Chapter I
Introduction

1.1 Textile industry
Textile industry is the largest industrial employer in the country, contributing to 6% GDP (Gross domestic product), 16% of export and about 18% of industrial production. The textile industry plays an important role in Indian economy. It contributes to 9% of excise collection, 30% of export revenue and 18% of employment in industrial sector. Since global trade in textile and clothing expected to reach USD 750 billions in 2012 from the level of USD 356 billions; there is an urgent need to augment our textile production capacity. At the same time, it is very essential that the environment problems associated with industrial development are properly addressed to sustain both industrial as well as economic growth.

1.2 Textile industry wastewater
The current worldwide production of more than 1,00,000 commercial textile dyes exceeds 6,00,000 tonnes annually. Globally it has been estimated that 2% of the dyes produced annually are discharged in effluents from manufacturing operations whilst 10% are discharged from textile and associated industries (Allen and Koumanova, 2005). The textile dyeing process requires large volume of water of fairly high purity and it discharges equal volume of wastewater after the dyeing process. The wastewater contains dyes at concentrations ranging from 10-200 mg/L along with other organic and inorganic accessory chemicals involved in the dyeing process (Murugesan and Kalaichelvan, 2003).

The treatment of textile effluents is of interest due to their toxic and esthetic impacts on receiving water. The release of coloured effluent into the environment is of growing concern as colour is visible pollutant that is increasingly being regulated. Since most dyes impart strong colour at concentrations even below 1 ppm, the persistent of colour is an aesthetic problem in receiving water. Without adequate treatment these dyes are stable and can remain in the environment for an extended period of time. For instance, the half-life of hydrolysed Reactive Blue 19 (RB19) is about 46 years at pH 7 and 25°C (Hao et al., 2000). The greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water which interferes with the growth of bacteria and hinder
photosynthesis in aquatic plants (Allen and Koumanova, 2005). In addition to the environmental problem, the textile industry consumes large amounts of potable water. In many countries where potable water is scarce, this large water consumption has become intolerable and wastewater recycling has been recommended in order to decrease the water requirements.

While much research has been performed to develop effective treatment technologies for wastewater containing dyes, no single solution has been satisfactory for remediating a broad diversity of textile wastes. Human and ecological health concerns have prompted the government to require textile effluent discharges to have increasingly lower colour and nitrogen levels. Despite being aware of the problem, many textile manufacturers have failed to adequately remove the dye compounds from their wastewater. Until dye and textile manufacturers are able to develop efficient technologies, allowing for increased dye - fiber bonding and lower dyehouse losses, the problem of treating these types of wastes will fall to the wastewater treatment facilities (Lewis, 1999).

1.3 Textile dye wastewater treatment methods

There are several methods used for the treatment of textile dye wastewater. These include physiochemical methods such as filtration, coagulation, use of activated carbon, chemical flocculation etc. Some of these methods viz., reverse osmosis, nanofiltration, multiple effect evaporator (MEE) are found to be effective but quite expensive (Do et al., 2002; Maier et al., 2004). Biological treatment offers a cheaper and environmentally friendlier alternative for colour removal in textile effluents. A number of microorganisms have been found to be able to decolourize textile dyes including bacteria, fungi and yeasts (Kirby et al., 2000; Wesenberg et al., 2003; Olukanni et al., 2006). They have developed enzyme systems for the decolourization and mineralization of dyes under certain environmental conditions. Although dye molecules display a high structural variety, they are degraded by only few enzymes. These biocatalysts have one common mechanistic feature. They are all redox-active molecules and thus, exhibit relatively wide substrate specificities (Duran and Esposito 2000; Mester and Tien 2000). Preferentially, suitable organisms excrete the active enzymes into the medium. On the other hand dye molecules are transported into the cells; another important requirement for these organisms is its resistance against toxic effects of dyes and other substances present in the effluent. It has been reported that after many studies decolourizing rates of dyes by microorganisms decreases with increasing dye
concentrations above certain levels. This may be a limiting factor for bio-elimination. Therefore, in cases where the target molecule or additives inhibit growth, isolated enzyme systems may be preferred.

1.4 Biological treatment

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolourization, 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 (Banat et al., 1996; McMullan et al., 2001; Fu and Viraraghavan, 2001). However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity towards diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation (Bhattacharyya and Sarma, 2003).

1.5 Sequential batch reactor (SBR)

The sequencing batch reactor (SBR) is an activated sludge process designed to operate under non-steady state conditions. SBR operates in a true batch mode with aeration and sludge settlement both occurring in the same tank. The major difference between SBR and conventional continuous flow activated sludge system is that the SBR tank carries out the functions of equalization, aeration and sedimentation in a time sequence rather than in the conventional space sequence. In addition, the SBR system can be designed with the ability to treat a wide range of influent volumes whereas the continuous system is based upon a fixed influent flow rate. Thus, there is a degree of flexibility associated with working in a time rather than in a space sequence.

SBR is an excellent reactor to treat a variety of wastewaters; they could be applied to treat domestic wastewater, landfill leachate, industrial wastewater, biological phosphorus and nitrogen removal, etc. The SBR has the following advantages in a small-scale system: flexibility in operation, low construction and maintenance cost and simultaneous removal of nitrogen and phosphorus. There are several literatures mentioning the applicability of this promising process in wastewater treatment (Jern et al., 1987; Yu et al., 1996; Hudson et al., 2001; Mohan et al., 2005; Boopathy et al., 2007; Tsang et al., 2007; Oliveira et al.,
The SBR technology has the advantage of being very flexible in terms of matching reaction and settling times to the strength and treatability characteristics of a particular waste stream. Process is easy to operate, mixed-liquor solids cannot be washed out by hydraulic surges and quiescent settling may produce lower effluent total suspended solids (TSS) concentration.

1.6 Simultaneous biodegradation and sorption of dyes in textile industry wastewater treatment

Textile dye industry wastewater is a high strength wastewater, which contain biodegradable substrates and inhibitory constituents. Thus, biological treatment alone may not be sufficient since non-biodegradable substrate cannot be removed. Certain difficulties have been encountered in the biomass growth and inhibition in textile dye industry wastewater treatment. It has been reported that the colour can often be removed by adsorption (Aktas and Cecen, 2001).

To enhance the performance of the SBR system in treating the textile dye wastewater, adsorbents have been added. The sorbent addition process involves simultaneous biodegradation and adsorption processes. The benefits of the addition of sorbent over conventional process are as follows:

- Improvement of the removal of COD and BOD
- Improvement of the stability to shock loads and toxic upsets
- Enhancement of the removal of toxic substances and priority pollutants
- Effective colour removal
- Improvement of sludge settling and dewatering
- Suppression of stripping of volatile organics
- Less tendency to foam in aerator

1.7 Need for this study

Previous research efforts have focused on various biological, chemical, and physical techniques for treating synthetic and real dye industry wastewater. There is evidence that all three areas have potential for remediating dye industry wastewater. However, chemical
treatment is often cost and application limited, while physical removal can lead to extra solid wastes and increased overhead. But, biological treatment has been effective in reducing dye industry wastewater, and when used properly has a lower operating cost than other remediation processes. Combinations of chemical and biological or physical and biological treatment have also proven to be effective. Hence this study is focused on the biological and combination of physical and biological process for the treatment of a textile effluent.

1.8 Objectives of this work
The main objective of this study is to examine the colour removal and COD reduction for the textile industry wastewater by biological and combined physical-biological method, which will minimize the treatment cost. Specific objectives include:

- To characterize the textile dye industry wastewater
- To decolourize and reduce the chemical oxygen demand (COD) of the textile industry wastewater using white rot fungus like Coriolus versicolor, Pleurotus floridanus, Ganoderma lucidum and Trametes pubescens in pure and mixed culture
- To optimize the process parameters namely pH, temperature, agitation speed and initial textile dye wastewater concentration for the decolourization of textile dye industry wastewater using Response Surface Methodology (RSM)
- To optimize the process parameters of the SBR like, air flow rate, sludge retention time, cycle time, sorbent dosage and particle loading etc., using RSM
- To compare the performance of SBR in treating textile dye wastewater with the addition of sorbent and plastic media at the optimized conditions
- To study the performance of SBR during the treatment of textile dye industry wastewater by varying the parameters such as hydraulic retention time and initial substrate concentration
- To study the decolourization kinetics in sequential batch reactor using first order model

- To model the performance of the SBR under various conditions using mathematical expressions

- To predict the performance of the SBR using Artificial Neural Network (ANN)

1.9 Structure of the thesis

Chapter I gives the introduction about the problem undertaken for research work. It also emphasizes on the scope of the present work. Chapter II presents literature review on textile wastewater, mainly covering the dyeing process, aspects of public health concerns and decolourisation techniques, with an emphasis on the biotechnological approaches. Also basic principles and operations of SBR are presented. Chapter III, describes the materials used and methods adopted in this work. In Chapter IV, the findings of this study are presented and discussed in a critical way. The modeling of SBR using mathematical model and ANN are given in Chapter V. In Chapter VI, the findings of this work are concluded and suggestions for further investigations are given.
Chapter II
Literature Review

2.1 History of dye
The use of natural dyes for painting and dyeing has been known since ancient times. The recent discovery in the Chauvet-pont-d'arc caves in France of 30000-year-old Paleolithic rock paintings provide the ancient’s testimony of the millenary use of inorganic pigments such as hematite, manganese oxide, soot and ochre (Chippindale, 1998). Organic natural colourants have also a long history, especially as textile dyes. Most dyeing techniques in use until the 19th century were established by the ancient Egyptians, who developed methods using plant extracts, sometimes in association with a mordant (Carr, 1995). Also other civilizations developed dyeing methods using not only plants, as the Indigo from Dyer's woad (Tinctoria isatis) or the red alizarin from Madder (Rubia tinctorum), but also from insects (Persian scarlet), mollusks (Tyrian purple), fungi and lichens. Due to the fact that these plants and materials were usually native from the regions where they were used in the dyeing processes the diffusion of these methods has not been possible for a long time (Carr, 1995). Until the 16th century the dyeing processes were well kept secret, but with the growth of commercial trips and the expansion of the knowledge they have had a rapid increment and diffusion.

