CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

The earth is a closed system like a terrarium means it rarely loses or gains extra matter. Water, one of the “Panch-Mahabhoota’s” is an important component of nature and is known as the universal solvent. Water is a source of life and energy, although millions of people worldwide are suffering with shortage of fresh and clean drinking water. It is well known that two-thirds of earth is covered with water. It dissolves more substances than any other solvent and carries chemicals, minerals, nutrients etc. wherever it flows. Most importantly, the temperature of earth is also regulated by this precious matter. Rapid industrialization, population expansion and unplanned urbanization have largely contributed to the severe water pollution and surrounding soils. It is well known that 70-80% of illnesses in developing countries are related to water contamination, particularly susceptible to woman and children.¹

The most tragic part of it is that due to rapid industrialization and advancement of technology, this water body, “live of all life” becomes polluted by either in the form of dye or heavy metal pollution. Hence, the challenge remains to the scientific community to maintain the norms so that the most important natural resources (water bodies) remains as pollution free from whatever may be dye or heavy metal.
1.2 POROUS CARBON

Porous carbons (PC) are basically carbonaceous materials having highly internal pore structure. These PC materials can be classified into three types based on their pore sizes as per the International Union of Pure and Applied Chemistry (IUPAC) recommendation: microporous < 2 nm; 2 nm < mesoporous < 50 nm, and macroporous > 50 nm. Lignocellulosic and cellulosic materials are good carbon precursors apart from other synthetic precursors for the preparation of porous carbon. There are two methods of preparing porous carbons viz.; chemical activation and physical activation.  

Table 1.1 Various chemical activating agents and carbon precursor for the preparation of PC

<table>
<thead>
<tr>
<th>Activating agent</th>
<th>Carbon precursor</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$PO$_4$</td>
<td>Peanut hull, almond shell, pecan shell, corn cob, bagasse, sunflower seed hull,</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>lignin, rice straw, oak, sewage sludge, chestnut wood, eucalyptus bark, rice</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hull, cotton stalk, jackfruit peel etc.</td>
<td></td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>Almond shell, apricot stone, bagasse, cattle-manure, corn cob, coconut shell,</td>
<td>4, 3(e),</td>
</tr>
<tr>
<td></td>
<td>macadamia nutshell, peanut hull, hazelnut shell, rice husk, tamarind wood,</td>
<td>3(i),3(g),</td>
</tr>
<tr>
<td></td>
<td>pistachio nut shell, sunflower seed hull</td>
<td>3(h)</td>
</tr>
<tr>
<td>KOH</td>
<td>Corn cob, rice straw, macadamia nut shell, peanut hull, olive seed, cassava peel,</td>
<td>5, 3(a),</td>
</tr>
<tr>
<td></td>
<td>petroleum coke, coal, cotton stalk, pineapple peel.</td>
<td>3(e), 16</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>Almond shell, bamboo, coconut shell, corn cob, cotton stalk, oil palm shell,</td>
<td>6, 3(a),</td>
</tr>
<tr>
<td></td>
<td>pineapple peel, pistachio shell, walnut shell.</td>
<td>5(c),</td>
</tr>
<tr>
<td>NaOH</td>
<td>Coconut shell, wood, bagasse and rice husk, waste news paper.</td>
<td>7</td>
</tr>
</tbody>
</table>
Chemical activation (CA): In this method the carbon precursor is impregnated with certain activating reagents [phosphoric acid (H₃PO₄), potassium hydroxide (KOH), sodium hydroxide (NaOH), zinc chloride (ZnCl₂), etc.] at specific ratios before carbonization. The impregnated carbon precursor is carbonized at low temperature under inert gas atmosphere. The most common chemical activating agents used for the preparation of PC from different carbon precursors are shown in Table 1.

Physical activation (PA): The physical activation method comprises two steps: a carbonization step where the carbon precursor is pyrolyzed at high temperatures in absence of air (usually in inert atmosphere using argon or nitrogen) and an activation step where the carbonized precursor is exposed to oxidizing agents (carbon dioxide, oxygen or steam) at high pressure and temperature.

The advantage of chemical activation over physical activation is to be performed in single step, shorter activation time, higher yields and development of better porous structure at relatively lower carbonization temperature. Pore development during preparation of PC from plant precursors is due to the conversion of cellulose, hemicellulose and lignin by the process of dehydrating, linkage breaking reactions and finally the structural ordering process of the residual carbon followed by polymerization reactions.

Porous carbons (PC) are of great interest now a day in many applications. Since the First World War, a major development in the use of PC has started and many new technologies were developed for preparation and its application. It had been widely used as adsorbents (gas separation, water purification etc.), catalyst/catalyst supports, electronic material, and electrodes for electrochemical double layer capacitor, fuel cells and energy storage material due to its high surface area, larger pore volume and physicochemical properties. Hence, the specific surface area, pore structure and surface chemical functional groups of PC mainly determine its applications. The most important part of this PC is that its porous structure could be controlled by various parameters such as activation conditions (activating agent, activation temperature and time), carbon precursor, templates etc. Moreover, surface functional groups of PC are
found to be responsible for the variety in physicochemical and catalytic properties. In order to improve the PC surface as adsorbents, the control of chemical and physical conditions might be harnessed to make it suitable for adsorption application. And this surface chemistry influences the electrostatic and non electrostatic interactions which can be responsible for the adsorption mechanism. PC’s are the most widely used adsorbent because of their excellent adsorption capacity for organic as well as inorganic pollutants such as dyes and heavy metals. The characteristics of PC depend on the physical and chemical properties of the precursor as well as on the activation method. Since the textural properties of PC is based on the nature of carbonaceous precursor and preparation method, therefore many natural as well as synthetic precursors, agricultural waste or industrial waste have been chosen for the preparation of PC in recent times. A few sources of carbon precursor from natural and agricultural waste have been listed in Table 1.2

**Table 1.2** List of raw materials used for the preparation of PC

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neem husk</td>
<td>16</td>
</tr>
<tr>
<td>Corn cob</td>
<td>17</td>
</tr>
<tr>
<td>Eucalyptus camaldulensisDehn bark</td>
<td>18</td>
</tr>
<tr>
<td>Oil palm stone</td>
<td>19</td>
</tr>
<tr>
<td>Bagasse and rice husk</td>
<td>20</td>
</tr>
<tr>
<td>Vetiver roots and sugarcane bagasse</td>
<td>21</td>
</tr>
<tr>
<td>Natural biomaterial bamboo</td>
<td>22</td>
</tr>
<tr>
<td>Physic nut (<em>Jatropha curcas L</em>)</td>
<td>23</td>
</tr>
<tr>
<td>Agricultural residues and bagasse</td>
<td>24</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>25</td>
</tr>
<tr>
<td>Gelam wood bark</td>
<td>26</td>
</tr>
</tbody>
</table>

The main sources of raw materials for the preparation of PC are lignocellulosic materials. Considering the cost of raw materials interests have been developing in search of other low cost and naturally abundant lignocellulosic agricultural waste materials as the carbon precursor for the preparation of PC. These plant based carbon precursors are especially attractive due to their renewable, biodegradable nature and can be sustainably managed, all of which contribute to making them suitable for accessible technologies.
1.3 DYE POLLUTION

A dye can be defined as a colored substance, which is in general, ionisable aromatic organic compounds, that shows affinity towards the substrate to which it is being applied. They are composed of a group of atoms responsible for the dye colour, known as chromophores, and auxochromes an electron withdrawing or donating substituents that cause or intensify the colour of the chromophores. The most important chromophores are azo (-N=N-), carbonyl (-C=O), methane (-CH=), nitro (-NO₂) and quinoid groups. Similarly, the most important auxochromes are amine (-NH₃), carboxyl (-COOH), sulphonate (-SO₃H) and hydroxyl (-OH). These dyes in general, are applied to the substrate in an aqueous solution and require a mordant to improve its fastness on the material.

