CHAPTER-1
INTRODUCTION

1.1 GENERAL

Water is an essential fluid for all living beings. Our mother Earth consists of 97.5% of salt water and the rest as fresh water. 70% of fresh water is in the frozen state in Antarctica and Greenland region. The major portion of water lies in deep underground to be accessible or exist as soil moisture. Merely 1% of the earth’s fresh water is available for withdrawal and human consumption [1]. In India, the per capita availability of water is reducing exponentially from 1951 to 2050 (projected) and the value is 5177 m$^3$ to 1140 m$^3$ [2]. Hasty industrialization is adversely brunting the environment worldwide. Pollution by inefficient management of industrial wastewater is one of the major environmental issues in India. Particularly in burgeoning small-scale industry. Cleaner production technologies and waste minimization initiatives are being encouraged to overcome pollution emanating from industries [3].

The inheritance of rapid urbanization and industrialization has an effect, in significant pollution problems, both in earthly and water environments [4]. Amid industries, textile industries consume a significant amount of water, allied chemicals, and energy [5]. Textile dyes show the property of high brightness, visibility at low concentration, resistant to light, chemical and microbial attack [6]. 20-50% of the dyes remains in the dye bath are unfixed hydrolyzed form, having no binding ability with the fabrics, resulted as colored effluent. Colored effluent from textile industries without proper treatment is objectionable when discharged in open water. Major pollutants
present in the effluent are organics, color, inhibitory compounds, toxicants, pH, salts, chlorinated compounds, etc. having high BOD, COD, turbidity, TDS, TSS [5]. Removing the color by the conventional method is highly complicated. [7]. Discharge of these recalcitrant contaminants into receiving water causes problem to the ecological system by the reduction of sunlight penetration and dissolved oxygen concentration, also, dyes are toxic and mutagenic, having potential to release carcinogenic amine [5, 8].

Among industries, textile industries are one of the oldest manufacturers in the world. A large volume of water and chemicals are consumed during the wet processing of textiles. Wastewater from these industries is of different types and qualities. They are rich in color, residues of coloring agents, and it needs an appropriate treatment.

In India about 2324 textile industries are functioning which includes composite and process houses. Out of which 83 are composite mills, and the rest are semi-composite and processing units. Tamil Nadu, Gujarat, Punjab and Maharashtra are major states having 81% of the total textile industries [3]. The state–wise distribution of the industries in India are given in Figure 1.1. Wastewaters from different units of a textile industry are from dyeing, chemical fiber production, wool scouring and dissolved fiber waste. Dyeing is the primary source of wastewater, which discharges a large volume of water containing dyes every day [3].
1.2 ENVIRONMENTAL CONCERNS OF TEXTILE INDUSTRIES

The textile industries are water and labor exhaustive and produce different forms of pollutants. Vapor formation is another form of pollutant formed during dyeing, printing and curing of dyes or color pigments; of these processes wet processing carried out on yarn and fabrics is concerned with major environmental issues [3]. The steps involved in the wet processes and their average water consumption are as follows:

1.2.1 Sizing or Slashing

Sizing provides tensile strength and smoothness to the yarn for weaving. The chemicals used are starch or polyvinyl alcohol (PVA) or carboxy methyl cellulose (CMC). Water requirement for this process is about 0.5 to 8.2 L/kg of yarn with an average of 4.35 L/kg.
1.2.2 Desizing

Desizing of a textile fiber is done through sulphuric acid or with enzymes. Water required de-sizing is 2.5 to 21 L/kg with the average of 11.75 L/kg.

1.2.3 Scouring / Kiering

Scouring is the next stage of operation which involves removal of impurities such as greases, waxes, fats and other impurities. Kier boiling and continuous scour are the two methods followed in souring. In the former method, Kiering liquor, an alkaline solution containing caustic soda, soda ash, sodium silicate, and sodium peroxide with a small amount of detergent is added. The water needed for this process varies from 20 – 45 L/kg with an average of 32.5 L/kg.

1.2.4 Bleaching

The natural coloring materials are removed through bleaching and make the clothes white in color. Alkaline hydrochloride or chlorine, peroxides are used. Bleaching the yarn both through hypo-chloride and hydrogen peroxide methods require same quantity of water and it varies between 24 to 32 L/kg, but the water requirement for cloth bleaching is much higher and it changes between 40 - 48 L/kg.