In 1548, Giovanventura Rossetti published the "Plichto dei tintori" in which not only described some dyeing and active constituent extraction methods but also chemical preparations such as hydrochloric acid (Welham, 2000). In 1671, Colbert in France established the first regulations for the control of the dyeing quality. In 1737, Dufay de Cisternay published the first truly scientific account about systematic fastness testing and quality classification in dyeing processes based on physical and chemical ideas (Welham, 2000). In 1856, English chemist Perkin, in the attempt to synthesize quinine, discovered and patented a substance with excellent dyeing properties that later would come to be known as aniline purple. In the following years other dyes have been developed, but it was only in 1865, with the Kekule’s discover of the molecular structure of the benzene, that the research followed a less empirical and more systematic approach. In the beginning of the 20th century the synthetic dyes had almost completely supplanted the natural dyes (Welham, 2000).
2.2 Dye and their classification

Dye molecules comprise of two key components: the chromophores, responsible for producing the colour, and the auxochromes, which cannot only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity (to attach) toward the fibers. The most important chromophores are azo (–N=N–), carbonyl (–C=O), methine (–CH=), nitro (–NO₂) and quinoid groups. The most important auxochromes are amine (–NH₃), carboxyl (–COOH), sulfonate (–SO₃H) and hydroxyl (–OH). It is worth to mention that the sulfonate groups confer very high aqueous solubility to the dyes. The auxochromes can belong to the classes of reactive, acid, direct, basic, mordant, disperse, pigment, vat, anionic and ingrain, sulphur, solvent and disperse dye (Welham, 2000). Fig. 2.1 shows an illustration of the chemical structure of several dye molecules.

It is estimated that almost 10⁹ kg of dyes are produced annually in the world, of which azo dyes represent about 70% by weight (Zollinger, 1987). This group of dyes is characterised by reactive groups that form covalent bonds with OH–, NH–, or SH– groups in fibres (cotton, wool, silk, nylon). Azo dyes are mostly used for yellow, orange and red colours (Christie, 2001). To obtain the target colour, normally a mixture of red, yellow and blue dyes is applied in the dyebaths. These three dyes do not necessarily have the same chemical structure. They might contain many different chromophores, in which azo, anthraquinone and phthalocyanine dyes are the most important groups (Hao et al., 2000). Anthraquinone dyes constitute the second most important class of textile dyes, after azo dyes (Baughman and Weber, 1994). Anthraquinone dyes have a wide range of colours in almost the whole visible spectrum, but they are most commonly used for violet, blue and green colours (Christie, 2001; Fontenot et al., 2003).

Dyes exhibit considerable structural diversity and are classified in several ways. These can be classified, both by their chemical structure and their application to the fiber type (Hunger, 2003). Dyes may also be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes. Besides this, either a major azo linkage or an anthraquinone unit also characterizes dyes chemically.
Fig 2.1. Examples of dye-auxochromes and chromophores for azo and anthraquinone dyes

Though, the classification of dyes on the basis of structure is an appropriate system and has many advantages, like it readily identifies dyes as belonging to a group and having characteristic properties, e.g., azo dyes (strong, good all round properties, cost effective) and anthraquinone dyes (weak, expensive), there are a manageable number of chemical groups (about a dozen). However, the classification based on application is advantageous before considering chemical structures in detail because of the complexities of the dye nomenclature from this type of system. It is also worth to point that classification by application is the principal system adopted by the Colour Index (C.I.). A five digit C.I. number is assigned to a dye when its chemical structure has been disclosed by the manufacturer. It is also worth to note here that though a dye has a C.I. number, the purity
and precise chemical constitution may vary depending upon the name. Some properties of dyes classified based on C.I. are given in Table 2.1 (Christie, 2001).

2.3 Textile dyeing process

The schematic operation involved in textile dye processing is shown in Fig. 2.2. The most common textile processing steps consists of desizing, scouring, bleaching, mercerising and dyeing processes. Sizing is the first preparation step, in which sizing agents such as starch, polyvinyl alcohol (PVA) and carboxymethyl cellulose are added to provide strength to the fibres and minimize breakage. Desizing is employed next to remove sizing materials prior to weaving. Scouring then removes impurities from the fibres by using alkali solution (commonly sodium hydroxide) to breakdown natural oils, fats, waxes and surfactants, as well as to emulsify and suspend impurities in the scouring bath. Bleaching is used to remove unwanted colour from the fibres by using chemicals such as sodium hypochlorite and hydrogen peroxide. Mercerising is a continuous chemical process used to increase dye-ability, lustre and fibre appearance. In this step a concentrated alkaline solution is applied and an acid solution washes the fibres before the dyeing step.

Finally, dyeing is the process of adding colour to the fibres, which normally requires large volumes of water not only in the dyebath, but also during the rinsing step. Depending on the dyeing process, many chemicals like metals, salts, surfactants, organic processing assistants, sulphide and formaldehyde, may be added to improve dye adsorption onto the fibres. Fig. 2.2 shows some potential pollutants from cotton processing operations in which the desizing/scouring and dyebath/rinsing wastewaters are mainly composed of organic pollutants and colour-causing pollutants, respectively (Snowden-Swan, 1995).
### Table 2.1 Classification of Dyes

<table>
<thead>
<tr>
<th>Class</th>
<th>Characteristics</th>
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</thead>
<tbody>
<tr>
<td>Acid dyes</td>
<td>Highly water-soluble due to the presence of sulphanic acid groups. Form ionic interactions between the protonated functionalities of the fibers (-NH$_3^+$) and the negative charge of the dyes. Also Vander Waals, dipolar and hydrogen bonds are formed. The most common structures are azo, anthraquinone and triarylmethane.</td>
</tr>
<tr>
<td>Reactive dyes</td>
<td>Form covalent bonds with -OH, -NH or -SH groups in cotton, wool, silk and nylon. The problem of coloured effluents associated to the use of these dyes is due to the hydrolysis of the reactive groups that occurs during the dyeing process. The most common structures are azo, metal complex azo, anthraquinone and phthalocyanine.</td>
</tr>
<tr>
<td>Direct dyes</td>
<td>Their flat shape and length enables them to bind alongside cellulose fibers and maximize the Vander Waals, dipole and hydrogen bonds. Only 30% of the 1600 structures are still in production due to their lack of fastness during washing. The most common structures are almost always sulphonated azo dyes.</td>
</tr>
<tr>
<td>Basic dyes</td>
<td>Basic dyes work very well on acrylics due to the strong ionic interaction between dye functional groups such as -NR$_3^+$ or =NR$_2^+$ and the negative charges in the copolymer. The most common structures are azo, diarylmethane, triarylmethane and anthraquinone.</td>
</tr>
<tr>
<td>Mordant dyes</td>
<td>Mordants are usually metal salts such as sodium or potassium dichromate. They act as “fixing agent” to improve the colour fastness. They are used with wool, leather, silk and modified cellulose fibers. The most common structures are azo, oxazine or triarylmethane.</td>
</tr>
<tr>
<td>Disperse dyes</td>
<td>Non-ionic structure, with polar functionality like -NO$_2$ and –CN that improve water solubility, Van-der-Waals forces, dipole forces and the colour. They are usually used with polyester. The most common structures are azo, nitro, anthraquinones or metal complex azo.</td>
</tr>
<tr>
<td>Pigment dyes</td>
<td>These insoluble, non-ionic compounds or salts, representing 25% of all commercial dye names, retain their crystalline or particulate structure throughout their application. The most common structures are azo or metal complex phthalocyanines.</td>
</tr>
<tr>
<td>Vat dyes</td>
<td>Vat dyes are insoluble in water, but may become solubilized by alkali reduction (sodium dithionite in the presence of sodium hydroxide). The produced leuco form is absorbed by the cellulose (Van-der-Waals forces) and can be oxidized back, usually with hydrogen peroxide, to its insoluble form. The most common structures are anthraquinones or indigoids.</td>
</tr>
<tr>
<td>Ingrain dyes</td>
<td>The term in-grain is applicable to all dyes formed in situ, in or on the substrate by the development, or coupling, of one or more intermediate compounds and a diazotized aromatic amine. In the Colour Index the sub-section designated Ingrain is limited to tetra-azaporphin derivatives or precursors.</td>
</tr>
<tr>
<td>Sulphur dyes</td>
<td>Sulphur dyes are complex polymeric aromatics with heterocyclic containing rings representing about 15% of the global dye production. Dyeing with sulphur dyes (mainly on cellulose fibers) involves reduction and oxidation processes, comparable to vat dyeing.</td>
</tr>
<tr>
<td>Solvent dyes</td>
<td>Non-ionic dyes that are used for dyeing substrates in which they can dissolve as plastics, varnish, ink and waxes. They are not often used for textile processing. The most common structures are diazo compounds that undergo some molecular rearrangement, triarylmethane, anthraquinone and phthalocyanine.</td>
</tr>
<tr>
<td>Other dye classes</td>
<td>Food dyes are not used as textile dyes. Natural dyes use in textile processing operations is very limited. Fluorescent brighteners mask the yellowish tint of natural fibers by absorbing ultraviolet light and weakly emitting blue light. Not listed in a separate class in the Colour Index, many metal complex dyes can be found (generally chromium, copper, cobalt or nickel). The metal complex dyes are generally azo compounds.</td>
</tr>
</tbody>
</table>
Fig. 2.2. Schematic of operations involved in textile cotton industry and the main pollutants from each step (EPA, 1997; Mattioli et al., 2002; Dos Santos et al., 2006)

2.4 Fixation mechanisms

Fibres can take up dyes as a result of van der Waals forces, hydrogen bonds and hydrophobic interactions. The uptake of the dye in fibres depends on the dye nature and its chemical constituents. The strongest dye-fibre attachment is a result of a covalent bond with an additional electrostatic interaction where the dye ion and fibre have opposite charges (Welham, 2000).
In alkaline conditions, i.e. pH 9–12 and salt concentration from 40 to 100 g/L, and at high temperatures (30-70°C), dyes form reactive groups such as vinyl sulfone (–SO₂–CH=CH₂) and chlorotriazinyl, that form bonds with the fibres. However, the reactive groups undergo hydrolysis, i.e. a spontaneous reaction that occurs in the presence of water, and because the products do not have any affinity with the fibres, they do not form a covalent bond. Therefore, a high amount of dye constituents are discharged in the wastewater (Hao et al., 2000). The fixation efficiency varies with the class of azo dye used, which is around 98% for basic dyes and 50% for reactive dyes (O’Neill et al., 2000). Large amounts of salts such as sodium nitrate, sodium sulphate and sodium chloride are used in the dyebath, as well as sodium hydroxide is widely applied to increase the pH to the alkaline range (Carliell et al., 1998). It is estimated that during the mercerising process the weight of these salts can make up 20% of the fibre weight (EPA, 1997).

2.5 Textile dye industry wastewater
Several steps in textile production generate highly contaminated liquid streams. The quantity and composition of these wastewaters depend on many different factors, including the processed fabric and the type of process. Type of machinery, chemicals applied and other characteristics of the processes also determine the amount and composition of the generated wastewater. In the textile sector, although processes should be considered separately, treatment of each process may not be considered individually. Combined selected streams can lead to a better treatable wastewater. A stream could be separated from the rest to facilitate the recovery of water or chemicals, or to prevent dilution of a compound difficult to remove.