Natural colourants includes all the dyes and pigments that are derived from natural resources such as plants, insects and minerals. The dyeing with the natural colorants one of the oldest techniques which was used by the ancient civilization people as is evident from the wall paintings called mural art of Ajanta, Ellora, Sittannavasal, Mithila etc. and Egyptian pyramids. Mineral earth and some other inorganic pigments like ferrous and ferric oxide for yellow and red respectively, copper carbonate for blue etc. have been extensively used in mural paintings in some of the Spanish caves of Altamira, Elcatillo and French Pyrene caves of Niaux. Since time immemorial, ancient craftsmen used natural dyes to dyeing primary colours such as blue from indigo, yellow from turmeric, saffron and brown from cutch and red from lac, safflower and madder. There are manifolds advantages of using natural dyes that includes safe for body contact, unsophisticated and harmonised with nature, obtained from renewable energy sources, no health hazards etc. and mainly no disposal problem. However, few limitations of natural dyes such as its availability, colour yield, fastness and brilliancy of shade, stability and complexity of dyeing processes restricts its use in various industries thereby increases the use of synthetic dyes now a days.

Dyes are considered to be one of the most threatening classes of pollutants to the human mankind among the other hazardous pollutants. As these dyes are very much stable and non-biodegradable because of their
complex molecular structure and is difficult to treat once these dyes enter into the water.\(^{34}\)

Dyes of various kinds are utilized to colour substances in textile industries and hence considered as a group of pollutants that affects fresh water bodies. There are several ways for dyes classification and each class are of unique Chemistry, structure and specific way of bonding either physical or chemical.

Although, dyes are classified based on many factors, these compounds can be classified in three broad categories based on ionic charge aspect: (i) anionic (direct, acid and reactive dyes), (ii) cationic (all basic dyes), and (iii) non-ionic (dispersed dyes).\(^{35}\)

**Table 1.3 Classification of dyes based on their application**

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Types of Dyes</th>
<th>Industrial Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Direct dyes</td>
<td>Cotton, leather, paper and Cellulosic and blended fibers</td>
</tr>
<tr>
<td>2</td>
<td>Vat dyes</td>
<td>Cotton and Cellulosic and blended fibers</td>
</tr>
<tr>
<td>3</td>
<td>Sulphur dyes</td>
<td>Cotton</td>
</tr>
<tr>
<td>4</td>
<td>Organic pigments</td>
<td>Cotton, cellulosic, blended fabric and paper</td>
</tr>
<tr>
<td>5</td>
<td>Reactive dyes</td>
<td>Cellulosic fiber and fabric (Cotton and wool)</td>
</tr>
<tr>
<td>6</td>
<td>Disperse dyes</td>
<td>Synthetic fibers (Polyester)</td>
</tr>
<tr>
<td>7</td>
<td>Acid dyes</td>
<td>Wool, silk, paper, synthetic fiber and leather</td>
</tr>
<tr>
<td>8</td>
<td>Azo dyes</td>
<td>Printing inks and pigments (Cotton)</td>
</tr>
<tr>
<td>9</td>
<td>Basic dyes</td>
<td>Silk, wool and cotton (Acrylic)</td>
</tr>
<tr>
<td>10</td>
<td>Food dyes</td>
<td>Food and cosmetics</td>
</tr>
<tr>
<td>11</td>
<td>Metal complexes dyes</td>
<td>Cotton</td>
</tr>
<tr>
<td>12</td>
<td>Mordant dyes</td>
<td>Wool</td>
</tr>
<tr>
<td>13</td>
<td>Whitening agent dyes</td>
<td>Plastics, paper and soap</td>
</tr>
<tr>
<td>14</td>
<td>Solvent dyes</td>
<td>Synthetics</td>
</tr>
</tbody>
</table>

Reactive and Basic (Anionic and Cationic) dyes are mostly used in textile industry as they possesses favorable characteristics such as bright colour, easily water soluble, simple application technique and consumption of low energy.\(^{36}\) On the other hand, non-ionic dyes are disperse dyes because they do not ionise in an aqueous medium and mainly used in polyester based materials. In Indian industries there are 14 groups of dyes based on their application that have been used and are presented in Table 1.3.
Textile dyeing industries uses lots of commercial synthetic dyes due to their superior dyeing properties. Wastewater discharge from these industries contains hazardous organic pollutants, which have detrimental effect on human as well as aquatic life. There are more than 100,000 different types of commercial dyes exists\textsuperscript{37} and about $7 \times 10^5$ tonnes are produced annually throughout the world.\textsuperscript{38} During the dyeing process approximately 10% to 15% of the dye is lost as effluent.\textsuperscript{39} Hence, more efficient technologies for their removal from waste water system are of great challenge to the scientific community.

### 1.3.1 Sources of Dye Pollution

Dyes are considered to be one of the most prominent organic compounds which have adverse effect to the environment.\textsuperscript{40} Dyes are used for thousand years by the mankind\textsuperscript{41} and the Neanderthal man was the earliest user of dyes about 1,80,000 years back. The first organic dyes blue dye indigo was used just 4000 years back, when it was discovered in the wrappings of mummies in Egyptian tombs.\textsuperscript{42}

Since Neolithic period, people have dyed their textiles using locally available common natural dyes. In the ancient and in medieval period, natural invertebrate dyes Tyrian purple and crimson kermes were used which have brilliant and permanent colours. Till late nineteenth century, almost all dyes were more or less natural, and these natural dyes are obtained mainly from different parts of plant sources, viz.; roots, berries, bark, leaves, wood, fungi and lichens. Later on, a few dyes of the plant based sources namely wood, indigo, saffron were produced commercially and becomes an important trade goods to enhance the economy of Asia and Europe. But due to the cost effectiveness, purer consistency and varieties of new colours for utilization of synthetic dyes replaces the traditional natural dies. The first synthetic dye, mauveine (basic) was manufactured for commercial use after the Perkin’s historic discovery in 1856 and was considered as the historic revolution of synthetic dyes.\textsuperscript{43}

