CHAPTER - I

INTRODUCTION
I. INTRODUCTION


The growth of population, society, science, technology in our world are reaching to new high breaks but the cost which we are paying or will pay in near future is surely going to be too high. The consequence of this rapid growth is due to environmental disorder which is a big pollution problem. Besides, other needs of the demand for water has increased tremendously with agricultural, industrial and domestic sectors consuming 70, 22 and 8 % of the available fresh water, respectively and the amount of wastewater generated is also large which is containing a number of ‘pollutants’ [1].

One of the important factors for the degradation of the environment is population growth [2]. Population growth has doubled the effect on environment with the improvement of cheap sources of energy from coal, petroleum, natural gas and hydroelectric power. To assure food for the individuals, man started using fertilizers, pesticides and demolished millions of hectors of forest land to convert it into cultivated land. The net disastrous effect is scarcity of rain and imbalance in the ecosystem thereby.

1.1. Importance of water

Water is an ubiquitous chemical substance and is necessary for all forms of life. Water covers 71 % of the earth's surface, and is found in the environment as sea water, river water, pond water, lake water and as water vapour in the atmosphere. Oceans hold 97 % of surface water; glaciers and polar ice caps constitute 2.5 % and other 0.5 % contributes to land surface water such as rivers, lakes, ponds, etc. Even though water covers about more than two-thirds of the earth’s surface only less than 0.08 % is available to human for real use [3].

Water is the most vital resource for our life and is also the resource which is most adversely affected both qualitatively and quantitatively. Water is a unique and universal
solvent, since it has the ability to dissolve almost all substances that come within contact. Water is also used in many industrial processes and equipments such as steam turbine and heat exchanger, in addition to its use as a chemical solvent.

1.2. Water pollution

The word polluted water is defined as water that does not meet the minimum standards to which it would be suitable in its natural state. The concept of water pollution may alternatively be defined as any alteration in the physical, chemical and biological properties of water as well as contamination with any foreign substance which constitute a health hazard or otherwise decreases the utility of water. One of the major environmental pollutions is wastewater from which comes from the various sources like homes, industries and public institutions. The contaminants such as heavy metal, cyanide, toxic organics, nitrogen, phosphorous, phenols, suspended solids, colour and turbidity from the industries and untreated sewage sludge from the domestics have caused great alarm to environment and public health.

The effluents, gaseous or liquid produced by some of our industries are harmful to the health and general wellbeing of human. When undesirable substances are present in liquid effluents, it may be disastrous as their presence pose severe threat to the immediate recipients. Wastewater from various industries, factories, laboratories, etc., is a serious problem to the environment. One of the significant classes of the pollutants is dyes and once they enter the water it is no longer good and sometimes difficult to treat as the dyes have a synthetic origin and complex molecular structures which makes them more stable and difficult to biodegrade [4,5].

The discharged waste which contains dyes is toxic to microorganisms, aquatic life and human being [6]. The adverse effects of chemicals on the ecosystem is a serious concern since a number of these chemicals such as azo dyes, herbicides and pesticides
actually present in rivers and lakes are suspected of being endocrine-disrupting chemicals (EDCs) [7-10]. Konstantinou and Albanis [11] reported that textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that correspond to an increasing environmental danger. It was estimated about 10,000 of different commercial dyes and pigments exist and over $7 \times 10^5$ tonnes are produced worldwide per annum [12]. Approximately 1-20 % of the total world production of dyes is lost during the dyeing process and is released as textile effluents [13].

The environmental issues due to the presence of colour in effluent is a continuing problem for dyestuff manufactures, dyers and water companies, since increasingly stringent colour consent standard is being enforced by regulatory bodies to reduce the quality of colour in effluent and water sources.

The presence of even very low concentrations of dyes in effluent is highly visible and undesirable. Moreover, some dyes and their degradation products may be carcinogenic and toxic. Subsequently they are important sources of water pollutions and their treatment becomes a major problem for environmental managers.

1.3. Impact of polluted water

The World Health Organization estimates that safe water could prevent 1.4 million child deaths from diarrhea each year [14]. In the world, 90 % of all wastewater still goes untreated into local rivers and streams [15]. Among 50 countries, roughly a third of the world’s population also suffers from medium or high water stress and 17 countries extract more water annually than its discharged quantity through their natural water cycles [16]. The strain not only affects surface freshwater bodies like rivers and lakes but also degrades groundwater resources.

Water pollution can cause pathogenic diseases like malaria, cholera, filariasis, etc [17]. It is estimated that half of the diseases commonly encountered in our country are
water borne. In villages, 80 % of children suffer from parasitic helminthic diseases caused by contamination of untreated surface or ground water [18]. Pollution of water is responsible for very large number of mortalities and incapacitations in the world. The ecological balance of nature is threatened by the increasing environmental pollution due to rapid industrialisation in the world with high population growth. Significantly large volumes of fresh water are used by the industries.

Among the modern industries textile industry occupies a unique place in the economy of India. It employs about 20 million people and earns as much as 27 % of the country’s total export revenue. The consumption of water for processing one kg of textile goods varies from 10 to 300 litres depending on the nature of the fiber form of textile goods and the processing to be carried out. Taking a conservative figure of 100 lit of water per kg, the amount of wastewater generated by the textile industry works out to a gigantic 4500 million kilolitres [3]. Handling of such a huge quantity of wastewater is not only a difficult task but also a highly significant risk in maintaining the supply of safe drinking water.

Of all the pollutants, colour is the first contaminant to be recognised because of its visibility to human eye [19]. Colour is mainly obtained by using dye which is the major ingredient of the textile, paper and plastic industries [20-22]. The discharge of highly coloured water is not only aesthetically displeasing but also interferes with the transmission of light. This upsets the biological processes and productivity in the receiving streams by decreasing the efficiency of photosynthesis in aquatic plants and hence has adverse impact on their growth. The release of these coloured wastewaters in the environment can originate dangerous by-products through oxidation, hydrolysis or by other chemical reactions taking place in the wastewater phase [23].
Dyes also can cause severe damages to human beings such as dysfunction of kidney, reproductive systems, liver, brain and central nervous system. The occupational exposure of workers in the textile industry is linked to a higher bladder cancer risk. The use of hair colouring product and breast cancer have also been linked. Hence industrial effluent treatment becomes essential prior to the discharge to keep our environment evergreen and to try to recycle as much of the water as possible. It is our concern to protect such limited and precious natural resources of water.

1.4. Principles of colour chemistry

Dyes are chemicals which on binding with material will give colour to the material. Unlike most organic compounds, dyes possess colour because they (1) absorb light in the visible spectrum (400-700 nm), (2) have at least one chromophore (colour-bearing group), (3) have a conjugated system, i.e., a structure with alternating double and single bonds and (4) exhibit resonance of electrons which is a stabilizing force in organic compounds. The colour disappears when any one of these features is lacking from the molecular structure. In addition to chromophores, most dyes also contain groups known as auxochromes (colour helpers). Examples are carboxylic acids, sulfonic acid, amino and hydroxyl groups.