Some processes in a textile mill hardly generate wastewater, such as yarn manufacture, weaving (some machines use water), and singeing (lightly polluted cooling water). The amount of wastewater produced in a process like sizing is small, but very concentrated. On the other hand, processes like scouring, bleaching and dyeing generate large amounts of wastewater, varying much in composition (Cervantes, 2001). In addition, there are many different types of dyes and different dyeing processes, making difficult that only a single treatment process answers satisfactorily to the treatment requirements in all situations (Soares et al., 2006).
Textile mill effluents are also characterized by high levels of colour caused by residual dyes that were not fixed to fibers in the dyeing process. Dye molecules are highly structured polymers that are toxic to organisms (Sevimli and Kinaci, 2002). Although effluent characteristics differ greatly even within the same process, some general values for major processes in a textile mill is given in Table 2.2. Mixed textile wastewater generally contains high levels of COD and colour, and usually has a high pH (Dos Santos et al., 2007).

### Table 2.2 Average and peak values for some quality parameters in wastewater from main processes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Desizing</th>
<th>Scouring</th>
<th>Bleaching</th>
<th>Dyeing</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>3580-5900</td>
<td>3200-40000</td>
<td>250-6000</td>
<td>550-8000</td>
</tr>
<tr>
<td>COD peak</td>
<td>11000</td>
<td>90000</td>
<td>13500</td>
<td>40000</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>200-5200</td>
<td>300-8000</td>
<td>80-400</td>
<td>11-2000</td>
</tr>
<tr>
<td>BOD peak</td>
<td>200-5200</td>
<td>300-8000</td>
<td>80-400</td>
<td>11-2000</td>
</tr>
<tr>
<td>TS (mg/L)</td>
<td>7600-42000</td>
<td>1100-30000</td>
<td>900-14000</td>
<td>200-2000</td>
</tr>
<tr>
<td>TS peak</td>
<td>7600-42000</td>
<td>1100-30000</td>
<td>900-14000</td>
<td>200-2000</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>400-800</td>
<td>200-20000</td>
<td>35-900</td>
<td>25-200</td>
</tr>
<tr>
<td>SS peak</td>
<td>6000</td>
<td>40000</td>
<td>25000</td>
<td></td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>1600-6900</td>
<td>-</td>
<td>40-5000</td>
<td>-</td>
</tr>
<tr>
<td>TDS peak</td>
<td>1600-6900</td>
<td>-</td>
<td>40-5000</td>
<td>-</td>
</tr>
<tr>
<td>Lipids (mg/L)</td>
<td>190-750</td>
<td>100-9000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lipids peak</td>
<td>190-750</td>
<td>100-9000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>6-9</td>
<td>7-14</td>
<td>6-13</td>
<td>3.5-12</td>
</tr>
</tbody>
</table>

### 2.6 Textile dye industry wastewater treatment methods

Common treatment methods for textile wastewater are: physical treatment, chemical treatment and biological treatment. These treatment methods and their efficiencies are reviewed in following sections.

#### 2.6.1 Physical - Chemical methods

In physical - chemical methods coagulant agents like ferric salts or aluminium polychloride are used to form flocs with the dyes, which are then separated by filtration or sedimentation. Polyelectrolyte can also be dosed during the flocculation phase to improve the flocs settleability (Vandevivere et al., 1998). The coagulation–flocculation method is one of the most widely used processes in textile wastewater treatment plants in many countries such as Germany and France. It can be used either as a pre-treatment, post-treatment, or even as a main treatment system (Gahr et al., 1994; Marmagne and Coste,
Marmagne and Coste (1996) reported that coagulation–flocculation methods were successfully applied for colour removal of sulphur and disperse dyes, whereas acid, direct, reactive and vat dyes presented very low coagulation–flocculation capacity.

On top of the problem of low colour removal efficiency with some dyes, physical-chemical methods demand large chemicals inputs, and produce high volumes of polluted sludge, which then must be treated (Robinson et al., 2001; Anjaneyulu et al., 2005).

### 2.6.2 Chemical methods

Chemical oxidation typically involves the use of an oxidizing agents such as ozone (O₃), hydrogen peroxide (H₂O₂) and permanganate (MnO₄⁻) to change the chemical composition of a compound or a group of compounds, e.g. dyes. Among these oxidants, ozone is the most widely used because of its high reactivity with many dyes, usually providing good colour removal efficiencies (Alaton et al., 2002). In a process called selective oxidation, ozone can be designed in such a way that only –N=N– bond occurs, and biodegradable compounds remain non-oxidised (Boncz, 2002). However, disperse dyes and those insoluble in water represent a drawback for the process, as well as the high cost of ozone (Hassan and Hawkyard, 2002; Anjaneyulu et al., 2005). The usual low efficiency of both colour and COD removals of conventional chemical oxidation techniques have been overcome by the development of the so-called advanced oxidation processes (AOP). In this process, oxidizing agents such as O₃ and H₂O₂ are used with catalysts (Fe, Mn and TiO₂), either in the presence or absence of an irradiation source (Anjaneyulu et al., 2005). Consequently, an improvement in the generation and use of the free hydroxyl radical (OH⁻) is obtained, which may represent a rate increase of one to several orders of magnitude compared with normal oxidants in the absence of a catalyst (Ince and Tezcanli, 1999).

At present, many different combinations of these AOP have been investigated for colour removal, all of which are capable of producing the free hydroxyl radical (HO). The first example is a reaction called the Fenton’s reaction, in which hydrogen peroxide is added in an acid solution (pH 2–3) containing Fe²⁺ ions:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO} + \text{HO}^- \quad (2.1)
\]
In comparison with ozonation, this method is relatively cheap and also presents high COD removal and decolourisation efficiencies (Van der Zee, 2002). The main drawbacks are the high sludge generation due to the flocculation of reagents and dye molecules (Robinson et al., 2001), as well as the need for decreasing the bulk pH to acidic conditions. Hassan and Hawkyard (2002) reported that a pre-ozonation of coloured wastewaters prior to Fenton reaction not only considerably accelerated the overall colour removal rates, but also decreased the sludge generation.

In H$_2$O$_2$/UV process HO radicals are formed when water containing H$_2$O$_2$ is exposed to UV light, normally in the range of 200–280nm (Metcalf and Eddy, 2003). The H$_2$O$_2$ photolysis follows the reaction:

$$H_2O_2 + UV \rightarrow HO^- + HO^-$$  \hspace{1cm} (2.2)

This process is the most widely used AOP technology for the treatment of hazardous and refractory pollutants present in wastewater, mainly because no sludge is formed and a high COD removal in a short retention time is achieved (Safarzadeh et al., 1997). Additionally, it has been successfully applied for colour removal. For instance, more than 95% decolourisation was achieved in treating reactive, basic, acid and direct dyes at pH 5, whereas disperse and vat dyes were only partially decolourised (Yang et al., 1998). A comparative study between ozone and H$_2$O$_2$/UV was carried out in treating a concentrated reactive dyebath from a textile factory. The H$_2$O$_2$/UV system presented decolourisation rates close to those rates obtained with ozone but with a lower cost (Alaton et al., 2002).

In some cases however, the H$_2$O$_2$/UV process presents low COD and colour removal efficiency due to inefficient use of UV light (mainly for highly coloured wastewater) (Moraes et al., 2000), or because of the low molar extinction coefficient of H$_2$O$_2$ (specific oxidation capacity), requiring high dosages of the latter.

The UV-based methods in the presence of a catalyst, e.g. a semiconductive material such as TiO$_2$, have also shown to distinctly enhance colour removal (So et al., 2002; Grzechulska and Morawski, 2002). Thus, different combinations such as ozone/TiO$_2$, ozone/TiO$_2$/H$_2$O$_2$ and TiO$_2$/H$_2$O$_2$ have been investigated, but they are enormously influenced by the type of dye, dye concentration and pH (Galindo et al., 2000). The utilization of solar technologies instead of UV-based methods has been attracting attention in the past decade (Wang, 2000).
2.6.3. Physical methods

Filtration methods such as ultrafiltration, nanofiltration and reverse osmosis have been used for water reuse and chemical recovery. In the textile industry these filtration methods can be used for both filtering and recycling not only pigment rich streams, but also mercerising and bleaching wastewater. The specific temperature and chemical composition of the wastewater determine the type and porosity of the filter to be applied (Porter, 1997). The main drawbacks of membrane technology are the high investment costs, the potential membrane fouling, and the production of a concentrated dyebath which needs to be treated (Robinson et al., 2001). The recovery of concentrates from membranes, e.g. recovery of the sodium hydroxide used in the mercerising step or sizing agents such as polyvinyl alcohol (PVA), can attenuate the treatment costs (Porter, 1997). Water reuse from dyebath effluents has been successfully achieved by using reverse osmosis. However, a coagulation and micro-filtration pre-treatment was necessary to avoid membrane fouling (Vandevivere et al., 1998).

Adsorption methods for colour removal are based on the high affinity of many dyes for adsorbent materials. Decolourisation by adsorption is influenced by some physical-chemical factors like dye-adsorbent interactions, adsorbent surface area, particle size, temperature, pH and contact time (Mattioli et al., 2002; Anjaneyulu et al., 2005). The main criteria for the selection of an adsorbent should be based on characteristics such as high affinity and capacity for target compounds and the possibility of adsorbent regeneration (Karcher et al., 2001). Activated carbon (AC) is the most common adsorbent and can be very effective with many dyes (Walker and Weatherley, 1997). However, its efficiency is directly dependent upon the type of carbon material used and the wastewater characteristics, i.e. types of dyes present in the stream (Robinson et al., 2001). Additionally, AC is relatively expensive and has to be regenerated offsite with losses of about 10% in the thermal regeneration process. In order to decrease the adsorbent losses during regeneration, new adsorbent materials have been tested for their ability for on-site regeneration.

Karcher et al., (2001) studied alternative materials such as zeolites, polymeric resins, ion exchangers and granulated ferric hydroxide. It was found that zeolites and microporous resins were unsuitable due to their low sorption capacity. Although the ion exchanger provides good sorption capacity, regeneration was sometimes difficult. A number of low-
cost adsorbent materials like peat, bentonite clay and fly ash, have been investigated on colour removal (Ramakrishna and Viraraghavan, 1997; Anjaneyulu et al., 2005). However, the efficiency of these materials varied with the dye class. For instance, fly ash presented high sorption affinity for acid dyes, whereas peat and bentonite presented high affinity for basic dyes. Table 2.3 shows the advantages and disadvantages of some non-biological decolourisation processes applied to textile wastewater.