The colour is the first public perception to measure the water quality and first contaminant recognized in waste water. Its presence even less than 1 ppm for some dyes is clearly visible and undesirable.\textsuperscript{44} Surface and
underground water ways contains numerous dyes with various chemical properties and becomes a great concern for the human being all around the world.\textsuperscript{45} Most of the dyes are stable and non-biodegradable because of their complex aromatic molecular structure.\textsuperscript{46}

Large quantities of dyes are released into the water system due to inefficiencies of textile industries dyeing technique and about up to 50\% of dyes may be lost into natural waterways when reactive dyes are used out of which azo dyes are also in the range of 5-1500 mgL\textsuperscript{-1}.\textsuperscript{47} There are 280,000 tons of textile dyes that are discharged from industrial effluents every year worldwide.\textsuperscript{48} Out of all dyes approximately 70\% azo dyes are used worldwide and are the largest and most common group of synthetic dyes released into the environment.\textsuperscript{49}

Including pigments, there are 40,000 dyes exists of which approximately 7,000 are of different chemical structures.\textsuperscript{50} It has been estimated that about 9\% (i.e., 40,000 tons) of the total amount (450,000 tons) of dyestuffs produced in the world are discharged in the textile wastewaters. Although there are less than 5\% loss in case of basic dyes in acrylic fiber but the loss of reactive dyes in cotton is approximately estimated to be 50\%.\textsuperscript{51} Studies reveal that approximately 12\% synthetic dyes are lost during manufacturing and processing in dyeing industries. Of which 20\% enters into the industrial wastewater stream.\textsuperscript{52} Different types of synthetic dyes are widely used in various industries such as textiles, leather, paper and pulp, food technology, light-harvesting arrays, photo-electrochemical cells, plastics, cosmetics, rubber and so forth.\textsuperscript{53} Approximately 1-2 million kilogram of active dye out of total production of 10 million kilogram per year dyestuff in the form of either dissolved or suspended form enters into the biosphere.\textsuperscript{54} Hence, these industrial effluents along with those from plant manufacturing dyes contain sufficient amount of dyes.

\textbf{1.3.2 Toxicological effects of Dyes}

The discharge of dye wastewater into the natural water bodies is a serious threat to many forms of life of the environment and is a matter of major concern for both toxicological and esthetical reasons.\textsuperscript{55} These dyeing
effluents are coloured in nature and can be easily recognized by human eye. These dye industries wastewater is considered to be problematic and to be treated before disposal due to their high chemical as well as biological oxygen demand, suspended solids and various toxic compounds. Hence, the discharge of these industrial effluents causes damage to the aesthetic nature of the environment and serious problems to the aquatic organisms in their photosynthetic phenomenon because of the reduced light penetration and may also be toxic to aquatic life due to the presence of aromatics, metals, chlorides etc.\textsuperscript{56}

An anionic and non-ionic dye contains chromophores and it consists of mainly azo groups or anthraquinone type. The formation of toxic amines in dyes effluent is the result of reductive cleavage of azo linkage.\textsuperscript{57} Reactive dyes are typically azo-based chromophores that can combine with various types of reactive groups, viz., vinyl sulphone, chlorotiazine, trichloropyrimidine, difluorochloropyrimidine etc. These dyes are different from all other dyes due to the formation of covalent bonding with the textile fiber (cotton) and are mainly used in textile industry. On the other hand, water soluble reactive and acid dyes are not treatable as they are unaffected by the conventional treatment technique. Anthraquinone-based dyes are non-degradable (most resistant to degradation) due to their fused and complex aromatic structures and remains coloured in wastewater.\textsuperscript{58} Cationic (basic) dyes are highly brilliant and intense in colour for which they are visible even in low concentrations of 1 mgL\textsuperscript{-1}.\textsuperscript{59} Metal complex dyes are mostly based on chromium metal and are carcinogenic in nature.\textsuperscript{60}

Disperse dyes (non-ionic) have the tendency to bioaccumulate easily and do not ionize in an aqueous medium. Many of these dyes are made from known carcinogens such as benzidine and other aromatic compounds.\textsuperscript{61} Sub-chronic exposure of these dyes resulted in hepatocellular carcinomas and hepatic neoplastic nodules in rats (National cancer Institute 1978) and carcinomas in very short duration (National Institute for Occupational Safety, 1980). It was also reported from a histopathological changes in testes of textile wastewater exposed rats that there is a reduction in the number of germ and Leydig cells, resulting in
impaired spermatogenesis. Chromosomal fractures, teratogenicity, respiratory toxicity, mutagenic and carcinogenic activities have been reported from the effluents of textile and other dye related industries. Maximum percentage (67%) of mutagenic effluents was reported while studying the mutagenic activity of textile wastewater effluents using salmonella/microsome assay. These dyes may cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, brain and even central nervous system.

It was reported that mainly textile effluent marked as the second in toxicity, among eight industrial sectors represented, by using a series of bioassays assessing the acute, sublethal and chronic toxicity at various trophic levels.

1.3.3 Guidelines and Need of Dye Removal

1.3.3.1 Guidelines

During the last few decades, application of synthetic dyes has been reduced for the increased awareness of environments by the harmful effects due to either toxicity or non-biodegradable nature. Recently, a ban has been imposed no to use some synthetic dyes all over the world including European Economic Community (EEC), Germany, USA and India. Since 1997, the environmental policy of UK becomes more stringent and states that zero synthetic chemicals should be released into the marine environment. This enforcement of law is to make ensure that dyeing industries must treat their effluent to the required standard. The Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) was formed in the year of 1974. The objectives of this association were to minimize the environmental damage, protect the users and consumers and to co-operate with Government and public concerns over the toxicological impact of dyes. As per the survey of this association it was found that more than 90% of some 4000 dyes had LD$$_{50}$$ value greater than 2 x 10$$^3$$ mgKg$$^{-1}$$ and highest rate of toxicity were found amongst basic and diazo direct dyes. Environmental Agency (EA) for England and Wales, and the Scottish Environment Protection Agency (SEPTA) looks after and regulates removal of dyes from industrial effluents. The Bureau of Indian
Standards (IS 10500) has prescribed new drinking water standards as colour standards at five colour units as the desirable limit and twenty five colour units as the permissible limit in the absence of alternate source.

**1.3.3.2 Need of removal**

Conventional wastewater treatment technologies are no more effective for the wastewater treatment of synthetic textile dyes because of their chemical stability.

It was reported that out of 18 azo dyes, 11 compound passed through the activated sludge process were practically untreated, 4 were adsorbed on the waste activated sludge and only 3 were able to biodegrade. Removal of dyes from waste effluents is of significant environmental, technical and commercial importance because of the presence of even a small quantity of it in water is highly visible and toxic. Further, the dyes have a tendency to sequester metal and may cause microtoxicity to fish and other organism. Hence, it is considered as an environmental challenge to remove dyes from wastewater and governmental legislation requires textile wastewater to be treated before coming to the natural water bodies. Therefore, constant effort is required to have an effective and efficient technique to remove these dyes.

