

CHAPTER - II

LITERATURE REVIEW

All the technologies and developments in which we are enjoying are the results of research in the past. Any research work can be formed by the effective analysis of the past studies. Because the analysis of the past research is very much essential for the formulation of a sound research methodology. The analysis of the results of the research work can seek novel materials and methodologies. Such a research will yield fruitful results. The subsequent paragraphs deal with various kinds of water pollutants and their impacts on the living things and also the merits and demerits of various kinds of treatment technologies.

2.1 Water pollution

All the freshwater resources are highly polluted due to the disposal of unwanted materials onto the water bodies by natural and man made activities. These additions of pollutants change the physical, chemical and biological characteristics of water beyond the permissible level. This ultimately deteriorated the quality of the environment and ecological balance. Various kinds of water pollutions and their impacts are reviewed in the following paragraphs.

2.1.1 Domestic sewage

Among the various kinds of water pollutants, domestic sewage occupies 75 to 80% (Haseena et al., 2017). The polluted freshwater contains less population of flora and fauna, owing to this 80% of world population is facing threats of water security (Owa, 2013). Most of the domestic sewages

are drained into river without proper treatment (Haseena et al., 2017). The domestic wastewater contains detergents, food wastes, plastics, papers and bacterial contaminants (Kamble, 2014). These categories of pollutants are released all around the world. Though some countries have installed domestic sewage treatment plants in selected places, but in general majority of domestic sewage discharged into the environment without proper treatment.

2.1.2 Agricultural wastewater

The developments in science and technology can improved the agricultural practice to a large extent and resulted in many fold increase in crop yield. But the usage of pesticides and fertilizers spoils the natural composition of the surface soil and the excess pesticides and fertilizers are washed with water and pollute the water bodies (Yonglong et al., 2015). These fertilizer and pesticides are highly hazardous and creates lot of ill effects to human beings (Khurana and Sen, 2008). These pesticides accumulated in human bodies through the food chain and create genetic disorders (Ebenstein, 2008). It is very difficult to treat the agricultural runoff, but the usage of synthetic pesticides and fertilizer may be restricted.

2.1.3 Industrial water pollution

Industrial wastewaters are of great impact on the deterioration of the quality of fresh water bodies. Most of the industrial wastewaters are very strong and contains toxic pollutants with varying degree of organic and inorganic contaminants. The composition varies from one industry to another and therefore it is essential to treat them at source (Peringer, 1997) and in some specific cases it is necessary to treat them in the production lines (Hu et

al., 1999). The composition of industrial wastewater is totally different from the domestic wastewater hence, multistage treatment system is required for these effluents (Meric et al., 1999).

Chemical industrial wastewater can be treated by some biological methods like trickling filters, rotating biological contractor, activated sludge, or lagoons (Nemerow and Dasguptha, 1991; Jobbagy et al., 2000). Owing to the large variation in characteristics of industrial effluent it is highly important to minimize the waste at source (Alvarez et al., 2004; Bury et al., 2002).

2.2 Dye pollution

Dyes are generally organic compounds containing more aromatic rings and different functional groups. Mostly dyes are used to colour paper, cloths, wool, pharmaceutical, paints, cosmetics and in some cases they are also used to colour the food materials. Especially in India, textile industries are the major consumers of synthetic organic dyes. Nearly 700 million tons of synthetic dyes are produced every year under 10,000 different categories (Zollingar 1999; Chequer et al., 2013).

Sandhya et al., (2005) have reported that an average mill in India producing 60 tons of fabric is discharging approximately 1.5 million litres of effluent every day. This type of discharge of untreated effluent into the water bodies reduced the sunlight penetration, the dissolved oxygen, creates aesthetic pollution and also causes chronic and acute toxicity (Arami et al., 2006; Kadirvelu et al., 2005). In such a context, it is highly imperative to treat the dye bearing wastewater before discharging them into the water sources.

There are different varieties of dyes are used in industrial applications. The nature of application and suitable treatment technology of some of the important dyes are discussed in the following paragraphs.

2.2.1 Acid dyes

Generally acid dyes are anionic dyes having ionisable sodium ions, i.e sodium salt of sulphonic acids. Most of the acid dyes are brightly coloured and water soluble. Acid dyes are used to colour polyamide and silk fabrics because they have direct affinity with polyamide and protein under acidic dye bath.

Intercalations of acid dyes with double layered hydroxides are used for slow dyeing process (Hussein et al., 2002). Geetha krishnan and Palanisamy (2006) have used acid blue as a film dopant for photosensitive chromophore used in optics and laser technology applications. Kengo and Yoshio (2001) used the same acid blue dye for ink jet technology.

The textile effluents containing acid dyes are treated with a process involving adsorption using low cost materials (Tsai et al., 2004; Li et al., 2003). It is proved that acid pH (pH of 3 to 5) and a temperature range of 95 to 105°C are ideal conditions for the adsorption of acid dyes (Attia et al., 2006; Alaton and Teksoy, 2007; Malik, 2003).

