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New Approaches of Biotechnology in Textile Coloration

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Abstract

The application of biotechnology in textile processing is gaining worldwide detection as one of the hopeful approaches to pollution issues and cost reduction. Hydrolase enzymes as amylases, pectinase, and cellulase have been successfully used in the wet process over the past 40 years. The application of these enzymes in one bath is a new challenge. Laccases enzymes are used in biosynthesis and decolorization of textile effluents. Application of enzyme in hydrolysis of starch thickeners which is the main component of the printing paste enzyme is one of the promising areas. Green synthesis of dyes, *in-situ* coloration, and polymer grafting are the new trends of enzymes application as it produces smart colored textile. The application of biotechnology in textiles is the solution to almost all the problems of this industry. The enzyme's researches illustrate the improvement in product quality at shorter times and lower energy and water consumption. This state of art highlights the novel approaches of application of enzymes in the textile coloration and industry covering both current types of research and pilot application.
Keywords: New approaches, Biotwcknology, Textile coloration

. Introduction

Environmental considerations are fundamental factors during the choice of consumer goods including textiles. On the other hand, social

Table 1. The ecofriendly aspect in textiles is one of the considerable issues because textiles present another skin layer. Application of biotechnology (enzyme and yeast) attract the pressures are increasing on textile processing units due to polluting effluents. [1, 2] The effect of chemicals used in wet processing on human health is listed in researches and textile factories to overcome the textile pollution problems that fulfilled the requirement of the customer and environment consideration.

Table 1: Health hazards associated with chemicals used in textile processing textile industries

Process	**Chemicals used**	**Health hazards**
Singeing	A small amount of exhaust gases, neglectable impact	-------
Desizing	Enzymes or H_2SO_4 for starch, detergents, and alkali for PVA and CMC	Bloating and diarrhea Irritant to eyes and skin
Scouring	NaOH, Na_2CO_3, surfactants, chlorinated solvents	The nonionic detergent may cause bloating and diarrhea Irritant to eyes and skin
Bleaching	Hypochlorite, hydrogen peroxide, acetic acid	Chlorine gases released cause severe irritation of respiratory tract and eyes tract and eyes toxic gases
Mercerization	NaOH, surfactants, acid, liquid ammonium	-------

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2. Enzyme classification

The enzyme's role in fermentation was known in Ancient Greece. By the time more knowledge of enzyme theory, extraction and the appearance of thermostable enzymes added up the new potential of industrial processes. [3, 4] Classification of enzyme according to its application are listed in **Error! Reference source not found.**.

The added-value of using enzymes in the textile industry

- An enzyme acts as a catalyst, meaning it helps in proceeding the reaction, and at the same time faster by decreasing the activation energy of the substrate and in the same time it remains at the end of the reaction
- Each reaction has its condition of temperature and pH depending on the enzyme used but overall, all enzymes act at the same condition of its natural source (bacteria, fungi,…etc) which are modest conditions.
- According to the hypothesis describe the reaction of enzyme-substrate. Enzymes bind with the substrate and under the optimum condition, ES compound dissociates to the required product only and the enzyme. That reduces pollution as no byproduct and the enzyme itself is biodegradable. [5, 6]

3. Industrial Enzymes: Production and Application

Novozyme Company was one of the leader's companies which have produced commercial enzyme formula ready for use in textile factories. Then different companies around the words have entered this field which increases the computation that affects the quality and the price of the commercial enzymes. Enzyme products are available at high concentrations suitable for the production of high-quality textiles and. the products are compatible with most chemical auxiliaries.

Genetic science help in the production of the new enzyme as it can identify the responsible gene on enzyme secretion. [5-7]

Textile enzymes are classified under the category of technical enzymes based on application classification (see **Error! Reference source not found.**). [8, 9] Commercial enzymes used in textiles are mainly hydrolysis enzymes. [10-12]

Table 2: Classification of enzyme according to its application

Group of enzymes	Reaction catalyzed	Example
Oxidoreductases	Transfer of hydrogen and oxygen atoms or electron from one substrate to another	Dehydrogenases Oxidases
Transferases	Transfer of a specific group (a phosphate or methyl, etc) from one substrate to another	Transaminase Kinases
Hydrolases	Hydrolysis of a substrate	Esterases Digestive enzymes
Isomerases	Change of the molecular form of the substrate	Phosphor hexo isomerase Fumarase
Lyases	Nonhydrolytic removal or addition of a group to the substrate	Decarboxylases Aldolases
Ligases (synthetases)	Joining of two molecules by the formation of new bonds	Citric acid synthetase

4. Enzyme applications in textile wet process

The application of enzymes in textile manufacturing were shown in

Figure 1, and will be discuss in details.

4.1. Cotton desizing

Amylases enzymes are proficient in digesting glycosidic linkages found in starch. Truncated enzymes are higher stability and activity comparing to other amylase enzymes used due to its altering structural conformations, and increased affinity withe the substrate. [4, 13]

The ultrasonic energy assists enzymatic desizing of cotton by reducing processing time to half with higher efficiency. [14]

4.2. Enzymatic scouring (bio-scouring)

The enzyme-catalyzed the removal of impurities from the surface of cellulosic fibers, in bleaching and dyeing improvement. Enzymatic scouring performed at neutral pH, low water consumption, and does not affect fiber strength and low percent of weight loss compared with processing in traditional ways. [15]

Combined desizing and scouring process for cotton fabric using each of the two commercial amylase enzymes namely BEISOL T2090 and BEISOL PRO were investigated. The optimum conditions were enzyme concentration at 2% of the weight of the fabric, time 30 minutes, temperature 90ºC, and pH 7.5. [16]

Treatment with one of those couples enzymes (pectinase + cellulase), (pectinase +

protease), (pectinase + cutinase) are capable of removing cotton noncellulosic impurities completely when used on an industrial scale. [17, 18]

4.3. Enzymatic bleaching (Biobleaching)

In the bleaching process, the natural coloring matter is removed which is directly related to the success of subsequent coloration operations such as dyeing and printing. Glucose is oxidized by glucose oxidase enzyme to hydrogen peroxide.

