

## TEXTILE EFFLUENT & WASTE WATER: A REVIEW

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### **Abstract:**

*Textile processing is a growing industry that traditionally has used a lot of water, energy and harsh chemicals. Textile industries consume over  $7 \times 10^5$  tons of dyes annually and use up to 1 litre of water per kg of dye processed and are third largest polluters in the world. As a characteristic of the textile processing industry, a wide range of structurally diverse dyes can be used in a single factory, and therefore effluents from the industry are extremely variable in composition. This needed for a largely unspecific process for treating textile wastewater.*

*Treatment methods that were perfectly acceptable in the past may not be suitable today or in the future. Some of the enzymes that are currently known in biotechnological processes such as amylases and proteases that are being used in the synthetic and biochemical reactions have evolved over millions of years to become efficient and selective for specific reactions taking place in living systems. Research on biological treatment has offered simple and cost effective ways of bioremediating textile effluents.*

*Biotechnology can be used in new production processes that are themselves less polluting than the traditional processes. Waste treatment is probably the biggest industrial application of biotechnology. The aims of this study represents a review of enzyme applications in bioremediating textile dye and their effluents. The aim is to provide the textile technologist with an understanding of enzymes and their use with textile materials.*

**Key words:** Enzymes, Eco-Friendly Characteristics, Biotreatments, Effluent, Pollution.

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### 1.Introduction:

As textile industry is one of the largest industries in the world and different fibres such as cotton, silk, wool as well as synthetic fibres are all pre-treated, processed, coloured and after treated using large amounts of water and a variety of chemicals, there is a need to understand the chemistry of the textile effluents very well. Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, colour, acidity, and other soluble substances whose chemistry will be emphasised.

Parrallel to usage of huge amounts of water and chemicals, the textile dyeing and finishing industry is one of the major polluters among industrial sectors, in the scope of volume and the chemical composition of the discharged effluent. Dyeing, desizing and scouring are the major sources of water pollution in textile effluent. Textile and dyestuffs waste waters are characterised by their highly visible colour, high COD (Chemical Oxygen Demand), suspended solids and alkaline pH (9 –11) [Manu and Chaudhari 2002] thus effluent discharge from these industries into the environment is a major cause for concern. Specific problems pertaining to the textile industry include colour removal from dyehouse effluent and toxic heavy metal compounds. Currently much research is being carried out to resolve these problems and biotechnology would appear to offer the most effective solutions.

Several chemical and physical decolourisation methods (adsorption, precipitation, flocculation, oxidation, electrolysis and membrane extraction) are effective for colour removal but use more energy and chemicals than biological processes [Bell et al. 2000; Robinson et al. 2001; Shaw et al. 2002]. Instead of using the chemical treatments, various biological methods can be used to treat the water from the textile industry.

Biological decolourisation (aerobic and anaerobic type) is the most common and widespread technique used in textile effluent treatment [Hunger 2003]. These methods include, biosorption, use of enzymes, aerobic and anaerobic treatments etc. [Nuran and Esposito 2000]. Only biotechnological solutions can offer complete destruction of the dyestuff, with a co-reduction in BOD (Biochemical Oxygen Demand) and COD.

## 2. Literature Review:

### 2.1 Classification of dyes

Dyes may be classified according to either chemical structure (chemical classification) or by usage (colouristic classification) [Trotman 1990]. Chemical classification is predominantly used by the practising dyechemists who use terms such as azo dyes, anthraquinone dyes, or phthalocyaninedyes. On the other hand, the dye technologist uses colouristic classification and speaks of “reactive dyes for cotton” and “disperse dyes for polyester” [Trotman 1990]. However, a review of the whole field of technical dyes reveals that the two classifications are interlinked.

### 2.2 Dye degrading enzymes

The potential to use these biocatalysts in industrial applications has been compromised by several obstacles as these processes involve substrates, organic solvents, metallic ions and other reaction conditions that are not normally encountered in their natural conditions. The introduction of protein engineering has facilitated the adaptation of potentially useful enzymes so that they can be used commercially. Controlling mutation efficiencies and screening for enhanced catalytic properties over multiple generations has led to the development of new enzymes that have 100-fold more activity than the natural enzymes.

Production of lignin modifying enzymes (LME) by white-rot fungi has shown great potential in degrading azo dyes and related effluents. The main LME include two types of peroxidases: lignin (LiP) and manganese (MnP) and a phenol oxidase, also called laccase. Research over the years has shown that expression of LME varies according to taxonomy and culturing conditions [Wesenberg et al. 2003].