1.5. Classification of dyes

The first human-made (synthetic) organic dye, mauveine was processed by William Henry Perkin in 1856. Many thousands of synthetic dyes have since been prepared. Synthetic dyes quickly replaced the traditional natural dyes. They offered a vast range of new colours and they imparted better properties to the dyed materials even at low cost. Dyes are now classified according to how they are used in the dyeing process.

Dyeing is a process which is used to transfer the colour to the substances being dyed. Dyes are classified in various ways according to (a) the method of application to the
dye (b) their chemical constitution (c) the types of material to be dyed and (d) the intermediates from which they are prepared. The first two types of classification of dyes are very important.

The main classifications of dyes are as follows [24],

1.5.1. Acid dyes

These are water-soluble anionic dyes which may contain sulphonic acid or phenolic group applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed by salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulose fibers. Most synthetic food colours fall in this category. The principal chemical classes of these dyes are azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso.

1.5.2. Basic dyes

These are water-soluble cationic dyes that are mainly applied to acrylic fibers, wool and silk but not unmordanted cotton. For dyeing cotton, the basic dyes need a mordant like tannic acid and tartar emetic or some synthetic organic substances. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the colouration of paper. The main chemical classes are diazahemicyanine, triaryl methane, cyanine, hemicyanine, thiazine, oxazine and acridine. Examples of basic dyes are methyl violet, crystal violet, methylene blue, magenta, rhodamine, etc.

1.5.3. Direct dyes

Direct or substantive dyeing is normally carried out in a neutral or slightly alkaline dye bath at or near boiling point with the addition of either sodium chloride (NaCl) or sodium sulfate (Na$_2$SO$_4$). Direct dyes are used on cotton, paper, leather,
wool, silk and nylon materials in most of the industries. They are also used as pH indicators and as biological stains. They are water-soluble anionic dyes and when dyed from aqueous solution in the presence of electrolytes have high affinity to cellulosic fibers. A typical direct dye is Congo red.

1.5.4. Azoic dyes

Azoic dyeing is a technique in which an insoluble azo dye is produced directly onto or within the fiber. This is achieved by azo coupling. The major applications of azoic dyes are dyeing and printing of cellulosic fibers, especially cotton.

1.5.5. Oxidation dyes

These dyes are produced in textile fibers by oxidation of a colourless compound. Example: 4-amino-2-hydroxytoulene.

1.5.6. Ingrain dyes

The term ingrain is applicable to all types of dyes formed on the substrate by the development or coupling of intermediate compounds which are not themselves true finished dyes.

1.5.7. Vat dyes

These are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces water soluble alkali metal salt of the dye which in this leuco form has an affinity for textile fiber. Subsequent oxidation reforms the original insoluble dye. Example: Indigo and anthraquinone dyes.

1.5.8. Sulfur dyes

Sulfur dyes are two parts "developed" dyes used to dye cotton with dark colours. The initial bath imparts a yellow colour and it is after treated with a sulfur compound in place to produce the dark black. Sulfur Black 1 is the largest selling dye by volume.
1.5.9. Disperse dyes

These are substantially water-insoluble non-ionic dyes used for hydrophobic fibers from aqueous dispersion. Their main use is to dye polyester but they can also be used to dye nylon, cellulose triacetate and acrylic fibers. In some cases, a dyeing temperature of 130 °C is required and a pressurised dyebath is used. They generally contain azo, anthraquinone, styryl, nitro and benzodifuranone groups.

1.5.10. Reactive dyes

These dyes form a covalent bond with the fiber and contain chromophoric groups such as azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc. Their chemical structures are simpler and absorption spectra show narrower absorption bands and the dyeing are brighter and making them advantageous over direct dyes.

1.5.11. Solvent dyes

These dyes are solvent soluble (water insoluble) and generally non-polar. These dyes are used for manufacture of stains, varnishes, inks, lacquers, copying paper, typewriter ribbons, candles, polishes, soap, cosmetic, etc.

It is seen that among the eleven classes of dyes, acid dyes are about 25.25 % of the total number of dyes made. This is followed by direct dyes with 18.11 %, disperse dyes with 14.70 %, reactive dyes with 8.40 %, mordant dyes with 8.04 % and basic dyes with 6.38 %. Colour wise, red dyes occupy 22.02 %, followed by blue 19.38 %, yellow 14.56 % and brown 13.19 %. Each of the rest amounts to less than 10 % of the total dyes. The primary colours (Yellow, Red and Blue) together amount to about 56 % of the total number of dyes [24].
Table 1.1. Disadvantages of different classes of dyes

<table>
<thead>
<tr>
<th>Dye class</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azo groups</td>
<td>Their reductive cleavage of azo linkages is responsible for the formation of toxic amines in the effluent.</td>
</tr>
<tr>
<td>Anthraquinone-based dyes</td>
<td>It is most resistant to degradation due to its fused aromatic ring structure and thus remains coloured for a longer time in wastewater.</td>
</tr>
<tr>
<td>Basic dyes</td>
<td>It has high brilliance and intensity of colours and is highly visible even in a low concentration.</td>
</tr>
</tbody>
</table>

1.6. Impact of colour pollutant

Overall, there are more than 100,000 commercial dyes with a rough estimated production of $7 \times 10^5$ to $1 \times 10^6$ tons per year [25-27]. Of such a huge production, the exact data on the quantity of dyes discharged in environment is not available. However, it is reported that 10-15 % of the used dyes enter the environment through wastes [28,29]. The big consumers of dyes are textile, dyeing, paper and pulp, tannery and paint industries and hence the effluents of these industries as well as those from plants manufacturing dyes tend to contain dyes in sufficient quantities. Dyes are considered an objectionable type of pollutant because they are toxic [30] generally due to oral ingestion and inhalation, leading to problems like skin irritation and skin sensitization and also due to carcinogenicity [31]. They impart colour to water which is visible to human eye and therefore, highly objectionable on aesthetic grounds. Not only this, they also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem [32].

From the ecological and physiological point of view the effluents from dying industries are the most expressively polluted because some dyes and their degradation products are carcinogenic and toxic [33]. For example, frequently used direct dye, Congo
red can cause severe damages such as malfunction of kidney, reproductive system, liver, brain and central nervous system [34] to human beings and its degradation product Benzidine has been identified as cancer producing agent [35].

1.7. Colour removal methods

Conventional biological wastewater treatment systems are inefficient in treating dye wastewater. This is due to the low biodegradability of dye. Usually dye contaminated wastewater is treated by physical or chemical treatment process. A variety of physical, chemical and biological methods are presently available for colour removal. Colour removal technique includes adsorption [36,37], coagulation [38], flocculation, chlorination, ozonation [39-41], electro-chemical methods [42,43], biological oxidation [44,45] and advanced oxidation using UV light [46-54].

