CHAPTER 2

REVIEW OF LITERATURE

Of all species on earth, human beings are the ones who, with their power of reasoning and analytical thinking have always tended to make their tasks easier and thereby their lives comfortable. But, such a world of development is not possible without a healthy population.

Hence, technology for sustainable development must focus on pollution prevention. Pollution prevention research has largely focused on the industrial sector. Yet till now, limited research have been devoted to the design of alternative synthetic pathways for green chemistry or process designs in order to increase product yield, improve selectivity or reduce unwanted reaction byproducts in chemical applications.

However, literature pertaining to general description of dyes and other chemicals used in textile processing, previous researchers done on treatment of dye effluents through various experiments and techniques have been presented here with a view to highlight the gap in those researchers, and to reiterate the rationale of the present study.

2.1 TECHNOLOGICAL ASPECTS OF DYES

Dyes are basically chemical compounds that can attach themselves to fabrics or surfaces to impart colour. Most dyes are complex organic molecules and are need to be resistant to many things such as weather and the
action of detergents. Synthetic dyes are extensively used in many fields of up to date technology.

Dyes are classified as follows, Anionic (Acid, Reactive and Direct Dyes), Cationic (Basic Dyes), Non-ionic (Disperse Dyes) (Mishra and Tripathy 1993, Fu and Viraraghvan 2001). The chromophores in anionic and non-ionic dyes are mostly azo groups or anthroquinone types. The reductive cleavage of azo linkages is responsible for the formation of toxic amines in the effluent. Anthraquinone based dyes are more resistant to degradation due to their fused aromatic structures and thus remain coloured in the waste water.

Acid dyes are water soluble anionic dyes and are applied to nylon, wool, silk and modified acrylcs (Reife 1993). Most of the acid dyes belong to azo and anthroquinone groups and give a wide range of bright colours on textiles and it is most difficult to remove. The largest class of dyes in the colour index is referred to as Acid dyes.

Basic dyes have high brilliance and intensity of colours and are highly visible even in very low concentration (Chu and Chen 2002). Basic dyes are cationic compounds that are used for dyeing acid group containing fibers, usually synthetic fibers like modified polyacryl. Most basic dyes are diaryl methane, triaryl methane, anthraquinone or azo compounds.

Reactive dyes form the second largest dye class in the colour index, with respect to the amount of active entries. Reactive dyes are typically azo-based chromophore combined with different types of reactive groups for example vinyl sulphone, chlorotriazine, trichloropyrimidine. They are extensively used in textile industries due to its favourable characteristics like bright colour, simple application techniques with energy consumption. Water soluble reactive and acid dyes are problematic as they pass through the conventional treatment system; they are unaffected and posing problems on to

Direct dyes are relatively large molecules with high affinity for especially cellulose fibers. Vander waals forces make them bind to fiber. The direct dyes form the second largest dye class in colour index with respect to the amount of different dyes. The use of direct dyes has continuously increased in the textile industry right from the development of synthetic fibres. Direct dyes are widely used due to its low cost, excellent colour change, good light fastness and ease of application to the material. These dyes are water soluble and contain one or more ionic groups, most often sulfonic acid/or amino groups. Most of the Direct dyes are highly toxic and potentially carcinogenic (Kaushik et al 2007, Bouyramoglu and Arica 2007).

2.2 TECHNOLOGIES FOR WATER TREATMENT

The wastewater characteristics from industries are highly variable depending on the type of dye, the type of fabric and concentration of the agents added. Water treatment process selection is a complex task involving the consideration of many factors which include available space for the construction of treatment facilities, reliability of the process equipment, waste disposal constraints, desired finished water quality and the capital and operating costs.
2.2.1 Biological Methods

Biological treatment is often considered the most economical alternative when compared to other physical and chemical processes. The use of micro organisms to remove contaminants from wastewater is an effective and wide spread method. It generally represents the phenomena of self purification that exists in nature. Self purification is the process by which an aquatic environment achieves the reestablishment of its original quality after the removal of pollutants.