2.2.2 Basic dyes

Basic or cationic dyes are the brightest among the all soluble dyes used in the textile industry (Stephen Inbaraj and Sulochana, 2006). The cationic dyes are the commonly used dyes with large quantities. The basic (cationic) dyes are preferably used for dyeing silk, cotton and wool (Chandrasekhar and Pramada, 2006). Another basic dye Rhodamine–B is widely used as a biological stains in biomedical laboratories (Stephen Inbaraj and Sulochana, 2006). But the basic dyes are generally harmful for human beings, if it is swallowed, it produces gastrointestinal tract infections with vomiting and diarrhoea.

The basic dyes also cause methenoglobinemia, cyanosis, convulsions, dyspnoea and cause skin irritation (Senthilkumaar et al., 2005). With a view of these complications, it is essential to remove the basic dyes from the wastewater. The coagulation and filtration methods are not suitable for the removal of cationic dyes as the cationic dyes do not coagulate at all. Adsorptions of cationic dyes using activated materials have been studied by many researchers (Oladoja and Asia, 2008; Sun and Yang, 2003). Sivakumar and Palanisamy (2008) have successfully demonstrated the removal of the basic dye (Basic Red 29) using a non-conventional activated carbon prepared from *Euphorbia antiquorum L.*

2.2.3 Reactive dyes

Generally the reactive dyes contain azo based chromophores having different types of reactive groups (Hu and Chiang, 1996). The reactive dyes are known for their excellent colour fastness, they can be applied on fabrics

using simple technology with low energy consumption. The reactive dyes are used for the colouring of cellulose and rayon fibres. The reactive dyes forms covalent link with oxygen, nitrogen or sulphur atoms of fibre, which provide great stability to the dye on the fabric (Trotman, 1984). The application of reactive dyes on cellulose fibres produces high colour fastness (Matyjas and Rybicki 2003).

The removal of reactive dyes are very difficult, they pass through all conventional treatment systems due to their high solubility (Dantas et al., 2004; Baskaralingam et al., 2006). Though the removal of reactive dyes are difficult but many researchers have demonstrated the removal of reactive dyes using various adsorbents like basic oxide furnace slag (Yongjie et al., 2009), dried biomass of activated sludge (Ju et al., 2008), metal hydroxide sludge (Netpradit et al., 2004), Calcined alunite (Turkey) 66 (Ozacar and Sengil, 2003) and Chitosan (Wu et al., 2001) etc.

2.2.4 Direct dyes

The usages of direct dyes are increasing day-by- day. These dyes are mainly used for the printing purpose in textile industry (Gupta et al., 1992). Most of the printing industry which uses the direct dyes in small scale industries, that do not have proper treatment systems (Hu, 1996; Wong and Yuen 1996).

Most of the direct azo dyes are proved to be carcinogenic and their degradation products are also highly toxic (Miller and Miller, 1953; Giri and Sharma, 2002). There are hundreds of studies have been demonstrated for the removal of direct azo dyes. Suresh kumar and Namasivayam (2008) have

used the activated carbon prepared from coir pith for the adsorption of Direct Red 31 and they have observed the maximum Langmuir mono layer adsorption capacity of 76.3 mg/g.

2.3 Methods of dye removal

Nearly three to four decades back the knowledge about the dye selection, application and usage are not given much importance with respect to their environmental implications (Gupta and Suhas, 2009). For the past two decades, there wear a lot of attention given on the health impacts of dye pollution and technologies needed for the treatment of dye bearing wastewaters. During the beginning, certain physical treatments like sedimentation and equalization where performed to maintain the pH, total dissolved solids (TDS) and total suspended solids (TSS). Later few secondary processes like filter beds for biodegradation and activated sludge process were included to improve the efficiency of dye wastewater treatment (Gupta and Suhas, 2009).

Most of the dyeing industry wastewater is treated with nearly similar way. The merits and demerits of general wastewater treatment technologies coming under any one of a) physical b) chemical and c) biological methods are discussed in the following paragraphs.

2.3.1 Sedimentation

It is a fundamental and basic form of primary treatment technology. Most of the domestic and industrial wastewater systems have this sedimentation process (Cheremissinoff, 2002). Instead of calling this as a technology, this can be treated as a primary step of all wastewater treatment

systems. This step mainly used for the removal of large particles, floating substances and some un-removed products. Specifically this step cannot remove the dissolved pollutants, this step is used for the removal of suspended matter only.

2.3.2 Filtration

This is also an essential stage of all wastewater treatment system. The general macro filtration is a common method for all wastewater treatment systems. Whereas, Microfiltration, Nano filtration, Ultra filtration, Nano filtration and Reverse osmosis using semi permeable membranes are special technologies for some specific requirements (Avlonitis et al., 2008). As far as the dyeing industry effluents are concerned, microfiltration is less effective when compared to that of ultra filtration and Nano filtration. (Marmagne and Cost, 1996). The main problem associated with these filtrations are high cost, frequent clogging of the membrane, high energy consumption and short membrane life. These limitations make these technologies not fit for small scale industries.