### Table 2.3 Advantages and disadvantages of non-biological decolourization processes applied to textile wastewaters (Andre B. dos Santos et al., 2007)

<table>
<thead>
<tr>
<th>Physical/chemical methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fentons reagent</td>
<td>Effective decolourisation of both soluble and insoluble</td>
<td>Sludge generation</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Applied in gaseous state: no alteration of volume</td>
<td>Short half-life (20 min)</td>
</tr>
<tr>
<td>Photochemical NaOCl</td>
<td>No sludge production</td>
<td>Formation of by products</td>
</tr>
<tr>
<td>Electrochemical destruction</td>
<td>Breakdown compounds are non-hazardous</td>
<td>High cost of electricity</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Good removal of wide variety of dyes</td>
<td>Very expensive</td>
</tr>
<tr>
<td>Membrane filtration</td>
<td>Removes all dye types</td>
<td>Concentrated sludge production</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Regeneration: no adsorbent loss</td>
<td>Not effective for all dyes</td>
</tr>
<tr>
<td>Irradiation</td>
<td>Effective oxidation at lab scale</td>
<td>Requires a lot of dissolved O₂</td>
</tr>
<tr>
<td>Electrokinetic coagulation</td>
<td>Economically feasible</td>
<td>High sludge production</td>
</tr>
</tbody>
</table>

**2.6.4 Biological treatment**

Biological treatment can be applied to textile wastewaters as aerobic, anaerobic and combined aerobic-anaerobic. In most cases, activated sludge systems (aerobic treatment) are applied. In all activated sludge systems, easily biodegradable compounds are mineralized whereas heavily biodegradable compounds need certain conditions, such as low food-to-mass-ratios (F/M) (<0.15 kg BOD₅/kg MLSS.d), adaptation (which is there if the concerned compounds are discharged very regularly) and temperature higher than 15°C (normally the case for textile wastewater) (Lacasse and Baumann, 2004).
Ineffectiveness of aerobic biological treatment in reducing colour caused by heavily biodegradable organics causes aesthetic problems in the receiving waters and encourages researchers to investigate alternatives. Dyes themselves are generally resistant to oxidative biodegradation, and a difficulty occurs in acclimation the organisms to this substrate. Acclimation presents a problem with textile wastewater due to constant product changes and batch dyeing operations (Reife and Freeman, 1996). Depending on the dyeing process; many chemicals like metals, salts, surfactants, organic processing assistants, sulphide and formaldehyde may be added to improve dye adsorption onto the fibers (Dos Santos et al., 2007). These chemicals are mainly in toxic nature and decrease the efficiency of biological treatment in colour removal regarding textile wastewater.

The treatment and safe disposal of hazardous organic waste material in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance. There is little doubt that biological processes will continue to be employed as a baseline treatment process for most organic wastewaters, since they seem to fulfill the above two requirements. However, biological processes do not always give satisfactory results, especially applied to the treatment of industrial wastewaters, because many organic substances produced by the chemical and related industries are inhibitory, toxic or resistant to biological treatment. Due to insufficiency of biological treatment in the removal of the dyes from textile and dyestuff manufacturing, this process requires the combination of physical, chemical, and physicochemical operations (Banat et al., 1996; Rai et al., 2005).

2.7 Dye decolourization using fungi
White-rot fungi such as Phanerochaete chrysosporium and Tinctoporia sp. to decolourize the lignin-containing pulp and paper wastewater was reported as early as 1980 (Eaton et al., 1980; Fukuzumi, 1980). Since then, P. chrysosporium has been examined for decolourization of pulp mill wastewaters and various dyes by many researchers (Spadaro et al., 1992; Ollikka et al., 1993; Bilgic et al., 1997; Young and Yu, 1997; Tatarko and Bumpus, 1998). In addition to P. chrysosporium, other white-rot fungi, also capable of decolourizing dyes, include T. versicolor (Young and Yu, 1997; Wong and Yu, 1999), Coriolus versicolor (Knapp and Newby, 1999) and Funalia trogii (Yesilada et al., 1995). Meanwhile, there are various fungi other than white-rot fungi, such as Aspergillus niger (Fu and Viraraghavan, 1999, 2000), Rhizopus arrhizus
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S.Sathian

(Zhou and Banks, 1991, 1993), *Rhizopus oryzae* (Gallagher et al., 1997; Polman and Breckenridge, 1996) which can also decolourize and/or biosorb diverse dyes. In fungal decolourization of dye wastewater, these fungi can be classified into two kinds according to their life state: living cells to biodegrade and biosorb dyes and dead cells (fungal biomass) to adsorb dyes.

### 2.7.1 Mechanisms

For living cells, the major mechanism is biodegradation because they can produce the lignin modifying enzymes, laccase, manganese peroxidase (MnP) and lignin peroxidase (LiP) to mineralize synthetic lignin or dyes (Michel et al., 1991; Raghukumar et al., 1996). However, the relative contributions of LiP, MnP and laccase to the decolourization of dyes may be different for each fungus. For the fungus *P. chrysosporium*, LiP was found to be responsible for the decolourization of the dyes (Glenn and Gold, 1983; Paszczynski et al., 1992; Pasti-Grigsby et al., 1992). Ollikka et al., (1993) reported that LiP played a major role in the decolourization of azo, triphenyl methane, heterocyclic and polymeric dyes by *P. chrysosporium* and that MnP was not required to start the degradation of these dyes. Young and Yu (1997) studied the decolourization of the eight synthetic dyes, including azo, anthraquinone, metal complex and indigo, by *T. versicolor* and also reported that MnP did not decolourize these dyes while ligninase-catalyzed oxidation removed over 80% of the dyes. However, Zhang et al., (1999) observed that MnP played an important role in the decolourization of cotton bleaching effluent by an unidentified white-rot fungus, while there was no obvious role for LiP in this decolourization. Because *T. versicolor* releases laccase as its major extracellular enzyme, its major mechanism in decolourizing anthraquinone, azo and indigo dyes was laccase activity (Wong and Yu, 1999). Vasdev et al., (1995) also observed that laccase activity reached a maximum during the decolourization of dyes by *Cyathus bulleri*.

In addition to biodegradation, a biosorption mechanism might also play an important role in the decolourization of dyes by living fungi. Mou et al., (1991) added wet cell cake (*Myrothecium verrucaria*) into the dye solution and they found that more than 50% of the dye was removed in the first few minutes and equilibrium was achieved in about 10 h, which indicated that adsorption was very fast. Then the cell-bound colour gradually degraded, depending on the type of the dye molecule, over a period
of a week or longer. Knapp et al., (1995) reported that the extent of colour removal by adsorption was always limited, generally less than 50%. Benito et al., (1997) studied colour adsorption by T. versicolor mycelium and reported that the adsorption accounted for only 5-10% of the total colour removal. Miranda et al., (1996) observed that the adsorbed colour was in the range 10-25% using A. niger. Boussaid (1995) used Sagenomella striatispora to remove colour from pulp mill effluent and reported that only 12% colour adsorption was observed in a total of 74% colour removal.

For dead cells, the mechanism is biosorption, which involves physico-chemical interactions, such as adsorption, deposition, and ion-exchange. Zhou and Banks (1991) studied the humic acid adsorption by dead Rhizopus arrhizus and they concluded that adsorption was a biphasic process, the first was fast and independent of metabolic energy while the second was slow and dependent on metabolic energy. They observed that no chemical reaction occurred between cell wall and humic acid; just a physical adsorption, according to the results of the infrared spectra. Banks and Parinson (1992) reported that active sites for humic acid adsorption on fungal biomass in R. arrhizus were on the fungal cell wall and were most probably the chitin/chitosan components. Gallagher et al., (1997) used Rhizopus oryzae biomass to adsorb Reactive Brilliant Red in solution and observed that both Freundlich and Langmuir isotherm models fitted biosorption well, which indicated adsorption by combined mechanisms onto a heterogeneous surface.

For the adsorption process, it is not clear whether external binding only or external binding plus internalization takes place. In order to investigate the possible role of intracellular compartmentation of dye in decolourization, Brahimi-Horn et al., (1992) studied the intact and disrupted cells incubated for 1h or 24 h in three dye solutions. After 1 h, they had adsorbed nearly the same amount of dye. But after 24 h the dye adsorption increased to a greater extent for the intact cells while this increase was only slight for disrupted cells. This suggested that the integrity of the cell was important for the binding capacity and some dye was internalized.
2.7.2 Influencing factors
In the decolourization process by fungi (living or dead cells), there are various influencing factors. They can be grouped into two kinds: one is related to fungal growth conditions; the other is related to the characteristics of the dye solution or wastewater.

2.7.2.1 Fungal growth conditions
As different components possess different abilities to decolourize dyes, it is necessary to create an optimal environment favorable to fungal growth and thus make the fungi possess the maximum ability to decolourize dyes in wastewater. Important fungal growth conditions are discussed as follows:

2.7.2.2 Medium
Fungi are usually grown in pure nutrient media, without dyes or dye wastewater, to develop a biosorbent using dead fungal biomass. Zhou and Banks (1993) studied *R. arrhizus* cultured on four different media: (1) yeast extract, malt extract, sucrose, and agar (2) yeast phosphate soluble starch (3) malt extract and (4) potato dextrose. The fungal biomass grown in potato dextrose had the highest biosorption capacity for humic acid. Fungi are mostly grown in a medium with dyes or dye wastewater to develop a biosorbent containing living fungi. The medium is mainly composed of carbon source, nitrogen source and other nutrients.

2.7.2.3 Carbon source
Zhang *et al.*, (1999) studied the carbon sources as effective co-substrate on decolourization of cotton bleaching effluent by an unidentified white-rot fungus and reported that glucose, starch, maltose and cellobiose were good carbon sources while sucrose, lactose, xylan, xylose, methanol and glyoxal were poor carbon sources. It was also reported that glucose concentration affected the decolourization and the most suitable concentration of glucose was about 5 g/L. In decolourization of melanoidin by *Coriolus sp.*, the effective sugars were glucose and sucrose (Watanabe *et al.*, 1982). Miranda *et al.*, (1996) reported that using the crystallized sucrose at an initial concentration of 10 g/L produced a maximum colour removal of 69%, but using molasses of 5 g/L equivalent sucrose only produced a colour removal of 45% for *A. niger*. Belsare and Prasad (1988) observed that the decolourization efficiencies of *Schizophyllum commune* with different carbon sources were: sucrose (60%), glucose (48%), cellulose (35%) and pulp (20%). Mou *et al.*,
(1991) studied the effects of glucose concentration on decolourization of dyes by *Myrothecium verrucaria* and observed that the influence of glucose concentration was not significant to the bio-decolourization process.