Each of these techniques offers special advantages and limitations. Adsorption had been found to be superior to other techniques for water reuse in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances [55]. The removal of coloured and colourless organic pollutants from industrial wastewater is considered an important application of adsorption processes [56].

A wide variety of materials such as peat, various types of silica, activated clay, banana pith, natural manganese mineral, shale oil ash, goat hair, alum sludge, natural zeolite and mixtures of fly ash and soil have been investigated as low cost alternatives to activated carbon [57-64]. Activated carbon has been generally used to remove composite reactive dye from dyeing unit effluent [65]. However, activated carbons are expensive due to their regeneration and reactivation procedures. In recent years, growing research interest in the production of carbon based dyes has been focused on agricultural residues [66]. Since all agricultural solid wastes used in this investigation are freely, abundantly and locally available, the resulting carbons are expected to be economically viable for wastewater treatment.
1.7.1. Physical and physico-chemical methods

These methods include adsorption, reverse osmosis, filtration and floatation. The dye adsorption on adsorbent involves diffusion of dye molecules from wastewater to the adsorbent surface, adsorption through molecular interactions and diffusion of dye molecules from the surface into the interior of the porous adsorbent.

Filtration is done by using cellulose acetate or polyamide membrane. The membrane technology is divided into nanofiltration, reverse osmosis, ultra filtration, hyperfiltration, etc [67]. Both nanofiltration and reverse osmosis membranes are effective in separating large dye molecules from the effluent. The procedure needs high capital and membrane fouling is a major problem. Moreover, colour residue remains to be disposed.

The nanofiltration membrane can retain ions as well as relatively small organic molecules from an aqueous solution. The first option is the solution of the dye bath goes directly to the nanofiltration unit where the contaminants are retained and clean recyclable water stream is produced. The second option is to give biological treatment to the waste dye bath followed by nanofiltration where the dye degradation products and the non-biodegradable organic compounds are removed.

Dye house wastewater may be treated in a reverse osmosis module for water recycling. It provides possibilities for reuse of specific dyes or chemicals and this can be readily isolated from wastewater. In ultra filtration method, ions, organic molecules, colloids or emulsified particles are filtered out with the aid of a semi permeable membrane under pressure. It finds application in removal of large molecular weight and water soluble dyes and pigments.

Ion separation method gives clean water free from colour and other organic compounds that can be used for recycling of water in process.
1.7.2. Chemical methods

Oxidation, reduction, photolytic treatment, flocculation, coagulation, electrochemical treatment and Fenton’s reagent process are some of the chemical methods used for colour removal. In oxidation process, the chromophore is destroyed or converted into biodegradable forms such as carbon dioxide, water, nitrogen, acids, sulphates, etc., by attacking weak bonds in the dye molecules with suitable oxidising agents. Advanced oxidation process has the potential to decolourise and detoxify textile dyeing effluent [67]. Chemical precipitation/flocculation techniques are used as a tertiary treatment to remove colour from the effluents. Decolourisation involves rapid precipitation followed by slow coagulation. Polymeric flocculent (Example: polyamines) can successfully remove the suspended particles and the colouring matter. Lime, either alone or with ferric salt is the most popular coagulant that is able to eliminate more than 90% of the colour present.

Fenton’s reagent is the most economical, effective and ecologically safe process that possesses the advantages of both oxidation and coagulation simultaneously increasing the amount of oxygen in water. The hydroxyl radicals generated up to pH 3.5 destroy the chromophore of dye molecule and decolourise it. The remaining dye molecules in wastewater can be coagulated and precipitated. For non ionic disperse dyes, this process is not suitable. In the presence of UV irradiation the activity of Fenton process increases.

The electro-chemical treatment of various types of dyes through electro-oxidation or by electro-coagulation causes decolourisation leading to the formation of corresponding amines. The electro chemical reduction of dyes is also possible. Although the azo dyes are readily decolourised by reduction, the resulting aromatic amines are
carcinogenic. In the case of anthraquinone dyes reduction may be reversible. A disadvantage of reduction process with sulphur dyes is the formation of sulphite and sulphate.

### 1.7.3. Biological methods

**Table 1.2. Some existing and emerging processes for dyes removal**

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional treatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coagulation Flocculation</td>
<td>Simple, economically feasible.</td>
<td>High sludge production, handling and disposal problems.</td>
</tr>
<tr>
<td>Biodegradation</td>
<td>Economically attractive, publicly accepted treatment.</td>
<td>Optimal favourable environment, maintenance and nutrition requirements.</td>
</tr>
<tr>
<td>Adsorption of activated carbon</td>
<td>The most effective adsorbent, produce a high quality treated effluent.</td>
<td>Ineffective against disperse and vat dyes. The regeneration is expensive.</td>
</tr>
<tr>
<td>Established recovery process</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane separations</td>
<td>Removes all dye types, produces a high quality treated effluent.</td>
<td>Expensive, incapable of treating large volumes.</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>No loss of sorbent on regeneration.</td>
<td>High cost and not effective for disperse dye</td>
</tr>
<tr>
<td>Oxidation</td>
<td>Rapid and efficient process.</td>
<td>Needs high energy and costly chemicals.</td>
</tr>
<tr>
<td>Emerging removal process</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Advanced oxidation process</td>
<td>No sludge production, little or no consumption of chemicals.</td>
<td>Economically unfeasible due to formation of by-products which leads to technical constraints.</td>
</tr>
</tbody>
</table>

Biological treatment of effluent is termed as secondary treatment. The objective of this treatment is to achieve bio-flocculation. The micro organisms convert the colloidal and dissolved carbonaceous matter into various gases and cell tissues. The cell tissues
have a specific gravity slightly higher than that of water and hence can be removed by gravity settling. Biological treatment includes aerobic and anaerobic treatments. Bio-aeration is ineffective in removing the colour from many types of dye wastes and is mainly used because of its efficiency in reducing the BOD from the textile effluent. Aerobic process is not exclusively used to decolourise azo dye containing wastewater. It is coupled with anaerobic treatment. The azo chromophore is non-specifically reduced under anaerobic conditions followed by aerobic oxidation of the generated carcinogenic and mutagenic aromatic amines. Biological treatment though appears to be quite simple, very tricky and needs proper attention [67].

The details of some existing and emerging processes for the removal of dyes are presented in table 1.2

1.7.4. Photo catalytic decolourisation

Industrial wastewater treatment using activated carbon as an adsorbent is a conventional technique which is being slowly replaced by other non-conventional methods. Wastewater treatment using photocatalyst is a very recent technique applied in the industrial wastewater treatment. The photocatalysts are used to convert UV energy to electro chemical energy capable of destroying organic waste in the process of decontaminations of water. Photooxidation process is also introduced as a possible method for completion of the wastewater treatment process and also used successfully for the detoxification of drinking water and ground water purification. At present photo catalytic processes for waste treatment method are the subject of investigations in order to develop the solar wastewater treatment plants [68].