2.3.3 Reverse osmosis

Reverse osmosis is the passage of water from higher concentration side to lower concentration side with the application of pressure on the higher concentration side. The efficiency of reverse osmosis for the treatment of dye bearing wastewater is good. The process can be applied for the removal of non-ionised weak acids and bases and also for the removal of smaller organic molecules having molecular weight below 200 (Al-bastaki, 2004; Marcucci et al., 2001; Sostar-turk et al., 2005). Another advantage of reverse osmosis is

that influent of varying composition can be effectively treated using this process. The major drawbacks of reverse osmosis are short membrane life, frequent clogging of pores of membrane and high cost of the membranes. These drawbacks limit the usage of RO by small scale industries.

2.3.4 Coagulation (or) flocculation

Coagulation (or) flocculation is one of the well-known chemical treatment technology used for the colour removal of wastewater (Shi et al., 199; Wang et al., 2006; Zhou et al., 2008). In this treatment method, flocculation agents like aluminium (Al^{3+}), calcium (Ca^{2+}) or ferric (Fe^{3+}) salts are mixed with dye effluent and deposit them as sludge (Mishra et al., 2006; Yue et al., 2008). In some cases two or more agents are used for effective coagulation (Wang et al., 2007). The advantages of this process are economically cheap and also this process is good for the removal of disperse, sulfur and vat dyes. The major disadvantage of this process is the generation of large quantity of concentrated sludge and the process is depended on solution pH (Kace and Linford, 1975; Lee et al., 2006). It was reported that this process is good for azo, reactive, acid and basic dyes but its scope is limited for highly soluble dyes (Hai et al., 2007; Raghavacharya, 1997).

2.3.5 Oxidation by chlorine

Chlorine is a powerful oxidizing agent used as such and also applied in the form of calcium hypochlorite and sodium hypochlorite. Predominantly used for the disinfection of potable water. It is also used for the removal of colour in pulp, textile bleaching, reactive, acid, direct and metal complex dyes (Namboodri et al., 1994a, b). This process is good for dyes having amino or

substituted amino groups on a naphthalene ring (Omura, 1994). When metal complex dyes are processed with chlorine, the decomposition products like transition metals further act as a catalyst and enhances the decomposition efficiency. Another advantage of this technique is that it is a low cost treatment technology. The drawbacks associated with this method are the unwanted side reactions that produce poisonous organo chlorine compounds, toxic trihalomethane and liberation of corrosive metals (Gupta and Suhas, 2009).

2.3.6 Oxidation with hydrogen peroxide (H₂O₂)

Hydrogen peroxide is a pale blue liquid on dilute condition it looks coloured and it is slightly viscous than water. Owing to its powerful oxidizing capacity, it is used as a bleaching agent for papers. It was estimated that in 1994 nearly 50% of the world's production of H₂O₂ is used for the bleaching of paper and pulp (Hage and Lienke, 2006). The peroxidase enzymes generated using H₂O₂ are used for the decolouration of dyes (Morita et al., 1996). The notable drawback of this process is the pH dependency and generation of more sludge.

2.3.7 Biological Treatment

It is most common and extensively used technology for the treatment of dye bearing wastewater (Barragan et al., 2007; Bromley-Challenor et al., 2000; dos Santos et al., 2007; Frijters et al., 2006). The decolourizations of dyes have been achieved using various species of micro organisms. The biological treatment offers considerable advantages like being relatively inexpensive, having low running costs and the end products of complete mineralization not being toxic (especially for the dyeing industry effluent).

The biological treatment is carried out in presence of oxygen (aerobic), in absence of oxygen (anaerobic) or combination of both aerobic and anaerobic.

2.3.7.1 Aerobic Treatment

The dye house wastewater treatment studies were widely studied using bacteria and fungi. The enzymes secreted by bacteria decomposes the organic dye molecules under aerobic conditions (Rai et al., 2005). The bacterial strain *kurthia sp.* effectively decomposed the dyes such as brilliant green, malachite green, ethyl violet, crystal violet and magenta dyes (Sani and Banerjee, 1999b). But it was also reported that all the dyes are not uniformly decomposed by aerobic treatment using activated sludge (Husain, 2006). Most studies showed that the results of some specific strains are active only on certain specific dye structure (Kulla, 1981).

Various studies have been performed to decolourize the azo and triphenyl methane dyes using fungal strains (Bumpus and Brock, 1988; Sani and Banerjee, 1999a). *Phanerochaete chrysosporium* fungi has been tried to decolourize various categories of dye for the past 20 years. (Fu and Viraraghavan, 2001a; Pazarlioglu et al., 2005). Along with fungi, other notable micro organisms such as *Rhizopus oryzae*, *Cyathus bulleri*, *Coriolus versicolour*, *Funalia trogii*, *Laetiporous sulphureus*, *Streptomyces sp.*, *Trametes versicolour* have been utilized for the treatment of dyeing industry wastewater (Nigam et al., 2000; Salony et al., 2006; Zhang et al., 1999). There are many environmental factors like Pollutant concentration, pH, temperature and other salts are responsible for the effective degradation of dyes using micro organisms (Christie, 2007). Though the aerobic treatment is

reported to be successful, certain dyes are highly resistant against aerobic degradations (Pagga and Brown, 1986; Rai et al., 2005).