1.2.5 Mercerising

Mercerisation gives gleam, strength, and dye affinity and abrasion resistance to fabrics. It is followed for cotton fabrics for easy dyeing in particular. Mercerisation can be carried out in cold caustic soda solution followed by water rinsing. The water required for this process varies from 17 to 32 L/kg, with an average of 24.5 L/kg.
1.2.6 Dyeing

The most complex step in wet processing is the dyeing. It imparts attractive color to the product. Dyeing can be carried out either at the fiber stage or as yarn or as fabrics. Hundreds of dyes and auxiliary chemicals are used for dyeing. The water requirement for dyeing purpose varies from 36 to 176 L/kg with an average of 106 L/kg. The effluent generation during dyeing process varies between 35 and 175 L/kg with an average of 105 L/kg [3]. The typical characteristics of textile waste are given in Table 1.1.

<table>
<thead>
<tr>
<th>Processes</th>
<th>pH</th>
<th>Total Suspended Solids mg/L</th>
<th>BOD mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sizing / Slashing</td>
<td>7.0 – 9.5</td>
<td>8500 – 22500</td>
<td>620 – 2500</td>
</tr>
<tr>
<td>Desizing</td>
<td>6 – 8</td>
<td>16000 – 32000</td>
<td>1700 – 5200</td>
</tr>
<tr>
<td>Scouring / Kiering</td>
<td>10 – 13</td>
<td>2200 – 17400</td>
<td>100 – 2900</td>
</tr>
<tr>
<td>Bleaching</td>
<td>6</td>
<td>6500 – 22000</td>
<td>-</td>
</tr>
<tr>
<td>Mercerising</td>
<td>12 – 13</td>
<td>430 – 2700</td>
<td>150 – 280</td>
</tr>
<tr>
<td>Dyeing</td>
<td>10.5</td>
<td>10200</td>
<td>-</td>
</tr>
</tbody>
</table>

Courtesy from Global good practices in industrial wastewater treatment and disposal/reuse, with special reference to common effluent treatment plants [3].

Dyes are soluble, colored organic compounds that are usually applied to fiber and fabrics. Dyes are designed to bind sturdily on the polymer molecules that make up the textile fiber. Pigments are insoluble compounds used in paints, printing inks, ceramics, and plastics. They are applied by using dispersion in a suitable medium. Mostly pigments are all organic compounds. In this section, we are discussing textile dyes [9].
Dyes are soluble, and impart color to a substrate. Resonance is required, to impart color and is made from an aromatic ring coupled with a side chain. Color has been consummate in the synthesis of dye using a chromogen-chromophore with auxochromes. An aromatic structure containing benzene, naphthalene, or anthracene rings are called Chromophore. Chromophore group is a color provider and is stand for by the following radicals, azo (–N=N–); carbonyl (=C=O); carbon (=C=C=); carbon-nitrogen (>C=NH or –CH=N–); nitroso (–NO or N–OH); nitro (–NO or =NO– OH); sulfur (>C=S, and other carbon-sulfur groups). The chromogen chromophore structure alone is not sufficient to impart solubility and cause adherence of dye to fiber. The autochrome or bonding affinity groups are the amine, hydroxyl, carboxyl, and sulfonic radicals, or their derivatives [9].

1.3 CLASSIFICATION OF DYES BASED ON AUXOCHROMES

**Acetate rayon dyes:** Cellulose acetate and some synthetic fibers

**Acid dyes:** Coloring animal fibers via acidified in combination with amphoteric protein

**Azoic dyes:** Cotton.

**Basic dyes:** Paper

**Direct dyes:** Cotton-wool, or Cotton silk combinations

**Mordant or Chrome dyes:** Paint and Inks

**Sulfur dyes:** Furnish dull shades with good fastness to light, washing, and acids but susceptible to chlorine and light