Biological treatments differ according to the presence or absence of oxygen. In biological treatment processes, bacteria and other such micro organisms are used to biochemically decompose the wastewater and stabilize the end product. Biodegradation, Adsorption by (living or dead) microbial biomass and bioremediation systems are the commonly applied methods for the treatment of industrial effluents. According to the difference in O$_2$ demand for the above processes, biological treatment methods can be divided into aerobic and anaerobic treatment.

2.2.1.1 Aerobic process

Bacteria consume the organic matter and helps convert it to CO$_2$ in the presence of O$_2$. On the other hand, sludge is fermented at a particular temperature in the absence of O$_2$. Because of high efficiency and wide application of the aerobic biological treatment, it naturally becomes the main stream biological treatment. It can be further divided into two major categories like activated sludge process and biofilm process.

Activated sludge process is an effective, highly economic system used for reducing organic pollutants in waste water. Activated sludge is a kind of floc which is mainly comprised of many micro organisms, which can easily
decompose and adsorb organics. The waste water can be clarified and purified after the separation of activated sludge. Activated sludge is used for the removal of Maxilon Red BL-N (Basibuyuk and Forster 2003).

Biofilm process is a kind of biological treatment that makes the numerous micro organisms attach to some fixed object or surface, while the wastewater is allowed to flow on its surface to be purified. Sludge from sewage has been successfully used for the degradation of dye stuffs (Calvo et al 2001).

2.2.1.2 Anaerobic process

Anaerobic (without O$_2$) and anoxic (oxygen deficient) treatments are similar to aerobic treatment, but with micro organisms that do not require the addition of O$_2$. These micro organisms use compounds other than O$_2$ to catalyse the oxidation of biodegradable organic and other contaminants resulting in innocuous byproducts.

Biodegradation of synthetic dyes by the application of microorganisms is an attractive and simple method by operation. However, the biological mechanisms can be complex. The process is relatively inexpensive, the running costs are low and the end products of complete mineralization are non-toxic. The microbial decomposition of synthetic dyes has been reviewed by Stolz (2001).

Unfortunately, the majority of dyes are chemically stable and resistant to microbiological attack. Further, it is a slow process and it is necessary to create an optimal favorable environment for desired results. The major pitfall of this method is the maintenance and supply of nutrition requirements for microorganisms.
The search for new technologies for the removal of dyes from industrial waste water has attracted attention, based on the binding capacities of various biological materials. Biosorbents are attractive since naturally occurring biomass/adsorbents or spent biomass can be effectively used. The biosorption process involves a solid phase (biosorbent- biological material) and a liquid phase (solvent, water) containing dissolved species to be sorbed (adsorbate-dyes, metals). Biosorption has several advantages when compared to conventional techniques (Volesky 1999). Biological treatment requires large land area, and it is constrained by sensitivity towards diurnal variation as well as toxicity of chemicals and less flexibility in design and operation. (Bhattacharya and Sharma 2003).

2.2.2 Physico-Chemical Methods

Chemical methods include coagulation, flocculation combined with flotation and filtration, Precipitation –flocculation with Fe (II) /Ca(OH)\textsubscript{2}, conventional oxidation by O\textsubscript{2}, Electro coagulation, Electrochemical and Hypochloride oxidation and electro kinetic coagulation processes.

2.2.2.1 Coagulation-Flocculation

Coagulation-flocculation treatments are generally used to eliminate organic substances. Even though this process is widely used, it is to eliminate only insoluble dyes effectively. A combination of aluminium sulphate and a cationic organic flocculant yields an effective treatment for the decolourisation of residual dye bath wastewaters (Golob et al 2005). The main drawback of this method is the disposal of large quantity of sludges. Organic polymers are developed as coagulants for colour removal treatment and they offer advantages over inorganic polymers since sludge production is much less and colour removal is significantly increased.
2.2.2.2 Electro Coagulation