Various methodologies have been employed for the removal of dyes and even reviewed too. Their advantages and disadvantages are listed in Table 1.4.
### Table 1.4 Advantages and Disadvantages of the current methods of dye removal from Industrial effluent

<table>
<thead>
<tr>
<th>Physical/Chemical methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton's Reagent</td>
<td>Effective decolourisation of both soluble and insoluble dyes</td>
<td>Sludge generation</td>
<td>75</td>
</tr>
<tr>
<td>Ozonization</td>
<td>Applicable in gaseous state: no alteration of volume</td>
<td>Short half life (20 min)</td>
<td>76</td>
</tr>
<tr>
<td>Photochemical</td>
<td>No sludge production</td>
<td>Formation of by-products</td>
<td>77</td>
</tr>
<tr>
<td>NaOCl</td>
<td>Initiates and accelerates azo-bond cleavage</td>
<td>Release of aromatic amines</td>
<td>78</td>
</tr>
<tr>
<td>Cucurbituril</td>
<td>Good sorption capacity for various dyes</td>
<td>High cost</td>
<td>79</td>
</tr>
<tr>
<td>Electrochemical destruction</td>
<td>Breakdown compounds are non-hazardous</td>
<td>High cost of electricity</td>
<td>80</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Good removal of wide variety of dyes</td>
<td>Very expensive, disposal problem</td>
<td>81</td>
</tr>
<tr>
<td>Peat</td>
<td>Good adsorbent due to cellular structure</td>
<td>Specific surface area for adsorption are lower than activated carbon</td>
<td>82</td>
</tr>
<tr>
<td>Wood chips</td>
<td>Good sorption capacity for acid dyes</td>
<td>Requires long retention time</td>
<td>83</td>
</tr>
<tr>
<td>Silica gel</td>
<td>Effective for basic dye removal</td>
<td>Side reaction in effluent prevent commercial application</td>
<td>84</td>
</tr>
<tr>
<td>Membrane filtration</td>
<td>Remove all types of dyes</td>
<td>Concentrated sludge production, need high pressures, expensive, incapable of treating large volumes.</td>
<td>85</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Regeneration: no adsorbent loss</td>
<td>Not effective for all dyes, economic restraints</td>
<td>86</td>
</tr>
<tr>
<td>Irradiation</td>
<td>Effective oxidation at lab scale</td>
<td>Requires a lot of dissolved oxygen</td>
<td>87</td>
</tr>
<tr>
<td>Electrokinetic coagulation</td>
<td>Economically feasible</td>
<td>Higher sludge production</td>
<td>88</td>
</tr>
<tr>
<td>Biodegradation</td>
<td>Efficient for specific dyes</td>
<td>Slow process, need to create an optimal favorable environment, maintenance and nutrition requirements.</td>
<td>89</td>
</tr>
</tbody>
</table>

#### 1.3.4 Existing Treatment Technologies of Dye Removal

With the growing concern on health mainly on aesthetic grounds, researcher started paying attention to the dye waste since 80's. Since then,
more information on the environmental consequences of dyestuff usage has become available and as a result the dye manufacturers, users and concerned government organizations are coming forward to take substantial measures to treat the dye containing wastewaters. Dyes containing wastewater is very difficult to treat by conventional techniques as they are recalcitrant organic molecules, resistant to aerobic digestion and even stable to light, heat and oxidizing agents. Due to the chemical stability and low biodegradability of dyes, conventional biological waste water treatment techniques and even conventional primary and secondary systems become inefficient and are not suitable to treat these dye wastewater. Hence, dye removal from industrial effluents in an eco-friendly way remains a major challenge to the present day research. A wide range of methods has been developed for the removal of synthetic dyes from dye containing industrial effluents to decrease their impact to the environment. Basically, there are three dye removal methods discussed under three categories: Chemical, Physical and Biological.

1.3.4.1 Chemical Treatments

Oxidative Processes: In this method wastewater is treated by using an oxidizing agent such as hydrogen peroxide (H₂O₂), Ozone (O₃), permanganate (MnO₄⁻), chlorine (NaOCl), fenton’s reagent (Fe²⁺-H₂O₂) etc. They are among the most commonly used methods for decolorization processes because of low quantity requirement and shorter reaction time.

Fenton’s reagent: Fenton’s reagent is a solution of hydrogen peroxide and an iron catalyst and is used to oxidise dye wastewaters. This is a suitable chemical means of treating wastewaters which are resistant to biological treatment or is poisonous to live biomass. It is effective in decolourizing both soluble and insoluble dyes though vat and disperse dyes are found to be resistant. This method not only removes colour but also reduced chemical oxygen demand (COD), total organic carbon (TOC) and toxicity. The main disadvantage is that it usually is effective within narrow pH range of <3.5, involves sludge generation and takes longer reaction time.
Ozonization: This method is capable of degrading chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons. This method shows a preference for double bonded dye molecules and major advantage is that it can be applied in its gaseous state and hence does not increase the volume of wastewater and sludge. The major disadvantage of this method is cost for its short half life period, typically being 20 minute.

Photochemical: This method is one of the advanced oxidation processes for pollutant degradation to CO\(_2\) and H\(_2\)O by using a light source of UV in presence of H\(_2\)O\(_2\). The rate of dye removal is influenced by the intensity of the UV radiation, pH, dye structure and dye bath composition. This method is suitable for a wide range of dyes including direct, reactive, vat and disperse. The major disadvantage of this method is that additional bye products such as halides, metal, inorganic and organic acids, aldehydes may be produced and they are quite expensive.

Sodium hypochlorite: Chlorine is a strong oxidizing agent and used as calcium or sodium hypochlorite. Dyes having amino or substituted amino on groups on naphthalene ring are more susceptible to chlorine and in addition, reactive, acid, direct and metal complexes dyes which are water soluble are decolourised by this method. Water insoluble disperses and vat dyes are resistant to decolorization by this method and it leads unavoidable side reactions producing toxic trihalomethane. Moreover, the liberation of metal from metal complex dyes causes corrosion on metallic vessels.

Cucurbituril: This is a cyclic polymer of glycoluril and formaldehyde. The mechanism behind the adsorption of reactive dye adsorption is the formation of host-guest complexes with aromatic compounds. Another probable mechanism is based on the hydrophobic interaction or the formation of insoluble cucurbituril-dye-cation aggregates since adsorption occurs reasonably fast. The major disadvantage is the cost of this method.

Electrochemical methodology: In this method, decolorization is achieved either by electro oxidation with non soluble anodes or by electro-coagulation using consumable material. This technique is effective in
decolorization of soluble and insoluble dyes with reduction of COD. But the main disadvantage is of consumption of high electricity and sludge production and also pollution from chlorinated organic and heavy metals due to indirect oxidation.