2.3.7.2 Anaerobic treatment

There are wide variety of organic dyes have been potentially degraded under anaerobic treatment conditions (Delee et al.,1998, Forgacs et al., 2004; Rai et al., 2005; Razo-flores et al. 1997) have successfully decolourized mordant orange 1 and azodi-salicylate using methanogenic granular sludge under anaerobic conditions.

Zee van der et al., (2001) have reported the total decolourization of 20 azo dyes using anaerobic granular sludge. The anaerobic pre-treatment is cheap treatment system when compared with aerobic treatment, as the latter require expensive aeration and also produces bulk sludge than the anaerobic method (Delee et al., 1998). The other advantages of anaerobic treatment are the dyes can be reductively decolourized, good improvement in BOD, no foaming problems, effluent with high temperature is also treated and degradation of refractory organics can also be initiated (Delee et al.,1998). But the problem associated with the anaerobic treatment are BOD removal not sufficient, dyes are not completely mineralised, nutrients (N,P) are not properly removed and finally the sulphates are converted to fouling sulphides (Delee et al., 1998).

2.3.8 Adsorption

Adsorption is one of the most widely used processes for the removal of dyes in wastewater (Bansal and Goyal, 2005; Danis et al., 1998; Freeman, 1989; Imamura et al., 2002; Liapis, 1987; Martel, 2001). In the adsorption process, the gaseous and solute molecules present in the solution are

accumulated on a solid surface. Right from the ancient times, the adsorption was performed using activated carbon. The ancient Egyptian papyrus in 1550 BC and Hippocrates in the later period used porous carbon adsorption for medical purpose.

However, based on the scientific records, the application of adsorption was observed by Sheele in 1773 for gas adsorption, Lowifzin 1785 for the reversible removal of colour and odour producing compounds from water using wood charcoal (Mantel, 1951; Tien, 1994).

Based on the interaction between the solute and solid surface, there are two type of adsorptions are possible. If the solute is adsorbed on the solid surface by weak forces of attraction (e.g physical forces like Van-der Waals forces), the adsorption is termed as physical adsorption or physisorption. Whereas the adsorbate molecules are attached with the solid surface by strong chemical forces, it is termed as chemical adsorption or chemisorption. The physisorption is weak and is reversible in nature, whereas chemisorption is strong and hence irreversible in nature.

2.3.9 Ion Exchange

Ion exchange is one of the chemical adsorption involving reversible process. The ions from the solution can be exchanged with similar ions present on the sorbent surface. Since ion exchange process has many common features like adsorption, hence both are grouped together as “sorption” (LeVan et al., 1997). The ion exchange finds greater application for the softening of hard water, in this process, hardness causing ions like Ca^{2+} and Mg^{2+} are exchanged with H^+ and Na^+ ions present in the ion exchange resins

(Clifford, 1999). There are plenty of studies have been reported for the removal of dyes from wastewater using ion exchange resins (Liu et al., 2007; Wu et al., 2008; Delval et al., 2003) have reported the preparation of starch based cross linked polymers using epichlorohydrin as a cross linking agent in presence of ammonia and its application for the recovery of dyes from wastewater.

The adsorption process has many advantages when compared with other technologies. The essential characteristics of adsorption are the quantity of adsorption that accumulates on the adsorbent is calculated using adsorption isotherms. The adsorption isotherm is nothing but the rate of adsorption with respect to equilibrium concentration of solution. The greater advantage of adsorption is that the adsorption can effectively remove the dyes which are highly resistant to other treatment technologies. A good adsorbent can possess high surface, which is the much essential requirement for wastewater treatment (Linsen, 1970; Tien, 1994).

There are few thousands of adsorbents with varying compositions and nature were reported in the past two decades. The subsequent paragraphs will deal the advantages and disadvantages of various adsorbents reported by the past researchers.

2.4 Inorganic Adsorbents

2.4.1 Alumina and silica

Alumina is a porous inorganic powder and available in various particle size with different surface area (Do, 1998). The surface area of alumina varies from 50 to 1200 m²/g (Zotov et al., 2018). Bauxite is a naturally occurring

crystalline porous alumina having surface area from 25 to 250 m²/g (Martel, 2001). There are plenty of researchers in the past have reported the use of alumina for the removal of dye from industrial wastewater (Adak et al., 2005; 2006; Huang et al., 2007). In a similar way, silica gel has been widely used as a inorganic adsorbent for the effective removal of pollutants present in wastewater. It is prepared by the coagulation of colloidal silica acid gives amorphous and porous silica powder of varying sizes. The surface area of silica gel is slightly higher than alumina (250 to 1700 m²/g) (Do, 1998). The applications of silica gel for the adsorptive removal of basic dyes were successfully demonstrated by Alexander and Mekay (1977) and Allingham et al., (1958). Though alumina and silica are highly inert and have very good mechanical stability but the high cost and lower surface area than activated carbon limits its application in the large scale industrial operations (Mckey, 1999).