Electro coagulation has been successfully used to treat a variety of industrial waste water. In this method three important processes occurs ie., electrolytic reaction at the electrodes with coagulation in aqueous phase, adsorption of soluble or colloidal pollutants on coagulation and finally the removal by sedimentation and flotation. The main advantage of this method is removal of small colloidal particles, low sludge production. (Pouet and Grasmisk (1995). Electro coagulation process is based on the principles involving responses of water contaminants to strong electric fields and electrically induced oxidation and reduction reactions. The main advantages of this method are no addition of lime, ferric and chemical coagulants, very low operation cost, less quantity of sludge generation. The drawbacks are the high pH of the treated effluent. Further, steel plates (electrodes) should be cleaned frequently using acid. But steel is soluble which introduces iron in the treated effluent.

2.2.2.3 Electro Chemical and Hypo Chloride Oxidation

Very high rate of colour removal is observed during electro chemical oxidation. The effluent is circulated in an electrolytic cell containing iron electrodes. The main disadvantage is the generation of iron hydroxide sludges (Lin and Peng 1994, Lin and Chen 1997). Colour and COD removal from textile wastewater using electrochemical oxidation has been studied by various researchers. (Vlyssides and Israilides 1998, Jia et al 1999).

2.2.2.4 Ozone Treatment

This is a very effective and fast decolourising treatment. Ozone is now used (either alone or in combination with other treatments, such as O$_3$-UV or O$_3$-H$_2$O$_2$) for the treatment of industrial effluents (Langlais et al 1991).
Ozone especially attacks the double bonds responsible for colour. Due to the above, decolourisation of wastewater by ozone alone is not always accompanied by significant reduction of the COD (Adams 1995). Moreover, the installation of an ozonation process involves additional costs. (Scott and Ollis 1995). When several dyes of different classes were studied, ozonation was found to be more effective for decolourisation of acid dyes. The colour removal increases with the applied ozone dose. Ozone can be applied in gaseous state and therefore it does not increase the volume of wastewater and sludge (Xu et al 1999).

### 2.2.3 Physical Methods

#### 2.2.3.1 Membrane Separation Process

It is a method that uses the micro porous membranes to filter and makes use of membrane’s selective permeability to separate certain substances in wastewater. It is a new separation technology with high separation efficiency, low energy consumption, easy operation and no pollution. Currently it is widely used for the treatment of wastewater containing dye effluents. It is mainly based on membrane pressure, such as reverse osmosis, ultrafiltration, nanofiltration and micro filtration. The main pitfall of this technology is the requirement of special equipment, high investment and membrane fouling (Ranganathan et al 2007).

#### 2.2.3.2 Reverse Osmosis

Decolourisation and elimination of chemical auxiliaries in dye house wastewater can be carried out in a single step by reverse osmosis. It is effective in the removal of all mineral salts, hydrolysed reactive dyes and chemical auxiliaries. The problem involved is the higher concentration of salt and greater energy requirement to give more pressure (Ramesh Babu et al 2007).
2.2.3.3  **Nanofiltration**

It has been used to remove both organics and inorganics in various wastewaters. It has been applied for the treatment of coloured effluents. It is a pressure related process, during which separation takes place, based on molecule size. Nanofiltration membranes retain organic compounds of low molecular weight, divalent ions, large monovalent ions, hydrolysed reactive dyes and dyeing auxiliaries.

When a combination of adsorption and nanofiltration was adopted for the treatment of a textile dye-house-effluent containing a mixture of two reactive dyes, the percentage removal of COD was greater than 99% and the salt recovery was in the order of 90% (Chakraborty et al 2005).

The treatment of dyeing effluent by nanofiltration represents one of the rare applications possible for the treatment of solutions of high concentration and complex solutions. A major handicap of this method is the accumulation of dissolved solids and high pressure.

2.2.3.4  **Ultrafiltration**

This method enables the elimination of macro molecules and particles, but the elimination of polluting substances such as colour is never complete (Watters et al 1991). This can be used as a pretreatment for Reverse Osmosis or in combination with biological reactor.

