CHAPTER I

1. INTRODUCTION

Clean drinking water is essential to human and other life forms. Access to safe drinking water has improved steadily and substantially over the last decades in almost every part of the world\textsuperscript{[1]}. There is a clear correlation between access to safe water and GDP per capita \textsuperscript{[2]}. However, some observers have estimated that by 2025 more than half of the world population will be facing water-based vulnerability \textsuperscript{[3]}.

The fast pace of industrialization, galloping demand for energy and reckless exploitation of natural resources during the last century have been mainly responsible for aggravating the problem of environmental pollution, which is now set to pose serious threat to biodiversity and ecosystem processes. The environmental problems in India are growing rapidly. The increasing economic development and a rapidly growing population that has taken the country from 300 million people in 1947 to more than one billion people today is putting a strain on the environment, infrastructure, and the country’s natural resources. Industrial pollution, soil erosion, deforestation, rapid industrialization, urbanization, and land degradation are all worsening problems. Over exploitation of the country's resources either soil or water and the industrialization process has resulted in environmental degradation of resources. Environmental pollution is one of the most serious problems facing humanity and other life forms on our planet today.

Environment consists of the following important components:

(i) Abiotic or nonliving

(ii) Biotic or Living

(iii) Energy components.
The abiotic or physical environment is subdivided into three categories, atmosphere (gaseous envelope), hydrosphere (water component) and lithosphere (solid earth). In resource management, all the factors associated with the environment have to be considered for the welfare of the present and future generations. The activities of the previous generations should not be questionable and detrimental to the current generations and those of the current to the future.

1.1 Water pollution

The hydrosphere includes all types of water resources – oceans, seas, rivers, lakes, streams, reservoirs, glaciers, polar ice caps and ground water. Water is the elixir of life and it is known as ‘Universal solvent’ or the ‘Liquid gold’. Water is one of the materials required to sustain all forms of life. For human beings, the higher animals, its important functions depend on its unique properties as a transport medium for heat and chemical substances and its effectiveness as an evaporative coolant. The other major uses are irrigation, transportation, hydroelectric power generation, industrial manufacturing, recreation and waste disposal.

Water is an indispensable requirement of life, as well as industries, which are working for the betterment of human life and health. Industrialization made a deep impact on human health directly or indirectly creating environment (air, water, soil) pollution by releasing wastes and untreated wastewater, into the environment.

Out of the total water resources, about 97% of the earth’s water supply is from the ocean, where the high salt content does not permit its use for human consumption. Of the remaining 3% water resources, 2% is locked in the polar ice caps and glaciers, while only 1% is available as fresh water (surface water – rivers, lakes, streams and ground water) for human consumption and other uses\[^{4,5}\].
Water pollution is a serious problem to the entire world. It threatens the health and well-being of humans, plants, and animals. Pure, unpolluted water is an essential resource to the environmental balance of the world. Water has life giving properties, which are crucial to the world's global ecosystem.

A substantial proportion of chemical substances in drinking water are of natural origin and results from complex interactions between precipitation (rain), soil and underlying geological strata. Various biological and microbiological processes occurring in soil and water are also important. In addition, there are anthropogenic constituents, which include agricultural chemicals and the components of urban run-off, industrial and domestic wastewater. In fact, virtually any chemical used by man could find its way into water and be detected given a sufficiently sensitive analytical technique.

Drinking water usually contains 50-500 mg/L of dissolved substances although in some arid regions water consumed contains more than 1500 mg/L of total dissolved solids. The dissolved solids consist almost entirely of bicarbonates, sulphates, chlorides and nitrates of calcium and magnesium, normally with low concentration of sodium and potassium. The trace inorganic components of drinking water include iron, manganese, aluminium, and a wide range of trace metals and metalloids including some for which limits have been prescribed on the grounds of toxicity.

Water has long been suspected of being the source of many human illnesses. It was not until approximately 150 years ago that definite proof of disease transmission through water was established. Owing to the development of urban areas, it became necessary, from public health and aesthetic considerations, to provide drainage or sewer systems to carry human wastes away from the area. The normal repository for such wastes was usually the nearest watercourse. This
has led to the major epidemics of cholera and typhoid in many countries during the 19th century, which are attributable to the proliferation of public water supply and waste disposal system. It soon became apparent that rivers and other receiving bodies of water have a limited ability to handle waste materials without creating nuisance conditions. Because of the success in controlling the spread of enteric diseases through the applications of engineering principles, a new concept of the potentialities of preventive medicine was born. For many years the major consideration was to produce adequate water supplies that were hygienically safe.