1.3.4.2 Physical Treatments

There are different physical methods that are widely used for dye wastewater treatment. Some of the important methods are discussed below:

Adsorption: Adsorption is recognized as the best method not only for the dye removal but also has the wide applicability in removal of metal and other hazardous organic pollutants. Adsorption refers to a process wherein a substrate is concentrated at the solid surface from its liquid or gaseous surroundings. Thus, the basic feature of adsorption is the surface accumulation of material. Based on the nature of attraction between the solid surface and the adsorbed molecule, it is divided into Physical adsorption or Physisorption and Chemical adsorption or Chemisorption. In Physisorption, Vanderwaals force is responsible for the attraction between solid surface and the adsorbed molecule and this force being weak in nature result in reversible adsorption. On the other hand, in Chemisorption chemical bonding is responsible for the attraction between the solid surface and the substrate. Hence, due to the higher strength of chemical bonding, it is difficult to remove the chemisorbed species from the solid surface.

Ion exchange: Ion exchange is basically a reversible chemical process wherein anion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. The largest application of this method to drinking water treatment is in the area of softening, i.e., the removal of calcium, magnesium, and other polyvalent cations in exchange for sodium. By this method, both cation and anion dyes can be removed from dye containing effluent. The major advantage of this method is that there is no loss of adsorbent on regeneration, reclamiation of solvent after use and the removal of soluble dyes. The disadvantage is cost effective as organic solvents are expensive and is not effective for disperse dyes.

Membrane separation: This technique has the ability to clarify, concentrate and separate dye constantly. It is resistant to temperature,
an adverse chemical environment and microbial attack. This method is suitable for water recycling within a textile dye plant of low dye concentration. But the major disadvantages of this method are that disposal problems of left out residue, high capital cost, possibility of clogging and membrane replacement.

**Irradiation:** In this method sufficient quantities of dissolved oxygen are required for organic substances to be broken down effectively. Some dyes and phenolic molecules can be oxidised effectively at laboratory scale.\textsuperscript{113} The major disadvantage of this method is being constant supply of dissolved oxygen, its cost matters.

**Electrokinetic coagulation:** In this method, ferrous sulphate and ferric chloride are added for removal of direct dyes from wastewater. This method is not applicable only for acid dyes. There is a large amount of sludge production which makes disposal problem and cost of ferrous sulphate and ferric chloride is the major disadvantages.\textsuperscript{114}

### 1.3.4.3 Biological Treatments

This is one of the most common and widespread technique used in dye wastewater treatment.\textsuperscript{115} This methodology offers considerable advantages like being relatively inexpensive, having low running cost, and the end products of complete mineralization not being toxic. This process can be divided into three categories: aerobic (in presence of oxygen), anaerobic (without oxygen) and combined aerobic-anaerobic.

**Aerobic treatment:** Bacteria and fungi are the two microorganism groups that have been widely used for dye wastewater treatment. In aerobic condition the bacteria present in the wastewater secrets enzyme and breaks down the organic compound. A number of triphenylmethane dyes (magenta, crystal violet, brilliant green, malachite green, ethyl violetetc) have been found to be decolorized by the strain *kurthia sp.*\textsuperscript{116} Fungal strains are also capable of decolourize azo and triphenylmethane dyes.\textsuperscript{117} *Phanerochaetechrysosporium* is another example of fungi that are extensively used to decolourize wide range of dyes.\textsuperscript{118} Various other microorganisms including *Rhyzopusoryzae, Cyathusbulleri, Coriolusversicolour, Funaliatrogii, Laetiporoussulphures* etc. have been tested
for their effective decolourization of dye. The decolourization process depends on various factors such as pollutants concentration, dyestuff concentration, initial pH, temperature of the effluent etc. Although this treatment is suitable for some dyes but most of them are recalcitrant to biological breakdown or are non transformable under aerobic condition.

Anaerobic treatment: This treatment is applicable to decolourizeazo and other water soluble dyes and involves oxidation-reduction reaction with hydrogen rather than free molecular oxygen in aerobic treatment. Methane and hydrogen sulphide yields in this anaerobic breakdown. Methanogenic granular sludge was used to decolourize two azo dyes mordant orange1 and azodisalicylate under anaerobic conditions. This treatment is a cheaper alternative compared with aerobic treatment as expensive aeration is omitted and bulking sludge problems are avoided.

Combined aerobic-anaerobic treatment: A combination of aerobic and anaerobic treatment gives more encouraging results for remediation of dyes from textile effluents. The advantage of this system is the complete mineralization due to synergistic action of different organisms. Moreover, the reduction of the azo bond can be achieved under the reducing conditions in anaerobic bioreactors and the resulting colourless aromatic amines may be mineralized under aerobic conditions, thereby making the combined azo dye technique more attractive. Hence, an anaerobic decolorization followed by aerobic post treatment is the best method for treating dye wastewaters.

Although the biological technique is cost competitive and suitable for variety of dyes, but it has several disadvantages also. It has low biodegradability of dyes, less flexibility in design and operation, larger land area requirement and longer times required for decolorization-fermentation processes thereby making it incapable of removing dyes from effluent on a continuous basis in liquid state fermentations.
1.4 HEAVY METAL POLLUTION

Heavy metals are referred as a metallic element with a specific gravity greater than or equal to 6 g cm\(^{-3}\), especially one that is poisonous, or a common hazardous waste, can damage organism at low concentrations and tend to accumulate in the food chain.\(^{128}\) From the environmental toxicity point of view, the heavy metal can also be defined as a group of elements which are toxic even at trace concentration and that lies between chromium and lead on periodic table with atomic weights 51.99 and 207.20 respectively with a specific gravity greater than 4 g cm\(^{-3}\). The most familiar heavy metals are Zinc (Zn-7.14 g cm\(^{-3}\)), Chromium (Cr-7.19 g cm\(^{-3}\)), Cadmium (Cd-8.65 g cm\(^{-3}\)), Cobalt (Co-8.9 g cm\(^{-3}\)), Nickel (Ni-8.91 g cm\(^{-3}\)), Copper (Cu-8.95 g cm\(^{-3}\)), Lead (Pb-11.34 g cm\(^{-3}\)) and Mercury (Hg-13.53 g cm\(^{-3}\)). Heavy metals are usually classified in three categories: toxic metals (Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn etc), precious metals (Pd, Pt, Ag, Au, Ru etc.) and radionucleids (U, Th, Ra, Am, etc.).\(^{129}\)

Most of the heavy metals are toxic to biota and living creatures. Pollution by toxic heavy metal is a global environmental problem. Heavy metal contamination to the environment has been increasing day by day as a result of industrial activities, especially in industries using electrolytic treatments, metallurgical and metal finishing industries, in engineering processes and in the manufacture of plastics and pigments. Moreover, agriculture and waste disposal also contribute to this kind of heavy metal contamination and as a result there is rapid increase in the heavy metals discharge into the environment.