**Vat dyes:** Fiber under reducing conditions and re-oxidized to an insoluble color.
1.4 SYNTHESIS OF DYES

Mauveine, the first ever synthetic dye was produced accidentally by William Perkin in 1856 while trying to synthesize quinine. Textile industries are exciting, a challenging industry which needs a continuous stream of novel products because of the rapidly changing world. Undeniably, except few dyes, all the dye types used on these days were discovered in 1800. The preamble of the synthetic fibers is nylon, polyester, and poly acrylonitrile during 1930. Reactive dyes discovered in 1954 and their commercial launch in 1956 signed a major step forward in cotton dyeing; intensive research in reactive dyes are still continuing today [10]. The size and growth of the dyes industry have been inextricably linked with the textile industry. World textile production has grown steadily to an estimated $35 \times 10^6$ tonne in 1990 [2, 3]. The two most imperative textile fibers are cotton, and polyester, as a result, dye manufacturers tend to concentrate their efforts on producing dyes for these two fibers. The estimated world production of dyes in 1990 was $1 \times 10^6$ t [2, 3]. The quantity is extensively smaller than that of textile fibers because a little dye is sufficient. For example, one ton of dye is sufficient to color 42000 suits [3, 10]. The steps involved in the synthesis of dyes by reaction are sulfonation, halogenation, amination, diazotization, coupling, distillation, precipitation, and crystallization. Naphthalene an organic compound reacted with an acid or an alkali along with nitrating or a sulfonating intermediate compound and a solvent form a dye mixture [9].

The molecules of colored organic compounds contain two divisions:

The color intensity can be increased by adding a lone pair of electrons to the aryl ring is known as auxochromes, and the entire structure is called chromogen [10].

\[ -\text{OH} \quad -\text{N} \quad -\text{N} \quad -\text{N} \quad -\text{N} \quad -\text{R}_1 \quad -\text{R}_2 \]
1.5 CLASSIFICATION OF DYES BY THEIR CHEMICAL STRUCTURE

(a) Azo dyes

(b) Anthraquinone dyes

(c) Phthalocyanines

1.5.1 Azo dyes

The azo dyes encompass the major chemical class, containing at least 66% of all colorants. The characteristic feature of the dye is one or more azo groups, together with hydroxyl groups, amine and substituted amine groups as auxochromes.

\[ \text{Yellow Green} \]

The molecular structures of some azo dyes showing the auxochromes are
Red

Blue
1.5.2 Anthraquinone dyes

The structure of Anthraquinone dyes are based on quinones, and it accounts for about 15%. The easiest quinone is benzoquinone, which has two isomers.

1,4 - Benzoquinone    1,2 - Benzoquinone

Examples of anthraquinones which are used as dyes are C.I. Disperse Red 60 and C.I. Disperse Blue 60.
1.5.3 Phthalocyanines

Phthalocyanines are made up of four molecules of isoindole: Isoindole molecules are connected to each other in a phthalocyanine by nitrogen atoms. It contribution among all colorants is 2% [10].

The structure of phthalocyanine is:

![Phthalocyanines](image)

1.6 DIRECT DYES

Direct dyes are predominantly used for dyeing fibers that are made from cellulose. More than 70% of all direct dyes are non-metallic azo compounds. Congo red, synthesized from benzidine is universally recognized to be a carcinogen. Direct dyes are primarily used for cotton and rayon and can also be applied to silk, jute, and wool. Direct dyes, are derived from benzidine and their molecule contains two azo groups -N=N-; they are, therefore, also known as ‘diamine colors.’
The structure of Direct Dyes

1.7 REACTIVE DYES

Reactive dyes are the juvenile and most imperative dye-class for cellulosic materials. The reactive dyes present a wide choice of dyes with varying shades, fastness, and cost with high brilliancy, easy applicability, and reproducibility. Pretreatment of the material is a prerequisite for the reactive dye. Mercerization helps in color yield and brilliancy of shades. Contrast to vat dyes; reactive dyes are not fast to chlorine bleaching, they are water-soluble anionic. Reactive dyes are tenaciously designed to have low substantivity, to facilitate the removal of hydrolyzed dye by soaping and rinsing. Reactive dyes are of stupendous importance for the dyeing of cotton, facilitating bright, intense coloration with high fastness. Around 95% of reactive dyes are azo dyes that almost cover all the range of colors. Anthraquinone and phthalocyanine structures provide blue and green color. The two stage dyeing involves dyeing and reaction, either both can take place separately or simultaneously. The characteristic structural feature is the presence of one or more reactive groups. On an average, the dyes are depicted as $D – B – RG$, where $D$ is the chromogen, $B$ a bridging group and $RG$ the reactive group. The most important reactive groups are the chlorinated triazines and vinyl sulfones.
Structure of reactive dyes