### 2.7.2.4 Nitrogen

Ryu and Weon (1992) investigated various organic or inorganic nitrogen sources to determine the most suitable nitrogen source for decolourization by *Aspergillus sojae* B-10. Sodium nitrate was the optimal nitrogen source and the highest colour removal occurred with NH$_4$NO$_3$ at 1.8 g/L for *A. sojae* B-10. But Vasdev *et al.*, (1995) reported that nitrogen had no effect on decolourization of dyes by the birds-nest fungus *Cyathus bulleri*. Zhang *et al.*, (1999) investigated the effect of concentration on decolourization and observed that the decolourization rate after adding ammonia was much lower than that without the addition of ammonia. Tatarko and Bumpus (1998) also reported that addition of supplemental nitrogen only inhibited decolourization of congo red in plates containing high amounts of nutrient nitrogen. As decolourization of dyes by *P. chrysosporium* occurs in secondary metabolic conditions, the important enzyme LiP is released by the fungal cells under either carbon or nitrogen limitation (Spadaro *et al.*, 1992; Zhen and Yu, 1998).

### 2.7.2.5 Nutrient concentration

Miranda *et al.*, (1996) reported that the highest colour removal took place at 1 g K$_2$HPO$_4$/L; and 0.5g MgSO$_4$.7H$_2$O/L for *A. niger*.

### 2.7.2.6 pH

pH is very important for fungal growth. Fungi can grow at low pH, normally ranging from 4 to 5. The optimum pH for decolourization by an unidentified white-rot fungus was pH 4-5 (Zhang *et al.*, 1999). Miranda *et al.*, (1996) studied the effect of initial pH on colour removal for *A. niger* and the optimal pH was 5. Raghukumar *et al.*, (1996) reported the effect of pH on colour removal by three marine fungi and effective pH was 4.5. Belsare and Prasad (1988) studied the optimal pH of *S. commune* and the most effective pH was 4-5.
2.7.2.7 Incubation time
Belsare and Prasad (1988) studied the incubation time of *S. commune* affecting colour removal and observed that 80% colour reduction was reached within one day and 82% in two days, but no increase was obtained in more than two days. So they suggested that two-day incubation was sufficient. Sumathi and Phatak (1999) observed that the major decolourization occurred during the exponential growth phase of the fungus *A. foetidus*. Soares and Duran (1998) observed that decolourizing efficiency using the fungus *T. villosa* did not change until the culture age was 15 days old. The fungal cell wall is the major site of sorption, especially for the chitin/chitosan components. Zhou and Banks (1993) observed that humic acid biosorption increased with culture age up to 4 days. They also suggested that the resulting increase in adsorption with culture age was due to the increase in cell wall mass, particularly the increased chitin/chitosan percentage.

2.7.2.8 Oxygen
Glenn and Gold (1983) also observed that decolourization of dyes by *P. chrysosporium* was strongly dependent on the oxygen concentration in the culture. Belsare and Prasad (1988) studied the effect of intermittent aeration three times a day on decolourization of the effluent. During aeration, dissolved oxygen (DO) ranged between 0.5 and 1.0 mg/L; prior to aeration DO was zero. They observed that intermittent aeration for a period of three days stimulated lignin breakdown and that colour removal was between 82% and 90%. Mou *et al.*, (1991) studied the effect of shaking and static incubation on decolourization and observed no adverse effect of shaking during the biodecolourization process. Yesilada *et al.*, (1995) also observed that there was not much difference in decolourisation between static and agitated cultures. Soares and Duran (1998) reported that agitation was essential for keeping a high rate of decolourization by *T. villosa*.

2.7.2.9 Temperature
Different fungi have different optimal growth temperatures. Most of them grow in the range of 25°C to 35°C. The optimal temperature for decolourization by *Coriolus sp.* was 35°C (Watanabe *et al.*, 1982) while that by an unidentified fungus was 27°C (Zhang *et al.*, 1999).
2.7.3 Characteristics of dye wastewater

2.7.3.1 Dyes

Different dyes have different molecular structures. So a fungus capable of decolourizing one dye may have different capacities for other dyes. This occurs more often for living cells than for dead ones. There are two divergent views about the effect of dye classes, structures, substitution patterns and substituent’s. Wong and Yu (1999) reported that dye decolourization by *T. versicolor* was dependent on dye structures. Anthraquinone dye was substrate of an enzyme laccase while azo and indigo dyes were not the substrates of laccase. Spadaro *et al.*, (1992) observed that aromatic rings with substituent’s such as hydroxyl, amino, acetamido, or nitro functions were mineralized to a greater extent than unsubstituted rings in dye decolourization by *P. Chrysosporium*. Brahimi-Horn *et al.*, (1992) observed that the divalent dye (Acid Red) was bound to a greater extent than the monovalent dye (Acid Orange II) by *M. verrucaria*. Knapp *et al.*, (1995) studied seven different fungi and fourteen structurally different synthetic dyes and they observed that Brilliant Yellow was easier to decolourize than chrysophenine, even though they have almost identical structures. They also reported that relatively small structural differences could markedly affect decolourization and this might be due to electron distribution and charge density as well as steric factors. On the other hand, Paszczynski *et al.*, (1992) reported that the substitution pattern of five sulfonated azo dyes did not significantly influence the susceptibility of the dyes to degradation by *P. chrysosporium*. Podgornik *et al.*, (1999) studied decolourization rates of dyes of different chemical classes and structures by using LiP of *P. chrysosporium* and reported that decolourization was not dependent on the chromophoric system and the sign and distribution of the charge, but slightly dependent on the auxochromic group. Further research is needed to establish the relationships between the structure of a dye molecule and fungal degradability and biosorption.

Dye concentration also affects the efficiency of colour removal. Zhang *et al.*, (1999) observed that the colour removal efficiency decreased with an increase in the concentration of the cotton bleaching effluent. Mou *et al.*, (1991) reported that high dye concentration resulted in low colour removal. Young and Yu (1997) also reported that high dye concentration decreased decolourization rates.
2.7.3.2 pH

pH affects not only the biosorption capacity, but also the colour of the dye solution and the solubility of some dyes. Therefore, pH is a very important factor in colour removal. Fu and Viraraghavan (1999, 2000) reported that initial pH of dye solution significantly influenced the chemistry of both dye molecules and fungal biomass. The effective initial pH of dye solution was 6.0 and 4.0 respectively, for Basic Blue 9 and Acid Blue 29. At pH of 2.0, no biosorption occurred for Basic Blue 9 due to the high concentration of protons, while at pH of 12, no biosorption occurred for Acid Blue 29. Zhou and Banks (1993) reported that the biosorption of humic acid by *R. arrhizus* increased with decreasing pH. At lower pH, more of humic acid functional groups were uncharged and humic acid had a lower solubility and was thus more adsorbable. On the other hand, the lower pH results in high concentrations of protons which neutralize the negative charge on both *R. arrhizus* and humic acid, leading to increased adsorption. De Angeli and Rodrigues (1987) studied the optimal pH for dye removal by yeast (*Candida sp.*) biomass and their results showed that the highest colour removal (98.7%) occurred at pH of 1.5 and the adsorption capacity decreased rapidly with an increasing pH.

2.7.3.3 Ionic strength

Dyeing processes consume large amounts of salt. So the concentrations of salt in dye wastewaters are normally high. Mou *et al.*, (1991) studied samples from a textile dyeing factory wastewater with as high as 15% (w/v) chloride ion. Zhou and Banks (1991, 1993) reported that high ionic strength (the concentration of NaCl) led to high biosorption of humic acid by *R. arrhizus*. So ionic strength is an important factor. The effect of ionic strength was similar to that of a colloid. At higher ionic strength, the electrical double layers of both *R. arrhizus* biomass and humic acid would be compressed thinner. Therefore biomass and humic acid could approach closer and thus this would increase van der Waals bonding and hence increase biosorption.

2.7.3.4 Metal ions

There is one class of dyes called metal-complex dyes, so there would be metal ions in some dye wastewater. Metal ions would be a factor influencing biosorption. They might compete with dye molecules for the binding sites or stimulate the biosorption of dye onto biomass. Zhou and Banks (1991, 1993) studied the effect of Cd$^{2+}$, Cu$^{2+}$ and Al$^{3+}$ on humic
acid adsorption by *R. arrhizus*. They observed that high concentrations of Cd$^{2+}$, Cu$^{2+}$ and Al$^{3+}$ resulted in high biosorption. They suggested that metal ion could be a bridge between *R. arrhizus* and humic acid, which were both negatively charged. So the addition of metal ions would neutralize their surface charge and thus reduce the repulsive forces between them, leading to their closer contact and increase bonding. The metal ions with di and tri valent cations could interact with humic acid to form precipitates or aggregates and thus reduce humic acid solubility and increase its biosorption potential.

### 2.7.3.5 Temperature

Various textile and other dye effluents are produced at relatively high temperatures (50-60°C) (Banat *et al.*, 1996). Hence temperature will be an important factor during the application of wastewater treatment. Zhou and Banks (1993) investigated the effects of temperature on humic acid sorption by *R. arrhizus*. They observed that low temperature (from 36°C to 16°C) caused a high biosorption. They suggested that biosorption between *R. arrhizus* and humic acid was an exothermic process and the mechanism was mainly physical adsorption, dominant at lower temperatures. Gallagher *et al.*, (1997) also confirmed by infrared analysis of the biosorbent that biosorption of Reactive Brilliant Red by *R. oryzae* was a physical adsorption.

### 2.7.3.6 Surfactant

In the process of dyeing, surfactants are occasionally used and thus may be present in dye wastewaters. Brahimi-Horn *et al.*, (1992) observed that the presence of detergent in wastewater may reduce the binding efficiency of the cells and reported that high concentration of Tween, a nonionic surfactant, results in a low adsorption and different dyes show different effects with the same concentration of Tween. The effect of Tween diminished with time.

### 2.7.4 Dye decolourization by white rot fungal in bioreactors

Few investigations have evaluated dye decolourization in fungal bioreactors for the design of continuous decolourization processes. Successful uses of such bioreactors are packed bed, fluidized bed, rotating bed biological reactor, SBR etc. *P.chrysosporium* is the most studied species for decolourization in bioreactors. In general, decolourization extents reported were reproducible and no external intervention was needed over a period of 9 to 12 days, after which, decolourization efficiency would decrease with the enzyme activity. Rodriguez Couto *et al.*, (2004) suggested that unstable enzyme production in an aged
culture was due to the secretion of extracellular proteases. Sustained enzyme production is an essential requirement for a stable decolourization process. It depends on the oxygen transfer and nutrient feeding rate (Swamy and Ramsay, 1999; Shahvali et al., 2000; Rodriguez Couto et al., 2004; Li and Jia, 2008). However, good oxygen transfer rate is hampered by the tendency of the fungal mycelium to excessive growth, adhesion to surfaces, which increases oxygen demand and the medium viscosity (Moreira et al., 2003). Zhang et al., (1999) operated a dye decolourizing fluidized bed reactor for two months by cleaning screens and removing excess mycelia in the reactor each week and maximized the operation. As the bioreactor was plugged and the decolourization efficiency decreased again the excess mycelia was removed and decolourization resumed. The use of rotating biological contactors (RBCs) for white rot fungi is relatively recent, as few investigations have reported its use for the decolourization of dyes (Kapdan et al., 2000; Ramsay and Goode, 2004; Guimaraes et al., 2005; Nilsson et al., 2006).