2.4.2 Bentonite

Bentonite generally consists of aluminium phyllosilicate, which is considered to be the impure clay mainly consisting montmorillonite (Adeyemo et al., 2017). Based on the principal component such as potassium (K), sodium (Na), calcium (Ca) and aluminium (Al) present, there are many varieties of bentonite are available (Adeyemo et al., 2017). Weathering of volcanic ash in the presence of water produces Bentonite. The clays which are similar to one another like bentonite and tonstein, has been used to describe clay beds of uncertain origin (Odom, 1984). Among the variants, sodium bentonite has swelling in water and adsorbs many times of solute when compared to its dry mass. For the liquid phase adsorption, calcium bentonite

is a useful adsorbent (Lagaly 1995). It also adsorbs fats and oils, and is a main active ingredient of fuller's earth, used for a long period of time as industrial cleaning agents (Robertson 1986).

The clay based bentonite reported to have a greater capacity to adsorb cationic dye as it exhibited high removal of Basic Blue 9 and Thioflavin T dyes (Ramakrishna and Viraraghavan 1997). There are many studies have suggested the usage of bentonite for the adsorptive removal of amines (Breen 1991) organic pigments (Gonzalez-Pradas et al. 1991) heavy metal ions like Ni and Zn (Stockmeyer and Kruse 1991), pesticides (Gonzalez-Pradas et al. 1993) non-ionic contaminants (Smith and Jaffe 1994; Espantaleon et al. 2003) and also chlorophyll (Gonzalez-Pradas et al. 1994). All the above studies proved that bentonite is a promising and low cost adsorbent for the removal of dyes (Bellir et al. 2010). But the problem associated with the bentonite is its poor mechanical stability and has the tendency to be leached with water.

2.4.3 Kaolinite

Kaolinite is a hydrated aluminium silicate with a formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ available as a main component in the soft and plastic Kaolin clay (Moore and Reynolds 1997; Murray 2002). In the kaolinite clay, the silicate sheets (Si_2O_5) bonded to aluminium oxide/hydroxide layers ($\text{Al}_2(\text{OH})_4$) called gibbsite layers (Moore and Reynolds 1997), owing to this nature, it is a layered silicate mineral with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedra (Deer et al. 1992). The polyvinyl alcohol / kaolinite composite was used as adsorbent for the removal of MB from aqueous solution by Abd El-Latif and co-workers

(Abd El-Latif et al. 2010). Another group of researchers have reported the composite made up of PVA and alginate and it exhibited rubber-like elastic properties; among the two components, PVA contributed strength and durability to the beads and alginate improved the surface properties and reduced the tendency of agglomeration (Dave and Madamwar 2006). They used the composite for the adsorptive removal of MB from aqueous solution and found to have excellent adsorption behaviour. Nwokem et al. (2012) used burnt clay for the removal of CR dye and demonstrated the excellent adsorption under given set of operating conditions. Again the problem of using the kaolinite alone for the adsorption is its poor abrasion resistance and forms colloids with water and regeneration is very difficult.

2.4.4 Industrial Waste as Adsorbents

The wastes and the by-products generated by many industries, such as ore processing, thermal power plants, steel and metal, sugar and fertilizer industries etc. have also been used as an adsorbent for the removal of wide range of pollutants. The advantages and disadvantages of few industrial wastes are discussed in the subsequent paragraphs.

2.4.4.1 Fly Ash

Fly ash is a waste by-product generated in large quantities during the combustion of coal based fuels in the thermal power plants. Since the fly ash is generated in huge quantities, the disposal of the fly ash is a major concern, also it is given at free of cost and it is being used for the construction of roads, bricks and cement etc. (Gupta and Suhas, 2009). As the fly ash is available in plenty and free of cost, there are hundreds of publications reported the use of

fly ash and modified fly ash as adsorbents. The removal of cationic and anionic dyes were studied by Ramakrishna and Viraraghavan (1997) using fly ash as adsorbent. Mohan et al. (2002) utilized fly ash as low-cost adsorbent for the removal of cationic dyes crystal violet (basic violet) and rosaniline hydrochloride (basic fuchsin). Wang et al. (2005) studied the effect of physical (heat) and chemical treatment and compared the adsorption behaviour with that of as-received fly ash. They observed that the heat treatment have some adverse effects on the adsorption capacity of fly ash whereas the acid treatment by nitric acid resulted in an increase of adsorption capacity of fly ash.

Various workers have investigated the adsorption behaviour of mixtures of various fly ash and fly ash mixed with other materials and reported good adsorption results (Gupta et al., 1990; Janos et al., 2003). Gupta et al. (1990) analysed the adsorption behaviour of fly ash mixed with coal mixtures for the removal of omega chrome red ME dye removal from its aqueous solutions. The fly ash adsorbent is economically cheap, available in plenty and free of cost. When compared with the activated carbon adsorbent, the fly ash has low surface area and low adsorption for the large organic dye molecules.

2.4.4.2 Blast Furnace Sludge

The byproducts/wastes generated from the blast furnace of steel industries are called as blast furnace dust and blast furnace slag. These blast furnace slag were investigated for their ability towards the adsorptive removal of acid dyes such as ethyl orange, metanil yellow, acid blue 113 and basic

dyes such as chrysoidine G, crystal violet, meldola blue, methylene blue (Jain et al., 2003a,b,c). Though blast furnace slag successfully used for the removal of above said dyes, on comparing their adsorption quantity with that of activated carbon, the removal capacities are less. The same blast furnace slag was investigated for its adsorption capability towards the removal of various other dyes (Gupta et al., 1997; Li et al., 2003). The blast furnace slag is a good adsorbent but not a better adsorbent when compared with that of activated charcoal.