Integrated desizing–bleaching–process for cotton towel then dyed with reactive dye without discharging each spent bath has revealed better eco-sustainability and economy. The desizing effluent discharge treated with Amyloglucosidase–pullulanase enzyme given glucose that will be oxidized by glucose oxidase enzyme generating hydrogen peroxide. In the next step, the catalase enzyme was added before reactive dyes to remove residual hydrogen peroxide. This method saves 400% and 50% of water and energy respectively. [10, 19]

Brewer's yeast enzymes (lipase, amylase, and cellulase) were applied on bamboo and bamboo/cotton knitted fabrics. The natural dye uptake increased for the two treated fabrics by improving the wettability. [20]

In another study combination of Brewer's yeast enzymes and microwave irradiation treatment of semi-finished rami fabric was investigated. The colorimetric data revealed that the treatment of rami fabrics in the microwave imparted bright color with excellent colorfastness properties at optimum temperature 60ºC, pH 4 for 20 min. [21]

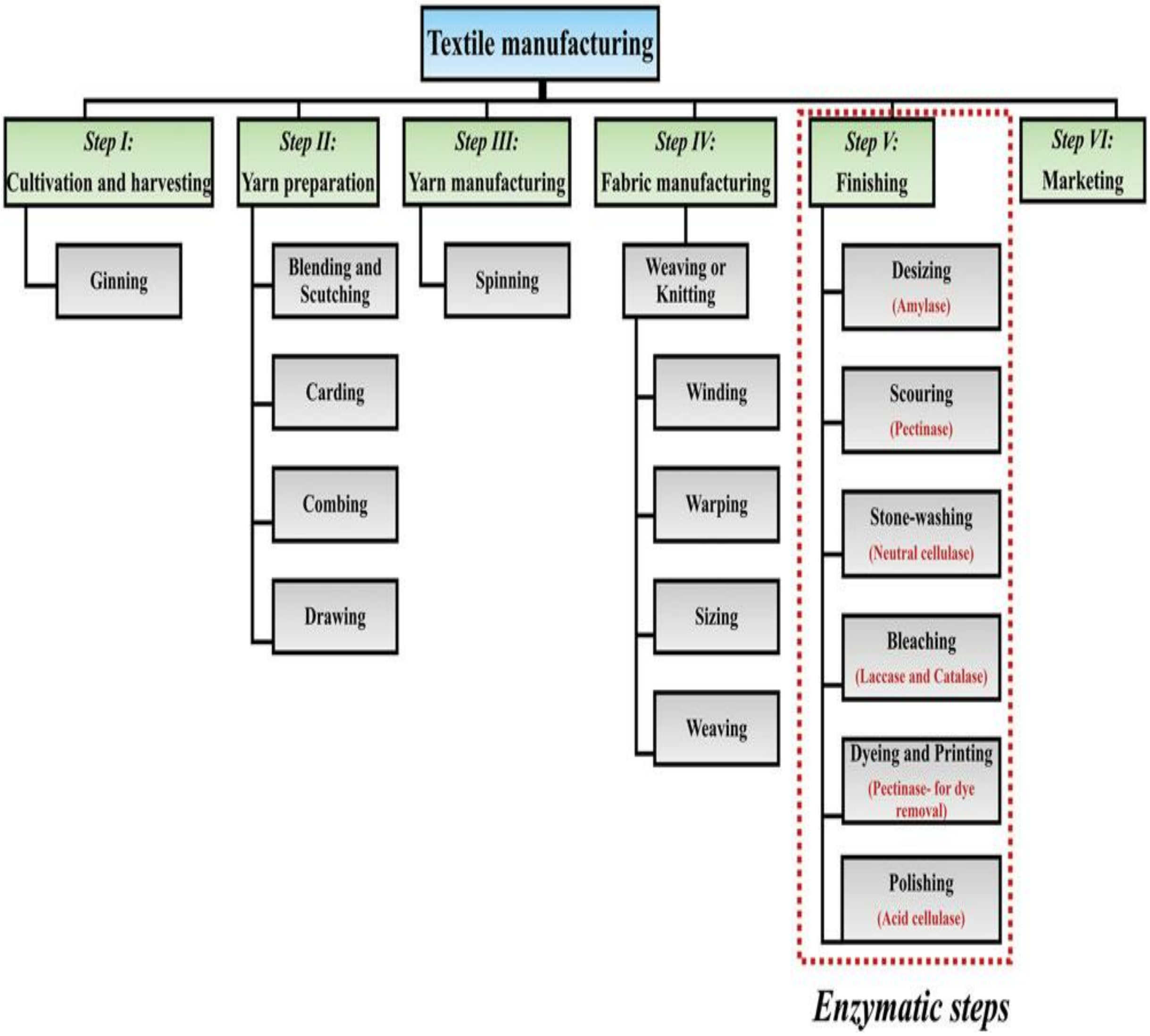

Figure 1: Application of enzymes in textile manufacturing

5. Denim fashion look

Denin washing technology is mainly used to make it soft, supple, and smooth which improves wearer's comfort besides modifying the appearance outlook. [22, 23] Sandblasting was the first finish method applied on denim fabric in which sand is sprayed at high pressure on the selected area of the denim fabric. The sprayed sand removes color from the required area of the denim fabric. [24]

In 2017 aloe gel was used for desizing cotton fabric as it contains enzymes like amylase, lipase, and cellulase besides different minerals like manganese. The Enzymatic cotton desizing conditions were 50-60 g/l aloe gel concentration with 5 g/l sodium chlorite at temperature 70-80°C for 60 minutes. The results of aloe gel desizing are compared with that of enzyme and there was a high amount of weight loss in aloe gel desizing which proves that this process is more efficient than synthetic enzyme desizing and also provides antibacterial finish. [25]

6. Enzymatic treatment of wool

Raw wool can't be colored either by dyeing or printing owing to the hydrophobic impurities of the epicuticular surface membrane. Convention chemical treatment used sodium carbonate for alkaline scouring or pretreatment using potassium permanganate, sodium sulfite or hydrogen peroxide. [26]

Treatment of wool fiber with different concentrations of protease enzyme improves it's physical and chemical properties compared to untreated fabric with a slight increase in weight loss and tensile strength (see **Figure 2**). [27]

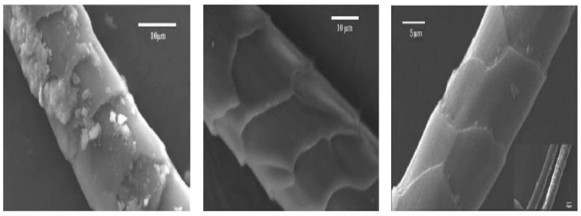

Figure 2: SEM of raw wool, chemically treated and protease treated wool [27]

Wool fabric has the affinity to shrink by wet processing. This is approved by the chemical commercial process using chlorine-Hercosett but its main drawback contamination of wastewater effluent with organic halogens (AOX). [28]

Glycerol diglycidyl ether was used to form cross-linking bridges in the wool at high temperature curing after protease treatment. This method produces complete shrink-resistance wool fabric dyed with reactive dyes. [29]