Kapdan et al., (2000) showed that the rotational speed, the biofilm thickness and the carbon source concentration impacted on the decolourization efficiency with C. versicolor. Thicker biofilms when nutrient concentration was high increased the mass transfer resistance to nutrient transfer and to enzyme secretion. Dye decolourization in fungal bioreactors needs additional investigations to determine efficient strategies to sustain a continuous enzyme production and control the growth of the mycelium as they are essential for a stable dye decolourization process in the reactor.

2.8 Sequential batch reactor (SBR)

SBRs are a variation of the activated-sludge process. They differ from activated-sludge plants because they combine all of the treatment steps and processes into a single basin, or tank, whereas conventional facilities rely on multiple basins. In a SBR, all necessary processes are taking place in a single basin as time sequenced rather than space sequenced simultaneously in separate tanks as such in conventional activated sludge (CAS) system.

SBR is successfully used to treat municipal and industrial wastewater, because of its simple configuration. Fill and draw batch processes similar to the SBR are not a recent development as commonly thought. Between 1914 and 1920, several full scale fill and draw systems were in operation. Interest in SBRs was revived in the late 1950s and early 1960s, with the development of new equipment and technology. Improvements in aeration
devices and controls have allowed SBRs to successfully compete with conventional activated sludge systems.

The SBR has received considerable attention since 1971 (Irvine and Davis, 1971) and studies of SBR process were originally conducted at the University of Notre Dame, Indiana (Irvine and Busch, 1979). Process operation and performance have been thoroughly described by Irvine et al., (1983, 1985 and 1987). They are uniquely suited for wastewater treatment applications characterized by low or intermittent flow conditions of 0 to 5 MGD (USEPA, 1999).

2.8.1 Basic treatment processes in SBR
In its most basic form, the SBR system is a set of tanks that operate on a fill-and-draw basis. Each tank in the SBR system is filled during a discrete period of time and then operated as a batch reactor. After desired treatment, the mixed liquor is allowed to settle and the clarified supernatant is then drawn from the tank.

The cycle for each tank in a typical SBR is divided into five discrete time periods: Fill, React, Settle, Draw and Idle as shown in Fig. 2.3. There are several types of fill and react periods, which vary according to aeration and mixing procedures. Sludge wasting may take place near the end of React, or during Settle, Draw, or Idle. Central to SBR design is the use of a single tank for multiple aspects of wastewater treatment. A detailed discussion of each period of the SBR is provided in the following subsections, along with a description of typical process equipment and hardware associated with each (Irvine and Ketchum, 2004).

2.8.1.1Fill
The influent to the tank may be either raw wastewater (screened and degritted) or primary effluent. It may be either pumped in or allowed to flow in by gravity. The feed volume is determined based on a number of factors including desired loading and detention time and expected settling characteristics of the organisms. The time of fill depends upon the volume of each tank, the number of parallel tanks in operation, and the extent of diurnal variations in the wastewater flow rate.
Fig. 2.3. SBR operating for each tank for one cycle for the five discrete time periods (Suresh et al., 2011)

Virtually any aeration system (e.g., diffused, floating, mechanical, or jet) can be used. The ideal aeration system, however, must be able to provide both a range of mixing intensities, from zero to complete agitation, and the flexibility of mixing without aeration. Level sensing devices, or timers, or in-tank probes (e.g., for the measurement of either dissolved oxygen or ammonia nitrogen) can be used to switch the aerators and/or mixers on and off as desired.

2.8.1.2 React

Biological reactions, which were initiated during fill, are completed during react. As in fill, alternating conditions of low dissolved oxygen concentrations (e.g., Mixed React) and high dissolved oxygen concentrations (e.g., Aerated React) may be required. The liquid
level remains at the maximum throughout react, sludge wasting can take place during this period as a simple means for controlling the sludge age. By wasting during react, sludge is removed from the reactor as a means of maintaining or decreasing the volume of sludge in the reactor and decreases the solid volume. Time dedicated to react can be as high as 50% or more of total cycle time. The end of react may be dictated by a time specification (e.g., the time in react shall always be 1.5 h) or a level controller in an adjacent tank.

2.8.1.3 Settle
In the SBR, solids separation takes place under quiescent conditions (i.e., without inflow or outflow) in a tank, which may have a volume more than ten times that of the secondary clarifier used for conventional continuous flow activated sludge plant. This major advantage in the clarification process results from the fact that the entire aeration tank serves as the clarifier during the period when no flow enters the tank. Because all of the biomass remains in the tank until some fraction must be wasted, there is no need for underflow hardware normally found in conventional clarifiers. By way of contrast, mixed liquor is continuously removed from a continuous flow activated sludge aeration tank and passed through the clarifiers only to have a major portion of the sludge returned to the aeration tank.

2.8.1.4 Draw (Decant)
The withdrawal mechanism may take one of several forms, including a pipe fixed at some predetermined level with the flow regulated by an automatic valve or a pump, or an adjustable or floating weir at or just beneath the liquid surface. In any case, the withdrawal mechanism should be designed and operated in a manner that prevents floating matter from being discharged.

The time dedicated to draw can range from 5 to more than 30% of the total cycle time. The time in draw, however, should not be overly extended because of possible problems with rising sludge.

2.8.1.5 Idle
The period between draw and fill is termed idle. Despite its name, this “idle” time can be used effectively to waste settled sludge. While sludge wasting can be as infrequent as once
every 2 to 3 months, more frequent sludge wasting programs are recommended to maintain process efficiency and sludge settling.

2.8.2 Continuous flow system
SBR facilities commonly consist of two or more basins that operate in parallel but single basin configurations under continuous flow conditions. In this modified version of the SBR, flow enters each basin on a continuous basis. The influent flows into the influent chamber, which has inlets to the react basin at the bottom of the tank to control the entrance speed so as not to agitate the settled solids.

Continuous flow systems are not true batch reactions because influent is constantly entering the basin. The design configurations of SBR and continuous flow systems are otherwise very similar. Plants operating under continuous flow should operate this way as a standard mode of operation. Ideally, a true batch reaction SBR should operate under continuous flow only under emergency situations. Plants that have been designed as continuous inflow systems have been shown to have poor operational conditions during peak flows. Some of the major problems of continuous inflow systems have been overflows, washouts, poor effluent, and permit violations (New England Interstate Water Pollution Control Commission, 2005).

The SBR system can be designed operation of the pilot plant is monitored by five on-line with the ability to treat a wide range of influent volumes whereas the continuous system is based upon a fixed influent flow rate. Thus, there is a degree of flexibility associated with working in a time rather than in a space sequence (Norcross, 1992). SBRs produce sludges with good settling properties providing the influent wastewater is admitted into the aeration in a controlled manner. Controls range from a simplified float and timer based system with a PLC to a PC based SCADA system with colour graphics using either flow proportional aeration or dissolved oxygen controlled aeration to reduce aeration to reduce energy consumption and enhance the selective pressures for BOD, nutrient removal, and control of filaments (Norcross, 1992). An appropriately designed SBR process is a unique combination of equipment and software. Working with automated control reduces the number of operator skill and attention requirement.
2.8.3 Common modifications
SBRs can be modified to provide secondary, advanced secondary treatment, nitrification, denitrification and biological nutrient removal. SBR manufacturers have adapted the sequence of batch treatment cycles described above in various ways. Some systems use a continuous inflow and provide a baffle to minimize short circuiting. SBRs were originally configured in pairs so that one reactor was filling during half of each cycle (while the wastewater in the other reactor was reacting, settling and being decanted). The modified configurations available include one SBR with an influent surge/holding tank; a three SBR system in which the fill time is one third of the total cycle time; and a continuous inflow SBR (USEPA, 1992).

In recent years, some modifications of SBR has been used by researchers, such as Intermittent Cycle Extended Aeration System (ICEAS) (USEPA, 1999), Continuous Flow SBR (Mahvi et al., 2004), Sequencing Batch Biofilm Reactor (SBBR) (Speitel and Leonard, 1992), Anaerobic Sequencing Batch Reactor (ASBR) (Dague et al., 1992) and Anaerobic - Aerobic Sequencing Batch Reactor (Bernet et al., 2000). An Anaerobic Sequencing Batch Reactor (ASBR) is similar to aerobic SBR, except that ASBR is not aerated during reaction phase and has a cover to exclude air (Fu et al., 2001).

2.8.4 Factors affecting SBR performance
The major factors affecting SBR's performance include Organic Loading Rate (OLR), Hydraulic Retention Time (HRT), Solid Retention Time (SRT), Dissolved Oxygen (DO), and influent characteristics such as COD, solids content and C/N ratio. Controlling these parameters, the SBR can be designed to have functions such as carbon oxidation, nitrification, denitrification and phosphorus removal (Hisset et al., 1982; Hanaki et al., 1990).

2.8.5 Advantages of SBR
The primary advantages of the SBR process are (Washington Department of Ecology, 1998; USEPA, 1999):

- Equalization, primary clarification (in most cases), biological treatment, and secondary clarification can be achieved in a single reactor vessel.
- Small space requirements.
- Common wall construction for rectangular tanks.
• Easy expansion into modules.
• Operating flexibility and control.
• Controllable react time and perfect quiescent settling.
• Elimination of return sludge pumping.
• Potential capital cost savings by eliminating clarifiers and other equipment.

A significant advantage of the SBR process is the space savings that results from providing treatment in single tanks (as opposed to separate aeration tanks, clarifiers, and RAS pumping facilities), which are generally square or rectangular in shape. This can allow for common wall construction, reduced site requirements, and the ability to design the facility to be readily expanded in modular steps (Washington Department of Ecology, 1998). A second significant advantage of the SBR process is process control and flexibility. Because the react time is not flow dependent, it can be adjusted to meet process objectives. By manipulating oxygen supply and mixing regimes, alternating aerobic and anoxic reactor environments can be created for nitrogen and phosphorus removal (Washington Department of Ecology, 1998).