C.I. Reactive Black 5, C.I. 20505

C.I. Reactive Blue
1.8 ADVANTAGES OF AZO DYES

- Azo dyes are strong in the orange, red and Bordeaux sectors. It covers the wide range of dark blue and black.
- Bright full depths are produced, not achievable by any other dyes.
- Excellent shade reproducibility.
- Exhibits exceptionally good wet fastness on cellulosic fibers. The light fastness is good to excellent in deep dark shades.
- Low dyeing cost.
- Fast to chlorine bleaching, but inefficiently fast to hydrogen peroxide.
- The fastness properties of azoic dyeing mercerizing and perspiration are admirable.
- Simplified dyeing procedure
- Easy washability
- Permanency of the color
- Good chemical binding
Permit for a wide range of chromophores to be used

1.9 DISADVANTAGES OF AZO DYES

- Procedures involved in applying these dyes are time-consuming and complicated.
- The fastness of rubbing has always been a problem. High substantivity of the coupling component and thorough soaping is essential for good rubbing fastness.
- There is a limitation of hues available and shade matching is difficult, if not impossible. Each azoic color is developed by reaction of a di-azo and a coupling component.
- The final shade can be noticeable only after coupling. Hence any unevenness, which may have occurred during naphtha lat on, may be left unnoticed and is visible after coupling when shading corrections difficult.
- They have poor light fastness in light shades.
  The main weakness of Naphthol dyeing is their limited fastness to organic solvents used in dry cleaning and spotting.
- Fastness to Rubbing varies and is largely dependent on the dyeing process.

1.10 EFFECTS OF TEXTILE DYE EFFLUENT

Around 100,000 commercial dyes have been produced with the capacity of $7 \times 10^5$–$1 \times 10^6$ tons annually [11-15]. In such a huge production, there is no proper data on dyes discharged in the environment. However it is reported, 20-50% of the dyes remains in the dye bath are unfixed hydrolyzed form, having no binding ability with the fabrics, resulted as colored effluent. Colored effluent from textile industries without proper treatment is objectionable when discharged in open water. Removing the color by a conventional method is highly difficult [7, 13, and 16]. Textiles, dyeing, pulp and paper, tannery and paint industries are the large consumers of the dyes. Textile dyes show the property of
high brightness, visibility at low concentration, resistant to light, chemical and microbial attack [6]. Discharge of these recalcitrant contaminants into receiving water causes problem to the ecological system by the reduction of sunlight penetration and dissolved oxygen concentration, also, dyes are toxic and mutagenic, having potential to release carcinogenic amine [5, 8]. Effluents of these industries and dye manufacturing plants contain dyes in large quantities. The presence of these dyes is considered as an objectionable pollutant because of its toxicity [11, 17]. Oral ingestion and inhalation, skin and eye contact, and skin sensitization lead to skin irritation and skin sensitization and also carcinogenicity [12, 18 & 19]. Dyes impart color to water which is highly objectionable due to its aesthetic nature it also interferes the light transmission and disturbs the biological metabolism processes which cause the annihilation of aquatic lives in the ecological unit [20, 21]. Further, the dyes having a tendency to confiscate metal and may cause micro toxicity to flora and fauna [21]. It is essential to treat colored effluents for the removal of dyes. Various methodologies have been offered to treat the textile dye effluent [22, 23].

1.11 TECHNOLOGIES IN TREATMENT OF WASTEWATER

The technologies in the treatment of wastewater are broadly categorized into i) physical (ii) chemical (iii) biological and (iv) acoustical, radiation, and electrical processes. Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are the filtration technologies, and in an integral component of drinking water and wastewater treatment. These filtration technologies have been investigated for color removal [24, 25]. Membranes of a particular process are very specific for particular water [25]. Ultra and Nano filtration are more effective for all class of dyestuffs; microfiltration is not applicable for dyestuff removal because of the large pore size [25, 26]. Chemical agents such as aluminum (Al\(^{3+}\)), calcium (Ca\(^{2+}\)) or ferric ions are best coagulant/flocculent for the removal of dyes in wastewater [27-29]. In addition to these other agents can also be used for the treatment [30, 31]. Occasionally a combination of two may also enhance the
process, and it is economically feasible with a reasonable removal of disperse, sulfur, and vat dyes [28]. Chlorine, hydrogen peroxide, Fenton's reagent, ozone, or potassium permanganate are the oxidizing agent used for treating the effluents. Chemical and UV-assisted oxidizing agent is more powerful and are commonly used for decolorization. Ozonation was found to be an effective way for decolorization of textile effluent [32-34]. Electrochemical methodology is a tertiary treatment method used to remove color by elector oxidation or electro-coagulation [35, 36]. If single oxidation system is not sufficient for effective dye removal. Advanced Oxidation Processes (AOP’s) can be adapted which has more than one oxidizing agent oxidizes simultaneously.