Heavy metals are nonbiodegradable and their presence at high concentrations in water bodies leads to bioaccumulation through food chain in living organisms and causes health problems in animals, plants and human beings even in relatively low concentrations.\(^{130}\) In history, few examples are there due to the adverse effects of heavy metal contamination in aquatic streams. “Minamata tragedy” in Japan is one of among past disasters due to methyl mercury contamination. Similarly, it is the “Itai-Itai” health effect in Jintsu river of Japan which is the consequences of cadmium contamination.\(^{131}\)
Uncontrolled discharge of heavy metals into the environment can create toxic or inhibitory effect on living systems and urban ecosystems.\textsuperscript{132} According to World Health Organization (WHO), the metals of most immediate concern are cadmium, chromium, cobalt, copper, lead, nickel, mercury and zinc. Therefore, it is the high time to prevent the entrance of these toxic heavy metals into the ecosystem. Hence, it becomes mandatory to control and reduce the levels of these metal ions in wastewaters and bring them to permissible values.\textsuperscript{133}

\subsection*{1.4.1 Sources of Heavy Metals}

Basically, the most hazardous components that exist in the environment can be identified and classified into two categories based on sources as natural and anthropogenic sources. Naturally a considerable amount of heavy metals have been often released into soil, water and air through chemical and physical weathering of igneous, metamorphic rocks and soils. They are also associated with volcanic activities, wind erosion, forest smoke fire and fossil fuels. But the level of metals of such natural origin is usually harmless to human beings and to the environment. Moreover, humans’ exploitation of world mineral resources and technological activities disperse metallic elements into the environment in unprecedented quantities and concentrations. The primary anthropogenic sources of heavy metals are industrial sector, which discharge a huge amount of contaminated wastewater due to highly toxic metal substances. Various industries such as mining and smelting of metalliferous, surface finishing industry, energy and fuel production, fertilizer and pesticide industry, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, metal surface treating, aerospace and atomic energy installation etc. produce and discharge different heavy metal containing wastes into the environment. Thus, metallic waste brings about serious environmental pollution, threatening human health and ecosystem.\textsuperscript{134} Distributions of heavy metals in various manufacturing industries are presented in Table 1.5.
Table 1.5 Distribution of heavy metals in Industrial effluents

<table>
<thead>
<tr>
<th>Heavy Metals</th>
<th>Name of Industries</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>Pesticides including wood preservatives, paints, desiccants, glass, alloys, electronic components (semiconductors), pigments and pharmaceuticals</td>
<td>135</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>Electroplating, batteries, smelting, pigments, plastic, iron and steel, mining and mineral processing, non-ferrous metal industry, printing and photographic paints</td>
<td>136</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>Electroplating, tanning and leather, textile, pigments, plastic and dye.</td>
<td>137</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>Mining, electronics, metallurgical, electroplating and paint industries</td>
<td>138</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>Electroplating, electrical, pipes and tubes, automobile, paper and pulp, paint, textile, fertilizer, petroleum</td>
<td>139</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>Battery, paper and pulp, mining, electroplating, lead smelting, metallurgical finishing industries, paints and pigments, metal dye, electricity and petroleum.</td>
<td>140</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>Mining, combustion of fossil fuels, pulp and paper, paints, oil refinery, plastic, battery manufacturing, electrical equipment, leather tanning, metal finishing, petroleum refinery, agriculture, smelters, chlorine and chloralkali manufacturing processes.</td>
<td>141</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>Paint industry, metal finishing, mineral processing, silver refineries, hydrometallurgical industries, leather tanning, electroplating, zinc base casting, storage battery industries and steam electric power plants.</td>
<td>142</td>
</tr>
<tr>
<td>Strontium (Sr)</td>
<td>Nuclear power plants, research applications, power remote weather stations, navigational buoys, fireworks, and satellite applications</td>
<td>143</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>Metals, chemicals, pulp and paper manufacturing, steel works with galvanizing lines, zinc and brass plating, viscose rayon yarn and fiber production industries.</td>
<td>144</td>
</tr>
</tbody>
</table>

1.4.2 Toxicological Aspects of Heavy Metals

It has been established beyond any doubt that dissolved heavy metals escaping into the environment pose a serious health hazard. The sad demise of Roman Empire in the past is also the consequence of threatening presence of heavy metals. With exponential increase of heavy metals emission into the environment, it is the high time to control these heavy metals before entering into the complex ecosystem. And once these metals come to the ecosystem, it becomes very difficult as they starts to move through from one ecological trophic layer to another. They accumulate in living tissues through the food chain which has humans at its top. The hazardous effect multiplies and humans eventually tend to receive the problems associated with the toxicity of heavy metals are concentrated and
CHAPTER 1

from many different directions. This resulting health problem demonstrates themselves on the acute as well as chronic levels to the health of human being and on aquatic organisms.

1.4.2.1 Effects of Heavy Metals on Human Health

As discussed above, the heavy metals are stable and persistent environmental contaminants because of their undegradable and stable nature for which it is difficult to destroy. But some heavy metals are essential to human health in their tolerable limit as the human body needs many friendly trace heavy metal elements for smooth functioning. To mention a few health benefits of heavy metals, we can mention as iron the main component of haemoglobin prevents anemia, zinc is a cofactor in over 100 enzyme reactions. Similarly copper and magnesium are also in minute amounts requiring for proper metabolism. Except few heavy metals, many others have no useful role in human physiology and even cause worst health condition. Arsenic, chromium, cadmium, lead, mercury, nickel etc. are toxic to the enzyme systems and metabolism of the human body even at trace amount of exposure. These heavy metals enter into the human body at very low concentrations by inhalation, ingestion and skin absorption. They tend to accumulate in the food chain and in the body and can be stored in soft (kidney etc.) and hard tissues (bone). When heavy metals are accumulated in human body tissue faster than the body’s detoxification pathway, toxins get buildup gradually in the human body. As these metals exist in positively charged form, they interact with negatively charged organic molecules to form complexes. Early ageing, stress, decreased sex drive and aggravation of menopausal symptoms are the results of overload of heavy metals in the adrenal gland that reduces the production of hormones. Moreover, heavy metal overloads leads to unresponsiveness of diabetic patients towards medication and neurological diseases such as depression and loss of thinking power, osteoporosis and hypothyroidism etc. Trace amounts of toxic heavy metals have negative health consequences that affect nutritional status, metabolic rate and the integrity of detoxification pathways. The most important threatening part of these heavy metals is that they have long half-life period, e.g.; it is decade for cadmium in kidney. Serious detrimental effects on behaviour, intellect and
developing nervous system of children are the results of heavy metals that readily transfer to the placenta and found in the breast milk.