7. Enzymatic treatment of silk

Raw silk structure contains the outer sericin layer which consists of amino acids that cover the fiber and decrease its wettability. The degumming process is typically performed in detergent at high temperature and alkaline pH to emulsify sericin. This method affects the silk's physical properties along with the release of detergent effluent in the environment (see **Figure 3**). A variety of commercially available proteolytic enzymes as lipases and bacterial proteases are being explored for degumming. [30-33]

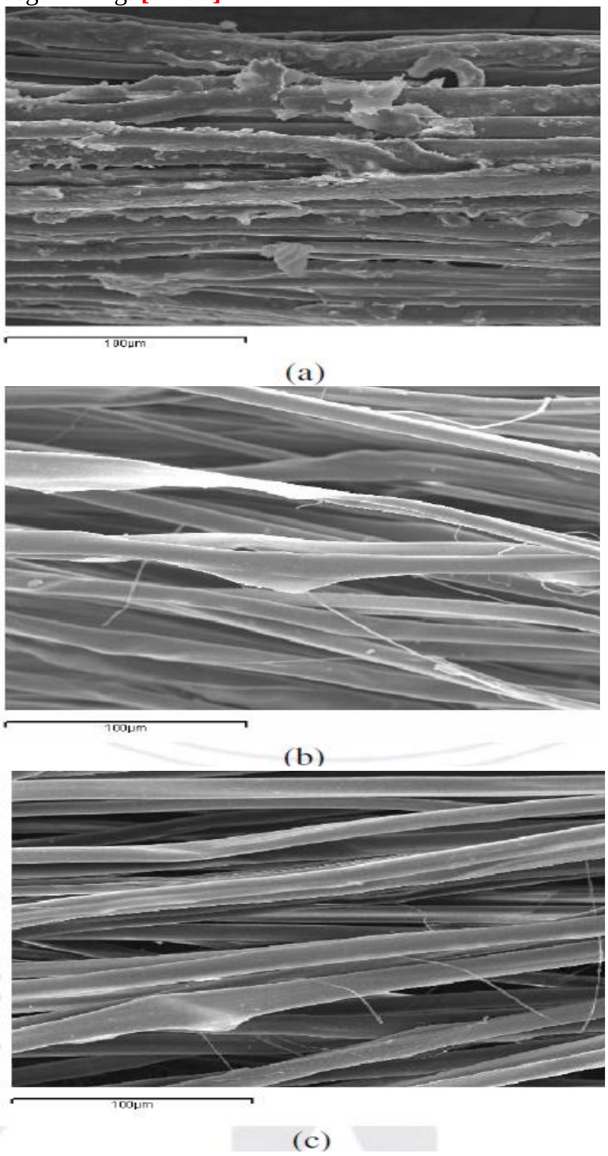

Figure 3: SEM of (a) raw silk (b) after degumming soap/alkali (c) degumming with protease enzyme

8. Surface modification of synthetic fibers

The hydrophobicity nature of synthetic polymers as polyamide (PA) and polyester (PET) make them uncomfortable to wear. [34]

Sodium hydroxide was used in the traditional chemical process to improve the hydrophilicity and flexibility of the synthetic textile but due to the increase in weight loss and yellowing of fibers, this process was unacceptable. Many proteases enzymes with a different commercial name such as Protex Gentle L, were used to induce changes in the nylon 6,6 polymer. Protease treatment of Nylon 6,6 showed significant high reactive and acid dye bath exhaustion. [35-37]

The role of enzymatic treatment of polyester is to improve the hydrophilicity by hydrolysis of ester bond using lipase and polyesterases enzyme (see **Figure 4**). [38-40] Hydrolysis of ester bond by cutinases, lipases, and esterases enzymes formed active polar hydroxyl and carboxyl groups. [41, 42]

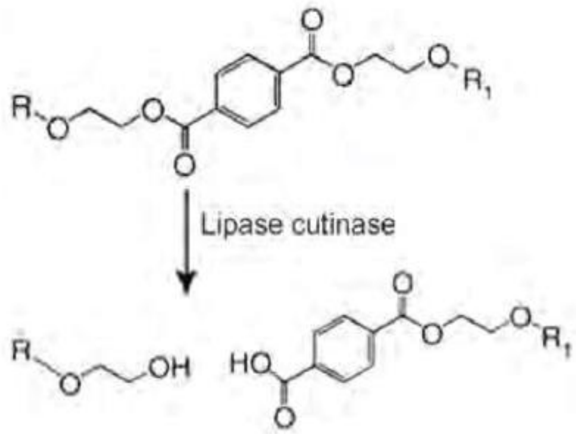

Figure 4: Enzymatic hydrolysis of polyester [38-40]

9. Textile coloration

9.1. Dyeing

Dyeing is one of the coloration methods of biotreated textile samples. The quality of dyed samples is measured by color evenness. Investigations were carried out to optimize one bath pretreatment and dyeing as it reduces the consumption of water, shorter process time, and economy. [43-47] Rapid Enzymatic Single-bath Treatment (REST) is a developed a new method to dye untreated woven cotton with reactive dye using a single bath combined process as shown in **Figure 5**. All tasks were completed in half the time of the conventional dyeing and without water replacement. The fastness properties of dyed cotton samples are very good and no effect on the tensile strength. [48]

Further experimental was carried out using an ultrasonic bath was used in biotreatment and dyeing of cotton fabric with natural dyeing (see **Figure 6**). The ultrasonic energy provided gave high color efficiency at lower water consumption and energy. [49]

Another experiment was carried out on cotton /polyester blend, at any ratio, shows that it could be dyed with no cleaning process. The colorfastness properties results are very good and hand feel was also found acceptable. This experiment could be exploitable on other blends of cellulosic/polyester fibers. [50]

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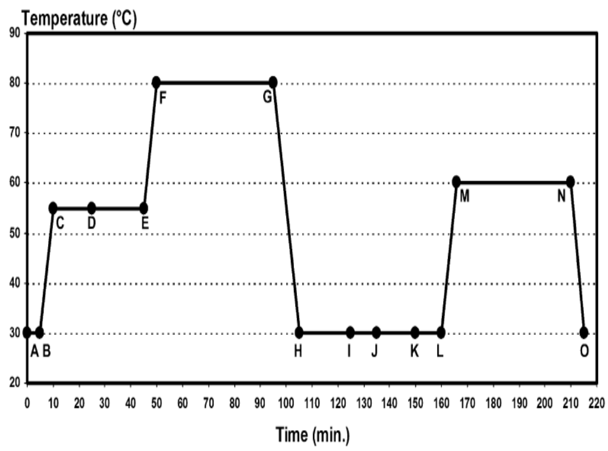

