzyme conformed this hypothesis, indicating a great increase in the amount of glucose: an average glucose generation of 199.8 mg/l for α-amylases and 3,544 mg/l for theamyloglucosidase/pullanase mixture. Iodine test results indicate a sufficient desizing performance for amg enzyme comparable to that of α-amylases.

despite the increase in glucose amount while using the amg enzyme, the glucose amounts were still under the required level of approximately 4,000 mg/l [10].recommended process parameters for the amg enzyme were not available for desizing, but ph 4.1 - 4.3 and temperature of 60 - 63 °c have been applied to produce glucose syrup from corn starch in food industry. A set of trials were performed to find optimum circumstances to generate maximum glucose during the desizing process.

FURTHER ACHIEVEMENTS:

PEROXIDE GENERATION IN DESIZING LIQUOR AND BLEACHING

In this, new research the desizing liquor is utilizing for the bleaching. The fabric used was a plain weave 100% cotton raw fabric with surface density of 175 g m-2. The fabric was sized with a 100% starch sizing agent, and 4% (owf) starch was present on the sized fabric.

The fabrics were desized with the amyloglucodidase/pullanase mixture enzyme in a desizing bath to produce glucose.

Glucose oxidase (EC 1.1.3.4) from Aspergillus niger (Biozymes) was used for peroxide generation process optimisation for the glucose oxidase enzyme was undertaken in order to generate hydrogen peroxide in the desizing liquor and then bleaching utilise desizing liquors of starch-sized fabrics using enzymes known as glucoseoxidase for bleach to produce hydrogen peroxide from glucose units of the starch removed;

Glucose -D-glucose using other oxidising substrates boxidase can oxidise besides molecular oxygen, including quinines and one-electron acceptors. D-glucono-1, 5-lactone (Fig. 2)can then hydrolyse spontaneously to produce gluconic acid.

Glucose oxidase is a dimeric protein composed of two identical subunits. Each subunit, or monomer, folds into two domains: one domain binds to the -D-glucose, while the other domain binds non-covalently tobsubstrate, a cofactor, flavin adenine dinucleotide (FAD), which it uses as a powerful oxidising agent. FAD is a common component in biological oxidation-reduction (redox) reactions, in which there is a gain or loss of electrons from a molecule. In glucose oxidase, FAD acts as an electron acceptor, which causes it to be reduced to FADH2; the FADH2 is then oxidised by the final electron acceptor, molecular oxygen, with the oxygen being reduced to hydrogen peroxide (H2O2). glucoseoxidase enzymes are efficient only at high glucose doses.

In this, process optimisation for the glucose oxidase enzyme was undertaken in order to generate hydrogen peroxide in the desizing liquor and then bleaching with the peroxide generated.

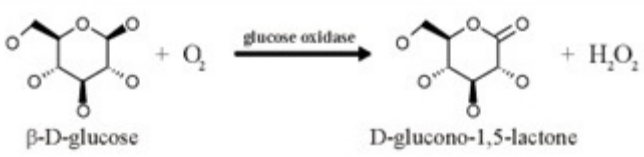

Fig. 2: Beta-D-glucose + O(2) <=> D-glucono-1, 5-lactone + H(2)O(2)

Results indicated that sufficient hydrogen peroxide, about 800 mg l-1, could be generated to perform successful enzymatic bleaching; however, the bleaching was compatible with the conventional peroxide type only in the alkali pH range. The maximum whiteness obtained by enzymatic treatment was 73.8 Stensby degree, whereas the whiteness of the conventionally treated fabric was 79.4 Stensby degrees.

ENZYMATIC ONE-BATH DESIZING — BLEACHING — DYEING PROCESS FOR COTTON FABRICS

This new process to desize, bleach, and dye starch-sized cotton fabrics in one bath using enzymes is successfully perform by engineering department bursa university Turkey .

Desizing was performed with an amyloglucosidase/pullanase enzyme (Dextrozyme DX, manufactured by Novozymes) instead of a conventional amylase enzyme in order to hydrolyze starch into single glucose units. The Multifect GO 5000L (Genencor) glucose oxidase enzyme was used to yield hydrogen peroxide from the glucose generated during desizing; bleaching was performed by this enzymatically generated hydrogen peroxide.

Decomposition of hydrogen peroxide after bleaching was done with Terminox Ultra 10L (Novozymes) catalase enzyme. The fabric was dyed in the same bath with the selected monochlortriazine reactive dyes (DyStar).
Starting with glucose as substrate for the GOD hydrogen peroxide is generated in situ [9], which is immediately used by the POD to oxidize colored compounds in dyeing baths. In this way the stationary peroxide concentration is nearly zero during the whole process and the enzymes are not degraded by the oxidizing agent. Moreover, experiments are carried out to check if this two compound- system is suitable for textile bleaching of natural cotton fibers.