2.2.3.5  **Microfiltration**

This method is suitable for treating dye baths containing pigment dyes as well as subsequent rinsing baths. It can be used as a pretreatment for nanofiltration or reverse osmosis.
These chemical technologies are mostly expensive and the accumulation of concentrated sludges creates disposal problems. This also gives rise to secondary pollution because of the excessive chemical use in treating the effluent. The high electrical energy demand and the consumption of chemical reagents are the other common problems. The major disadvantage of this processes is the limited lifetime of the membranes and the high cost involved for periodic replacement.

2.3 ADSORPTION

Adsorption has been proven to be superior to other water treatment technologies around the world. Adsorption separation in Environmental Engineering is now an aesthetic attention and consideration abroad the nations, owing to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solution (Foo and Hameed 2010). Adsorption does not result in the formation of harmful substances.

Morris and Weber (1962) suggested that adsorption is a physico chemical treatment process, which has gained acceptance for the removal of dyes from waste water since it produces a high quality treated effluent. Decolourisation is a result of two mechanisms; adsorption and ion-exchange which is influenced by many factors including dye/sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time (Slokar and Le Marechal 1998).

2.3.1 Activated Carbon

Different adsorbents have selective adsorption of dyes. Charcoal, the forerunner of modern activated carbon has been recognized as the oldest adsorbent known in wastewater treatment. Activated carbon is still the best
adsorbent of dye wastewater. Because of its selectivity to adsorb dyes, it can effectively remove the water soluble dye in waste water, such as reactive dyes, basic dyes and azo dyes, but it can’t adsorb the suspended solids and insoluble dyes. Activated carbon with high porosities (macro to micro structures) makes it an efficient adsorbent to adsorb low molecular weight chemicals such as metal ions, dyes and other organic compounds. This is achieved through adsorption processes, where the atoms and molecules are fixed to the carbon surface via physical interactions or chemical bonds. Activated carbon is produced by treating organic precursors at high temperature.

**Low cost sources of Activated Carbon**

The precursor for activated carbon should be abundant in nature or produced in large quantities as by products or wastes in industry and it also requires little processing. Using the agricultural and industrial wastes for the production of activated carbon appears to be a most beneficial venture due to the environmental and economic aspects involved. The market for activated carbon has increased considerably in the last two decades and the tendency will continue in the near future (March and Rodriguez-Reinoso 2006).

Plentiful agricultural and wood by products may also offer an inexpensive and renewable additional source of activated carbon. These waste materials have little or no economic value and often present a disposal problem. Agricultural wastes are rich sources for activated carbon production due to its low cost and reasonable hardness (Ahmedna et al 2000). So their conversion into activated carbon would add not only economic value to such material but also helps to reduce the cost of waste disposal and, above all, it provides a potentially inexpensive alternative to the existing commercial activated carbon.
A wide variety of carbon have been prepared from agricultural and wood wastes, such as Bagasse (Juang et al 2002, Valix et al 2004), Bamboo waste (Chan et al 2008), Banana pith (Kadirvelu et al 2003), cane pith (Jung et al 2001), coir pith (Namasivayam and Kavitha 2002, Namasivayam et al 2001), date pits (Banat et al 2003), Rice husk (Mohamed 2004, Malik 2004, Guo et al 2003), Olive waste cake (Baccar et al 2010), Pine wood (Tseng et al 2003), Ground shell (Malik et al 2007), Rubber seed coat (Hameed and Daud 2008).

Activated carbon productions from various wastes and industrial by-products have been reported such as waste PET bottles, waste tires (Nakagawa et al 2004), sewage sludge (Rozada et al 2003, Otero et al 2003a,b, Graham et al 2001), waste carbon slurries (Jain et al 2003).

However, the adsorption capacity of a carbon depends on the raw materials, the history of its preparation and the treatment conditions such as pyrolysis temperature and activation time. Besides, the physical structure and surface area, the adsorption capacity of activated carbon is strongly influenced by the chemical nature of the surface. The adsorption capacity also depends on the accessibility of the pollutants to the inner surface of the adsorbent, which depends on their size.