Stage	Application	Stage	Application
A-B	Wetting out of the fabric for 5 minutes	J	Addition of dye(s) to the bath
C-D	Enzymatic desizing	K	Addition of the first portion of the alkali
D-E	Enzymatic scouring, set pH 8-9	L	Raising temperature to 60°C by a 5°C/min. heating rate
F-G	Hydrogen peroxide bleaching	M	Addition of the second portion of the alkali
H-I	Anti-peroxide treatment by catalase addition	M-N	Dyeing
I	At pH 7, salt addition for dyeing	O	Rinsing stage

Figure 5: Temperature and time condition of REST [48]

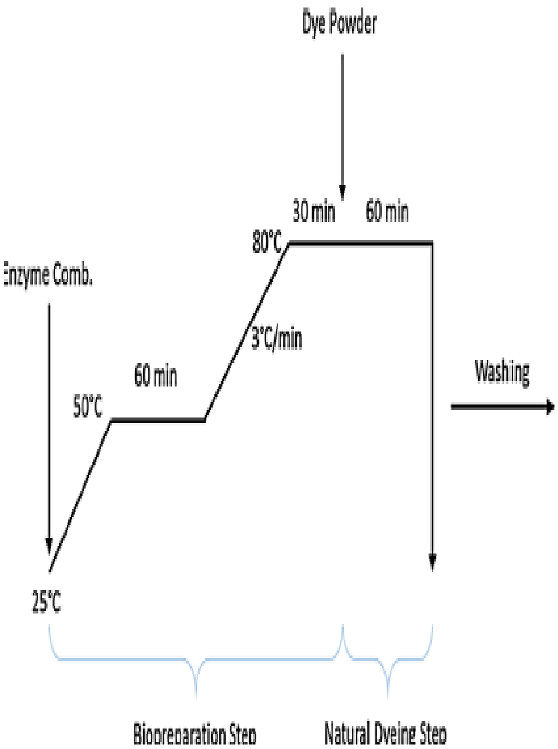

Figure 6: Experimental condition of biotreatment and dyeing cotton with natural dyes [49]

9.2. Digital printing

Digital printing has more advantages than screen printing as it is flexible, creative since there are no limits of colors or designs, and eco-friendly. The main drawback is the high price of used inks (see **Figure 7**).

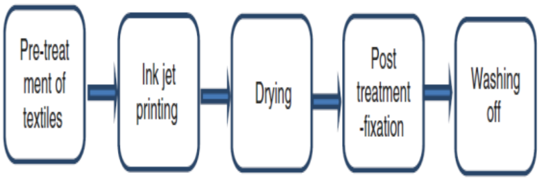

Figure 7: Digital printing steps

Table 3. The optimum condition used was pH adjusted at 4 and 10 at optimum 70◦C and 50◦C

Polyester fabric is widely used in inkjet printing due to its characters as high strength and flexibility but on the other hand, it had low wettability that gives dull colors and even bleeding. Enzymatic pretreatment of polyester meant for inkjet printing was carry out using different enzymes like lipase, cellulase, and brewer's yeast. The results show a significant increase in the color strength and its percentage over 200% of biotreated inkjet printed polyester, linen, and linen polyester blend fabrics as shown in

for 60 min for Brewer's yeast suspension upon using the two Valumax enzymes relatively. [51-53]

Table 3: Effect of enzymes concentration on color strength of biotreated digital printing fabrics

Enzyme used	Concentration	Fabric					
		Linen/polyester		Linen		Polyester	
		K/S	%K/S	K/S	%K/S	K/S	%K/S
Untreated	-	0.76	100	1.76	100	12.02	100
Brewer's yeast	50 ml/kg	0.88	115.79	0.55	31.25	0.28	2.33
	100 ml/kg	0.93	122.37	0.73	41.48	0.49	4.08
	300 ml/kg	1.01	132.90	0.92	52.28	0.72	5.99
	600 ml/kg	2.40	315.79	2.17	123.30	3.62	30.11
	900 ml/kg	4.01	527.63	3.11	176.71	7.60	63.22
Valumax A356	50 g/kg	1.56	205.26	3.20	181.82	9.51	79.12
	100 g/kg	1.70	223.68	3.25	184.66	9.72	80.86
	200 g/kg	2.78	356.79	4.10	232.95	11.23	93.43
	220 g/kg	2.60	342.11	3.48	197.73	10.75	89.43
	240 g/kg	2.53	332.89	2.84	161.36	10.47	87.10
	260 g/kg	2.21	290.79	2.78	157.95	10.28	85.52
Valumax A828	50 g/kg	1.19	156.58	3.05	173.30	7.11	59.15
	100 g/kg	1.45	190.79	3.16	179.55	8.28	68.88
	200 g/kg	3	394.74	4.16	236.36	12.69	105.57
	220 g/kg	2.62	344.74	3.62	205.68	10.75	89.43
	240 g/kg	2.23	293.42	2.83	160.80	10.55	87.77
	260 g/kg	1.69	222.37	2.10	119.31	9.93	82.61

10. Decolorization of dyes

The textile industry consumes about 60 % of the dyestuff market. [54] The reactive azo dyes come at the top of the dyes used that is related to the high demand for bright colored cotton fabrics. The washing effluent of the colored garment after dyeing or printing contains an different metal ions and unfixed hydrolyzed dye that released into the environment. [55, 56] Sometimes the color of the effluent can be noticed, due to the high percentage of dye, given colored streams or lakes. [57] These effluents are toxic for aqua life beside it prevents the sunlight leading to reduce photosynthesis and percentage of dissolved oxygen. Several physical and chemical treatments are used in the wastewater treatment but they have their limitations which render them unattractive (see **Figure 8**). [58, 59]