#### 2.2.1 Laccases (benzenediol: oxygen oxidoreductases, EC.1.10.3.2)

These phenol oxidase enzymes have broad substrate specificity. The mechanism of laccase involves removal of an H<sup>+</sup> atom from the hydroxyl and amino groups of the *ortho*- and *para*-substituted mono and polyphenolic substrates, and aromatic amines. As a result laccases have found application in the treatment of a wide range of industrial effluents such as textile, paper and pulp, tannery and other industrial effluent containing chloro-lignins or phenolic

compounds. The application of laccases to such processes requires development of efficient production systems [Kahramann and Yasilada 2001].

### 2.2.2 Peroxidases

Lignin peroxidase (oxygen  $H_2O_2$  oxidoreductases EC.1.11.1.14 and manganese peroxidase (II)  $H_2O_2$  oxidoreductases EC.1.11.1.13) are glyco-proteins containing one iron protoporphyrin IX heme prosthetic group [Wesenberg et al. 2003]. Studies have shown that LiP catalyzes the oxidation of non-phenolic aromatic lignin moieties and structurally similar compounds. Also, it has been reported that LiP has the ability to catalyze the cleavage of aromatic ring structures including azo dyes [Wesenberg et al. 2003]. LiP degrades azo dyes by oxidation of the phenolic group to produce a radical at the carbon bearing the azo linkage. The phenolic carbon is then attacked by a water molecule resulting in its break down to produce phenyldiazene which is easily oxidised by a one electron reaction to generate nitrogen [Rodriguez et al. 1999].

Manganese peroxidase is the most commonly produced enzyme by white-rot basidiomycetes. This enzyme has generated a lot of interest in enzyme biotechnology because of its high degradative potential. It is a specific enzyme that oxidizes  $Mn^{2+}$  to  $Mn^{3+}$  ions which are highly reactive [Ziegenhagen and Hofrichter 2000]. The resultant products consist of low molecular mass fragments, quinones, ring-fission products, organic acids and carbon dioxide, all of which can serve as substrates for other reactions [Ziegenhagen and Hofrichter 2000].

### 2.2.3 Azoreductases

These are non-specific cytoplasmic enzymes that catalyze the cleavage of the characteristic (-N=N-) azo bonds. There are two broad classes of azoreductases; - the true azoreductases produced under aerobic conditions and those that are said to be produced under anaerobic conditions. Aerobic azoreductases catalyze reductive metabolism of azo dyes in the presence of molecular oxygen.

### 2.2.4 Hydrogenases

Hydrogenases are a class of enzymes that catalyze the reversible reduction and oxidation of molecular hydrogen.

Three types of hydrogenases are known to date: on the basis of their metal content, two groups have been described, namely [Fe] and [Ni-Fe] hydrogenase. The third type does not contain any

metals, instead they attribute their catalytic activity to the presence of an organic factor [Zadvorny et al. 2004].

Nickel-Fe hydrogenases have low specific activities and have been shown to function in the oxidation of hydrogen. They are found predominantly in all *Desulfovibrio* species. A lot of research has been done on this type of enzyme from *D. gigas* (Albracht 1994).

### 2.3 Textile effluent and waste water

Textile industries consume large volumes of water and chemicals during wet processing of textiles. Slashing, bleaching, mercerizing and dyeing are the major consumption activities as well as wastewater generation. The chemical reagents used during manufacture and processing are diverse in chemical composition ranging from inorganic compounds to polymers and organic products. The pollutant features of textile wastes differ widely among various Organic substances such as dyes, starches and detergents in effluent undergo chemical and biological changes which consume dissolved oxygen from the receiving stream and destroy aquatic life. Such organics should be removed to prevent septic conditions and avoid rendering the stream water unsuitable for municipal, industrial, agricultural and residential uses.

Treatment of wastewater will definitely reduce the waste, prevent and make positive effects on its further uses. Strong rinse waters from dye operations may be used to make up new dye baths, while weak rinses may be recycled through in-plant water treatment units. The savings in material in the first case may be enough to pay for the cost of treatment of the later case.

The nature of the processing exerts a strong influence on the potential impacts associated with textile manufacturing operations due to the different characteristics associated with these effluents (Table 1). Specific water use varies from 60-400l/kg of fabric, depending on the type of fabric. Every process and operation within a textile dyeing and finishing plant has an environmental aspect that should be considered and for which environmental performance can potentially be improved. This is in addition to the input of a wide range of chemicals, which, if not contained in the final product, become waste treatment and disposal problems.