2.4.5 Biomaterials

Recently there is a growing attention towards the usage of biomaterials and bio-polymers like chitin and chitosan (Wan Ngah et al., 2011). These polymers can be derived from natural sources through some simple steps. They have a lot of advantages like cationicity, high adsorption capacity, macromolecular structure, abundance and low price (Muzzarelli., 2011). The biopolymer as such or modified biopolymers are used for the adsorption of various kinds dyes from aqueous solutions. Dotto and Pinto (2011) reported the adsorption ability of chitosan powder derived from shrimp wastes for the batch mode adsorption of acid blue 9 and yellow 3 (which are used as a food colourants). Chitosan flakes were synthesized and tried for the removal of methyl orange dye from wastewater under batch mode (Saha et al., 2010). They observed that the adsorption was influenced by pH, dye concentration, and temperature.

The positive factors for the use of biopolymers like chitin and chitosan are low cost, have high adsorption capability and selectivity, versatility,

environmental friendly and biodegradability. However, chitosan generally used as a flakes or powder, which has crystallized structure, leads to low adsorption capacity. Mostly the adsorption occurs in the amorphous regions and the crystallite regions are not useful for the adsorption purpose.

2.4.6 Agricultural waste materials

The byproducts from the agricultural wastes and waste products of biological nature could serve as low cost adsorbents. As the agro based products are available in plenty, renewable in nature and also economically cheap. Another advantage of agricultural by products is that they have good carbon percentage (Ahmedna et al., 2000)

2.4.6.1 Fruit and nut shells

There are large number of research is being done on the conversion of fruits and nuts based agricultural wastes into activated carbon. The shells which have some considerable rigidity like nuts, peanuts, dates, almond seeds, apricot stones etc. these materials are converted in to activated carbon through physical and chemical activation process. Sudaryanto et al., (2006) prepared activated carbon from cassava peel using KOH as an activating agent. The obtained products have maximum surface area and pore volume using an impregnation ratio of 5:2 and activation temperature of 750°C. Olive pit was converted into activated carbon using KOH as a chemical activating agent (Martinez et al., 2006). Date pit also used as a precursor for the preparation of activated carbon using various chemical activating agents like H₃PO₄ and ZnCl₂ (Bouchenafa-Saib et al., 2005; Girgis and El-Hendawy, 2002). They obtained activated carbon with excellent surface characteristics and also the

authors have demonstrated the role of activating agents for the development of porosity (Girgis and El-Hendawy, 2002).

Similar to the nuts, pits and fruits shells have also been successfully converted into activated carbon. Stavropoulos and Zabaniotou (2005) have developed an activated carbon using olive seed by KOH activation method. The prepared AC was used for the removal of methylene blue from aqueous solution and the adsorption performance of the activated carbon was comparable to commercial variants even higher at high degrees of activation. Large surface area activated carbon was prepared from Almond shell and pecan shell and it was used for the removal of pollutants like VOC, metal ions and organics (Bansode et al., 2003; Johns et al., 1999; Vaghetti et al., 2009). The authors have reported that the prepared GAC has a surface area equal or greater than commercial AC (Johns et al., 1999).

2.4.6.2 Activated Carbon from Wood Wastes

The wood based waste materials are available in plenty with free of cost. The conversion of these materials into activated carbon can solve the problem of waste disposal and also the prepared AC will be economically cheap.

Cedar wood and its shavings are converted into activated carbon under physical activation with CO₂ and a pre-treatment with H₂O₂ (Lopez de Letona Sanchez et al., 2006). They reported that the pre-treatment with H₂O₂ successfully eliminated the surface complexes and thereby created an excellent porosity on the carbon surface. Cuerda-Correa et al., (2006) prepared AC from cedar wood, using H₂SO₄ pre-treatment and CO₂

activation. H_2SO_4 acts as a dehydrating agent and enhances the formation of greatly developed pore structure.

Fir wood used a precursor material for the preparation of AC using chemical activation with KOH and physical activation with steam (Ismadji et al., 2005). The synthesized carbon had a surface area of $1096 \text{ m}^2/\text{g}$ and the AC showed high rate of external adsorption and low rate of intra particle diffusion (Ismadji et al., 2005; Lopez et al., 1996) compared the physical activation with CO_2 and chemical activation with $\text{H}_3\text{PO}_4/\text{ZnCl}_2$ for an activated carbon prepared from Tropical tree wood as a precursor. They reported that the chemical activation was more effective than physical activation. Lopez et al., (1996) proved that the selection of precursor was a fundamental criteria for the development of a good surface activated carbon.