Activated carbon prepared from agricultural wastes such as silk cotton hull, coconut tree saw dust, sago waste, maize cob and banana pith have been used for the removal of dyes from aqueous solution (Kadirvelu et al 2000). Choice of raw material depends on what is available locally at low cost, provided it will lead to the production of a carbon with reasonably large adsorptive capacity that is economically viable too.
2.3.2 **Low Cost Alternative Adsorbents**

Raw agricultural solid wastes and waste materials from industries such as saw dust and bark have also been used as adsorbents. These materials are available in large quantities and may have the requisite potential as sorbents due to their physico-chemical characteristics and their low cost.

a) **Agricultural Wastes**

Agricultural materials particularly those containing cellulose have potential sorption capacity and they can adsorb various pollutants. The basic components of the agricultural waste materials include hemicelluloses, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starch.

Saw dust is easily available in the countryside at zero or negligible price (Garg et al 2004a). Saw dust has proven to be a promising effective material for the removal of dyes from wastewaters. (Ozacar and Sengil 2005, Garg et al 2004a,b, Baaouab et al 2001, Ho Mckay 1998a). The sorption results are strongly pH dependent. (Garg et al 2003, 2004b, Khattri and Singh 2000, Ho and Mc kay 1998). Chemical pretreatment of saw dust has been done to improve the sorption capacity and also to enhance the efficiency of saw dust adsorption (Batzias and Sidiras 2004). Bark from timber industry is an effective adsorbent because of its high tannin content (Bailey et al 1999, Morais et al 1999). Tree fern, an agricultural by-product, has recently been investigated to remove pollutants from aqueous solutions (Ho et al 2005). Maximum adsorption capacity of tree fern for Basic Red13 was 408 mg/g, involving mechanism of chemical bonding and ion-exchange. Other solid wastes from cheap and readily available resources such as orange peel (Rajeshwari sivaraj et al 2001), Banana peel has been experimented for the removal of Basic dyes (Annadurai et al 2002), Pine saw dust for the removal of acid dyes is also undertaken (Ozacar and Sengil 2005).
Numerous researches has been done on chemically modified agricultural wastes such as ginger waste treated with ZnCl₂ (Rajeev kumar and Rais Ahmed 2011), treated ginger waste (Ahmad and Kumar 2010), chemically modified rice husk (Shamik Chowdhury et al 2011). The possible utilization of rice husk was investigated as an adsorbent for the removal of methylene blue and saramine from aqueous solutions (Mckay et al 1999). The adsorption potential of wheat husk was studied for the removal of reactive dyes such as Reactive Blue19, Reactive Red195 and Reactive Yellow145 (Fatma et al 2007). Spent tea leaves were examined for the removal of cationic dye Methylene Blue (Hameed 2009). Adsorption of Neutral Red onto peanut husk in aqueous solution was investigated (Han et al 2008). Orange peel waste was examined for the removal of textile dyes Direct Red23 and Direct Red 80 (Arami et al 2005). The potential of garlic peel to remove Methylene Blue from aqueous solution was evaluated in a batch process (Hameed and Ahmed 2009). Wood apple shell was examined for the removal of two basic dyes Methylene Blue and Crystal Violet by Jain and Jayaram (2010). Hameed (2009) and Hameed et al (2009) investigated the feasibility of papaya seeds and pine apple stem waste for Methylene Blue adsorption. The potential of cotton plant wastes-stalk (CS) and hull (CH)-as sorbents for the removal of Remazol Black B was investigated (Tunc et al 2009). Sun and Xu (1997) examined sun flower stalks as adsorbent for the removal of two basic dyes (methylene blue and basic red 9) and two direct dyes (congo red and direct blue 71). Kohlrabi peel has also been investigated for the removal of cationic dyes (Gong et al 2007).

b) **Industrial and Municipal waste**

The waste materials generated by various industrial activities do not find proper utilization and are dumped in remote areas as unwanted materials. These materials are available almost free of cost and if these wastes could be
used as low cost adsorbents, it would manifest a twin-advantage in protecting the environment from pollution and utilization of waste material.