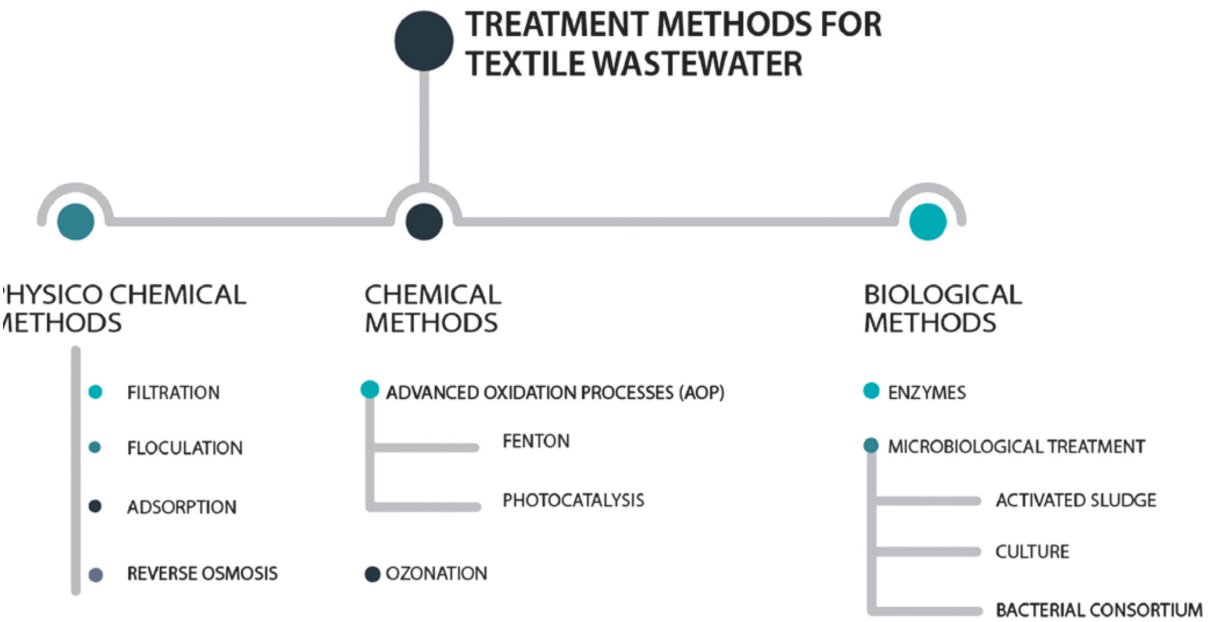

Figure 8: Textile wastewater treatment methods [58, 59]

Enzymatic degradation is viewed as a promising process for waste treatment if designed to be cost-effective. Oxidative enzyme as Laccase can convert the mean pollutants into less toxic or insoluble compounds that can be removed from effluents. [60-63] Studies state the capability of laccase to degrade textile effluent dyes but its application on industrial processes is not always successful due to the loss of the enzyme of stability and activity. [64] The use of redox mediators and emulsions can improve catalytic reactions. Immobilized enzyme provides several economic advantages included the improvement of thermal stability and possible reuse (**Figure 9**). [65]

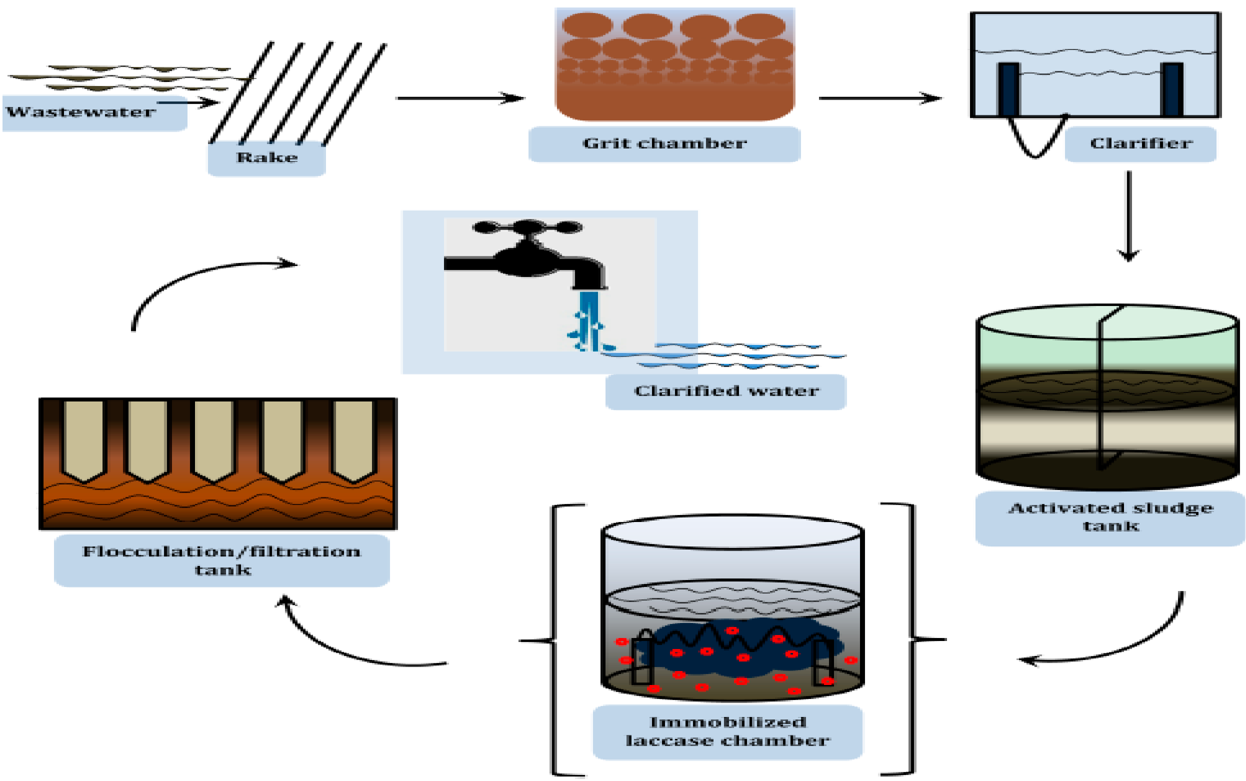

Figure 9: Suggested scheme of wastewater treatment using immobilized Laccase enzyme [65]

Commercial laccase formula produces from Novozyme Company for denim washing was used for decolorization of simulated textile effluent consist of a mixture of three reactive dyes and auxiliaries. The results were promising as Laccase catalyzed degradation of around 55% of dyes. Effluent treated analysis as COD, BOD, and toxicity were found to be in the permitted limits of wastewaters. **[66]**

11. Enzymes used in the detergent industry

Detergents which are a prime application area for enzymes represent 25–30 % of the total enzyme sales. The enzymatic containing detergent entered the market in 1960. **[67]** Since then the detergent companies started to introduce more enzymes in its detergent to reduce the phosphate percentage to an eco-friendly limit along with the bleaching agent. The new trend in the detergent using a mix of enzymes (lipase, protease, and amylase) and softener. Application of detergent is not limited to laundry only, it was extended to others as dishwashing and industrial cleaning (see

Table 4). **[10, 68-70]**

Table 4: The role of different enzymes in the detergent formula

Name of enzyme	Effective as stain remover for
Proteases	Grass, blood, egg, sweat stains
Lipases	Lipstick, butter, salad oil, sauces
Amylases	Spaghetti, custard, chocolate
Cellulases	Color brightening, softening, soil removal