2.8.6 Disadvantages of SBR
The primary disadvantages of the SBR process are (Washington Department of Ecology, 1998; USEPA, 1999):
• A higher level of sophistication is required (compared to conventional systems), especially for larger systems, of timing units and controls.
• Higher level of maintenance (compared to conventional systems) associated with more sophisticated controls, automated switches, and automated valves.
• Potential of discharging floating or settled sludge during the draw or decant phase with some SBR configurations.
• Potential plugging of aeration devices during selected operating cycles, depending on the aeration system used by the manufacturer.
• Potential requirement for equalization after the SBR, depending on the downstream processes.
• Installed aeration power based on percent toxic of the treatment time.
• Batch feeding from storage or bioselectors required to control bulking.
2.8.7 Application of SBR for the treatment of textile dye industry wastewater

The kind of industrial activity associated with textiles can lead to major negative impact on the environment, both in terms of pollutant discharge as well as of water and energy consumption. The major pollutant types identified in textile wastewater are organic load, colour, nutrients (N and P), sulfur, toxicants, and refractory organics. There are literatures describing the effective performance of the SBR technology for the treatment of dye/textile wastewater (Shaw et al., 2002; Fongsatitkul et al., 2004; Kapdan and Alparslan, 2005; Abu-Ghunmi and Jamrah, 2006; Isik and Sponza, 2006; El-Gohary and Tawfik, 2009). A laboratory scale SBR showed a removal efficiency of 76.4% TOC, 60-70% COD and 78.1% SS in 60 - 70 days retention time, (Shaw et al., 2002) for textile dye wastewater.

Table 2.4 Literatures on textile dye wastewater treatment in SBR

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>%COD reduction</th>
<th>%Decolourization</th>
<th>Microorganism</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remazol Brilliant Violet and Remazol Black B</td>
<td>60-70%</td>
<td>90%</td>
<td>Mixed microbes</td>
<td>Lourenco et al., 2001</td>
</tr>
<tr>
<td>Textile</td>
<td>83.3</td>
<td>35.5</td>
<td>Mixed microbes</td>
<td>Fongsatitkul et al., 2004</td>
</tr>
<tr>
<td>Acid red 151</td>
<td>&gt;90</td>
<td>&gt;80</td>
<td>Mixed microbes</td>
<td>Soon-An Ong et al., 2005a</td>
</tr>
<tr>
<td>Orange – II</td>
<td>99</td>
<td>95</td>
<td>Mixed microbes</td>
<td>Kapdan and Rukiye Ozturk, 2005</td>
</tr>
<tr>
<td>Remazol Red RR</td>
<td>70</td>
<td>95</td>
<td>Mixed microbes</td>
<td>Abu-Ghunmi and Jamrah, 2006</td>
</tr>
<tr>
<td>Vat yellow dye</td>
<td>70</td>
<td>75</td>
<td>Mixed microbes</td>
<td>Suntud Sirianuntapiboon et al., 2006</td>
</tr>
<tr>
<td>Remozol rot RR</td>
<td>85</td>
<td>90</td>
<td>Ilgi Karapinar Kapdan and Rukiye Oztekin, 2006</td>
<td></td>
</tr>
<tr>
<td>Textile</td>
<td>80-95</td>
<td></td>
<td></td>
<td>El-Gohary and Tawfik, 2009</td>
</tr>
<tr>
<td>Acid black 210</td>
<td>92</td>
<td>100</td>
<td>Mixed microbes</td>
<td>Venkata Mohan et al., 2009</td>
</tr>
</tbody>
</table>

Table 2.4 Literatures on textile dye wastewater treatment in SBR
Fongsatitkul et al., (2004) investigated treatment of textile wastewater by single process as well as in association with chemical oxidation at different conditions. In single biological process, the high reduction in 83.3% COD, 94.1% Total Kjeldah Nitrogen (TKN), 77.4% total phosphorus (TP) and 35.5% colour was found in the period of 60 days. They concluded that process was found to be independent of variation in the anoxic time period, however, an increase in solids retention time (SRT) improved COD and colour removal, although it reduced the nutrient (TKN and TP) removal efficiency. Abu-Ghunmi and Jamrah (2006) examined the feasibility of initial substrate and cell growth in the ratio of 0.13-0.5. The composition of the influent was 400-1520 mg/L COD, pH-9.5 and 1-3mg/L DO. A pilot scale-SBR with simulated sludge, removals efficiency was 80-95% COD and 95% BOD. Table 2.4 summarizes some of characteristics and removal percentages of dye/textile wastewaters by laboratory and pilot/full scale-SBR used in the last decade. Kapdan and Alparslan (2005) studied the biological treatment of textile wastewater with an anaerobic SBR. They found that 85% colour removal and 90% COD in a 12-72 h cycle.

2.9 Artificial neural network (ANN)

Artificial neural networks have been established as a tool for effortless computation and its application in environmental engineering field is very promising and has gained extensive interest. ANN has been successfully employed in solving problems in environmental engineering (Hack and Kohne, 1996; Hamoda et al., 1999; Bongards, 2001; Oliveira-Esquerre et al., 2002; Molga et al., 2005; Rajasimman et al., 2009; Turan et al., 2010). The purpose of using artificial neural networks in wastewater treatment system is to reduce the number of experiments that are being carried out to characterize the system.

Neural networks, inspired by the information processing strategies of the human brain, are proving to be useful in a variety of engineering applications. ANN may be viewed as paralleled computing tools comprising of highly organized processing elements called neurons which control the entire processing system by developing association between objects in response to their environment. ANN has been developed as generalizations of mathematical models of human cognition or neural biology. ANN is generally based on information processing that occurs at many simple elements called neurons and signals that are passed between neurons over connection links. Each connection link has its associated weight that multiplies the signal transmitted and each neuron applies an activation function to determine its output signal.
A neural network is characterized by its pattern of connections between the neurons - called its architecture, the method of determining the weights on the connections - called its training or learning algorithm and its activation function. The researches have proposed many architectures of the network. Two widely used network for non-linear problems are the backpropagation and radial basis function networks.

### 2.9.1 Advantages of ANN

The Advantages of neural networks are:

- **Adaptive learning**: An ability to learn how to do tasks based on the data given for training or initial experience.
- **Self-organization**: An ANN can create its own organization or representation of the information it receives during learning time.
- **Real time operation**: ANN computations may be carried out in parallel.
- **Fault tolerance via redundant information coding**: Partial destruction of a network leads to the corresponding degradation of performance. However, network capabilities may be retained even with major network damage.
- **ANN has the ability to account for any functional dependency**: The network discovers (learns, models) the nature of the dependency without needing to be prompted. No need to postulate a model, to amend it, etc.
- **Network is insensitive to (moderate) noise or unreliability in the data**.
- **Handling the network is easy**, as it requires lesser human effort than traditional statistical analysis. ANN has higher speed of use in order of few milliseconds.
- **ANN can be developed solely from the input-output data**.

### 2.9.2 Backpropagation networks

In backpropagation, input vectors and the corresponding output vectors are used to train the network until it can approximate a function, associate input vectors with specific output vectors, or classify input vectors in an appropriate way as defined. Networks with biases, a sigmoid layer, and a linear output layer are capable of approximating any function with a finite number of discontinuities.

Trained backpropagation networks tend to give reasonable answers when presented with inputs they have never seen. Typically, a new input will lead to an output similar to correct output for input vectors used in training that are similar to the new input being presented.
This generalization property makes it possible to train a network on a representative set of input/target pairs and get good results without training the network on all possible input/output pairs.

The backpropagation training may lead to a local rather than a global error minimum. The local error minimum that has been found may be satisfactory, but if it is not, a network with more neurons may do a better job. Each input is weighted with an appropriate weight - $w$. The sum of the weighted inputs and the bias forms the input to the transfer function $F$. Neurons may use any differentiable transfer function $F$ to generate their output. Backpropagation networks often use the log-sigmoid transfer function.

### 2.9.3 Limitations of backpropagation

A simple backpropagation is very slow because it requires small learning rates for stable learning. There are many techniques to improve the speed and general performance of backpropagation such as momentum and adaptive learning rates. Multi layered networks are capable of performing just about any linear or non-linear computation, and can approximate any reasonable function arbitrarily well. The error surface of a nonlinear network is more complex than the error surface of a linear network. Picking the learning rate for nonlinear network is a challenge. As with linear networks, a learning rate that is too large leads to unstable learning. Conversely, a learning rate that is too small results in incredibly long training times. Unlike linear networks, there is no easy way of picking a good learning rate for non-linear multi-layered networks.

The problem is that non-linear transfer function in multi-layered networks introduces many local minima in the error surface. As gradient descent is performed on the error surface it is possible for the network solution to become trapped in one of these local minima. Settling in local minima may be good or bad depending on how close local minimum is to the global minimum and how low an error is required. Networks are also sensitive to the number of neurons in their hidden layers. Too few neurons can lead to under fitting. Too many neurons can contribute to over fitting, in which all training points are well fit, but the fitting curve takes wild oscillations between these points. The recent studies show that radial basis neural network overcomes the limitations of the conventional back propagation technique (Govindarajan, 2005; Rajasimman, 2007). Hence
in this thesis radial basis neural network has been employed for the modeling of treatment of textile dye industry wastewater in SBR.

2.9.4 Radial basis function network
Radial basis function networks form one of the essential categories of neural networks. A radial basis function (RBF) network is a two-layer network, whose output units form a linear combination of the basis functions computed by the hidden units. A function is radially symmetric (or is an RBF) if its output depends on the distance of the input sample (vector) from another stored vector. Neural networks whose node functions are radially symmetric functions are referred to as Radial Basis Function Nets.

2.9.5 RBF neuron model
The transfer function for a radial basis neuron is radbas. The radial basis neuron receives as net input the vector distance between its weight vector w and the input vector p, multiplied by the bias b. The basis functions in the hidden layer produce a localized response to the inputs i.e each hidden unit has a localized receptive field. The basis function can be viewed as the activation function in the hidden layer. The outputs of the hidden unit lie between 0 and 1. The closer the input to center of the Gaussian, the larger the response of the node. The node produces an identical output for inputs with equal distance from the center of the Gaussian; it is called a radial basis. The output unit form a linear combination of the nonlinear basis functions and thus the over all network performs a nonlinear transformation of the input.

RBF network is capable of approximating any arbitrary mapping. The main difference between the RBF network and the back propagation network is in their basis functions. The radial basis function covers only small regions whereas the sigmoid function assumes nonzero values over an infinitely large region of the input space. Classification tasks are more amenable to the RBF network than the backpropagation network in the case when the problem is extended to higher dimensions.

2.9.6 RBF training procedure
The radial basis neural networks have been designed by using the function newrb available in the neural network toolbox supported by MATLAB. The function newrb iteratively creates a radial basis network by including one neuron at a time. Neurons are added to the
network until the sum squared error is found to be very small or the maximum numbers of neurons are reached. At each iteration the input vector, which will result in lowering the network error most, is used to create a radial basis neuron.

During the training, each of the connecting weights of the individual neuron is compared with input signals. The distance between the connecting weights determines the output of hidden neurons and input vector, which is further, multiplied by bias an additional scalar quantity being added between neuron and fictitious neuron.