2.4.6.3 Rice husk carbon

Since 1940 rice husk is one of the most versatile sources for the development of activated carbon with high surface area. Depending upon the geographical region, climatic conditions and nature of soil, the composition of rice husk varies. Generally the rice husk contains nearly 20% silica along with other metal oxides, during the ashing process, the silica content increases upto 90%. The activated carbon prepared from rice hulls were successfully employed to bleach cotton seed oil and sun-flower oil by Tanin and Gargey (1988). The industrial textile dyes like Sandocryl orange and Lanasyne black were removed from their aqueous solutions using an activated carbon prepared from rice husk (Nawar and Doma, 1989). Activated carbon synthesized from rice husk carbon was demonstrated for their ability for the

removal of Basic green 4 (Guo et al., 2003), Basic blue 9 (Kannan and Sundaram, 2001), Basic blue 9 (McKay et al., 1999), Acid blue (Mohamed 2004), Congo red 28 (Chou et al., 2001) and Acid yellow 36 (Malik, 2003).

2.4.6.4 Coconut shell carbon

Starting from the ancient times to till date the activated carbon prepared from coconut shell have occupied a dominant position in the activated carbon industry. The great advantage of coconut shell based activated carbon is its excellent hardness and mechanical stability. These properties may provide advantages to coconut based AC for its commercial application worldwide (Bansal and Goyal, 2005). In addition the coconut shell based carbons have high surface area, which is more or less equal to that of commercial carbons (Mortley et al., 1988). Alaerts et al., (1989) have utilized the coconut based activated carbon for the adsorptive removal of Cr(VI). The authors have compared the adsorption efficiency of the coconut based AC with commercial carbon and found that they both have similar surface area.

2.4.6.5 Coir pith carbon

Coir pith is one of the most abundantly available agro based waste material around Tamil Nadu and Kerala states in India. The coir fiber processing industries generate huge volume of coir pith, which hardly finds any application in industry as well as in the Agriculture. These advantages make the coir pith carbon as cost-effective and also the non-conventional adsorbent and also helps to reduce the solid waste disposal problems for the coir processing industries. The activated carbon prepared from coir pith carbon was reported to be effective for the removal of chlorophenols

(Namasivayam and Kavitha, 2004) and metals (Kadirvelu et al., 2001). Namasivayam et al., (2001) effectively utilized the coir pith carbon for the adsorptive removal of Acid violet and Basic violet 10. Direct red 28 was removed from its aqueous solution using coir pith activated carbon (Namasivayam and Kavitha 2002). Suresh kumar and Namasivayam, (2008) utilized the surfactant modified coir pith as an adsorbent for the removal of textile dyes namely Direct Red 12B (anionic direct dye) and Rhodamine B (cationic dye) present in its aqueous solution.

Activated carbon prepared using agricultural waste material have the advantages of low cost, easily renewable and also makes a way for the solid waste disposal problems when compared with that of coal based activated carbon. These advantages makes agricultural by-products are good sources of raw materials for the preparation of activated carbon (AC).

2.5 Nano Adsorbents

2.5.1 Metallic nanomaterials

Metal based nanomaterials have also studied extensively for the adsorptive removal of pollutants present in the water. The nano sized adsorbents such as titanium dioxide (Lee et al., 2007), zinc oxide (Salehi et al., 2010), magnesium oxide (Li et al., 2012) and zero valent iron etc. has been utilized for the adsorptive removal of dye from aqueous solutions. This type of nano materials show difference in their physical and chemical properties and proportionally their adsorption mechanisms are significantly different. As for as nano materials are concerned, their adsorption dependent

on the physical and structural morphology and in such a context, their adsorption is predominantly physical in nature.

2.5.2 Nano Titania

Highly active mesoporous nano titania was successfully synthesized and used for the adsorptive removal of reactive red 198 (Belessi et al., 2009). The authors have observed an excellent adsorption capacity of 86.96 mg/g and the adsorption completed within 10 min. The hydrothermal method is one of the widely used synthesis method for the production of nano titania. Kasuga et al., (1998) reported the production of titanate nanotubes (TNTs) using hydrothermal method. They compared the surface area, pore volume of nano titania with that of titanate nanotubes and they observed that the TNTs generally have a relatively higher pore volume, ranging from 0.67 to 0.89 cm³/g (Hai-chao et al., 2010). Lee et al., (2008) have studied the effect of synthesis temperature on the morphology and pore structure titanate nano tubes and used the nano tubes for the adsorptive removal of basic dyes. Xiong et al., (2010) synthesized titanium nano tubes and used the material for the adsorptive removal of basic methylene blue dye and found a maximum adsorption capacity of 133.33 mg/g.

2.5.3 Nano zero-valent iron

Metallic iron when in zero oxidation state has a particle size of nano scale is proved to be a good candidate as an adsorbent for the removal of pollutants present in the wastewater (Wang and Zhang, 1997). Wang and Zhang (1997) proposed a simple method for the synthesis of nano sized Zerovalent Iron nZI, as per the following reaction scheme:



The synthesized nZI is proved to be a cheap and efficient adsorbent. Based on its superior qualities, the nZI was employed by various research groups for the removal of water polluting agents such as nitrates (Huang and Wang, 1998), chlorinated compounds (Chang and Cheng, 2006), heavy metals (such as arsenic from groundwater (Kanel et al., 2005), lead ions (Ponder et al., 2000), and copper ions (Xiao et al., 2011). Zhao et al (2008) developed a new type of cation exchange resin composite with nZI for the removal of acid orange 7, acid orange 8 and sunset yellow and successfully demonstrated the applicability.