Photo-Fenton reaction had been exposed to enhance the competence of the Fenton process and had been found to be successful in treating dye wastewaters [37]. Decolorization and degradation of dyes can be done through ultrasonic waves. The mechanism of sono chemical processes is based on the formation of short-lived radical species generated in violent cavitation actions [38]. The most common and extensive technique used in dye wastewater treatment is Biological treatment [39, 40]. A wide range of species has been used for decolorization and mineralization of various dyes. The advantage of the biological method is relatively inexpensive, low running costs and the end products of complete mineralization are nontoxic. The biological process can be aerobic, anaerobic or facultative. Bacteria and fungi have the ability to treat dye wastewaters under aerobic condition. Enzymes secreted by bacteria and fungi present in the wastewater break down the organic compounds. The potential of anaerobic treatment for the degradation of a large number of synthetic dyes has been well established and recognized [41, 42]. For better color removal from textile effluent, a combined aerobic and anaerobic treatment is suggested. The advantage of such a system is the complete mineralization which is often achieved due to the synergistic action of different organisms [43], and the consequential colorless aromatic amines may undergo mineralization under aerobic conditions [44]. Hence it is advised for treating dye wastewaters [45]. Adsorbents such as alumina, silica, zeolites, activated carbon and low-cost natural
adsorbents can also use to remove color from the textile effluent. Among the treatment technologies, biological method of treatment is more efficient, low cost and highly specific towards the target pollutant. As a result, it is an enduring need to spot and utilize resourceful microbes for the decolorization and degradation of synthetic and real textile dye effluent.

In this study synthetic dyes such as Reactive Black 5, Reactive Blue, Reactive Red and Congo red were used in treatment studies and real textile dye effluent collected from industries were used for the treatment studies. Optimized conditions in the flask level were taken in the inverse fluidized bed reactor.

**Objectives:**
To select the promising fungal and bacterial strain for textile dye effluent treatment.

1. To optimize the process parameters such as pH, volume of the bed to volume of reactor ratio ($V_b/V_r$) and initial dye concentration, for the decolorization of aqueous textile dye wastewater and real textile dye effluent using *Pleurotus ostreatus* by Response Surface Methodology (RSM).
2. To optimize the process parameters such as glucose, pH, salinity and initial effluent concentration for the decolorization of real textile dye wastewater using *Pseudomonas putida* by RSM.
3. To compare the modeling and optimization of process parameters using RSM and Artificial Neural Network-Genetic Algorithm (ANN-GA) for the optimal color removal.
4. To design the inverse fluidized bed reactor for the treatment of synthetic and real textile dye effluent.
5. To investigate the effect of color and COD removal, under optimized process parameters in the Erlenmeyer flask and inverse fluidized bed reactor under semi-continuous mode.
6. Determination of kinetic parameter using first order kinetics for flask and reactor level.

1.12 OVERVIEW OF THE THESIS

Chapter 1 deals on the significance of water in our mother earth, wastewater treatment from textile dye industries and its importance in the exponential growth of industries and population.

Chapter 2 gives a complete review of the literature on the physical, chemical and biological methods employed for dye removal. Design of Experiments (DoE) and models involved in treatment studies, Artificial neural network (ANN) for modeling and Genetic algorithm (GA) for the optimization of designed model and finally the types of reactors involved in the treatment of textile dye effluent under batch and continuous mode.

Chapters 3 explain the materials and methods involved in the decolorization and degradation studies on synthetic and real textile dye effluent. Experimental design by Box-Behnken Design (Response Surface Methodology), modeling and optimization by ANN–GA and design of Inverse Fluidized Bed Reactor.

Chapter 4 elucidate the experimental results, models by RSM, ANN-GA, compares the RSM with ANN and discusses the kinetic studies on treatment, in flask and reactor level under optimized condition and validation of pseudo-first order kinetics.

Chapter 5 declares the abridgment of the work carried out and scope for the future work.