2

REVIEW OF LITERATURE

A comprehensive review of the literature is important because it provides an up to date understanding of the proposed research work and identifies the methods used in previous research on the topic. This chapter deals with the literature review on various types of dyes and their removal from aqueous solution using various conventional and nonconventional methods.

2.1 TYPES OF DYES

Dyes are classified based on its origin into two types

Natural Dyes

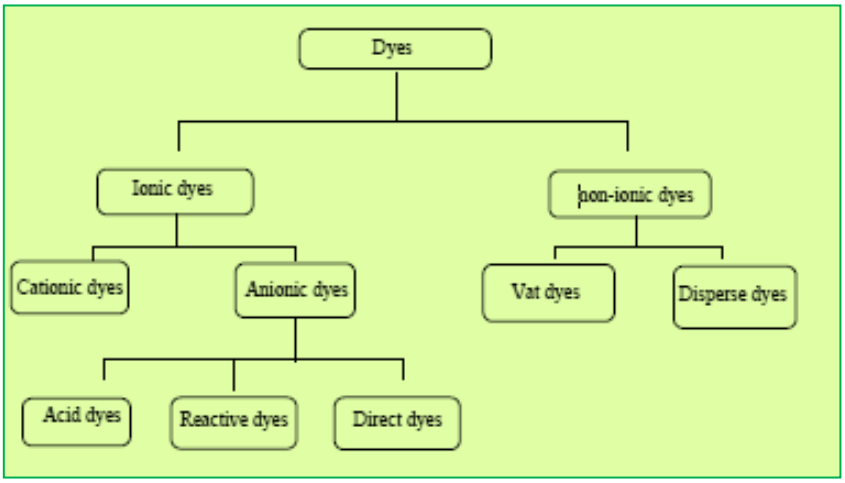
These are used since ancient times for colouring and printing fabrics and are extracted from plants, insects, animals and mineral sources. Since natural dyes do not meet the industrial demand their applications have been limited in textile industry. Some of the common natural dyes used in textile industry are Turmeric, Henna, Teak, Indigo, Alizarin, Onion and Eucalyptus **(Dawood and Sen, 2014).**

Synthetic Dyes

The first synthetic purple colour cationic dye “MAVUE” was prepared by William H.Perkin in 1856. Most of the synthetic dyes were derived from aromatic intermediate chemicals obtained from coal tar distillation, these dyes are also called as coal tar dyes **(Chatwal, 2009).** A few synthetic dyes are listed below

Classification of dyes according to the ionic charge (Mishra and Tripathy, 1993 ; Purkait *et al.,* 2005)

Dyes usually used in textile industry are cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (disperse dyes) depending on their particle charge dissolution in aqueous solutions **(Ruan *et al.,* 2019)**



Classification of dyes based on application

2.2 ANIONIC DYES

Acid Dyes

Acid dyes are used to dye fibres having basic groups such as wool, silk, nylon(poly amide) and poly urethane fibres. Acid dyes are soluble in water, which may contain one or more sulphonic groups and give very bright hue. Some important examples of acid dyes are Picric acid, Metanil Yellow, Congo Red, Methyl Orange, Acid Blue etc., **(Dawood and Sen, 2014)**

Direct Dyes

These are water soluble anionic dyes used for dyeing cotton, wool, silk, leather and paper. Most of the direct dyes are azo dyes (Matius Yellow, Direct Black, Direct Orange) except a few dyes Dioxazine and Phthalocyanines. **(Dawood and Sen, 2014)**

Reactive Dyes

Reactive dyes are used in the dyeing of cellulosic fibers, wool and poly amides. These are structurally similar to acid dyes and form covalent bonds with fibers. Example Reactive Red, Reactive Blue, Reactive Yellow, Reactive Black, Remazol Blue, Remazol Yellow, Remazol Red etc**., (Dawood and Sen, 2014)**

2.3 CATIONIC DYES

Basic Dyes

The cationic dyes are used for dyeing cotton, wool, silk, poly ester and modified nylon. These dyes are soluble in water and have basic amino group. Examples of basic dyes are Methylene Blue, Basic Brown, Crystal Violet, Aniline Yellow, Magenata etc., **(Dawood and Sen, 2014).**

NON IONIC DYES

Disperse Dyes

These dyes are used for dyeing cellulose acetate, nylon, poly ester and poly acrylonitrile fibres. Disperse dyes are largely water insoluble non-ionic dyes and have some hydroxyl and amino groups to give finite solubility at dyeing temperature. Example Disperse Blue, Disperse Red, Disperse Orange, Disperse Brown etc., **(Dawood and Sen, 2014)**

Vat Dyes

Vat dyes are insoluble in water however their reduced forms are soluble. They are used to dye wool, cellulosic fibers, rayon and cotton. Examples of vat dyes are Indigo, Vat Blue, Vat Green etc., **(Dawood and Sen, 2014)**

The classification of dyes based on application mode was shown in **Table 1a (Ruan *et al.,* 2019)**