Fly ash is the major solid waste by-product of thermal power plant based on coal burning. The main uses of fly ash include construction of roads, bricks, cement production etc. Fly ash is used as a low cost adsorbent for the removal of cationic and anionic dyes (Viraraghavan and Ramakrishna 1999). The potential of fly ash modified with nitric acid has been used for the removal of methylene blue (Nang et al 2005).

Slag has also been used for dye removal. The utilization of treated basic oxygen furnace slag (BOF slag) was successfully carried out to remove synthetic textile dyes Reactive Blue 19, Reactive Black 5 and Reactive Red 1200 from aqueous solutions (Xue et al 2009).

Red mud is a solid waste product of aluminium industry produced during bauxite processing. The adsorption potential of Red mud for the removal of congo red from aqueous solution was investigated by Namasivayam and Arasi (1997). Fly ash and Red mud have been used as an adsorbent for the removal of methylene blue (Wang et al 2005).

Using the waste generated from leather industry buffing dust for the removal of dyes such as Acid Brown was successfully employed by Sekaran et al (1995). Use of paper mill sludge was investigated for the removal of Orange G from aqueous solution (Bhatnagar et al 2007). Waste metal hydroxide sludge has been used as low cost adsorbent for removing Remazol Brilliant Blue (Santos et al 2008).

Solid wastes from distillery waste (DW), the by product of the ammonia-soda process for the production of soda ash, has been used as an alternative adsorbent for removing the anionic dyes from aqueous medium
Boron waste produced from boron processing plant was investigated for the removal of Basic Yellow 28 and Basic Red 46 (Olgun and Atar 2009).

c) Natural Materials

Clay used as a low cost potential adsorbent because of its abundance and high sorption properties. They are classified based on the differences in their layered structures. The adsorption capabilities of clay results from a negative change on the structures of minerals and their surface area and high porosity (Alkan et al 2004).

Montmorillonite clay has the largest surface area and the highest cation exchange capacity. Ozdemir et al (2004) investigated the removal of reactive dyes Reactive Black 5, Reactive Red 239, Reactive yellow 176 by Sepiolite (Turkey) and Zeolite (Turkey). Organo-bentonite has been investigated for the removal of Acid Green 25 from waste water (Raymond Koswojo et al 2010).

Kaolin has been used for the removal of cationic dyes Basic Yellow 28, Methylene Blue, Malachite Green from waste water (Tehrai et al 2011). MCM-22 a novel Zeolite was proven effective for the removal of common dyes (Wang et al 2006).

Clay minerals exhibit a strong affinity for both hetero atomic, cationic and anionic dyes. However, the sorption capacity for basic dyes is much higher than for acid dyes because of the ionic charges on the dyes and the character of the clay. The adsorption of dyes on clay minerals is carried out mainly through ion-exchange processes. The feasibility of using diatomite for the removal of the problematic reactive dyes has been investigated (Al-Ghouti et al 2003).
Modified sepiolite has been used as an adsorbent for variety of azo reactive dyes (Ozdemir et al 2004). For effluent remediation and to remove cationic dyes from aqueous solution, Kaolinite has been used as an adsorbent (Ghosh and Bhattacharyya 2002, Harris et al 2006, Ziolkowska et al 2009). Acid activated clay was used as a low cost adsorbent for the adsorption of dyes and the adsorption capacity was found to be comparatively high for basic dye and was lower for other kind of dyes (Juang et al 1997). Bentonite was examined for the removal of Congo Red from aqueous solution by Lian et al (2009).

d) Siliceous Materials

The use of natural siliceous sorbents for waste water treatment is increasing because of their abundance, availability and low price. Their porous structure, high surface area and mechanical stability make them an effective sorbent for decontamination applications.