**Table 1.6** Toxic effects of heavy metals on human health (US Department of Health and Human Services, 1991)

<table>
<thead>
<tr>
<th>Heavy Metals</th>
<th>Toxicological effects on human health</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>Skin cancer, hyper pigmentation, carcinogen and mutagen, dermatitis, skin damage or problems with circulatory systems, and may have increased risk of getting cancer</td>
<td>146</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>Kidneys and respiratory disorders, carcinogenic, prolonged concentrations affect liver, kidney, pancreas, thyroid, and hypertension suspected effect</td>
<td>147</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>Skin and respiratory disorders, Cr(VI) is carcinogenic and corrosive on tissue, long term skin sensitization and kidney damage</td>
<td>148</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>Lungs, pneumonia, wheezing and asthma problems</td>
<td>149</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>Its long term exposure causes irritation of the nose, mouth, eyes, headaches, stomachs, dizziness, vomiting and diarrhea. High uptake may cause liver and kidney damage and even death.</td>
<td>150</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>Long term exposure may cause brain nervousness, kidney damage, birth related complexities, disruption of the biosynthesis of haemoglobin and anaemia. Declined fertility of men through sperm damage.</td>
<td>151</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>Vapour inhalation may cause nerve, brain, kidney damage, lung and eye irritation, skin rashes, vomiting and diarrhea.</td>
<td>152</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>Excess quantity uptake causes lung, nose, larynx and prostate cancer, respiratory failure, birth defects, asthma and chronic bronchitis.</td>
<td>153</td>
</tr>
<tr>
<td>Strontium (Sr)</td>
<td>Strontium chromate causes lung cancer, and problems with bone growth and radioactive effects.</td>
<td>154</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>Zinc poisoning can cause desiccating muscles, electrolytes imbalance, stomach ache, vertigo and disharmony.</td>
<td>155</td>
</tr>
</tbody>
</table>
Similarly, silent chronic symptoms, low level heavy metal accumulation in tissues of adults’ results in steady decline in energy, productivity and quality of life to accelerated cardiovascular disease, premature dementia and total debilitation. Various heavy metals toxicity on human health is represented in Table 1.6.

1.4.2.2 Effects of Heavy Metals on Aquatic Organisms

Heavy metals enter into the aquatic system mainly through three possible pathways causing various disorders.

Free metal ions can either readily or passively diffused into the blood system by the adsorption through respiratory surface (gills) and through body surface respectively. And metals which are adsorbed onto food and particulates may be ingested from free metal ion bearing water bodies.\textsuperscript{156}

1.4.3 Guidelines and need for the removal of Heavy Metals

1.4.3.1 Guidelines

As a result of development of advanced analytical techniques and better health monitoring technologies, the acceptable minimum concentrations of these metals are progressively decreasing. The compounding toxic effects of heavy metals in the environment are being recognized and their hazardous effects are better understood in recent times. Various regulatory bodies have set the maximum prescribed limits for discharging toxic heavy metals in industrial wastewater effluent into the aquatic system to minimize health hazards and environmental degradation. Under the public and media pressure, Governments introduce and progressively enforce stringent regulations for metal discharge from industrial operations. These guidelines are intended to support the development and implementation of hazardous risk management strategies that will ensure the safety of drinking water supplies through the control of hazardous constituents of water system.\textsuperscript{157} These guidelines for industrial effluents not only restrict the quantity of pollutants but also set the desired degree of treatment. The guidelines from WHO and the Indian Standards (IS) for some of the heavy metals for drinking water and industrial effluents are presented in Table 1.7.
Table 1.7 Guidelines of heavy metals for drinking water and industrial effluents

<table>
<thead>
<tr>
<th>Heavy Metals</th>
<th>Permissible limit (mg/l) of industrial effluent as per CPCB*</th>
<th>Allowable drinking water standards (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inland surface water</td>
<td>Public sewer</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>0.10</td>
<td>2.00</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>0.10</td>
<td>0.30</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Nickel (Ni)</strong></td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.10</td>
<td>1.00</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>5.00</td>
<td>15.00</td>
</tr>
</tbody>
</table>

* Central Pollution Control Board, India, ** Bureau of Indian Standards, *** World Health Organization

1.4.3.2 Need for the Removal of Heavy Metals

Heavy metals cannot be destroyed by biological degradation once it comes to the food chain. Incidence of heavy metal contamination in fish, oysters, mussels, sediments and other components of aquatic ecosystems have been reported from all over the world.\textsuperscript{158}

Excessive amounts of some heavy metals can be toxic through direct action of the metal, through their inorganic salt or via organic compounds from which the metal can become easily detached or introduced into the cell. Some of the heavy metals are toxic to aquatic organisms even at very low concentration and hence needs continuous monitoring and surveillance and need to remove these toxic heavy metals from the aquatic system.

Continuous efforts have been in streamline for a cost effective treatment and technologies for metals-contaminated wastewater to get rid of toxicological effects of heavy metals on environment, animals and human beings. Considering various hazardous effects of heavy metals, it becomes
imperative to treat these toxic heavy metal contaminated effluents before discharging into fresh water bodies.

1.4.4 Existing Treatment Techniques for Heavy Metal Removal

Municipal sewage treatment plants are not well designed and equipped for handling toxic wastewaters as metals toxicity persists even in the sludges and by-product streams of these treatment plants. These toxic heavy metals need to be removed at the source in a specially designed pre-treatment set up, but need to be cheap so that it can deal with large volumes of effluents.\textsuperscript{159}

There are various conventional methods for removal of metal ions from aqueous solutions that includes chemical precipitation, ion exchangers, chemical oxidation/reduction, reverse osmosis, electrodialysis, ultra filtration etc.\textsuperscript{160} Although heavy metal removal from aqueous solution can be achieved to some extent by conventional treatment as mentioned above, but each treatment has its own inherent limitations such as less efficiency, sensitive operating conditions, production of secondary sludge and further costly disposal affair.\textsuperscript{161}

As such, Chemical precipitation and electrochemical treatment are ineffective when metal ion concentration in aqueous solution is within the range of 1-100 mg/l (ppm), and also produce large quantity of sludge again required to treat with great difficulty.
Table 1.8 Advantages and disadvantages of conventional existing techniques