As population increases, the demand for water grows accordingly and at much more rapid rate if the population growth is to be accompanied by improved living standards. The combinations of these two factors are placing greater and greater stress upon the environment for adequate supplies. In many cases, inferior quality and often-polluted water must be utilized to meet the demand. It is to be expected that this condition will continue and grow more complications as long as population and industrial growth and increased use of agricultural chemicals occur.

To meet the demands of the growing population and the modern living standards, the existing old industries have increased their production enormously and many new industries have started coming up. There is also a dramatic increase in the production and consumption of fertilizers. For instance, the production and consumption of fertilizers (NPK) during 1960-´61 was 150 and 292 thousand tons of nutrients, respectively. This has increased to 11300 and 15665 thousand tons of nutrients during 1995-´96 [6].

Historically, the major concern with regard to pollution of surface waters was their oxygen resources. However, in the past two decades, an increasing concern is the pollution of surface waters and ground waters with other pollutants of primarily industrial or agricultural
origin. The lowland drivers, which are used for water supply, are exposed to effluent disposal by a series of sources and recycling can occur with a consequent increase in the concentration of those components most resistant to biodegradation. The situation can even be worse with ground water supply as in this case the effect of pollution may be everlasting and even irreparable. Today, finished waters after treatment that are free of colour, turbidity, taste, odour, nitrate, harmful metal ions and a wide variety of organic chemicals such as pesticides and chlorinated solvents are required. Health problems associated with some of the chemicals include cancer, birth defects, central nervous system disorders and heart disease. In addition, the public desires water that is low in hardness and total solids, non-corrosive and non-scale forming \[7\].

Surface water and groundwater have often been studied and managed as separate resources, although they are interrelated. Sources of surface water pollution are generally grouped in two categories based on their origin.

1.1.1 Point source pollution: Point source pollution refers to the contaminants that enter a waterway through a discrete conveyance, such as a pipe or ditch. Examples of sources of this category include discharges from sewage treatment plant, factory or a city storm drain.

1.1.2 Non-point source pollution: Non-point source (NPS) pollution refers diffused contamination that does not originate from a single discrete source. Non-point source pollution is often a cumulative effect of small amounts of contaminants gathered from a large area. Nutrient run off in storm water from "sheet flow" over an agricultural field or a forest area are sometimes cited as examples of NPS pollution.
The specific contaminants leading to pollution in water include a wide spectrum of chemicals, pathogens and physical or sensory changes such as elevated temperature and discoloration.

1.1.3 Pathogens: Coliform bacteria are the commonly-used bacterial indicator of water pollution, although not an actual cause of disease. Other microorganisms sometimes found in surface waters which have caused human health problems include, Cryptosporidium parvum, Giardia lamblia, Salmonella, Novo virus and other viruses, Parasitic worms[^8,9].

1.1.4 Chemicals and other contaminants:

Contaminants may include organic and inorganic substances.

Organic water pollutants are:

- Detergents
- Disinfection by-products such as chloroform.
- Food processing waste, which can include oxygen-demanding substances, fats and grease.
- Insecticides and herbicides, a huge range of organohalides and other chemical compounds.
- Petroleum hydrocarbons, including fuels (gasoline, diesel fuel, jet fuels, and fuel oil) and lubricants (motor oil), and fuel combustion byproducts, from stormwater runoff[^10].
1.1.5 Effect of Water Pollution

Waterborne diseases caused by polluted drinking water are Typhoid, Amoebiasis, Giardiasis, Ascariasis and Hookworm and by polluted beach water rashes, ear ache, pink-eye, respiratory infections, hepatitis, encephalitis, gastroenteritis, diarrhoea, vomiting, and stomach ache.

Water polluted by chemicals (such as pesticides, hydrocarbons, persistent organic pollutants, heavy metals, etc.) causes cancer, non-Hodgkin’s lymphoma, hormonal problems that can disrupt reproductive and developmental processes, damage to the nervous system, liver, kidney and DNA.

Nutrients from fertilizers such as Nitrogen, phosphates etc. cause overgrowth of toxic algae. Oil pollution affects the development of marine organisms. Environmental pollution causes a lot of distress not only to humans but also to animals, driving many animal species to endangerment and even extinction \[11\].

1.2 Heavy metal pollution

Pollution from human made sources creates the conditions wherein metal presence is elevated to toxic levels in natural water resources. The major causes of water pollution include sewage, waste water, industrial waste, marine dumping, radioactive waste, oil pollution, underground storage leakages, atmospheric deposition and global warming. Now, water pollution has become a major problem globally and a leading cause of diseases worldwide with approximately 14000 people daily losing life because of water pollution \[12, 13\].