Table 1. Effluent Characteristics From Textile Industry

Process	Effluent composition	Nature
Sizing	Starch, waxes,	High in BOD, COD

	carboxymethyl cellulose (CMC)	
Desizing	Starch, CMC, PVA, fats, waxes, pectins	Sodium hydroxide, cotton wax
Bleaching	Sodium hypochlorite, Cl <sub>2</sub> , NaOH, H <sub>2</sub> O <sub>2</sub> , acids, surfactants, NaSiO <sub>3</sub> , sodium phosphate, short cotton fibre	High alkalinity, high SS
Mercerizing	Sodium hydroxide, cotton wax	High pH, low BOD, high DS
Dyeing	Dyestuffs urea, reducing agents, oxidizing agents, acetic acid, detergents, wetting agents	Strongly coloured, high BOD, DS, low SS, heavy metals
Printing	Pastes, urea, starches, gums, oils, binders, acids, thickeners, cross-linkers, reducing agents, alkali	Highly coloured, high BOD, oily appearance, SS slightly alkaline, low BOD

### 2.3.1 Chemicals used in Textile Industry

Synthetic organic dyes, bleaches and detergents. Some chemicals are biodegradable-starch, however others such as dyes are non-biodegradable. Thus the effluents could have lower dissolved oxygen concentrations which means higher BOD and COD.

Solids in textile wastewater come from fibrous substrate and process chemicals, this disturbs the aquatic life by showing oxygen transfer and reducing light penetration.

- High concentrations of soluble inorganic salts may make the discharge water stream unsuitable for industrial and municipal use
- Metals such as chromium and zinc are toxic to aquatic life and should be removed before discharge
- Certain carrier chemicals used in dyeing , such as phenol may add bad taste and odor as well.

### 2.3.2 Standards for textile effluent

In the last few years, environmental legislature about the appearance of colour indischarges (Table 2), combined with increasing cost of water in the industrial sector has made treatment and re-use of dyeing effluents increasingly attractive to the industry [Maier et al. 2004]. Effluent discharge from textiles and dyestuff industries into water bodies and waste water treatment systems is currently causing significant health concerns to environmental regulatory agencies. Government legislation is increasingly becoming more stringent especially in the more developed countries, regarding the removal of dyes from industrial effluents.

Textile effluent discharge has to meet the following guidelines: coloration, toxicity, Total Organic Carbon (TOC) content, absorbable of organic halogens, presence of metals, and salt content [Robinson et al. 2001].

Table 2. Standard and Allowed for aqueous effluent discharge

Parameters	Standard/Allowed
Temperature	Below 42°C at point of discharge
pH	Between 6-9 at the point of discharge
BOD	30mg/l to surface water
COD	50mg/litre to surface water consented to sewer
Suspended solids	20mg/litre to surface water consented to sewer
Color	Below 1 ppm consented
Toxic substances	Restricted by legislation
Volume and flow	Basis for the charging consented

The municipalities calculate effluent charges based on the organic load of the effluent (usually determined by COD), and therefore the discharge of desizing and scouring effluents usually results in extremely high effluent treatment penalties. Therefore, there is need to develop cheap cost effective methods for removal of these contaminants before discharge into the environment.

### 2.3.3 Treatment of Textile Effluents

Dyes in wastewater can be eliminated by various methods. The wastewater from the dye house is generally multi-colored. The dye effluent disposed into the land and river water reduces the depth of penetration of sunlight into the water environment, which in turn decreases

photosynthetic activity and dissolved oxygen. The adverse effects can spell disaster for aquatic life and the soil. Many dyes contain organic compounds with functional groups, such as carboxylic (-COOH), amine (-NH<sub>2</sub>), and azo (-N=N-) groups, so treatment methods must be tailored to the chemistry of the dyes. Effluents from textile industries are the most expressive from an ecological and physiological perspective. Based on the fact that azo dyes constitute the largest percentage of textile dyes, most treatment methods are based on the decolourisation of azo dyes [Raghavacharya 1997]. These dyes are inevitably discharged in industrial effluents. Azo dyes have a serious environmental impact, because their precursors and degradation products (such as aromatic amines) are highly carcinogenic [Szymczyk et al. 2007]. Numerous biodegradability studies on dyes have shown that azo dyes are not prone to biodegradation under aerobic conditions [O'Neill et al. 2000]. These dyes are either adsorbed or trapped in bioflocs, which affects the ecosystem of streams, so they need to be removed from wastewater before discharge. Currently the main operational methods used in treatment of textile waste water involve physical and chemical processes [Shaw et al. 2002; Liu et al. 2005].