Semiconductor photocatalysts are preferred in photocatalytic treatments of dye wastewater for the following reasons: (i) they are inexpensive, (ii) they contain low to no toxicity, (iii) they exhibit tunable properties that can be modified such as by size
reduction, doping, or sensitizers, (iv) they contain an affording facility for a multielectron transfer process and (v) they are capable of extending their use without substantial loss in photocatalytic activity.

Photocatalytic degradation using a semiconductor such as TiO$_2$, ZnO, WO$_3$, SnO$_2$, ZrO$_2$, CeO$_2$, and CdS as photocatalyst is one of the various advanced oxidation processes used now a days. ZnO is used as an excellent catalyst in the photocatalytic degradation of these dyes. ZnO with a high surface reactivity owing to large number of active sites has emerged to be an efficient photocatalyst as compared to TiO$_2$. ZnO is an attractive material for water treatment as it can be tailored to absorb visible light and is capable of ushering in the era of solar photocatalysis.

Large number of activated carbons has been prepared for the water treatment applications. The activated carbons derived from naturally available waste materials would be of great concern as they are eco friendly. Photocatalytic degradation of these dyes has also been carried out using ZnO as co-catalyst for one of the best adsorbent which has been getting good adsorption results. Equilibrium, thermodynamic and kinetic studies have been performed in order to propose suitable mechanism and feasibility for these dyes removal by activated carbons.

The degradation of the organic pollutant is normally initiated from an electronic excited state which can undergo homolytic bond scission to form radicals that will react towards final products in a chain reaction with the participation (or not) of molecular oxygen or initiate a process of electron transfer to a ground state oxygen molecule.

\[ \text{hv} \quad R \rightarrow R^* \]

\[ R^* \rightarrow R_1 + R_2 \rightarrow \text{Products} \]

\[ R^* + O_2 \rightarrow R^+ + O_2^- \]
The resulting radical cation can undergo hydrolysis or mesolytic bond scission to low molecular weight products. The super oxide radical ion (\(O_2^-\)) is known to be capable of degrading aromatic molecules although the emission for the removal of substituted aromatics with a more favourable adsorption spectrum can undergo efficient degradation. A schematic diagram of photocatalytic oxidation/reduction process is presented in Fig. 1.1.

![Fig. 1.1. Schematic diagram of photocatalytic oxidation/reduction process](image)

The colour of dyes results from conjugated chains or rings which absorb light at visible wavelength. The UV degradation can be achieved by the cleavage of conjugated chains. It is also reported that the photocatalytic efficiency could be increased by adding a co-adsorbent such as commercial activated carbon. This effect has been explained by the formation of a common contact interface between the different solid phases in which activated carbon acts as an efficient adsorption trap to the organic pollutant which is immediately photocatalytically degraded.

### 1.8. Review of literature

This review is based on adsorptive and photocatalytic mode of Rhodamine B (RhB) and Acid Orange 7 (AO7) dye removal from wastewater using activated carbons.
Many scientists and researchers have done a lot of work for the removal of dye. A brief view of work by different researchers is presented. All researchers in the following papers have studied the Physico-chemical parameters like dye concentration, solution pH, temperature and contact time to study the adsorption phenomenon.

Namasivayam and Yamuna [69] have studied the basic dye removal by biogas waste slurry from aqueous solution. Here rate controlling step is mainly intra-particle diffusion. Adsorption rate constant was found to be 0.029 min⁻¹ at 20 mg/L initial dye concentration. They found that the adsorption is following Freundlich isotherm. In the pH range 2.3 to 11.2, dye removal was found to be at least 90 %. Desorption of dye in 50 % (v/v) acetic acid to the extent of 69.7 % indicates that most dye is held by the chemisorption.

Namasivayam et al., [70] have examined sorption onto the adsorbent prepared from waste orange peel. The adsorption obeyed both Langmuir and Freundlich isotherms and the process was following first order rate kinetic. Adsorption capacity was 3.2 mg/g and acidity pH 3 favourable for adsorption of RhB dye. Desorption studies showed that alkaline pH was efficient for desorption of RhB dye.

Stephen Inbaraj and Sulochana [71] took jackfruit peel as agricultural waste, for the removal study of the RhB dye from aqueous solution. Maximum adsorption capacity was 121.47 mg/g at an initial pH 6 and at 32 ± 0.5 °C. Adsorption capacity was increased with an increase in temperature. The influence of pH on dye removal was not significant. An optimum carbon dose of 1.2 g/L was required for maximum removal (96 %) of dye from its 60 mg/L solution. A significant portion of the dye was recovered from the spent carbon using 50 % acetic acid.

Hameed and Daud [72] have investigated the acidic dye removal by using activated carbon from rubber (Hevea brasiliensis) seed coat. The equilibrium adsorption
data of activated carbon was analyzed by the Langmuir, Freundlich and Tempkin isotherm models. The isotherm data were well described by the Freundlich isotherm model. The monolayer adsorption capacity was 227.27 mg/g at 30 °C. Pseudo-first-order; pseudo-second-order and intra-particle diffusion models were used to analyze the kinetic data obtained at different concentrations. The adsorption kinetics was well described by the pseudo-second-order kinetic model. Rubber seed coat-based activated carbon was shown to be a promising material for adsorption of aqueous solutions.

Arivoli and Thenkuzhali [73] analysed Phoenix sylvestris leaves as adsorbent in indigenous agricultural waste treated with Sulphuric acid and tested for its efficiency of RhB removal. The adsorption followed first order reaction equation and the rate was mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The temperature variation study showed that the adsorption was endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the solutions. Almost 90 % removal of dye was observed at 60 °C. The Langmuir and Freundlich isotherms obtained, positive ΔH° value, pH dependent results and desorption of dye in mineral acid suggested that the adsorption of on adsorbent involved physisorption mechanism.

Hema and Arivoli [74] studied the effective removal of RhB using acid treated carbonaceous Thespesia populnea bark adsorbent. The temperature variation study showed that the RhB adsorption was endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on the varying the pH of the RhB solution. Almost 79 % removal was observed at 60 °C. The Langmuir and Freundlich isotherms obtained positive ΔH° value, pH dependent
results and desorption of dye in the mineral acid suggested that the adsorption of RhB on adsorbent involved physisorption mechanism.

Panda et al., [75] took Jute stick powder as a promising material for adsorptive removal of RhB dye from aqueous solutions. Favourable adsorption occurred at around pH 7 whereas temperature had no significant effect on adsorption of both dyes. The maximum adsorption capacity had been calculated to be 87.7 mg/g of the biomass. The adsorption process was in conformity with Freundlich and Langmuir isotherms. Adsorption occurred very fast initially and attained equilibrium within 60 min. Kinetic results suggested that the intra-particle diffusion of dyes as rate limiting step.