Though the nZI is efficient for the pollutant removal, the major drawback is the slow attainment of equilibrium. This makes it difficult to employ for the large scale industrial operations. The major drawback of the usage of nano materials for the adsorption process is their hazardous nature during handling. Since, the nano materials are very fine in size, they can easily fly in air and create respiratory illness and also they are carcinogenic. Another drawback is that the removal and recovery of the spent adsorbent, due to nano size it takes longer time for the settling and removal.

2.5.4 Carbonaceous nano materials

Carbon based nano materials like graphene, fullerene, carbon nano tubes, carbon balls have attracted the researchers to explore new materials with greatly enhanced properties. The covalently bonded carbon network gives very strong mechanical and thermal properties. These carbon based nano materials are generally synthesized using the organic hydrocarbon raw

materials such as methane and acetylene under controlled conditions using chemical vapour deposition method. Among the different carbon nano materials, carbon nanotubes (CNTs) and nano diamonds have been studied effectively for the wastewater treatment technologies.

2.5.5 Carbon nanotubes

Iijima (1991) who reported the synthesis of carbon nano tube very early even though the carbon nano tubes had been synthesized in advance. Subsequently the electronic, optical and mechanical properties of the CNTs were studied. de Jonge et al., (2002) studied the high brightness electron beam from a multi-walled carbon nanotube. Later on, the CNTs have been widely used as an adsorbent for the treatment of wastewater discharged from various industries. The advantages associated with the CNTs are their physico chemical stability, high selectivity and structural diversity (Lu et al., 2005). For the past ten years there are numerous research have been carried out for the application of carbon nanotubes for remediation of wastewater. The CNTs have demonstrated for their superiority towards the removal of certain heavy metals like Cd (II), Zn (II) and Pb (II) (Cho et al., 2009; Wang et al., 2007). Fugetsu et al., (2004) synthesized and utilized the CNTs for the adsorption of textile dyes such as acridine orange, ethidium bromide, eosin bluish, and orange G under laboratory scale.

Exploration of materials in the nano scale has great advantages due to high surface area, uniform properties, excellent process ability etc. Carbon in nano scale has some exciting morphologies like nanotubes, nano spheres for example fullerenes, single layered nano sheets and so on. The nano carbon

variants namely hollow carbon nano spheres and carbon nano-tubes have been successfully used as a composite for hydrogen storage (Ampoumogli et al., 2012), PEM fuel cell cathode (Marie et al., 2009), adsorptive removal of pollutants (Wang et al., 2014; Saha et al, 2014) and super capacitors (Fan et al., 2015). It is also used for the remediation of water contaminated with oil (Murugesan et al., 2017). Hollow carbons, bamboo shaped tubes and smooth tubes have been successfully synthesized from benzene, ethylene and acetylene using mixture of metal salt catalysts (Fe, Ni and Co) at high temperature by Kovalevski et al., (1998). Synthesis of nano sized carbon materials using biologically renewable precursor or environmentally unimportant materials will certainly be beneficial for the environment as well as the society. The usage of nano carbon materials for the adsorptive removal of pollutants has some limitations like floating on the surface of water and easy leaching with water owing to their small size and low density. In-order to overcome these sort of difficulties, the carbon is immobilized with some magnetically active nano materials like Fe, Ni oxides, which will certainly enhance the recovery of the spent carbon.

2.6 Aim and Objectives

The present study has been carried out with the following aim and objectives:

1. The objective of the work is to synthesize highly active Nano Sized Carbon Balls (NCB) using *Madhuca longifolia* (Mahuwa) oil with a uniform and average size <100 nm using an indigenous reactor assembly through air controlled, low temperature direct pyrolysis with the help of multi-metal catalyst derived from *Alternanthera sessilis* stem.
2. The synthesized carbon balls will be doped with Fe₃O₄ using sol-gel co-doping method to get the magnetic carbon balls with high surface area.
3. To analyse and evaluate the surface characteristics using SEM, XRD and other characterization studies.
4. The Fe₃O₄ immobilized magnetic nano carbon balls will be used for the removal of Methylene Blue (MeB), Acid Green 25 (AG25) and Direct Red 81 (DR 81) from its aqueous solutions using Batch and column mode adsorption.
5. Various kinetic and Isotherm parameters were studied to analyze the applicability of the selected adsorbent for the removal of dye from wastewater.
6. Application of the adsorbent for the treatment of various dyeing industrial effluents was also demonstrated in this study.

7. From the results of the preparation, characterization and adsorption studies, one can advise the industries to go for cheap and efficient low-cost method of effluent treatment.
8. Thus, the present investigation is an applied research, in which the findings will be highly useful to the industries, society and to the country, to protect, safeguard and sustain the environment.
9. The objective of the study will be fulfilled only if the comparative cost analysis is made. In this regard the operating cost of wastewater treatment was compared for the commercial carbon with the prepared adsorbent.