12. New trends in the application of enzyme in textile

12.1. Immobilization

Fabrics (cotton, polyester, and polyamide) are attractive support for enzyme immobilization as they are flexible, cheap, and lightweight. Immobilized enzymes are thermostable, easy to recover, and reused several time. The using methods for immobilization are illustrated in **Table 5**. Immobilization enzymes are used in several industries manly food but still need to be induced in textile especially wet operations. **[71-75].**

Table 5: Methods for immobilization of different enzymes on textile

Enzyme	Fabric type	Activation/binding material
Peroxidase (HRP)	Polyester, polyethylene	Glutaraldehyde, plasma
Catalase	Polyester, polyamide 6,6	Photochemical
Catalase	Cotton	Oxidation by sodium periodate
Tyrosinase	Silk fibroin, polyamide 6,6	Glutaraldehyde
Laccase	Polyamide 6,6	Enzymatic hydrolysis, Glutaraldehyde, and spacer
Glucose oxidase	Silk fibroin, polyamide 6, viscose, polyester, polypropylene	Various activation strategies
Alkaline phosphatase	Silk fibroin	Low-temperature plasma
Lysozyme	Cotton	Esterification with glycine/ glutaraldehyde
	Wool	Glutaraldehyde
Organophosphate hydrolase	cotton	Esterification with glycine/ glutaraldehyde
Thrombin	Polyester	Ethylenediamine

12.2. Biodischarge printing

Discharge printing based on the destruction of the ground dye in the printed areas to obtain the required pattern. The commonly used discharging agents are based on formaldehyde sulphoxylates and thiourea dioxide. Formaldehyde sulphoxylate $(NaHSO_2CH_2O.2H_2O)$. Those agents are carcinogenic as it dissociates producing formaldehyde (**see Figure 10**).

The optimum condition of applying the Peroxidase enzyme in textile discharge printing was at pH 8.5 at 70°C for 60 min. **[76]** In another research, the commercial enzyme formula of Laccase and cellulase beside brewer's yeast suspension has been applied successfully in discharge printing. The higher percent removal of ground dye follows the order laccase enzyme, Brewer's yeast suspension, and cellulase enzyme commercial product at the end. **[77]** Laboratory experiments reached the optimum conditions (temperature and treatment time, pH) of all used enzymes and brewer's yeast filtrate for their utilization as discharging agents. The next step was to apply the results on an industrial scale at Egyptian Knitted Service Company in comparison with rongalite C. Laccase enzyme removed 94.8, 95.0, and 96.8% of the ground color on using sunzol yellow and sunzol blue dischargeable reactive dyes. All the aforementioned biomaterials were used either alone or mixed with rongalite C. Samples with different halftones have been obtained by changing the nature of the biomaterial and/or its ratio with rongalite C in the mixture. **[78]**

In another lab study, the laccase enzyme was used in the discharge printing of cotton, silk, and wool dyed with natural dyes. The laccase was added to the printing paste then printed on the naturally dyed samples. Halftone samples were obtained at the optimum conditions of enzymes (pH 4.5, treatment temperature 70°C for 1 hour). **[79]**

*Figure 10: The action of cellulases in discharge printing (a),*White discharge printing (b) and Halftone (c)

12.3. Biodegradation of starch thickener

Different Kinds of starches were subjected to gelatinization under the action of sodium hydroxide solution then treated with an alpha-amylase enzyme in the gelatinized form. The modified starches were evaluated as thickeners in printing wool fabrics with acid dye and polyester using disperse dye. The results demonstrated that increasing the apparent viscosity by increasing starch concentration.

12.4. Green catalysts for Synthesis of dyes

A wide range of dyes is produced by the oxidation reaction of colorless compounds as phenols derivatives using laccase enzymes. [80, 81]

The oxidation mechanism of laccase depends on the presence of copper atom (II) at its core (see **Figure 11**). The scientist named them according to their spectroscopic adsorption band to T1, T2, and T3. The T1 copper is responsible for the blue color of laccase as it has an absorption band at 610 nm. [82-86] The oxidation-reduction reaction catalyzed by laccase depends on two factors the pH of the medium and the redox potential of the substrate. Phenols consider the best substrate of laccase because of its low redox potentials. The role of the laccase enzyme copper's atoms in proceeding the oxidation-reduction mechanism of phenol derivatives start its attach to T1 copper permit the electron transfer from the substrate to copper T1 given phenoxyl radical then the second Step is the electron transfer, T2/T3 coppers, given the reduced enzyme form. [80, 87, 88] The produced phenoxyl radical is the starter of further reaction. The chemical reactions catalyzed by laccase can be divided into three groups (**Table 6**):

- *Group 1*: direct oxidation of phenolic derivatives
- *Group 2*: Using mediator (compound of low molecular weight and low redox potential) to assist the oxidation of phenolic and non-phenolic substrates
- *Group3:* homomolecular reaction by coupling the produced reactive radicals.

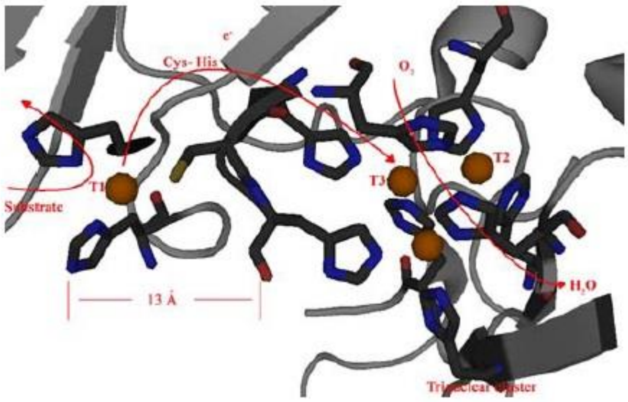

Figure 11: Oxidation–reduction mechanism of laccase

1. Phenolic and non-phenolic dyes

   Dyes of wide color range from yellow, brown to red, and blue are the result of the phenoxyl radicals produced from laccase oxidation reaction with the phenolic or non-phenolic compound as derivative of benzoic acid. [89-94]

2. Phenoxazinone

Phenoxazinone compounds are colorful, non-toxic and some if they have fluorescence properties used as probes in the field of molecular biology and can be used in textiles for dyeing of natural fabrics. [95, 96]

3. Azo dyes

Synthesis of azo dye without using the forbidden amino acid could be achieved by using the laccase enzyme. it has been reported that red azo dye is the end product oxidation reaction, catalysis with methoxy phenols with benzothiazoles. These results lead to the eco-friendly synthesis of azo dyes. [89, 97, 98]