Heavy metals, though natural in origin, have been considered as pollutant in view of their dislocation from the geological sources, use in various spheres of human activities, consequent
higher concentration in many compartments of the total environment, transport through unusual path ways and affects target and non-target organisms based on their role and concentration in them. Living organisms require varying amounts of "heavy metals". Iron, cobalt, copper, manganese, molybdenum and zinc are required by humans. Excessive levels can be damaging to the organism. Other heavy metals such as mercury, plutonium, and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can cause serious illness.

1.2.1 Toxicity of Heavy Metals

The power of toxicity differs from metal to metal. Toxicity of some important heavy metals are given below:[14]

**Copper (Cu):** Excess of Cu (470 mg) in human body is toxic and causes hypertension, sporadic fever, uremia, coma and even death. Cu also produces pathological changes in brain tissue.

**Silver (Ag):** Excess of Ag (100 mg) in human body causes changes in blood cells, gastroenteritis, diarrhoea, and fall in blood pressure and decrease in respiration.

**Gold (Au):** Soluble gold compounds are toxic. Au toxicity in man is fever, violent diarrhoea, gastritis, colitis.

**Zinc (Zn):** Zinc salts are relatively non-toxic but heavy doses (165 mg) for 26 days cause vomiting, renal damage and cramps. Inhalation of air containing ZnO at 1-34 mg /m³ causes metal fume fever and pneumonitis in humans.

**Cadmium (Cd):** Cigarette-smoke inhalation is a source of exposure of Cd. The total Cd in cigarette smoke varies from 10 to 18 µg per 20 cigarettes. Cadmium dust, fumes and mists pollute the atmosphere in zinc, Cu, and lead industries. Cadmium is toxic to all men and animals. Cd toxicity (50 mg) causes vomiting, diarrhoea, abdominal pains and loss of consciousness. It
also causes growth retardation, bone deformation, impaired kidney functioning, impaired reproductive function, hypertension, tumor formation and teratogenic effects. Inhalation Cd causes choking, coughing, bronchitis and damage to renal tissues.

**Mercury (Hg):** Hg containing insecticides and fungicides causes Hg toxication. The retention of absorbed Hg in soft tissues is high and follows the distribution: Kidney > liver > intestinal and colon walls > brain > heart > lung > respiratory mucosa > skin. The kidney retains maximum concentration of Hg in human body. Mercury and its salt toxicity are worldwide problems. Hg is found in water due to the disposal of industrial mercury waste. Excess of Hg (more than 100 mg) may cause headache, abdominal pain, diarrhoea, haemolysis and tremors. Hg vapour causes acute tightness and pain in chest causing great difficulty in breathing. Hg compounds affect central nervous system also.

**Lead (Pb):** About 800 mg of Pb creates toxicity in human beings. The toxicity symptoms are mild anemia, brain damage, vomiting, loss of appetite, convulsion, unco-ordinated body movements and stupor, eventually producing coma and death (when Pb > 500 mg). Lead toxicity is due to the formation of metallothionein.

**Chromium (Cr):** It is used in industries in the manufacture of steel, jet engines, tools, paints, photography, electric cell, rubber goods and matches. Trivalent Cr is least toxic of trace elements while hexavalent Cr (greater than 70 mg) is very toxic. It causes cancer, anuria, nephritis, gastrointestinal ulceration and affects central nervous system.

**Manganese (Mn):** It is least toxic of essential metals. At concentration greater than 100 ppm, Manganese is toxic both to man and mammals. It causes growth retardation, fever, sexual importance, muscular fatigue and eye blindness. Permanganate appears to be the most toxic
among Mn forms when given intravenously and MnO4⁻ ion is less toxic by subcutaneous route. Divalent Mn²⁺ ion is 3 times more toxic than Mn³⁺ ion.

**Iron (Fe):** More than 10 mg/kg level) causes rapid increase in respiration, pulse rates, congestion of blood vessels, hypertension and drowsiness.

**Cobalt (Co):** High doses (27 mg) cause paralysis, diarrhoea, low blood pressure, lungs irritation and bone defects.

**Nickel (Ni):** Small amount of Ni is non-toxic but higher amount (more than 30 mg) may cause changes in muscle, brain, lung, liver and kidney function and can also result in cancer. Sometimes it causes tremor, paralysis and even death.