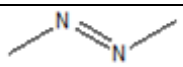
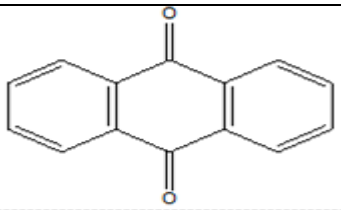
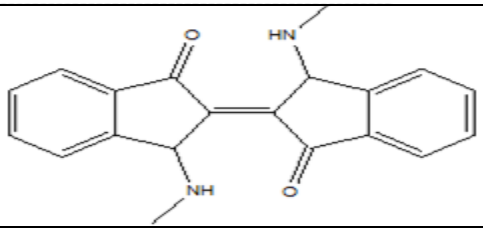
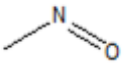
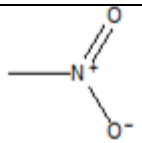
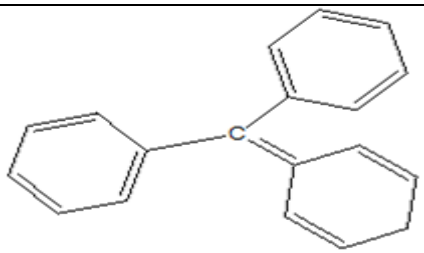
Table 1a. Application and toxicity of different dyes (Hunger, 2003)

Dyes	Example	Application	Toxicity
Acid	Sunset yellow, Methyl orange	Wool, Silk, Paper Leather	Carcinogenic (Benign and Malignant Tumors)
Cationic	Methylene blue, Rhodamine 6G	Paper, Modified Polyester	Carcinogenic (Benign and Malignant Tumors)
Disperse	Disperse Orange 3, Disperse Red	Nylon, Acrylic Fiber	Allergenic (Skin), Carcinogenic
Direct	Congo Red, Direct 23	Cotton, Paper, Leather	Bladder cancer
Reactive	Reactive Red 120, Reactive Red 198	Cotton, Wool, Nylon	Dermatitis, Allergic conductivities
Vat	Vat Orange 15,Vat Orange 28	Cellulosic Fibers	-

Classification of dyes based on the chemical structure

Azo dyes, anthraquinone dyes, phthalocyanine, indigoid dyes, nitroso dyes, nitro dyes and triarylmethane dyes based on the classification of chemical structure are presented in **Table 1b**. **(Ruan *et al.,* 2019)**

Table 1b Classification of dyes based on the chemical structure (Yagub *et al*., 2014)

Class	Chromophores	Examples
Azo Dye		Reactive Black 5
Anthraquinone Dye		Reactive Blue 4
Indigoid Dye		Acid Blue 71
Nitroso Dye		Acid Green 1
Nitro Dye		Acid Yellow 24
Triaryl methane dye		Malachite Green

2.4 METHODS OF DYE REMOVAL

During the dyeing processes all the dyes that are applied to the fabrics and other materials are not fixed on them and a portion of these dyes that remains unfixed to the fabrics gets washed out and discharged as dyeing industrial effluent. In addition to dyes, the waste water released from textile industries contains large amount of pollutants like acids, alkalis, toxic organics, inorganics and dissolved solids **(Ghaly *et al.,* 2014).** Waste water effluent containing synthetic dyes and chemicals may cause a potential hazard to the environment. There is no single standard methodology / treatment procedure available for the removal of all types of dye wastes. A few decades past as there was no discharge limits, the removal of waste water from dyeing units started with a few primary physical treatment methods like sedimentation, equalization to maintain pH, assessment of total dissolved solids (TDS) and total suspended solids (TSS) **(Gupta and Suhas, 2009).**

Subsequently secondary treatments like the use of filter beds for biodegradation were used to treat the dyeing effluent. The third process is the tertiary treatment (Physical and Chemical treatments) involving ion exchange, electro coagulation, adsorption, chemical oxidation and membrane separation techniques **(Gupta and Suhas, 2009).**

2.4.1 PHYSICAL TREATMENT PROCESS

Sedimentation / Flocculation

These two techniques are the primary treatments utilized at municipal and industrial wastewater treatment plants **(Cheremisinoff, 2002).** There are number of other treatments such as chemical flocculants, sedimentation basins and clarifiers are also available to increase gravity settling of suspended particles. **(Gupta and Suhas, 2009)**

Membrane Filtration / Reverse Osmosis

Membrane filtration is used to remove dyes in the waste water. It involves utilization of microfiltration, ultra filtration, nano filtration and reverse osmosis for waste water treatment process **(Avlonitis *et al.,* 2008).** Each membrane process is best suited for a particular waste treatment function. Among them microfiltration is of not much use for wastewater treatment because of its large pore size **(Cheremisinoff, 2002).** Ultrafiltration and Nanofiltration techniques are effective for the removal of all classes of dyestuffs. The main drawback of this process is the high cost of membrane and frequent clogging of the membrane pores reducing the membrane life making the separation system of limited use for textile effluent treatment process **(Cheremisinoff, 2002).**

Reverse osmosis is successful water treatment process which forces water under pressure, through a membrane that is impermeable to most contaminants. It is a valuable decolorizing and desalting process against various ranges of dye wastes and the water obtained by reverse osmosis will be close to pure water and has been successfully employed for recycling waste wate (**Al-Bastaki, 2004; Sostar-Turk *et al.,* 2005).**

Adsorption Process

In adsorption process atoms, molecules or ions of the adsorbate get transferred and sticks to the surface of the adsorbent **(Dawood and Sen, 2014).** Charcoal was used for filtration of drinking water by ancient Hindus in India and carbonized wood was used as a medical adsorbent and purifying agent by the Egyptians as early as 1500 BC **(Cheremisinoff, 2002).** The first documented use of activated carbon in a large scale water treatment application was in 19th century England, where it was used to remove undesirable odours and taste from drinking water **(Cheremisinoff, 2002).**

Adsorption technique is divided into two types – physical adsorption and chemical adsorption. In physical adsorption or physisorption the adsorption process is reversible in nature and the attractive forces exist between the adsorbed molecules and the solid surface are weak forces like Van der Waals forces, hydrogen bonding, dipole-dipole interaction etc., **(Dawood and Sen, 2014),** whereas in chemical adsorption or chemisorptions, the dye molecules are chemically bound with the surface of the adsorbent due to exchange of electrons **(Artioli, 2008).** Because of strong bonding in chemisorptions it is difficult to remove chemisorbed species from the solid surface **(Hassler, 1974).**

Selection of the adsorbent is based on the adsorption capacity and surface area of the adsorbent as well as its availability and cost (Dawood and Sen, 2014).