Typically textile effluent would involve the following steps:

- Reactive dye concentrates can be treated in a conventional anaerobic digester
- Exposure to the biomass to achieve de-colorization and tolerance of the micro organisms to concentrations of the dye
- Additional carbon source (eg. glucose) is necessary to maintain the microbial metabolic state
- The presence of Nitrate in the system inhibits de-colorization
- Adsorption of the dye to the biomass also causes de-colorization
- The degradation products of the dye after anaerobic digestion may be isolated and identified

Each dye removal technique has its limitations and one individual process may not be sufficient to achieve complete decolourisation (Table 3). To overcome this problem, dye removal strategies involve a combination of different techniques [Raghavacharya 1997].

Table 3. Advantages and disadvantages of physical and chemical textile effluent treatment

Physical/ Chemical Methods	Advantages	Disadvantages
Ozonation	Applied in gaseous state; no	Short half life

	alteration of volume	
NaOCl	Initiates and accelerates azo bond cleavage	Release of aromatic amines
Photochemical	No sludge production	Formation of bi – products
Electrochemical destruction	Breakdown compounds are non hazardous	High cost of electricity
Activated carbon	Good removal of a variety of dyes	Very expensive to operate
Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Removes all dye types	Concentrated sludge production
Electro kinetic coagulation	Economically feasible	High sludge production

### 2.3.4 Treatment of Wastewater

After every effort that can be made to reduce waste strength and volume, there still remains the problem of disposing the final remains of polluted waste into any water stream, thus the waste may be treated in various methods either singly or in combination and the best combination of methods differs from plant to plant.

The various types of treatment practices are as follows:

- Segregation
- Lagooning and storage
- Screening
- Mechanical Filtration
- Pre-aeration and Post-aeration

- Neutralization
- Chemical precipitation
- Chemical Oxidation
- Biological Oxidation

These include traditional physical-chemical techniques such as ultra filtration, reverse osmosis, ion exchange and adsorption on various adsorbents (activated carbon, peat, fly ash, and coal, wood chips, and corncob). Adsorption techniques are more popular due to their efficiency in the removal of pollutants too stable for conventional methods. Physical treatment methods have the advantage that they are non destructive, but the major set back is that they do not effectively remove the colour but they simply transfer the pollutant from the liquid phase (water) to a solid matrix, (adsorbent). This normally requires expensive regeneration operations of the adsorbent materials thus post treatment of the solid waste is required.

Widely used techniques include oxidation reactions, photochemical oxidations and electrochemical treatment [Shaw et al. 2002], of which, oxidation processes are the most common. This is primarily due to its simplicity of application with hydrogen peroxide being the main oxidizing agent. Chemical oxidation removes the dye from the dye –containing effluent by oxidation resulting in aromatic cleavage of the molecules [Raghavacharya 1997].

A wide range of structurally diverse dyes are consumed within a very short time during textile processing. Therefore, textile effluents are extremely variable in composition. This underlines the need for a largely non-specific treatment process of textile effluents. Alternative approaches utilizing microbial biocatalysts to remove dyes in textile effluent offers potential advantages over conventional processes due to minimal impact on the environment and cost effectiveness [Hiroyuki et al. 2002]. These treatment textile processes are essentially self sufficient and do not require rigorous monitoring. Options for biological treatment of textile effluent may be single phase aerobic or anaerobic or a combination of the two [Stolz 2001].

### 3. Future Directions:

The combined effect of the increasing population growth and industrial development has inevitably led to an increased volume of industrial based pollutants which have a serious impact on the environment. While, the advent of technology has brought about

simplified and modern products onto the market, the downstream effects of these products tend to pose hazardous effects on both the users and the environment. Textile production results in production of potentially carcinogenic and harmful waste water, which if untreated are discharged into the ecosystem either by seepage into aquifers to underground water bodies or into established mainstream water bodies. Traditional treatment methods have not only managed to remove the effluent from the water, but have rather aggravated the problem by introducing secondary effluent through chemicals used in the 'effluent treatment'. This has led man to try, where application of micro-organisms in the treatment of various industrial wastes including dye containing effluent has been investigated for the last two decades. Enzymes are not only beneficial from ecological point of view but they are also saving lot of money by reducing water and energy consumption which ultimately reduce the cost of production. It seems that in the future it will be possible to do every process using enzymes.

#### 4. Conclusion:

Effluent generated by the industries is one of the sources of pollution. Since the textile industries is the one of major water consumers, the problem faced by the textile industries is of effluent and waste disposal. Also red listed chemicals and banned dyes are carcinogenic and highly toxic. These chemicals are not only poisonous to humans but also found toxic to aquatic life and they may result in food contamination.

Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light. A synthetic dye in wastewater cannot be efficiently decolorized by traditional methods. The technologies for colour removal can be divided into three categories: biological, chemical and physical. All of them have advantages and drawbacks. Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants.

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