Table 6: laccase assist the synthesis of dyes using different chemicals

Substrate of laccase + reaction partner	Type of reaction product
Phenolic and non-phenolic dyes	
Phenoxy- and aminoderivatives of benzene- and naphthalene-sulfonic acid; dihydroxynaphtalene; phenylphenol; pyridine	Yellow, orange, red, purple, brown and green/grey products phenoxazinone dye
Phenoxy-, amino-, methoxy-, methyl-, sulfo- and carboxy-derivatives of benzoic acid	Yellow, orange, red, purple, brown, green/grey, violet and blue products
Indole + TEMPO + dioxygen over pressure	Trimer 2,2-bis(3′-indolyl)-indoxyl yellow compound
Catechol + polyoxometalate	Dark coloured heterogenic polymers
Ferulic acid + hydro-organic biphasic system	Yellow product (possible food colourants)
3-Methyl-2-benzothiazolinone hydrazone + 3-dimethylaminobenzoic acid	Indamine dye (blue) (for enzymatic activity measuring)
Alkylated pyrogallol derivatives	Benzotropolone structures (orange solids)
3-Methylcatechol + primary linear amines with alkyl chain lengths (C4—C9)	Secondary amines as red solid (pharmaceutically valuable)
Natural phenols (gallic acid + syringic acid; catechin + catechol; ferulic acid + syringic acid)	Yellow, orange, red, purple, brown and black products
Aromatic amine	Binuclear and trinuclear aromatic compounds
ABTS	Cation radical $ABTS^{\bullet +}$ dication $ABTS^{2+}$ purple and green colouration of fabrics
Phenoxazinone dyes	
3-Hydroxyanthranilic acid	Cinnabarinic acid
4-Methyl-3-hydroxyanthranilic acid	2-Amino-4,6-dimethyl-3-phenoxazinone-1,9-carboxylic acid (actinomycin-like cytotoxic derivative)
3-Hydroxyorthanilic acid	2-Amino-3-oxo-3H-phenoxazine-1,9-disulfonic acid water soluble red dye (LAO)
3-Amino-4-hydroxybenzenesulfonic acid	2-Amino-3-oxo-3H-phenoxazine-7-sulfonic acid from yellow to red water soluble phenoxazinone dye
3-Amino-4-hydroxybenzenesulfonic acid	2-Amino-3-oxo-3H-phenoxazine-7-sulfonic acid phenoxazinone dye
2-Amino-3-hydroxy-benzenephosphoric acid	2-Amino-3-oxo-3H-phenoxazine-1,9-diphosphonic acid (aminophenoxazinone water soluble dye)
Azo dyes	
3-Methyl-2-benzothiazoline hydrazone + methoxyphenols	Azo dye (for enzymatic activity measuring)
Anthraquinonic acid dye (Acid Blue 62)	Azo dye (Acid Red 1)
Anthraquinonic acid dye (Acid Blue 62)	Azoanthraquinone dye (LAR 1)
4-Methylaminobenzoic acid	Coloured azo intermediates

12.5. Biosynthesis of Indigo dyes

Indigo dyes were first extracted from the plants but this method isn't economic as it gives a limited amount of dye after long extraction time. Synthesis of indigo dye in the lab was the best solution by increasing demand on vat dyes. Indigo and indirubin are classified carcinogenic compounds besides the last medicals reports estate that it causes Alzheimer's disease. [99] Successful attempts of producing indigo from the microbial process have been proceeding but they give low dye yield. [100, 101] A promising method was produced using

Pseudomonas sp. HOB1 and anionic surfactant and the indigo produced dye used in dyeing cotton. [102]

12.6. In situ coloration

Flavonoids such as quercetin, rutin, and morin are colorless compounds that undergo oxidation and polymerization on the surface of natural fibers given colored yellow to brown colored samples. [103] this was applied in textile printing by adding the laccase enzyme, flavanoid as rutin, buffer to the gelatinous thickener. the cotton samples were printed using a screen-printed technique then put in the oven at the optimum temperature and time to have colored samples.

In other research fabrics like cotton, wool, and (PET) undergo polymerization reaction catalysis by laccase under high pressure. The phenol derivatives used were catechol and *p*-phenylenediamine. **Figure 12** shows a promising methodology approach proposed for *in situ* coloration of fabrics assisted by laccase to produce colored antimicrobial fabrics with enormous potential applications in different fields including medical. [104]

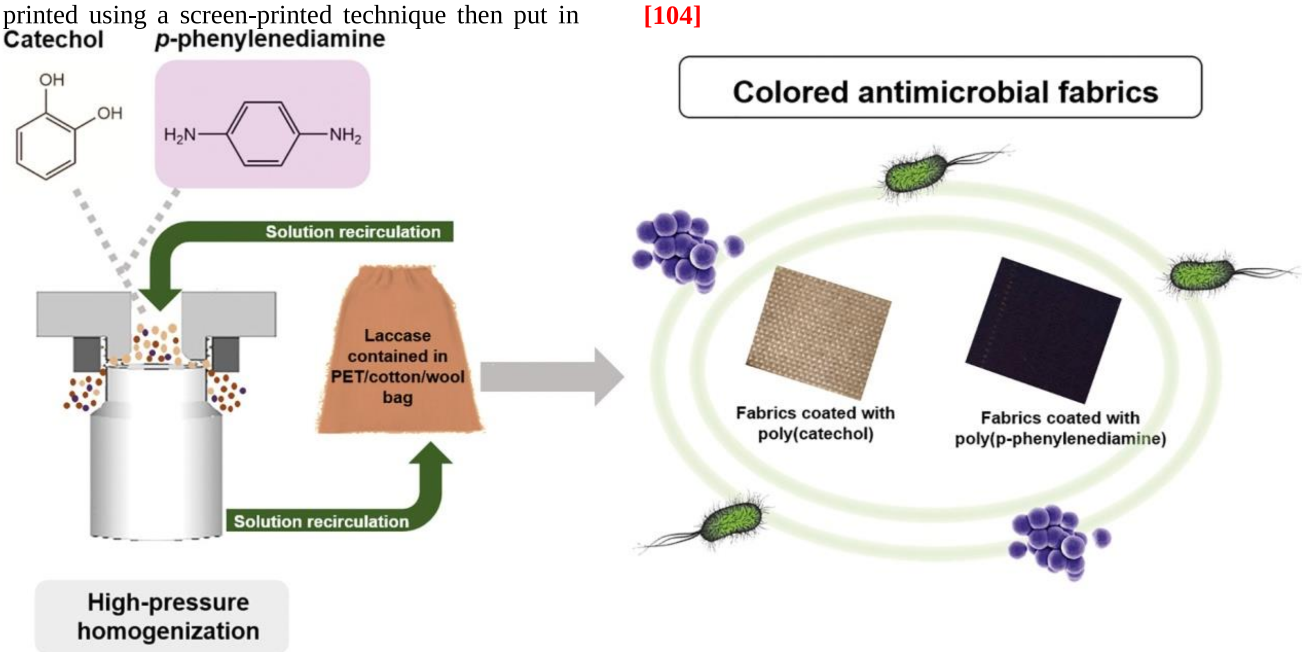

Figure 12: Methodology of preparation of colored antimicrobial fabrics

12.7 Application of Enzymes in grafting functional polymer

Producing fabrics with UV protection, antimicrobial, and/or antioxidant activities are an added value to the fabrics. [105]