The extent of adsorbate accumulated on the surface of adsorbent is generally calculated from the adsorption isotherms (**Gupta and Suhas, 2009**). A superior adsorbent material should have a porous structure, high surface area and time required to reach equilibrium should be short . (**Gupta and Suhas, 2009**).

Activated carbon is the earliest adsorbent known and is generally prepared either physical or chemical activation methods using wood, coal, lignite and coconut shell **(Carrott *et al.,* 2003)**. The physical activation needs high temperature and extended activation time whereas in chemical activation the activated carbon requires a careful washing due to the use of chemical agents (**Gupta and Suhas, 2009**).

Activated carbon is obtained in two forms: powdered activated carbon (PAC) and granular activated carbon (GAC) (**Gupta and Suhas, 2009**). Removal of pollutants from water using GAC is more advantageous because of the fact that the granular form is more adaptable to continuous contacting and there is no need to separate the carbon from the bulk fluid. Conversely the use of PAC exhibits some practical problems because of the necessity to separate the adsorbent from the liquid after use. Despite these problems PAC is still used for wastewater treatment due to low capital cost and lesser contact time requirement **(Najm *et al.,* 1991; Gupta and Suhas, 2009).**

To expose the usefulness of activated carbon, various workers have been using this adsorbent for the removal different types of dyes. **McKay, (1982)** utilized activated carbon for the removal of dyes such as acidic, basic, disperse and direct dyes and found to be effective for the removal of all dyes except direct dyes. Activated carbons are good material for the removal of different types of dyes, its use is sometimes limited due to its high cost coupled with its production and regeneration (**Gupta and Suhas, 2009**).This shows the way by various workers to built-up large number of

alternative adsorbents at low cost for dye removal applications **(Alireza *et al.,* 2013; Aadil *et al.,* 2012).**

2.4.2 CHEMICAL METHODS

Advanced Oxidation Technologies

Oxidation process is the conventional method used for the removal of pollutants from industrial effluent. This method is based on the production of hydroxide radicals (oxidizing reagent) which attack the chromophores of the dye molecules and create peroxides further converted to inorganic salts, water and carbondioxide at the end **(Antoniadis *et al.,* 2010)**. Oxidation by using Chemicals is a very successful technique used for water decontamination applications, but the efficiency depends upon the nature of the oxidant used **(Forgacs *et al.,* 2004).** The various oxidants used are ozone, chloride, Fenton's reagent, chlorine dioxide, hydrogen peroxide and potassium permanganate **(Dawood and Sen, 2014)**.

. Chlorine is a strong oxidizing agent used and applied as sodium hypochlorite or calcium hypochlorite. Water soluble dyes such as reactive, acid, direct and metal complex dyes are decolourized readily by hypochlorite, but water insoluble disperse and vat dyes are resistant to this process. **(Namboodri *et al.,* 1994 a,b)**.Though chlorine gas is used as a low-cost technique for decolorizing dyes, its use causes side reactions, producing organochlorine compounds and toxic trihalomethane, thereby increasing the absorbable organic halogens content of the treated water **(Gupta and Suhas, 2009).**

Ozonation Process

It is a very effective process in treating wastewater and removal of textile effluents **(Dawood and Sen, 2014)**. Ozone selectively attacks the nitrogen conjugated double bonds associated with the structure of coloured synthetic dyes **(Gao *et al.,* 2012; Turhan *et al.,* 2012).** Because of complete decomposition of dyes occur in ozonation process, it does not form sludge and hence reduces the toxicity of by-products **(Sharma *et al.,* 2013).** The short $t_{1/2}$ of ozone and high power consumption restricts this technique in large scale water decontamination applications. **(Robinson *et al.,* 2001).**

2.4.3 Electrokinetic Coagulation:

An effective physiochemical process used for water decontamination process is electrokinetic coagulation **(Dawood and Sen, 2014)**. The metal ions produced from metal electrodes during electrolysis flocculates the coagulated particles and create hydroxides of metal that is used to precipitate and adsorbe dissolved pollutants (**Chen *et al.,* 2004; Aoudj *et al.,* 2010).** The drawbacks connected with this process are the further treatment is needed by flocculation and filtration, high electricity cost and high amount of sludge formation.

2.4.4 Photocatalytic Process

An extensive range of dyes are removed by Photocatalytic degradation process. Excitation of electrons between the valence and conduction bands of the catalyst produces hydroxyl radicals which oxidise the dye molecules due to its high oxidizing potential. Oxides like zinc oxide, ceric oxide, titanium di oxide, zirconium oxide, cadmium sulphide

and zinc sulphide are used as photo catalysts **(Gupta and Suhas, 2009).** The drawback of this process is degradation of some photo catalysts release toxic products **(Chong *et al.,* 2010).**

Titanium dioxide (TiO_2), used as the photocatalyst, is owing to the photogeneration of charge carriers (electrons and holes). TiO_2 is a semiconductor with the band gap of 3.2 eV, which can be irradiated by ultraviolet (UV) and visible light. Upon the exposure of the photocatalyst to radiation, electrons (e-) on the surface of TiO_2 are excited to the conduction band (CB), and positive holes (h+) are produced in the valance band (VB). The positive hole can oxidize water to generate hydroxyl radical and the electron can reduce molecular oxygen in the solution.