Mohammadi et al., [76] did research on palm shell activated carbon utilized as a potential adsorbent to remove RhB dye from aqueous solution. The ability of the prepared activated carbon for dye adsorption was examined in a series of batch experiments. The obtained results revealed that the adsorption of RhB on activated carbon followed a pseudo-second-order kinetic model. Maximum dye removal efficiency of 95 % was achieved at an initial dye concentration of 62.6 μmol/L at pH 3 and temperature of 50 °C.

Li et al., [77] found the activated carbon derived from solid hazardous waste scrap tires evaluated as a potential adsorbent for cationic dye removal. The adsorption process with respect to operating parameters was investigated to evaluate the adsorption characteristics of the activated pyrolytic tire char (APTC) for RhB. Systematic research including equilibrium, kinetics and thermodynamic studies was performed. The results showed that APTC was a potential adsorbent for RhB with a higher adsorption capacity than most adsorbents. Solution pH and temperature exert significant influence while ionic strength showed little effect on the adsorption process. The adsorption equilibrium data obeyed Langmuir isotherm and the kinetic data were well described by the pseudo-
second-order kinetic model. The adsorption process followed intra-particle diffusion model with more than one process affecting the adsorption process.

Theivarasu and Mylsamy [78] studied the removal the RhB from aqueous solutions by cocoa (*Theobroma cacao*) shell activated carbon (CSAC) in a batch adsorption system. The adsorption studies include both equilibrium adsorption isotherms and kinetics. The kinetic data were well described by the pseudo-second-order kinetic model. The mechanism of the adsorption process was determined from the intra-particle diffusion model. The results indicated that CSAC could be employed as a low cost alternative for the removal of RhB from diluted industrial effluents.

Gupta *et al.*, [79] studied removal of wastewater effluent from Mustard cake, obtained from local oil mills which are an inexpensive and effective adsorbent. The influence of various factors on the adsorption capacity has been studied by batch experiments. Thermodynamic parameters indicated the feasibility of the process. The desorption profile revealed that a significant portion (80 %) of RhB dye could be desorbed by using 50 % ethanol as eluting agent. Desorption studies indicated the possibility of recycling and regeneration of both adsorbent and the dye.

Ahamed *et al.*, [80] explored carbonaceous adsorbent prepared from an agricultural waste, *Azadirachta indica* bark (AIC) for its efficiency in removing RhB dye. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity \( Q_e \) obtained from the Langmuir isotherm plots with temperature variation study showed that the RhB adsorption was endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the RhB solutions. Almost 94 % removal of RhB was observed at 50 °C. Thermodynamic parameters such as \( \Delta H^\circ \), \( \Delta S^\circ \), and \( \Delta G^\circ \) were
evaluated. The positive $\Delta H^\circ$ value, pH dependent results and desorption of dye in mineral acid suggested that the adsorption of on AIC involved physisorption mechanism.

Parimaladevi and Venkateswaran [81] studied the adsorbent prepared from fruit waste digested with phosphorous (V) oxy chloride for RhB removal. Behavior of adsorption followed pseudo-second-order kinetics and the rate was mainly controlled by intra-particle diffusion. Langmuir and Freundlich models were applied to the equilibrium data. The adsorption capacity ($Q_e$) obtained from the Langmuir isotherm plots at 302 K were 34.48 and 35.71 mg/g, respectively at pH of 7.1 and 6.2. The temperature variation study showed that the adsorption was endothermic and spontaneous with increased randomness at the solid solution interface. By varying the pH of the dye solution significant effect on adsorption was observed. Langmuir and Freundlich isotherms obtained. Positive $\Delta H^\circ$ value, pH dependent results and poor desorption of indicated that adsorption of these dyes on PFR involved chemisorption mechanism.

Haddad et al., [82] studied the adsorptive removal of a cationic dye, RhB from aqueous solutions achieved by the use of animal bone meal as a new low cost adsorbent. Adsorption of RhB Dye was measured by studying the effects of contact time, adsorbent amount, dye concentration and temperature. Dye adsorption equilibrium was rapidly attained after 60 min of contact time. The isotherms of adsorption data were analyzed by the Langmuir and Freundlich adsorption isotherm models. Thermodynamic parameters such as $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ were calculated and which indicated that the adsorption was spontaneous and endothermic nature. The characteristic results and dimensionless separation factors $R_L$ showed that animal bone meal could be employed as an alternative to commercial adsorbents in the removal of RhB dye from aqueous solution and wastewater.
Vijaya kumar et al., [83] studied the feasibility of removal of basic dye RhB from aqueous solutions by using a low cost natural adsorbent perlite. Batch adsorption experiments were carried out as a function of pH, contact time, initial concentration, adsorbent dosage and temperature. Dye adsorption equilibrium was rapidly attained after 50 min of contact time and it was described by the Langmuir and Freundlich adsorption isotherms over the entire concentration range from 20 to 100 mg/L. Thermodynamic parameters such as $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ were calculated and which indicated that adsorption was spontaneous and exothermic nature which was evident by decreasing the randomness of the dye at the solid and liquid interface. Adsorbent used in this study, characterized by FTIR and SEM before and after adsorption of RhB. The characteristic results and dimensionless separation factors ($R_L$) showed that perlite could be employed as an alternative to commercial adsorbents in the removal of RhB from aqueous solution and wastewater.

Aliabadi et al., [84] studied adsorption of RhB from aqueous solutions using almond shell (*Prunus dulcis*) as a biosorbent. Almond shell had been selected as an adsorbent because of advantages such as high adsorption capacity, non-toxicity, availability and low cost. The effects of contact time, initial dye concentration, adsorbent dosage, particle size and solution pH were studied. The results showed that the removal efficiency increased by increasing contact time, adsorbent dosage and initial dye concentration. In addition, the adsorption was dependent on solution pH and the maximum adsorption was observed at a solution pH of 2. The Langmuir, Freundlich and Tempkin isotherms were used to describe the adsorption equilibrium data. Freundlich isotherm was best fit for the experimental data’s while comparing Langmuir and Tempkin isotherms.
Venkatraman et al., [85] studied the RhB adsorption from an aqueous solution to acid activated cynodon dactylon carbon had been studied experimentally using batch adsorption method. Adsorption kinetics and equilibrium were investigated as the function of contact time, initial dye concentration, pH and adsorbent dosage. Kinetic studies indicated that the adsorption followed reversible first order reaction. Equilibrium data’s were analyzed using Langmuir and Freundlich isotherm models. The adsorption capacity of cynodon dactylon was found to be 94 % on the basis of experimental results and the model parameters, it can be inferred that the carbonaceous cynodon dactylon was effective for the removal of RhB from aqueous solution.