The phenomena of yellowing of wool by exposure to sunlight have attracted the researchers. [106] Wool fabric was treated in aqueous–ethanol medium 80/20 (v/v%) with aquanordihydroguaiaretic acid (NDGA) in the presence laccase to enhance the formation of inters/intramolecular bonds and cross-links in wool were efficient to protect wool against the undesirable photo yellowing. [107]

laccase-catalyzed grafting of functional molecules on cellulose confers new properties to fiber in an eco-friendly manner. [108]

Antibacterial and antioxidant linen fabric was obtained by its pretreatment by laccase enzyme to produce free radical on the fabric surface from the oxidation of nature phenols derivatives then chitosan was added followed by catechin and laccase. [109]

Lipase enzymes assist the synthesis of polyester onto the cotton surface to render it hydrophobic in a novel bio-approach to change the physical properties of cellulosic fabrics. [110]

Figure 13 shows a suggested mechanism of laccase catalyze synthesis of conductive PANI-ES (A) aniline oxidation follow dimer (PADPA) and polymeric formation. (B) using template molecules containing sulfonate groups (C) IR spectra of the obtained PANI-ES-type polymers. All polymeric products consisting of conductive PANI-ES units that could use in producing conductive textiles. [111, 112]

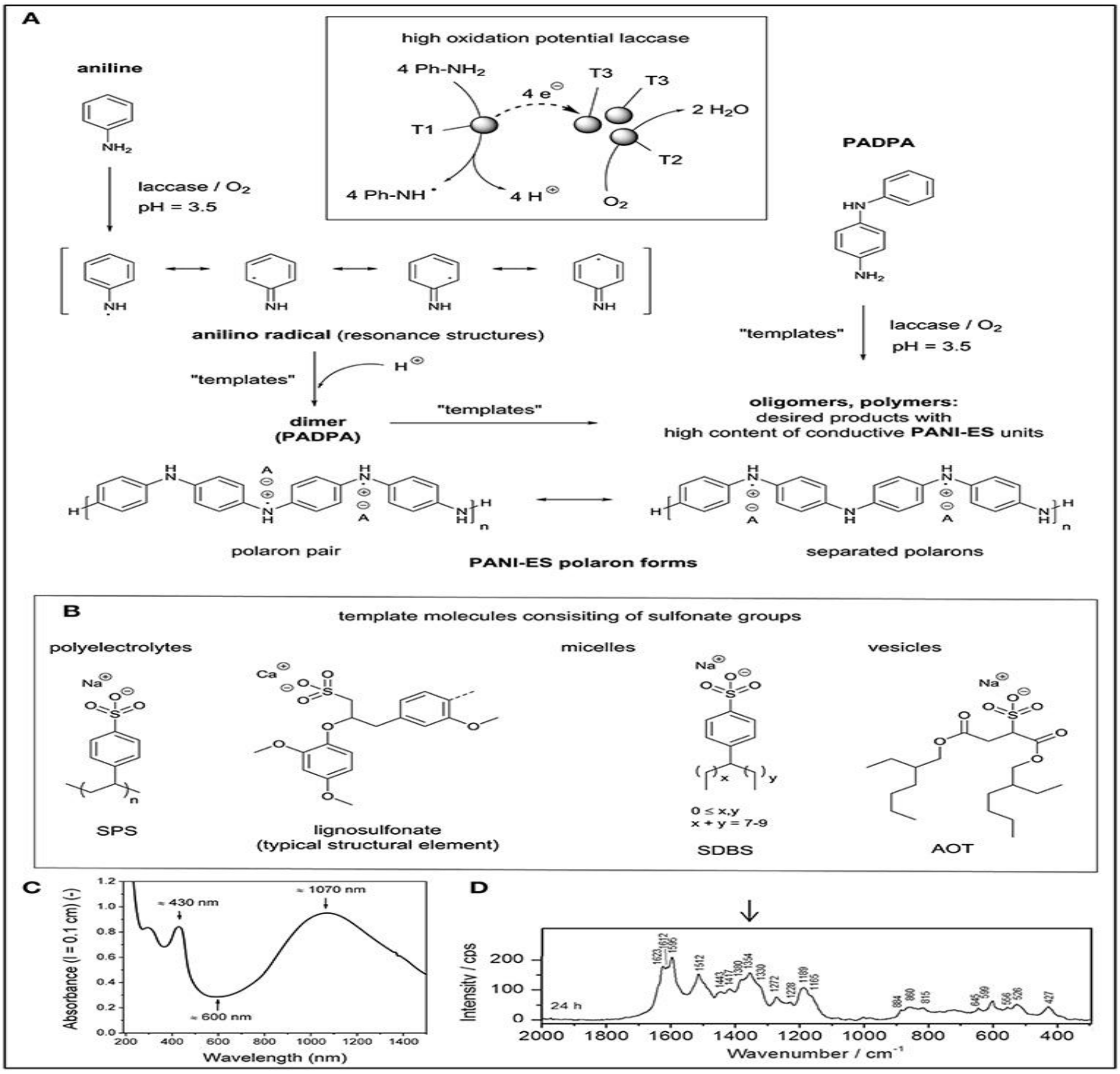

Figure 13: Suggested reaction of synthesis of PANI-ES6 catalyze by laccase

13. Future Directions

Further research is needed for:

- Producing of the commercial enzyme such as cutinase, esterase, and polyesterase for the modification of synthetic fibers.
- Search for new enzyme-producing micro-organisms.
- Different immobilized enzymes that could be applicable in either wastewater treatment or fiber treatment.
- One bath treatment of cellulosic fabrics using enzymes will solve almost all the environmental problems associate with the wet process.
- Enzyme assist synthesis of dyes and in-situ coloration needs to get more attention to get it from the lab to the pilot scale.
- The future of textile industries is in the production of colored functional fabrics due to its high price and high demand.
- Producing of biological detergent formula work at low temperature.
- The biosynthesis of indigo dyes is very promising but needs more work on reducing production cost and time and increase the yield.
- The polymeric products obtained from aniline are difficult to isolate to be analyzed despite their promising electrochemical properties. Further researches on PADPA separation, the effect of templates, and its application on textiles are needed.

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