The photo catalytic mechanism using TiO_2 is given below **(Ruan *et al*., 2019)**

$$TiO_2 + h\nu \rightarrow h^+ + e^-$$

$$e^- + O_2 \rightarrow O^{\gamma}$$

$$h^+ + H_2O \rightarrow OH^{\gamma} + H^+$$

.

2.4.5 Ion Exchange Method

Ion exchangers are materials which adsorb cations and anions and release equivalent amount of other ions into the solution. Cation and anion exchangers with excellent adsorption capacities for the dyes have been reported **(Wu Jen-Shiou *et al.,* 2008 ; Labanda *et al.,* 2009).** The limitation of this process is high capital cost of the membrane restrict its use to some extent.

2.4.6 Biological Treatment Methods

Biological materials, such as yeast, fungi, bacteria, chitin, chitosan and peat are used as adsorbents to remove dyes from aqueous solution **(Sanghi *et al.,* 2013).** A considerable number of biosorption studies on the removal of dyes from aqueous solution have been conducted worldwide which has been compiled by **Asgher (2012).** Diverse functional groups such as carbonyl, hydroxyl, sulphate, and amino groups which are originally present on the biosorbent are responsible for possible binding mechanism **(Bhatti *et al.,* 2015).** The raspberry like TiO_2 @yeast was prepared via an electrostatic self assembly approach and evaluated as an adsorbent for adsorption of Methylene Blue from aqueous solution **(Lan Chen and Bo Bai, 2013).** The maximum adsorption capacity of 397.97mg/g was observed according to the Langmuir isotherm model. The TiO_2 @yeast composites could be effectively regenerated in situ by TiO_2 photolysis on the surface of yeast.

2.4.7 Aerobic Degradation

Dye degradation under aerobic conditions is mainly catalyzed by a specific enzyme called azo reductase. Some aerobic microorganisms in the presence of enzyme azo reductase mainly reduce azo dyes and produce aromatic amines, which can be further degraded by microorganisms under aerobic conditions **(Yingying Gao *et al.,* 2018).** Bacteria and fungi are microorganisms used for dye removal applications.

Effective decolorization of azo dyes such as Direct Blue 151(DB151) and Direct Red 31 (DR31) was carried out using a bacterial consortium isolated from soil samples of saline environment. This study reported that an enriched bacterial consortium can efficiently decolorize DB 151 and DR 31 up to 97.57% and 95.25%, respectively in 5 days **(Sylvine *et al.,* 2016).**

2.4.8 Anaerobic Degradation

Anaerobic degradation process takes place without oxygen. **Cao *et al.,* (2013)** investigated the use of bacteria Shewanella oneidensis MR-I for decolourisation of dyes such as Methyl Orange (MO) and Naphthol Green B (NGB) under anaerobic conditions. **Balamurugan *et al.,* (2011)** studied the effective decolourisation of Reactive Red dye using bacteria Halomonas variabilis and Halomonas glaciei by determining Chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Statistical analysis showed that the BOD and COD reduction rate were optimal in the concentration of 1297 mg l^{-1} for the time duration of nearly 100 hours. In general, some simple azo dyes can be completely biodegraded under anaerobic conditions, but the aromatic amines of azo dyes often cannot be fully degraded under this condition resulting in the accumulation of toxic by-products. These aromatic amines are biodegradable under aerobic conditions. Thus in order to get better results in treating dye waste water combined aerobic-anaerobic process is suggested **(Yingying Gao *et al.,* 2018).**

Li *et al.,* 2017 studied the effect of the electrochemically active bacterium Shewanella oneidensis MR-1 to decolourise an azo dye cationic red X-GRL. Shewanella oneidensis MR-1 showed complete decolorizing capacity for X-GRL under optimal anaerobic conditions of pH 5.5-8.0, temperature 30-40 °C, and reaction time of 12 hours. **Liu *et al.,* 2017** investigated the decolorization of Methyl Orange dye and Cr(VI) under an aerobic condition using Bacillus circulans BWL1061, a newly isolated salt tolerant strain. The results showed that azo reductase, NADH-DCIP reductase and laccase were involved in the degradation of Methyl Orange by BWL1061. The strain BWL1061 also degrades aromatic amines, thereby reducing the toxicity of the dye. **Song *et al.,* 2017,** isolated a salt-tolerant yeast strain pichia occidentalis G1 to study the decolorization performance of azo dye Acid Red B (ARB). Under optimal conditions, more than 98% of ARB was decolorized within 16 hours.

2.4.9 Agricultural / Industrial / Domestic Wastes as Adsorbents

Natural materials or the waste / agricultural by-products, industrial by-products or synthetically prepared materials which cost less can be used as such or used after some

minor chemical treatment as adsorbents. They are generally called low-cost adsorbents and they also act as substitutes for activated carbon **(Gupta *et al.,* 2009).**

Agricultural by-products are available in huge amount all around the world as waste products. The adsorption of dyes onto agricultural by-product is becoming a suitable alternative for the removal dyes from aqueous solution. Recently many researchers mentioned the effective removal of dyes using various agricultural solid wastes as adsorbents **(Yagub *et al.,* 2014).**

Hajira *et al.,* (2016) studied the removal of Malachite Green (MG) dye using carbonaceous bagasse as low-cost adsorbent. Chemical treatment of sugar cane bagasse (SB) was carried out with formaldehyde and sulfuric acid. The chemically treated bagasse C-SB shows about 89% removal, due to the formation of new modified surface and enhancement in its surface area.