Silva et al., [86] studied the adsorption of AO7 using Spent brewery grains (SBG) a by-product of the brewing process, a mono azo acid dye currently used in paper and textile industries The adsorption process followed a pseudo-first-order model. The equilibrium process showed to be well described by both Freundlich and Langmuir isotherm models at 20 and 30 °C. The maximum adsorption capacity was estimated to be 30.5 mg/g AO7 on SBG at 30 °C. Free energy of adsorption (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes were calculated to predict the nature of adsorption. The positive value for ΔH° indicated that the adsorption of AO7 dye to SBG was an endothermic process. The positive value of entropy reflected the affinity of the adsorbent for AO7 dye. The obtained results were very promising since high levels of colour removal (> 90 %) were achieved with low contact time adsorbent/dye (less than 1 h contact) and the whole SBG could be successfully used as adsorbent of AO7 dye in aqueous solution without needing any previous treatment such as milling and/or sieving.

Gupta et al., [87] studied the removal of AO7 [p-(2-hydroxy-1-naphthylazo) benzene sulfonic acid] by adsorption over two waste materials namely bottom ash, power plant waste and de-oiled soya, by-product obtained during the processing of soybean in
soya oil extraction mills. Both waste materials showed excellent adsorption abilities and can be treated as low cost adsorbents. The adsorbents were characterized using FTIR spectroscopy and differential thermal analysis (DTA). Preliminary investigations were carried out by batch adsorption method to examine the effects of pH, adsorbate concentration, sieve size, adsorbent dosage, contact time and temperature. A possible mechanism for the ongoing adsorption process and thermodynamic parameters were also obtained from Langmuir and Freundlich adsorption isotherm models. Experiments were also performed for the recovery of loaded dye through chemical regeneration of spent columns and an estimate of the operating costs were also calculated.

Park and Choi [88] reported that the visible light sensitized degradation of dyes were enhanced with Nf/TiO$_2$ not only for cationic dyes like methylene blue (MB) and Rhodamine B (RhB) but also for an anionic dye (AO7) that is less adsorbed on Nf/TiO$_2$. The unexpected behavior in AO7 degradation seems to be related to the role of the nafion layer in retarding the charge recombination.

Hariprasad et al., [89] prepared Pt deposited TiO$_2$ which was found to be capable of mineralizing the dye RhB in the presence of UV as well as direct sunlight. Pt incorporated in the TiO$_2$ matrix extended the light absorption of TiO$_2$ from UV to the visible range which made the composite a good photocatalyst for solar decontamination of polluted water. Pt/TiO$_2$ is more effective than TiO$_2$ alone for the removal of the pollutant.

Silva et al., [90] studied the photochemical and photocatalytic degradation of aqueous solutions of solophenyl green dye with different activated carbons. The kinetics of photo catalytic dyestuff degradation was found to follow a first order rate law. It was observed that the presence of the activated carbon enhanced the photo efficiency of the titanium dioxide catalyst. Different activated carbon materials induced different rates
which increased the apparent first order rate constant of the process. The effect was quantified in terms of a synergy factor already described in the literature. The kinetic behaviour could be described in terms of a modified Langmuir-Hinshelwood model. The values of the adsorption equilibrium constants for the organic molecules $K_c$ and for the reaction rate constant $k_c$ were 0.0923 and 1.58 mg/L for the TiO$_2$/UV process and 0.0928 and 2.64 mg/L for the TiO$_2$ + AC/UV system with highest synergy factor, respectively. The mechanism of the TiO$_2$ photosensitization by the activated carbon has also been proposed.

Jain et al., [91] studied the photocatalytic and adsorptive treatment of a hazardous xanthene dye and RhB in wastewater. The photocatalytic degradation was carried out in the presence of the catalyst TiO$_2$ and the effects of pH, concentration of the dye, amount of TiO$_2$, temperature and electron acceptor H$_2$O$_2$ on the degradation process were observed. It was found that photocatalytic degradation by TiO$_2$ was an effective, economical and faster mode of removing Rhodamine B from aqueous solutions. Attempts were also made to utilize activated carbon and rice husk as potential adsorbent to remove Rhodamine B from wastewater. The adsorption studies were carried out at 40, 50 and 60 °C and the effects of pH, temperature, amount of adsorbents, concentration of adsorbate, etc., on the adsorption were measured. On the basis of adsorption data the Langmuir and Freundlich adsorption isotherm models were also confirmed. The adsorption isotherm constants thus obtained were employed to calculate thermodynamic parameters like Gibb's free energy, change in enthalpy and entropy.

Byrappa et al., [92] investigated photocatalytic degradation of RhB dye using hydrothermally synthesized ZnO. It was found that the photocatalytic degradation of RhB was dependent on various kinetic parameters like nature and concentration of the dye, concentration of the semiconductor, pH, temperature of the dye solution, etc. The ZnO
could be used for a number of cycles which would reduce the cost of operation. The fairly high positive values of thermodynamic parameters $\Delta H^\circ$ and $\Delta G^\circ$ indicated that the transition state was highly solvated. $\Delta S^\circ$ value $-0.17$ which was almost positive indicated that the complex formed was less ordered than the reactants and the bonds are not strongly associated.

Guo et al., [93] investigated the adsorption of RhB by rice husk-based porous carbons and commercial carbons from aqueous medium. Three samples of carbons prepared by NaOH activation, three samples prepared by KOH activation and two samples of commercial carbons have been used. The adsorption isotherms were determined after modifying the carbon surface by oxidation with nitric acid and hydrogen peroxide and after degassing at 800 °C. The adsorption capacity of RhB on oxidized carbon was increased and the adsorption capacities on carbons with heat treatment were higher than that obtained from the oxidized adsorbent.

Elizalde-Gonzalez and Hernandez-Montoya [94] studied the removal of AO7 by using guava seed carbon from aqueous solution. In this study four samples of carbon were obtained by thermal treatment at 1000 °C using as precursor the guava seed with different particle sizes. The Taguchi method was applied as an experimental design to establish the optimum conditions for the removal of AO7 in batch experiments. The chosen experimental factors and their ranges were pH (2–12), temperature (15–35 °C), specific surface area (50–600 m$^2$/g) and adsorbent dosage (16–50 mg/mL). The orthogonal array L9 and the larger the better response category were selected to determine the optimum removal conditions pH 2, temperature 15 °C and dosage 30 mg/mL. The influence of the different factors on the adsorption of AO7 from solution was explained in terms of electrostatic interactions by considering the dye species and the character of the surface.
Aber et al., [95] investigated the adsorption of AO7 from aqueous solutions by powdered activated carbon and modelling of experimental results by artificial neural network. Maximum equilibrium removal of AO7 was 96.24 % for its initial concentration of 150 ppm at pH_i = 2.8 and minimum equilibrium removal was 48.05 % for initial concentration of 350 ppm at pH_i = 5.8. It was found that the adsorption system followed the second-order adsorption rate expression and the constants of the rate expression at different conditions were calculated. Comparisons of R^2 values showed that fitting of Freundlich equation to experimental data’s were better than Langmuir equation.