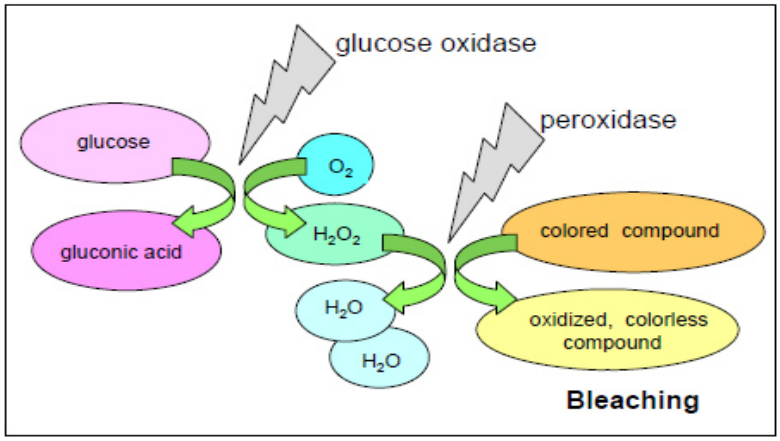

Fig. 3 Generation of Peroxidase [9]

The amount of glucose generated during desizing was 4000 ± 135 mg/l and it yielded 765 ± 15 mg/l hydrogen peroxide during glucose oxidase enzyme treatment. The whiteness index of the enzymatically bleached fabric was 71.0 ± 1.2 stensby degree. The color yields of the enzymatically treated samples were comparable to the conventionally treated samples. All enzymes used in this study were commercial grades having the advantages of easy storage and supply compared to the pure enzymes used in earlier studies. The advantages of the new one-bath process were: less auxiliary demand; lower environmental impact; and energy and water savings compared to the conventional desizing, scouring, bleaching, and dyeing sequence.

NOVEL BIOTECHNOLOGICAL TRENDS IN WET PROCESSING

DYEING IN CATALASE-TREATED BLEACHING BATHS:

Catalase is a tetrameric haein-enzyme, which contains four ferriprotoporphyrin groups per molecule. Chelating agents may remove the iron atom from the heam group of the catalase and thereby inactivate it. Bleach formulations usually contain sequestering agents such as silicates. This classifical hydrogen per oxide stabilizer acts as an anti-catayst. Catalysts, which decompose hydrogen peroxide are inserted into the water glass colloids and thereby are inactivated.

ENZYMES FOR WOOL AND SILK FINISHNG

The enzymes were introduced for the Bio-polishing of wool. Wool is made of protein and therefore this treatment features a protease, which modifies the wool fibers. “Facing up” is the trade term for the ruffling up of the surface of wool garments by abrasive action during dyeing. Enzymatic treatment reduces facing up, which significantly improves the pilling performance of garments and increases softness. Proteases are also used to treat silk. Threads of raw silk must be degummed to remove sercin, a proeinaceous substance that covers the silk fiber. Traditionally degumming is performed in an alkaline solution containing soap. This is a harsh treatment because the fibre itself, the fibrin, is also attacked. However, because they remove the sercin without attacking the fibrin.

ENZYMETIC BLEACHING OF DENIM

Laccase is a redox enzyme using molecular oxygen as the electron acceptor. Madiator is a low molecular weight organic compound, named PPT, which mediates electron transfer from indigo to molecular oxygen. In the presence of aqueous medium, the enzyme gets oxidized and attacks the mediator and converts it into free radicals. The free radicals are generated and then attack the indigo and convert it into oxidized products.

DECOLORIZATION OF TEXTILE TEXTILE WASTE WATER

Enzymes such as laccases and manganese peroxidases can cleave aromatic rings. These have potential for destroying dyes though individual enzymes capable of breaking down one type of dye molecular structure may be blocked from attacking another dye structure.

POLYESTER HYDROPHILIZATION

Lipase has an ability to hydrolyze ester linkages. The wetting and absorbency properties of sulphonated polyester and micro-denier polyester fabrics can alas be improved by lipase.

FUTURE SCOPE

Biotechnology also offers the potential for new industrial processes that require less energy and are based on renewable raw materials. It is important to note that biotechnology is not just concerned with biology, but it is a truly interdisciplinary subject involving the integration of natural and engineering sciences [11]. Biotechnology is like an enormous factory which not only provides other industries with innovative ideas, but also supplies the appropriate know-how. Now familiar with the application of modern biotechnology in medicine and agriculture: so-called red and green biotechnology. There is less general awareness of the white variety: the use of biotechnology for industrial applications. It has been shown here that mechanical energy plays a dominant role in the performance of enzymes [10] in textile treatment processes. Therefore, it is not easy to translate the performance obtained on a laboratory scale to the performance on an industrial scale. This is because the deformation factor α is different in different systems. The best way would be to set up laboratory- scale experiments in such a way that they have an α-factor which is the same as its value on full-scale equipment. To prevent the phenomenon of enzyme exhaustion in the pores of the fabric, it is possible to enhance the enzyme concentration in the enzyme padding system. However, this will be very costly and therefore not a realistic option. The current installed base in textile treatment companies are based on traditional chemistry. It has been shown here that enzymes require another approach and, thus, it is expected that a breakthrough in the application of enzymes will only occur if machine manufacturers develop special systems in which the squeezing factor is as high as possible. Incorporation of ultrasound in such new systems could lead to the desired performance.

CONCLUSION

Textile processing is a growing industry that traditionally has used a lot of water, energy and harsh chemicals. Starting from pesticides for cotton growing to high amounts of wash waters that result in waste streams causing high environmental burdens. As textile fibers are polymers, the majority being of natural origin, it is reasonable to expect there would be a lot of opportunities for the application of white biotechnology to textile processing. Enzymes nature's catalysts are the logical tools for development of new biotechnology-based solutions for textile wet processing. Developments in genetic and protein engineering have led to improvements in the stability, economy, specificity and overall application potential of industrial enzymes. When all the benefits of using enzymes are taken into consideration, it's not surprising that the number of commercial applications for enzymes is increasing every year.

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