Formaldehyde-treated Simarouba glauca seed shell powder, a low cost agricultural byproduct, was used as the adsorbent for the removal of cationic dye Malachite Green (MG) from aqueous solution. Optimum adsorption of MG was found at pH 8 in 60 min of contact time with an adsorbent dose of 0.15 g **(Jeyagowri *et al.,* 2016).**

Activated carbon produced from pomelo peels (PPAC) was tested for its effectiveness in the removal of Malachite Green (MG) dye from aqueous solution. The authors found that dye removal was pH dependent, resulting in 95.06% removal at pH 8.0 **(Bello *et al.,* 2015).** The effectiveness of adsorption process for Congo Red dye removal from waste water using a wide range of adsorbents has been critically reviewed and compiled by **Raval *et al.,* (2016).**The authors concluded that nano particles and nano composite adsorbents have demonstrated outstanding adsorption capabilities for Congo Red.

Methylene Blue dye removal of from aqueous solution using various activated carbons prepared from *Acacia auriculiformis* scrap wood with activating agents such as hydrochloric, sulphuric, phosphoric and nitric acid was carried out by **Monal Dutta *et al.,* (2011)**. The results showed that a typical honeycomb pattern with pores of varying size was observed on the surface of the scrape wood char. The monolayer adsorption capacity of the phosphoric acid activated carbon was found to be 250 mg/g.

Yakout and Deen (2016) studied the characterization of activated carbon prepared using phosphoric acid activation (60, 70 and 80 weight percentage phosphoric acid) of Olive stones. The concentration of phosphoric acid solution plays an important role in

controlling the processes of impregnation and carbonization. The BET surface areas and pore volumes of the carbons produced (Surface area 257 m^2/g and pore volume 0.123 cc/g using 60% H_3PO_4, Surface area 779 m^2/g and pore volume 0.35 cc/g using 70% H_3PO_4 and Surface area 1218 m^2/g and pore volume 0.6 cc/g using 80% H_3PO_4) indicates that the surface area and pore volumes are found to be greater with 80 weight percentage phosphoric acid.

Kumar and Jena (2016) prepared and characterized high surface area activated carbon from Fox nut (*Euryale ferox*) shell by chemical activation with H_3PO_4. The results showed that the surface area of activated carbon was 2636 m^2/g with total pore volume 1.53cm^3/ produced at 700 °C with 1.5 impregnation ratios and one hour of activation time. The FTIR spectroscopy analysis of the prepared carbon confirmed the existence of abundant functional groups on the carbon surface. The FESEM images of the prepared carbon confirmed that a porous structure formed during activation process.

Adsorption of textile dyes (Maxilon Blue GRL and Direct Yellow DY 12) on activated carbon prepared from Coconut shell was studied by **Aseel Aljeboree *et al.,* (2017).** Results showed that the pseudo second order kinetic rate equation exhibited the best fit and Fritz Schlunder (F-S) adsorption isotherm model best describe the uptake of dyes.

Adsorption of Methylene Blue (MB) on activated carbon prepared from Bael Tree Bark was studied by **Valliammmai *et al.,* (2013).** The mean energy of adsorption (E) values was in the range of 18.53 to 20.82 kJ/mol indicating that chemisorption might be the mode of adsorption of MB over the activated carbon. The lignocellulosic biomass jute fiber (JF) was chemically modified with polyphenolic tannin in aqueous medium by epoxy activation under mild condition and applied as a potential adsorbent for the removal of Congo Red (CR) dye from aqueous solution **(Aparna Roy *et al.,* 2013).** The rate of adsorption of the dye onto treated JF was very high due to the availability of hydroxyl and other polar functional groups on the fiber surface and equilibrium was attained within 15 – 30 minutes of contact time. The adsorption process followed pseudo second order kinetic model and the low value of Arrhenius activation energy (9.31 kJ/mol) suggests that CR adsorption on treated JF is a physisorption process. Adsorption of Reactive Yellow 145 and Remazol Black RL onto pine needles was investigated by **UCAR (2014).** As the pH decreased, adsorption density increased gradually and the highest adsorption density (91.57 and 64.77%) was obtained at pH 2 with both adsorbents

Kaur *et al.,* (2013) studied the removal of Congo Red dye from aqueous solution using two low cost adsorbents namely Ground nut shell charcoal (GNC) and Eichhornia

charcoal(EC) under various experimental conditions. Results imply that adsorption of Congo Red on these adsorbents followed second order kinetic model with maximum adsorption capacity of 117.6 and 56.8 mg/g for GNC and EC at 318K. Freundlich isotherm described the isotherm data with high correlation co-efficients.

Adsorption of Methylene Blue dye from aqueous solution using beach sand coated with poly aniline was carried out by **Ansari *et al.,* (2013)**. The results showed that the reaction followed pseudo second order kinetics and adsorption process is endothermic and spontaneous. Spent tea leafs (STL) a solid waste that is available in large amount worldwide was investigated as a potential low cost adsorbent for the removal of two azo dyes Reactive Green 19 (RT19) and Reactive violet 5 (RV5) **(Zuorro *et al.,* 2013).** After thermal exposure of STL to 300°C for one hour, removal efficiencies of 98.8% and 72.8% were observed for RG19 and RV5 dyes. Structural and chemical changes that occurred in the lignocellulosic material were responsible for the enhancement in adsorption properties.