Lara Abramian and Houssam El-Rassy [96] studied the removal of azo-dye AO7 onto highly porous titania aerogel from aqueous solution. The adsorbents also exhibit a high porosity with a pore volume equal to 2.86 cm^3/g and a surface area around 500 m^2/g. At pH smaller than the titania PZC (i.e., pH < 6.0), the adsorbent’s surface was partially protonated and favouring the electrostatic interaction with the dye existing at this pH in its anionic form. In addition, AO7 molecules were attracted by the titania surface due to Yoshida hydrogen bonding between the titanol groups, the aromatic rings, the nitrogen atoms and the oxygen atoms. The optimum uptake capacity was found at pH 2. Fast adsorption of the dye was noticed within the first 30 min of the experiment where more than 12 mg of AO7 (50 % of the initial dye amount) were adsorbed onto 1 g of titania aerogel. A weak influence of the temperature on the adsorption was observed with the experiments performed at 50 °C revealing the lowest adsorption. The modification of the adsorbent dose indicated that 10 mg or less of titania aerogel was able to remove more than 94 % of the dye molecules existing in the solution. The uptake capacity of 30 mg of titania aerogel was the maximum for dye concentrations around 200 mg/L.

Hashem Akhlaghi [97] studied the photodegradation of AO7 using Zinc Oxide (ZnO) nanostructure which was prepared using zinc acetate and activated carbon (as matrix).
The ZnO nanostructure was characterized by BET, XRD and SEM and consisted of ZnO nanoparticles with a size of 21–31 nm and its surface area was 17.78 m$^2$/g. The efficiency of the catalyst was evaluated in the photocatalytic decomposition of aqueous solution of azo dye, Acid orange 7. Major parameters such as pH, amount of catalyst, stirrer effect, initial concentration and solution oxygen effect were considered and activity measurements performed under UV radiation showed acceptable results for the Photodegradation of AO7.

Han Yanhe et al., [98] investigated the integrated electrochemically enhanced adsorption with electrochemical regeneration for removal of AO7 using activated carbon fibers (ACS). Electrochemical polarization can cause an increase of the adsorption rate and capacity for AO7 on the ACFs. The adsorption rate and capacity at the polarization of 600 mV increased by 120 and 115 %, respectively. In all these cases the adsorption isotherms were in good agreement with Langmuir isotherm model. The effective electrochemical regeneration of ACFs saturated with AO7 was realizable. The regeneration efficiency of over 90 % was achievable at −5V, and the regeneration potential higher than −5V was not advantageous to desorption of AO7. The results of the integrative electrosorption/regeneration cycle experiment showed that the regeneration efficiency still maintained over 70 % after 10 cycles.

Houa et al., [99] studied the electro-photocatalytic degradation of AO7 using a novel TiO$_2$/ACF photo anode. Results demonstrated that by applying a 0.5 V bias (vs. SCE) across the TiO$_2$/ACF electrode, the AO7 degradation rate increased significantly compared to that of photocatalytic (PC) oxidation. The application of an electric field promoted the separation of photogenerated electrons and holes as confirmed by electrochemical impedance spectroscopy (EIS) measurements. The morphological features of the photo anode facilitated the passage of solution as well as UV light through
the felt-form electrode and created a three dimensional environment favourable to EPC oxidation. Both large outer surface areas of the 3D electrode and the good organic adsorption capacity of the ACF support to high contact efficiency between AO7 and TiO$_2$ surface. Anatase was the major crystalline TiO$_2$ deposited. UV-vis spectrophotometry, TOC (total organic carbon) analysis and HPLC technique were used to monitor the concentration change of AO7 and intermediates as to gain insight into the EPC degradation of AO7 using the TiO$_2$/ACF electrode.

Kousha et al., [100] investigated the adsorption of AO7 dye by raw and chemically modified brown *macroalga stoechospermum marginatum*. Adsorption was studied as a function of initial solution pH 2–10, initial dye concentration (30–90 mg/L), contact time (5–60 min), biomass dosage (0.2–2.2 g/L) at constant temperature and agitation speed. The biosorption process depends significantly on the initial solution pH of the dye solution and was favoured at pH 2. The kinetic data’s were well described with the pseudo-second-order model. The results revealed that amine functional groups were mainly responsible for the adsorption of AO7 dye. The modification of biomass with propylamination enhanced the dye adsorption capacity about two times of the untreated algal biomass. These findings were confirmed by Fourier transform infrared spectroscopy (FTIR).

Liu et al., [101] studied the degradation of azo dye AO7 in water by Fe$^0$/granular activated carbon (GAC) system in the presence of ultrasound. The AO7 degradation efficiency by Fe$^0$/GAC was dramatically enhanced by ultrasound, and it had a little effect on the degradation. Effects of Fe$^0$/GAC ratios and initial pH values on AO7 degradation were studied in the US–Fe$^0$/GAC system. The degradation followed the pseudo-first-order kinetics model. The pseudo-first-order rate constant of AO7 degradation by Fe$^0$/GAC was $8.74 \times 10^{-3} \text{ min}^{-1}$ while that by US–Fe$^0$/GAC was $3.91 \times 10^{-2} \text{ min}^{-1}$. A
significant synergetic effect was observed between US and Fe\textsuperscript{o}/GAC. Ultrasound swept the reactive intermediates or products from Fe\textsuperscript{o} surface and thereby the surface of Fe\textsuperscript{o} was cleaned and reactivated. Granular activated carbon was added as cathode to increase the unit of internal batteries and enhance the current efficiency of the internal electrolysis. The suitable Fe\textsuperscript{o}/GAC ratio (v/v) for the degradation of AO7 in the presence of ultrasound was 1:1. The degradation was highly dependent on pH and a decrease of the initial pH values from 12 to 4 led to the increase of degradation efficiencies.

Ong et al., [102] investigated the comparative study on photocatalytic degradation of mono azo dye AO7 and methyl orange (MO) under solar light irradiation. The performance on the photocatalytic degradation of AO7 and MO was enhanced with solar light irradiation, a higher dosage of TiO\textsubscript{2}, lower initial dye concentration and with air aeration. The pseudo-first-order rate constants derived from Langmuir-Hinshelwood kinetic model showed that the photocatalytic degradation of AO7 was more rapid than MO which could be ascribed to the different molecular structure of the azo dyes and the adsorption capacity onto TiO\textsubscript{2}.

Quan et al., [103] studied the regeneration of Acid orange 7 exhausted granular activated carbons with microwave irradiation. The three GACs were made from different materials, i.e., coconut shells, almond nucleus and coal. The AO7 adsorption process was carried out in a continuous flow adsorption column. After adsorption, the AO7 saturated GAC was dried at 120 °C and then regenerated in a quartz reactor by 2450 MHz microwave (MW) irradiation at 850 W for 5 min. The efficacy of this procedure was analyzed by determining the rates and amounts of AO7 adsorbed in successive adsorption-MW regeneration cycles. Effects of this regeneration on the structural properties, surface chemistry and the AO7 adsorption capacities of GAC samples were examined. It was found that after several adsorption-MW regeneration cycles, the
adsorption rates and capacities of GACs could maintain relatively high levels even higher than those of virgin GACs, as indicated by AO7 breakthrough curves and adsorption isotherms.