<table>
<thead>
<tr>
<th>Treatment Techniques</th>
<th>Heavy Metals</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Precipitation</td>
<td>Cd(^{2+}), Cr(^{6+}), Cu(^{2+}), Fe(^{3+}), Pb(^{2+}), Sn(^{2+})&amp; Zn(^{2+})</td>
<td>Simple process, not metal selective and inexpensive</td>
<td>Difficult separation for higher concentration, not effective for mixed metals, resulting sludge and high cost for sludge disposal, high maintenance cost.</td>
<td>162</td>
</tr>
<tr>
<td>Chemical Oxidation or Reduction</td>
<td></td>
<td>Chemicals required (not universal), slow rate of biological system, climate sensitive.</td>
<td></td>
<td>Mineralization</td>
</tr>
<tr>
<td>Electrochemical Treatment</td>
<td>Cr(^{6+}), Cu(^{2+}), Fe(^{3+}), Pb(^{2+}), Bi(^{3+})&amp; Zn(^{2+})</td>
<td>Rapid process, effective for certain metal ions, can treat effluent &gt; 2000 mg/l and metal recovery</td>
<td>Expensive, formation of by products, high initial capital cost and production of hydrogen, filtration process for flocs.</td>
<td>163</td>
</tr>
<tr>
<td>Ion Exchange</td>
<td>Cr(^{3+}), Cu(^{2+}), Fe(^{3+}), Pb(^{2+}) &amp; Ni(^{2+})</td>
<td>Withstand at shock loading, metal selective, limited pH tolerance, high regeneration</td>
<td>particles sensitive, expensive resins, fouling of bed by organic components, plugging of resin bed by suspended solids, high maintenance cost</td>
<td>164</td>
</tr>
<tr>
<td>Membrane Filtration</td>
<td>Cr(^{6+}), Cu(^{2+}), Fe(^{3+}), Pb(^{2+}), Ni(^{2+})&amp; Zn(^{2+})</td>
<td>Good removal, low solid waste generation, low chemical consumption, small space requirement and possible to be metal selective</td>
<td>Requires extensive pretreatment, high initial capital, maintenance and operation cost, membrane fouling and limited flow rates</td>
<td>165</td>
</tr>
<tr>
<td>Biological Treatment</td>
<td>Cd(^{2+}), Cu(^{2+}), Pb(^{2+}), Hg(^{2+}) &amp; Ni(^{2+})</td>
<td>Low cost and effective for many metals</td>
<td>Treatment not yet to be established and commercialized</td>
<td>166</td>
</tr>
<tr>
<td>Adsorption (CAC)</td>
<td>Cd(^{2+}), Cu(^{2+}), Pb(^{2+}), Hg(^{2+}) &amp; Ni(^{2+})</td>
<td>Wide variety of target pollutants, high capacity, fast kinetics, selective dependent on adsorbent</td>
<td>Performance depends on type of adsorbent, require chemical regeneration to improve its sorption capacity</td>
<td>167</td>
</tr>
<tr>
<td>Coagulation and Flocculation</td>
<td>Cr(^{6+}), Fe(^{3+}), Sb(^{3+}), Bi(^{3+})&amp; Zn(^{2+})</td>
<td>Bacterial inactivation capability, good sludge settling and dewatering characteristics</td>
<td>High chemical consumption, increased sludge volume generation</td>
<td>168</td>
</tr>
</tbody>
</table>
Similarly, ion exchange, membrane technologies, and activated carbon adsorption process are extremely expensive when treating large amount of water and wastewater containing heavy metal in low concentration, they cannot be used at large scale.\textsuperscript{169} The advantages and disadvantages associated with each conventional treatment technique are presented in Table 1.8.

Amongst all the available treatment techniques, adsorption using activated carbon has become one of the popular, most effective alternative treatments for the heavy metal removal from waste water. This technique is considered to be superior to other techniques in view of its comparatively low cost, wide range of applications, simplicity of design, easy operation, low harmful secondary products and facile regeneration of the adsorbents.

Basically adsorption is a mass transfer process by which a substance is transferred from liquid phase to the surface of the adsorbent, and bound by physical or chemical interactions.\textsuperscript{170}

Therefore, search of low cost and easily available materials of agricultural and biological origin along with industrial by-products as precursor for activated carbon has been geared up since last few decades.
1.5 REQUIREMENT OF ALTERNATIVE TREATMENT TECHNIQUE

As discussed in each section of dye and metal pollution, the existing conventional wastewater treatment techniques are having a few advantages and many of its own disadvantages. When pollutants are present in moderate concentrations, these techniques are usually expensive. United States Environmental Protection Agency (USEPA) has been cited the adsorption by AC as one of the best available control technologies.\textsuperscript{171} Hence, attempts have been made to find inexpensive alternative adsorbents for economical waste water treatment rather than commercially available AC. In recent years, numerous approaches have been studied the technical feasibility for the development of cheaper and effective adsorbents. Many workers have been studied various non-conventional low cost adsorbents, including natural materials, biosorbents, and waste material from industry and agriculture. Some of the reported and established adsorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton).

The major application of PC (about 80% of the world production of AC) is the aqueous phase adsorption of both organic and inorganic pollutants.\textsuperscript{172} Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications.\textsuperscript{173} It has been found to be superior to other existing techniques in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. The most important characteristic of the process is that it does not result in the formation of any harmful substances throughout the process. Therefore, adsorption of dyes as well as toxic heavy metals by PC prepared from easily available, inexpensive carbon precursor source becomes a challenge in present day context.
1.6 IMPORTANCE AND OBJECTIVE OF THE PRESENT STUDY

As of now, adsorption is universally accepted as the latest technology of treating industrial wastewater bearing variety of dye pollutants and toxic metals for the removal of soluble toxic components. In this regard, technically feasible and economically viable pre-treatment procedures with suitable biomaterials based on better understanding of the adsorbate adsorbent mechanisms are gaining importance. Various PC of agricultural waste products as low cost adsorbents have been reported till now. However, there is weakness in adsorption efficiency and an additional cost involved in the processing of solid waste generation after the single usage of the agricultural materials, which is posing economic difficulties necessitating research on alternate adsorbents with high potential and reuse capability. In adsorption process, detailed understanding of adsorbate binding mechanisms with active sites facilitates to determine the rate determining step. This information is important for the rational design and optimization of the adsorbents and adsorption conditions.

However, there are no detailed studies considering IOSH and ANH as the carbon precursor for the preparation of adsorbents and subsequent use in the removal of dyes and metal. Therefore, keeping all the environmental, ecological, societal health issues and other unexplored research directions in interest, it is considered to be necessary to find novel adsorbents which will provide easy, feasible and economical solution for the removal of certain industrially important cationic and anionic dye and heavy metals from aqueous solutions.

Hence, the present work has been undertaken to achieve the above goals with the following objectives:

- Development of high potential adsorbents from industrial (Tea Waste and Areca Nut Husk Fiber) as well as agricultural waste material (Indian Oleander Seed Hull) as the carbon precursor.
- Characterization of laboratory synthesized adsorbents for its optimization of surface area and pore texture, surface morphology, surface functional characteristics and other important properties by sophisticated analytical instruments.
CHAPTER 1

✓ Find out the suitability of these synthesized PC’s as low cost adsorbents and optimum operating parameters such as agitation/equilibrium time, initial dye/metal concentration, pH of the aqueous solution, adsorbent dosage as well as the maximum adsorption capacity of targeted dyes (Methylene blue and Eosin Yellow) and heavy metals (Cr\(^{6+}\), Cd\(^{2+}\) and Ni\(^{2+}\)).

✓ Development of appropriate equilibrium isotherm model, thermodynamic and kinetic studies to analyze the adsorbate-adsorbent interaction.

✓ Finding the possible adsorbate binding mechanism of studied adsorbents with the help of surface chemistry.

Therefore, it is of extreme relevance to find suitable low-cost natural and agricultural waste carbon precursors that are economically attractive and at the same time present similar or even better characteristics than the conventional ones for the adsorptive removal of dyes as well as toxic heavy metals from aqueous solutions.

1.7 SUMMARY

As discussed in the previous sections and from literature citations it indicates the urgent demand of finding low cost carbon precursor for the preparation of PC and subsequently removal of dyes and toxic heavy metals contaminants from its wastewater. Considering the importance and alarming threat of dyes and toxic heavy metals to the human as well as aquatic organism, the objective of this present study is made to utilize three locally available waste carbon precursors for the preparation of environment friendly and low cost adsorbents for dyes [cationic (MB) and anionic dye (EY)] as well as toxic metal [Cr(VI), Cd(II) and Ni(II)] contaminant removal from aqueous solutions.
1.8 REFERENCES


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CHAPTER 1