Alunite is another sorbent from siliceous materials to adsorb dyes. Modified Alunite has been used as a potential adsorbent for the removal of acid dyes and reactive dyes from waste water (Ozacar and Sengil 2002, 2003). Alunite is cheap and its regeneration is not necessary. Silica modified with humic acid was used to adsorb indigo carmine dye (Prado et al 2003).

Dolomite is both a mineral and a rock used as a potential adsorbent for the removal of reactive dye (Walker et al 2003). Zeolites are highly porous aluminosilicates with different cavity structures. Higher aluminium content, higher ion exchange capacity make zeolites as effective agents for the removal of pollutants from water, as well as catalysts and molecular sieves used in other applications (Logar and Kaucic 2006). Although the removal efficiency of zeolites for dyes may not be as good as that of clay materials,
their easy availability and low cost may compensate the drawbacks associated with it.

e) Biosorbents

Chitin and Chitosan

The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials is termed as biosorption. In this method, biological materials such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass are used as chelating and complexing sorbents in order to concentrate and to remove dyes from solutions. They are selective than traditional ion-exchange resins and can reduce dye concentration to ppb levels. It is a novel approach and is considered effective and cheap.

Chitin and chitosan are abundant, renewable and biodegradable resources. The sorption of dyes using biopolymers is one of the emerging biosorption methods for the removal of dyes. Chitosan is a low cost option for the adsorption of pollutants from wastewater and it has been proved efficient for the removal of dyes (Ramanani and Sabharwal 2006, Sakkayawong et al 2005).


Chitin is a naturally occurring derivative of cellulose. The major derivative of chitin is chitosan and it refers to polymer derived from chitin by deacetylation. Chitin will display no significant attraction to basic dyes. Cross linked chitosan beads has been used as a potential adsorbent for the removal
of reactive dyes, acid dyes and direct dyes (Reactive Blue 2, Reactive Red 2, Reactive Orange 14, Reactive Yellow 86, Acid Orange 12, Acid Red 14, Acid Orange 07 and Direct Red 81) (Chiou et al 2004).

The performance of chitosan as an adsorbent for the removal of acid dyes has been demonstrated by Wong et al (2004). The usefulness of chitosan for the removal of reactive dyes has been studied and it has been found that chitosan beads have higher adsorption capacities than the flake type due to its greater surface area (Wu et al 2000).

However, it is difficult to develop chitosan based materials as adsorbents at an industrial scale, because traditional method of extraction of chitin creates its own environmental problems as it generates large quantities of waste and production of chitosan involves a chemical deacetylation process also.

**Peat**

Peat is a porous and rather complex soil material with organic matter in various stages of decomposition. This material is plentiful, relatively inexpensive and a widely available biosorbent, which has adsorption capabilities for a variety of pollutants.

Peat is a low grade carbonaceous fuel containing lignin, cellulose and humic acids as major constituents. For acid and basic dyes, the removal performance was comparable with that of activated carbon while for disperse dyes, the performance was much better. Peat has been modified by mixing peat with sulphuric acid, poly vinyl alcohol and formaldehyde to produce a peat-resin particle and utilized for the adsorption of Basic Magenta and Basic Brilliant Green (Sun and Yang 2003). Because of polar character, peat can effectively remove dyes from solution (Allen et al 2004, Ho and Mckay 2003,
Sun and Yang 2003). However, raw peat has many limitations such as low mechanical strength, high affinity for water, poor chemical stability, a tendency to shrink and/or swell and to leach fulvic acid (Smith et al 1977, Couillard 1994).

**Miscellaneous Sorbents**

Starch is the most abundant carbohydrate next to cellulose in the world and it is used as a low cost adsorbent. It is a unique raw material and is with abundant polymers, apart from being inexpensive and widely available. It has biological and chemical properties such as hydrophilicity, biodegradability, polyfunctionality, high chemical reactivity and adsorption capacities.

Starch based material has been used as an adsorbent for the removal of Acid Blue 25 (Delval 2002). Adsorption of Acid Blue 25 by cross linked cyclodextrin polymer has also been investigated (Crini 2003). However, the efficiency of adsorption depends strongly on the control or particle size and the expansion of the polymer network (Crini 2003). The non-porous nature and low surface area are other handicaps.