Sartape *et al.,* (2017) studied the use of low cost abundantly available adsorbent-Wood Apple Shell (WAS) as an alternative adsorbent to remove Malachite Green dye (MG) from aqueous solution. The removal of MG dye was found to be 98.87 % when the initial concentration of dye was 100 mg/l and at pH 9. The adsorption equilibrium data fitted well with Langmuir model and the adsorption kinetics followed pseudo second order equation for adsorption of MG onto WAS.

Pyralized paper sludge adsorbent was used for the removal of Methylene Blue (MB) and Procin Red (PR) dyes by **HU and Hu (2013).** The maximum adsorption capacity for MB and PR dyes calculated from Langmuir equation was found to be 119.05 and 65.79 mg/g respectively**.** The adsorption behavior of both dyes fitted the pseudo second order kinetic model and the respective activation energies calculated from the Arrhenius equation for MR and PR dyes were 12.32 and 2.88kJ/mol. Malachite Green dye removal from aqueous solution using paper industry waste sludge as an adsorbent was investigated by **Thakur *et al.,* (2016)**. Using one gram of adsorbent 97.30% of dye has been removed within 60 minutes for 100 mg/l dye concentration. The kinetics of adsorption has been best described by pseudo-second-order model and is supported by intra-particle-diffusion model.

Industrial by-products such as metal hydroxide sludge **(Netpradit *et al.,* 2003)** , fly ash (**Acemioglu 2004)**, red mud (**Namasivayam *et al.,* 2007)**, bio-sludge ash (**Weng *et al.,* 2006)** and palm ash waste slurry (**Ahmad *et al.,* 2007)** are classified as low cost and locally available materials and used as adsorbents for dye removal**.** Adsorption of

Congo Red dye with adsorption capacity of 270.8 mg/g using metal hydroxide sludge as an adsorbent was done by **Golder *et al.,* (2006)**

Fly ash is a residue that results from the combustion of coal in thermal power plants. The major components of fly ash are alumina, silica, iron oxide, calcium oxide, magnesium oxide and residual carbon **(Sivamani and Leena, 2009).** The use of low-cost, abundantly available coal fly ash (FA-CO), HCl-treated coal fly ash (TFA-HCl), and biomass fly ash (FA-BM) has been studied as an alternative adsorbent for the removal of Reactive Black 5 (RB) and Reactive Yellow 176 (RY) dyes from aqueous solution **(Pengthamkeerati *et al.,* 2008).** The author found that increase in the initial dye concentration enhances the interaction between dye molecules and biomass fly ash, resulting in greater adsorption capacity. The equilibrium data of both dyes were fitted to both Langmuir and Freundlich isotherms. The monolayer adsorption capacity of the biomass fly ash was found to be greater for the Reactive Black 5 (4.38 mg g−1) than the Reactive Yellow176 (3.65 mg g−1). The adsorption process followed the second-order kinetic model.

Removal of Acid Red 37 from aqueous solution has been studied using red mud waste material after its modification with Laccase from Russulaceae by **Nadaroglu *et al.,* (2014).** The results indicated that the optimum pH for efficient adsorption of AR37 is 4. The adsorption capacity is strongly dependent on the temperature and increases significantly with increase in temperature from 20 to 30ºC. For equilibrium studies, the Freundlich equation was found to have the highest value of r^2 compared with the Langmuir model. Thermodynamic parameters (Gibbs free energy, enthalpy and entropy changes) indicated that the adsorption of acid red 37 onto laccase-modified red mud was feasible, spontaneous and endothermic.

The adsorption potential of pumice was investigated as geomaterial adsorbent for the removal of two cationic dyes Malachite Green (MG) and Crystal Violet (CV) from aqueous solution **(Shayesteh *et al.,* 2016).** The maximum adsorption capacities calculated were 22.57 and 6.99 mg/g for MG and CV at 25℃ respectively. The kinetic data for both dyes were better described by pseudo second order kinetic model.

Sea shell was used as low cost adsorbent for the removal of Malachite Green dye **Shamel *et al.,* (2016)**. The carboxyl group on the surface of the sea shell was primarily responsible for the adsorption of Malachite Green dye. The percentage removal increased from 79.42 to 94.84% by increasing the initial concentration of MG dye from 5 to 30 mg/l at pH 10.

A high efficiency and eco friendly porous cellulose based bioadsorbent was synthesized by grafting acrylic acid and acrylamide to remove anionic dye Acid Blue 93 (AB93) and cationic dye Methylene Blue (MB) from single and binary dye solutions **(Lin Liu *et al.,* 2015)**. The maximum adsorption capacities of the bioadsorbent for both AB93 and MB were 1372 mg/g at initial concentration of 2500 mg/l. The adsorbent behaviors were due to electrostatic interactions between the bioadsorbents and dye molecules.

Vaishakh Nair and Vinu (2016) prepared a mesoporous activated biochar with high surface area using Prosopis juliflora biomass with H_2O_2 treatment followed by microwave pyrolysis for the removal of Remazol brilliant Blue and Methylene Blue dyes. H_2O_2 impregnation time of 24 hours and microwave power of 600 W produced nano structured biochar with high surface area of 357 m^2/g. Langmuir – Freunlich isotherms described the adsorption equilibrium, while pseuo second order model explained the kinetics of adsorption.