The output is propagated in a feed forward direction to output layer neuron, which will give output if the connection weights are close to input signal. This output is compared with target vector. If the error reaches the error goal then training is completed otherwise the next neuron will be added. The connecting weights are modified each time by changing maximum neurons and spread constant. The value of maximum neuron and spread constant are keep on changing till the network is trained properly. Radial basis networks can be used to approximate functions. newrb adds neurons to the hidden layer of a radial basis network until it meets the specified mean squared error goal.

Larger the spread, smoother will be the function approximation. Too large a spread means a lot of neurons will be required to fit a fast changing function. Too small a spread means many neurons will be required to fit a smooth function, and the network may not generalize well. The function newrb creates a two-layer network. The first layer has radbas neurons, and calculates its weighted inputs with distance, and its net input. The second layer has purelin neurons, and calculates its weighted input and its net inputs. Both layers have biases. Initially the radbas layer has no neurons.

The following steps are repeated until the network’s mean squared error falls below goal as given in Fig 2.4.

- The network is simulated
- The input vector with the greatest error is found
- A radbas neuron is added with weights equal to that vector
- The purelin layer weights are redesigned to minimize error
2.9.7 Advantages of radial basis network

- The time taken in designing a radial basis network is often less when compared to the training a sigmoid / linear networks
- The number of neurons required for designing the network is considerably less when compared to standard back propagation network

2.9.8 Artificial neural networks in wastewater treatment

Hamoda et al., (1999) examined plant dynamics and modeling techniques with emphasis placed on the digital computing technology of ANN. A backpropagation model was developed to model the municipal wastewater treatment plant at Ardiya, Kuwait City, Kuwait. Results obtained proved that Neural Networks present a versatile tool in modeling full-scale operational wastewater treatment plants and provides an alternative methodology for predicting the performance of treatment plants. The overall suspended solids and organic pollutants removal efficiencies achieved at Ardiya plant over a period of 16 months were 94.6 and 97.3 percent, respectively. Plant performance was adequately predicted using the backpropagation ANN model. The correlation coefficients between the predicted and actual effluent data using the best model was 0.72 for TSS compared to 0.74 for BOD.

Choi and Park (2001) developed software sensor techniques to estimate the water quality parameter from other parameters using the correlation between water quality parameters. They focus on the preprocessing of noisy data and the selection of the best model feasible.
to the situation. They proposed a hybrid neural network as a software sensor inferring wastewater quality parameter. Multivariate regression, ANN, and a hybrid technique that combines principal component analysis as a preprocessing stage are applied to data from industrial wastewater processes. The hybrid ANN technique shows an enhancement of prediction capability and reduces the over fitting problem of neural networks. The result shows that the hybrid ANN technique can be used to extract information from noisy data and to describe the non linearity of complex wastewater treatment processes.

Lee et al., (2002) chose a full-scale coke-plant wastewater treatment process as a model system. Initially, a process data analysis was performed on the actual operational data by using principal component analysis. Next, a simplified mechanistic model and a neural network model were developed based on the specific process knowledge and the operational data of the coke-plant wastewater treatment process, respectively. Finally, the neural network was incorporated into the mechanistic model in both parallel and serial configurations. Simulation results showed that the parallel hybrid modeling approach achieved much more accurate predictions with good extrapolation properties as compared with the other modeling approaches even in the case of process upset caused by, for example, shock loading of toxic compounds. These results indicate that the parallel hybrid neural modeling approach is a useful tool for accurate and cost-effective modeling of biochemical processes, in the absence of other reasonably accurate process models.

Hamed et al., (2004) developed ANN model to predict the performance of a wastewater treatment plant (WWTP). The data used in this work were obtained from a major conventional treatment plant in the Greater Cairo district, Egypt, with an average flow rate of 1 million m$^3$/day. Daily records of biochemical oxygen demand (BOD) and suspended solids (SS) concentrations through various stages of the treatment process over 10 months were obtained from the plant laboratory. Exploratory data analysis was used to detect relationships in the data and to evaluate data dependence. Two ANN-based models for prediction of BOD and SS concentrations in plant effluent are presented. The appropriate architecture of the neural network models were determined through several steps of training and testing of the models. The ANN-based models were found to provide an efficient and a robust tool in predicting WWTP performance.
Daneshvar et al., (2005) studied the influence of the basic operational parameters such as initial concentration of $\text{H}_2\text{O}_2$ and irradiation time on the photo degradation of MTBE. Their results showed that MTBE could be treated easily and effectively with the UV/$\text{H}_2\text{O}_2$ process. The proposed model based on artificial neural network (ANN) could predict the MTBE concentration during irradiation time in optimized conditions. The comparison between the predicted results of the designed ANN model and experimental data shows the model predicted the values well.

Rangasamy et al., (2007) investigated anaerobic treatability of synthetic sago wastewater in a laboratory anaerobic tapered fluidized bed reactor (ATFBR) with a mesoporous granular activated carbon (GAC) as a support material. The experimental protocol was defined to examine the effect of the maximum organic loading rate (OLR), hydraulic retention time (HRT), the efficiency of the reactor and to report on its steady state performance. An ANN model using multilayer perceptron (MLP) has been developed for a system of two input variable and five output dependent variables. For the training of the input-output data, the experimental values obtained have been used. The output parameters predicted have been found to be much closer to the corresponding experimental ones and the model was validated for 30% of the untrained data. The mean square error was found to be 0.0146.

Farouq S. Mjalli et al., (2007) developed ANN program and implemented and validated using plant-scale data obtained from a local wastewater treatment plant, namely the Doha West wastewater treatment plant (WWTP). It is used as a valuable performance assessment tool for plant operators and decision makers. The ANN model provided accurate predictions of the effluent stream, in terms of biological oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solids (TSS) when using COD as an input in the crude supply stream. It can be said that the ANN predictions based on three crude supply inputs together, namely BOD, COD and TSS, resulted in better ANN predictions when using only one crude supply input.

Pai et al., (2007) employed grey model (GM) and ANN to predict suspended solids (SS) and chemical oxygen demand (COD) in the effluent from sequence batch reactors of a hospital wastewater treatment plant (HWWTP). The results indicated that the minimum mean absolute percentage errors of 23.14% and 51.73% for SS and COD could be
achieved using genetic algorithm ANN (GAANN). GM required a small amount of data and the prediction accuracy was analogous to that of GAANN. Furthermore, it was observed that influent pH has affected effluent SS and COD significantly. It suggested that if the influent pH could be adjusted appropriately, a better effluent SS and COD could be obtained.

Jose S. Torrecilla et al., (2008) designed an integrated artificial neural network (ANN)/laccase biosensor for the determination of concentrations of phenolic compounds (catechol). The data collected (current signals) from amperometric detection of the laccase biosensor were transferred into an ANN trained computer for modeling and prediction of output. Such an integrated ANN/laccase biosensor system is capable of prediction of catechol concentration of olive oil mill wastewater, based on the created models and patterns, without any previous phenomenological knowledge. The predicted results using the ANN were compared with the amperometric detection of phenolic compounds obtained at a laccase biosensor in olive oil wastewater during the 2004–05 harvest season. The difference between the real and the predicted values was less than 1%.

Yue Shi et al., (2009) establishes an artificial neural network (ANN) model which adopts a back propagation algorithm with momentum and adaptive learning rate, based on the prototype experiment of treating herb wastewater by Upflow anaerobic sludge bed and anaerobic filter reactor. The effect of each parameter to the performance of the reactor was compared, using the method of partitioning connection weights (PCW). The result is pH values > influent of COD > HRT > alkalinity. In addition, many strategies were proposed to optimize the working condition of the system.

Mohtada Sadrzadeh et al., (2009) applied ANN to predict separation percent (SP) of lead ions from wastewater using electrodialysis (ED). The aim was to predict SP of Pb²⁺ as a function of concentration, temperature, flow rate and voltage. Optimum numbers of hidden layers and nodes in each layer were determined. The selected structure (4:6:2:1) was used for prediction of SP of lead ions as well as current efficiency (CE) of ED cell for different inputs in the domain of training data. The modeling results showed that there is an excellent agreement between the experimental data and the predicted values.
Erkan Sahinkaya (2009) used ANN to model the Sulfidogenic treatment of sulfate (2–10 g/L) and zinc (65–677 mg/L) containing simulated wastewater in a mesophilic (35°C) CSTR. The developed ANN model was very successful as an excellent tool. Reasonable match was obtained between the measured and the predicted concentrations of sulfate ($R = 0.998$), COD ($R = 0.993$), acetate ($R = 0.976$) and zinc ($R = 0.827$) in the CSTR effluent.

Pai et al., (2009) employed three types of adaptive neuro fuzzy inference system (ANFIS) and artificial neural network (ANN) to predict suspended solids ($SS_{eff}$) and chemical oxygen demand ($COD_{eff}$) in the effluent from a hospital wastewater treatment plant. The results indicated that ANFIS statistically outperforms ANN in terms of effluent prediction. The minimum mean absolute percentage errors of 11.99% and 12.75% for $SS_{eff}$ and $COD_{eff}$ could be achieved using ANFIS. The maximum values of correlation coefficient for $SS_{eff}$ and $COD_{eff}$ were 0.75 and 0.92, respectively. The minimum mean square errors of 0.17 and 19.58, and the minimum root mean square errors of 0.41 and 4.42 for $SS_{eff}$ and $COD_{eff}$ could also be achieved.

Rajasimman et al., (2009) modeled a laboratory scale inverse fluidized bed reactor using ANN. A Radial Basis Function neural network has been successfully employed for the modeling of the inverse fluidized bed reactor. In the proposed model, the trained neural network represents the kinetics of biological decomposition of organic matters in the reactor. The neural network has been trained with experimental data obtained from an inverse fluidized bed reactor treating the starch industry wastewater. Experiments were carried out at various initial substrate concentrations of 2250, 4475, 6730 and 8910 mg COD/L and at different hydraulic retention times (40, 32, 24, 16 and 8h). They found that the neural network based model has been useful in predicting the system parameters with desired accuracy.

Turan et al., (2010) simulated the performance of the upflow anaerobic filter (UAF) reactor treating cyanide using three different neural network techniques (ANNs) – multi-layer perceptron (MLP) neural network, radial basis neural network (RBNN), and generalized regression neural network (GRNN). The performance of UAF reactor over a period of 130 days at different cyanide concentrations was evaluated with these robust models. Influent COD, HRT and influent cyanide concentration were the inputs of the
models, whereas the output variable was effluent COD. The models results were compared with each other using four statistical criteria - root mean square error (RMSE), mean absolute error (MAE), mean absolute relative error (MARE) and determination coefficient ($R^2$). The results showed that the MLP neural network with Levenberg Marquardt algorithm was found to be better than the RBNN and GRNN techniques.

In this thesis, the Neural Network has been used for the modeling of SBR performance by evaluating the effluent concentrations of textile dye industry wastewater treated in the reactor.