Rego et al., [104] studied the decolouration of AO7 solutions by TiO$_2$ and ZnO active layers screen-printed on ceramic tiles under sunlight irradiation. Optimal processed layers showed an interesting decolourisation performance, as denoted by an attenuation degree of 90 % and decolouration rate, assuming an apparent first order reaction reaching $2.9 \times 10^{-3}$ min$^{-1}$. In the actual conditions, TiO$_2$ layers showed superior performance than ZnO. The previous alkalisation of the dye solution was not recommended since better performance is achieved under the naturally resulting pH (6.7) of the solution (20 g/L).

Wu et al., [105] studied the degradation of AO7 in aqueous solution by a novel electro/Fe$^{2+}$/peroxydisulfate process. The decolourization efficiency could be significant enhanced by the combination of these two processes. The decolourization efficiency increased with the increase of peroxydisulfate concentration and ferrous ion concentration while it was nearly independent of initial pH between 3 and 9. The current densities had little effect on the decolourization of AO7 at the beginning of the reaction. However, the decolourization efficiency as well as the decomposition percentage of peroxydisulfate increased with the increase of current densities after 60 min reaction. The COD removal efficiency reached 57.6 % after 60 min reaction and it achieved 90.2 % when the reaction time extended to 600 min. The immobilization rate of the initial AO7 was 25 % which reached the maximum after 20 min reaction and then decreased to zero after 40 min reaction.

Farzana and Meenakshi [106] have studied the facile synthesis of chitosan/ZnO composite (CZC) for the photodegradation of Rhodamine B dye. In order to enhance the photoresponse of ZnO towards visible light, the modification of ZnO was done with
chitosan, a well known biopolymer and the modified photocatalyst was synthesized in the form of composite. The photocatalysts ZnO and CZC were characterized by diffuse reflectance spectra (DRS), Fourier transform-infrared spectra (FTIR), scanning electron microscope (SEM), energy dispersive X-ray analysis (EDAX) and X-ray diffraction (XRD) studies. The results signified that the decolourization was mainly affected by the irradiation time, catalyst dosage, pH, co-ions, as well as with the initial dye concentration. The pseudo-first-order kinetics for the photodegradation of RB dye using CZC was well supported by Langmuir-Hinshelwood mechanism. The photodetoxification was studied by reduction in COD of the RB dye using ZnO/vis and CZC/vis systems respectively and the mineralization achieved was higher in the case of CZC/vis system. The photodegradation of the RB dye was measured in terms of decolourization and the reduction in chemical oxygen demand (COD) at optimized conditions. The rate of photodecolourization of RB dye follows pseudo-first-order kinetics which is well supported by Langmuir-Hinshelwood mechanism.

Ravichandran et. al., [107] studied the comparison between adsorption and photodegradation methods for the removal of basic violet 10 (BV) dye. Adsorption studies were carried out using activated carbon prepared from rice husk (RC). The photocatalytic degradation reactions using RC + TiO₂ mixture were carried out under UV irradiation. The influence of operating parameters governing dye removal such as contact time, pH, effect of dose, adsorption isotherms and kinetics were investigated. The negative ΔG° values revealed that the dye removal process is spontaneous. The percentages of dye removal using TiO₂/UV, RC and RC + TiO₂/UV are 35.3, 49.8 and 61.5 % respectively. The Freundlich and Langmuir adsorption isotherms were found to be applicable to both adsorption and photocatalytic degradation of BV. The Freundlich isotherm was more suitable for the removal of BV using the RC alone and the Langmuir
isotherm was more suitable for the removal of BV using RC + TiO$_2$/UV. The adsorption process is found to be second order with the intra-particle diffusion as one of the rate determining steps for both of the systems.

1.9. Scope and objectives of the present study

During the past three decades, several physical, chemical and biological decolourisation methods have been reported and a few have been accepted by the paper and textile industries. Amongst the numerous techniques to dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of colouring materials. Several materials have been identified for the removal of colour from effluents. The use of activated carbons however has been widely favoured because of their high adsorption capacities and amphoteric properties which enable the adsorption of both cationic and anionic dyes. Since adsorption technique using activated carbon can remove dyes even in trace amount due to its ease of operation, cost effectiveness and selectivity. If the adsorption system is designed correctly, it will produce a high quality of treated effluent. In most of the present commercial systems, activated carbon is used as sorbent to remove dyes in wastewater because of its excellent adsorption ability.

Therefore in the present investigation, the research interest was focused on using simple low cost adsorbents for colour removal. Lignocellulosic materials are very porous and have a very high free surface volume that allows accessibility of aqueous solutions to the cell wall components. All of the fibers with lignin content greater than about 10 % readily adsorb pollutants. The textile fiber of cotton, saw dust, bagasse and wood pulp are a few examples of novel cellulosic and low cost adsorption materials for removing the pollutants. *Ailanthus exelsa*, Bagasse, Eucalyptus hybrid, Deinked pulp sludge and soybean hull are of particular interest because they are all renewable resources, abundant
and cost effective. Hence these materials were used as precursors for preparing the activated carbons for the present investigation. The most commonly used dyes in the industries viz., Rhodamine B (RhB) and Acid orange 7 (AO7) were selected for sorption and photodegradation studies.

Among the methods, adsorption seems to be efficient, economical and eco-friendly. Although many studies have been made on the removal of dyes, no such systematic studies have been made on the removal of above said dyes using the prepared carbons viz., Ailanthus exelsa, bagasse, eucalyptus hybrid, deinked pulp sludge and soybean hull. Hence the present investigation aims to carry out the sorption studies of dyes viz., RhB and AO7 using the prepared carbons. The present investigation was carried out with the following aims and objectives.

- To prepare and characterize low cost activated carbons from industrial wastes viz., bagasse, eucalyptus hybrid, deinked pulp sludge and biowastes like Ailanthus exelsa and soybean hull for decolourisation of dyes
- To study the suitability of prepared Ailanthus exelsa, bagasse, eucalyptus hybrid, deinked pulp sludge and soybean hull carbon for the removal of two commonly used dyes RhB and AO7
- To optimize suitable conditions like contact time, dose, pH, temperature, initial dye concentration, etc., for the best sorptive capacity of the prepared adsorbents in the removal of dyes
- To carry out the isotherm, kinetics and thermodynamic studies and to establish the mechanism of dye removal capacity of the sorbents by adsorption method
To investigate the photocatalytic degradation of RhB and AO7 using ZnO in the presence of identified best adsorbent as co-sorbent under identical conditions

To optimize various conditions like irradiation time, dosage, pH, co-ions, initial concentration, light intensity etc., for the maximum removal of dyes by photocatalytic degradation

To propose the rate of photocatalytic degradation of dyes by Langmuir-Hinshelwood kinetics