2.4.10 Siliceous Materials

The natural siliceous materials such as silica beads, alunite, dolomite and perlite are increasingly used for wastewater treatment because of their abundance, high adsorption properties and low-cost. Among inorganic materials, silica beads receive more attention **(Phan *et al.,* 2000)** due to its chemical reactivity of their hydrophilic surface, their high surface area, porous texture and mechanical stability that make them as suitable adsorbents for the dye removal applications **(Ahmed *et al.,* 1992). Ali Shamel *et al.,* (2016)** studied adsorption of cationic dye Malachite Green onto sea shell as low cost adsorbent. The authors suggested that carboxyl group on the surface of the sea shell were primarily responsible for the adsorption of Malachite Geen dye. **Na Liu *et al.,* (2018)** utilized a naturally occurring borosilicate mineral Powdered Tourmaline (PT) as adsorbent for the removal of Direct Red 23 dye. A maximum adsorption capacity of 153 mg/g was determined according to Langmuir isotherm. The PT was subjected to a total of 5 regeneration runs without losing much of its dye adsorption capacity.

2.4.11 Zeolites

Zeolites having cavity structures, highly porous three dimensional framework, negative charge, high specific surface areas, high ion-exchange capacity and low-cost make zeolites attractive adsorbents **(Babel *et al.,* 2003).**

2.4.12 Metal Oxide Nanoparticles

Metal oxides and composite nanoparticles play an important role in wastewater treatment industry. Iron oxides nanoparticles with size of 20-100 nm have received much

attention due to their outstanding magnetic properties, nanoparticle size, high surface area and high adsorption capacity **(Giri *et al.,* 2011).** The behavior of magnetic nanoparticles depends on size, state of aggregation, surface chemistry and preparation methods.

Literature Review (Additional Recent Literature Information's)

1. The impact of different parameters like current density, anode type, temperature, pH, and electrolyte concentration on the removal of Reactive Red 120 in synthesized wastewater through electrocoagulation using solar energy was studied by **Pirkarami and Olya (2013).** Current density of 45 Am-2 proved to be optimum level for dye removal. The obtained optimum conditions were applied to the treatment of six samples of real textile effluent. Electrocoagulation was satisfactory in only four of the cases. The study indicates that dye removal is more complicated in the case of real effluent than with synthesized wastewater.
2. To provide a better framework for a safer and cleaner environment, **Adegoke and Bello (2015)** made an extensive literature survey and demonstrated outstanding removal capabilities of various dyes. They concluded that dye contaminants from waste waters using agricultural based activated carbon has offered promising results with maximum efficiency in the field of adsorption technology because they show outstanding removal capabilities for various classes of dyes and could be used in place of commercial activated carbon.
3. **Wijannarong *et al*., (2013)**, explored removal of Reactive Dyes from Textile dyeing industrial effluent by Ozonation Process. Results of decolorization showed that the colour of wastewater is reduced when the reaction time is increased. At reaction times 5 and 120 minutes, the decolorization efficiency is 32.83 % and 56.82 %, respectively. However, the waste water after primary experimental still have colour although the intensity of colour will be soft. The ozonation can reduce colour in the wastewater more than 90% at reaction times 6 hours.
4. **Popuri *et al*., (2016)**, carried out the analysis for the utilization of orange peel as an adsorbent for the removal of dyes from wastewater and to establish it as a standard wastewater treatment process for textile dyeing industry. The experiment showed that the removal percentage is 88.04 at pH of 10, dosage of 2.5g/l, retention time of 120 minutes and RPM of 90.
5. An overview of treatments for the removal of textile dyes was carried out by **Karthik *et al*., (2014).** The author concluded that adsorption is found to be most economical among all effluent treatment methods.
6. **Hussein *et al*., (2014)** studied the colour removal of Reactive Blue 19 from textile wastewater by electrocoagulation using iron electrodes. Effects of various parameters

such as pH on dye removal, current density, electrolysis time, initial dye concentration, supporting electrolyte concentration, temperature were analysed. The optimum operating conditions for the effective removal was at pH 11.5, applied current density of 50mA/cm^2, electrolysis time of 20 minutes, 100mg/l dye concentration, supporting electrolyte concentration of 5g/l NaCl and room temperature. Under these conditions, 99.60% of dye effectively removed

7. **Stercipoulous *et al*., (2014)** investigated electrochemical decolourization and removal of Indigo carmine dye from textile wastewater. Indigo carmine decolourized by electro oxidation process using Ti / Pt and graphite electrodes in the presence of NaCl as supporting electrolyte.

8. **Sendhil *et al*., (2012)** studied that electrochemical oxidation reduces the colour and COD of Acid green dye V textile effluent. As effluent flow rate is lowered percentage colour removal of dye increases. Energy utilization is affected by flow rate, current density and initial dye concentration.

9. **Milica Javic *et al*., (2013)** proved that electrochemical oxidation is capable of destroying the chromophore groups, and full decolorization of dyes found in textile effluents at short treatment times. Indirect electrochemical oxidation via hydroxyl radicals is a convenient way for the degradation and mineralization of reactive dyes and offers approach to developing new technology for removal of reactive dyes in real textile industry effluents with low energy expenditure.

10. **Balachandran (2013)** investigated removal of Methylene Blue dye using prepared nano titanium dioxide (TiO_2). Anatase phase TiO_2 nanoparticles were produced by sol-gel method. Lower concentration level of Methylene Blue after 5 hour reaction indicated that dye molecules were successfully decomposed.