**Biomass**

A wide variety of micro organisms including algae, yeasts, bacteria, fungi and biomass are capable of decolourising a wide range of dyes with a high efficiency (Swamy and Ramsay 1999, Nigam et al 1996). Decolourisation and/or bioadsorption of effluent by (dead or living) biomass was studied. The use of biomass for wastewater treatment is increasing because of its availability in large quantities and its low price.
Biosorption is a promising, potential alternative to conventional processes for the removal of dyes (Aksu 2005, Aksu and Tezer 2005). However, the major advantage of biosorption technology is its effectiveness in reducing the concentration of dyes to very low levels and the use of inexpensive biosorbent material. Biosorption is also an emerging technology that attempts to overcome the selectivity disadvantage of conventional adsorption processes.

There is growing research interest in the production of cheaper adsorbents. The sorption potential of adsorbent material can be improved by modification process. Modification reactions including cross-linking and functionalisation are commonly applied to enhance the adsorption capacity and adsorbent stability of the components present in biomass. Modified biosorbents exhibit good potential for the biosorption of dyes from contaminated media (Oei et al 2009, Bayramoglu et al 2006). Orange bagasse used as a potential adsorbent to remove Reactive Blue 5G dyes (Fiorontin et al 2010). Various agricultural waste biomass such as pinus bark powder (Ahmad 2009), deoiled soya (Mittal et al 2010), tomato plant root and green carbon (Kannan et al 2009), alligator weed, japonica, rice bran, wheat bran (Wang et al 2008), skin almond waste (Atmani et al 2009), almond shell (Senturk et al 2010) have been analysed for biosorption process.

Saw dust is reported to be a good adsorbent for the removal of cationic dyes such as Methylene Blue and Malachite Green and poor adsorbent for anionic dyes (Ahmed et al 2009, Wang et al 2008, Ansari et al 2009). The adsorption capacity of saw dust can be enhanced by surface modifications. Polyaniline, a widely studied conducting polymer, has been used in many fields including electrochromic devices, rechargeable batteries and sensors for its good combination of properties, environmental stability and ease of synthesis.
One efficient way of improving adsorption behavior of saw dust is to synthesise the conducting electro active polymers such as polyaniline and polypyrrole on the saw dust surface. Polymer coated saw dust has been used for the removal of Eosin Y from aqueous solutions and also metal ions (Ansari and Mosayebzadeh 2010, Ansari 2006, Ansari and Fahim 2007, Ansari and Dellavar 2008).

Generally, a suitable non-conventional low cost adsorbent for dye adsorption should meet several requirements such as

i) Efficient for removal of wide variety of dyes

ii) High capacity and rate of adsorption

iii) High selectivity for different concentrations

iv) Tolerant of a wide range of wastewater parameters

Adsorption using modified saw dust or polymer coated saw dust (polymer composite) will be a most promising technology and a potential alternative to conventional processes for the removal of dyes.

2.4 AIM AND OBJECTIVES

This research was aimed to study the adsorptive removal of various classes of dyes by using activated carbon and polymer coated saw dust composites in batch systems. The objectives of this research are

i) To synthesise and characterize the activated carbon and polymer composite adsorbents

ii) To study the adsorptive removal of dyes such as Acid Orange 10, Basic Violet 3, Reactive Red and Direct Blue onto activated carbon and polymer coated saw dust composites in
batch mode adsorption under varying operating conditions like initial dye concentration, contact time, pH and temperature.

iii) To test and compare the applicability of several kinetic models for the adsorption of various dyes by chosen adsorbents in order to determine the rate parameters for assessing the effectiveness of each model.

iv) Calculation of adsorption capacity and intensity using Langmuir and Freundlich isotherm models

v) Prediction of nature of adsorption by using thermodynamic parameters

vi) To extend the application of adsorbents for the adsorptive removal of colour from industrial effluents