11. **Rameshwar Amete (2014)** investigated the photo catalytic degradation of Methylene Blue using calcium oxide. The various factors such as effect of pH, effect of dye concentration, effect of amount of CaO, effect of light intensity were studied. The study revealed that photo catalysis is very effective technology for degradation of Methylene Blue dye.

12. **Bakhtyar Kamal Aziz *et al*., (2013)** examined the removal of textile dyes from waste water using natural clay. Red clay & Yellow clay were selected from two different locations from Kiffry region. Adsorption of textile dye onto the clay was studied at 25°C. Equilibrium time of adsorption was found out after 35 min and it follow the Freundlich isotherm model. The adsorption capacity of the Congo red onto the red and yellow clay was 22&12.5mg.g-^{1} respectively.

13 **Umpuch *et al*., (2013)** investigated adsorption of organic dyes from aqueous solution by cationic surfactant modified Corn Straw to increase the adsorption capacity of the adsorbent. The adsorption isotherm well fitted in Langmuir & Freundlich models. The kinetic data were studied by pseudo second order kinetic model.

14. **Deshuai sun *et al*., (2013)** studied adsorption of Reactive Dyes on activated carbon developed from Enteromorpha Prolifera by $znCl_2$ activation. Adsorption capacities of three reactive dyes Reactive Red 23, Reactive blue 171, and Reactive blue 4 by activated carbon were 59.88, 71.94 & 131.93 $mg.g^{-1}$ at 27°C respectively. Thermodynamic study& kinetic study proposed that reaction was an endothermic reaction & second order kinetic model were well fitted to the equilibrium data. Freundlich isotherm model were fitted well to the experimental data.

15. **Ansari *et al*., (2016)** used Cauliflower Leave, an agricultural waste bio-mass adsorbent, for the removal of MB Dye from aqueous solution. The sorption data were found to follow pseudo-second-order kinetics. Equilibrium data were fitted very well in Freundlich isotherm equation with a sorption capacity of 149.22mg g^{-1} .

16. **Ashraf *et al*., (2019)** studied adsorption studies of textile dye Chrysoidine from aqueous solutions using raw saw dust and sulphuric acid activated sawdust. They concluded that Sawdust, in both raw and sulphuric acid treated forms, proved to be an efficient adsorbent for chrysoidine dye from aqueous solution. The adsorption of Chrysoidine followed Langmuir's isotherm.

17. **Kandisa *et al*., (2016) and Ruan *et al*., (2019)** made an extensive literature information regard to dyes, its classification and toxicity, different methods for dyes removal including the removal of dyes by Nano Materials(NM) by adsorption technique. It is evident from the literature survey that NMs have shown good capability for the removal of dyes.

18. **Uddin *et al*., (2017)** investigated mango leaf powder (MLP) as a potential adsorbent for the removal of Methylene Blue (MB) from aqueous solutions. The amount of dye uptake (mg/g) was found to increase with increasing initial dye solution concentration. Equilibrium data fitted very well in the Langmuir isotherm equation, confirming the monolayer adsorption of Methylene Blue onto MLP with a monolayer adsorption capacity of 156 mg/g which The kinetics of the adsorption process was found to follow the pseudo second-order kinetic model.

19. A review of various types of activated carbon adsorbents have been presented by **Razi *et al*., (2017).** The review provides literature information about different basis materials used to produce activated carbon like agricultural waste (sugarcane bagasse, olive stone, bamboo, pomegranate peel) and industrial waste (fly ash and red mud) as well as the operational parameters factors in term of contact time, adsorbent dosage, pH solution and initial dye concentration that will affect the process in removing textile dye.

20. **Yu *et al*., (2017)** studied CO_2-activated porous carbon derived from cattail biomass for removal of Malachite green dye and application as super capacitors. The activated carbon exhibited exceptional electrochemical performance as super capacitors, with specific capacitance reaching 126.5 F/g at a current density of 0.5 A/g within a

potential range of 1.0 to 0 V in a 6 M KOH solution. The excellent adsorption capacities and electrochemical performance suggested that the obtained activated carbon could be a promising candidate as adsorbent and as well as super capacitor.

21. **Mouni *et al*., (2018)** studied the removal of Methylene Blue from aqueous solutions by adsorption on Kaolin. The results revealed that the the dye removal process was more efficient at higher temperatures and with raw kaolin sample, and it can be successfully utilized for the adsorption of Methylene Blue dye from aqueous solutions.

22. **Islamuddin *et al*., (2019)** made a review on study of eco-friendly agricultural wastes as non-conventional low cost adsorbents. The authors suggested that in India alone more than 400 million tons of agricultural wastes is produced every year, which incorporates bagasse, stalk, coir substance, rice husk etc and use of these agricultural wastes as adsorbents in the treatment of domestic and industrial effluents is found to be a reasonable option in effluent treatment..

23 **Giraldo *et al*., (2017)** prepared adsorbents from wood wastes (cedar and teak) by chemical activation (ZnCl2). Activated Cedar (AC) and Activated teak (AT) showed a good fit of their experimental data to the pseudo second order kinetic model and Langmuir isotherms. The maximum adsorption capacities for AC were 2000.0 and 444.4mg·g^{-1} for MB and CR, respectively, while for AT, maximum adsorption capacities of 1052.6 and 86.4mg·g^{-1} were found for MB and CR, respectively.

24. A Review was carried out by **Sulyman *et al*., (2016)** on low-cost adsorbents derived from agricultural by-products/wastes for enhancing contaminant uptakes from wastewater: The authors suggested that wide spectrum of carbonaceous adsorbent materials derived from agricultural by-products were found to be good alternative low-cost adsorbents.