Heavy metal pollution can arise from many sources but most commonly from the purification of metals and preparation of nuclear fuels. Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation. Some well-documented environmental disasters associated with heavy metals are Minamata disease and heavy metal waste thrown into the Mississippi River from 1986 to 1996.

In medical usage, heavy metals are loosely defined\(^{[15]}\) and include all toxic metals irrespective of their atomic weight: "heavy metal poisoning" can possibly include excessive amounts of iron, manganese, aluminium, mercury or beryllium (the fourth lightest element) or semi-metal such as arsenic. This definition excludes bismuth, the heaviest of stable elements, because of its low toxicity.

### 1.2.2 Health Effects Due To Heavy Metals

The international community is beginning to recognize the adverse health effects of heavy metals \(^{[16]}\). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver,
and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals (or their compounds) may cause cancer. For some heavy metals, toxic levels can be just above the background concentrations naturally found in nature. Therefore, it is important to learn about heavy metals and take protective measures against excessive exposure\textsuperscript{[17]}.

Heavy metals are associated with myriad adverse health effects, including allergic reactions (e.g., beryllium, chromium), neurotoxicity (e.g., lead), nephrotoxicity (e.g., mercuric chloride, cadmium chloride), and cancer (e.g., arsenic, hexavalent chromium). Humans are often exposed to heavy metals in various ways—mainly through the inhalation of metals in the workplace or polluted neighborhoods, or through the ingestion of food (particularly seafood) that contains high levels of heavy metals or paint chips that contain lead\textsuperscript{[18]}.

\section*{1.3 Dye Pollution}

Dyes are the most important class of water pollutants emanated from textile as well as from dye manufacturing industries. Based on Chemical composition, dyes are grouped into azo, nitro, diphenyl methane, tri phenyl methane, anthraquinone dyes etc.\textsuperscript{[19]}.

Dyes are problematic due to their high water solubility and low bio degradability\textsuperscript{[20]} and they interfere with the transmission of sunlight into stream thereby reducing the photo synthesis activity\textsuperscript{[21]}. 
Frequent charges of dye and Chemicals in the dyeing process are reported to cause considerable variation in the wastewater characteristics like pH, BOD and COD. Large swing in pH of recipient water is especially troublesome.

Dyes or dyestuffs are coloured substances capable of imparting their colour, fast to light, water, soap, etc., to the fibres. The first synthetic dyestuff was prepared in 1856 by W.H. Perkin called Perkin’s violet dye, commonly known as mauve. This discovery stimulated the study and research on the synthetic dyes and the progress was very rapid. Through hundreds of years, the scale of production and nature of dyes changed drastically and now it has been estimated that there are more than 3000 dyes in use worldwide. Dyes are widely used in textile, paper, carpet, printing, leather, food and cosmetic industries. Some dyes are also used in medicine and biological stains and for colouring plastics, gasoline, varnish, fats, oils and waxes. Textile mills engaged in dyeing nylon, polyacrylonitrile modified nylon, wool, silk and cotton is the main consumer of dyes.

The dye-bearing wastewaters are disposed in two ways: (i) into the sewer and (ii) into a nearby river/stream. In many cases, the effluent is discharged into a sewer to be treated with other domestic and industrial wastes. In the absence of any sewer passing sufficiently nearby the effluent is discharged to a river or a stream. In either case, restrictions are likely to be applied limiting the concentration or load of contaminants that may be discharged.

The problems of discharging these wastewaters are compounded by the concentration of dyestuff industries/dyeing units in small areas. For example, in India the dyestuff industries are concentrated in the western states of Maharashtra and Gujarat, accounting for over 90 percent of the dyestuff's production in the country. Similarly, most of the dyeing units are concentrated in cities like Coimbatore, Tirupur, Erode and Karur, situated in southern part of
India. In Tirupur alone, there are around 500 dyeing industries[^26] and the effluent from those industries has already started polluting the ground waters making them unfit for any use.

Recent estimates indicate that, approximately, 12% of synthetic textile dyes used each year is lost during manufacture and processing operations and that 20% of these lost dyes enter the environment through effluents that result from the treatment of residual industrial waters. Though the dye bearing wastewaters contain various pollutants, the most obvious impact is the high degree of colour that the residual dye often imparts. Dyes being one of the important recalcitrant, colour persists for long distances in flowing waters, retards photosynthetic activity in streams, inhibits the growth of aquatic biota, decreases recreational value of the streams and has a tendency to sequester metal ions producing micro toxicity to fish and other organisms[^27].

Many dyes are visible in water at concentrations as low as 1 mg L\(^{-1}\). Textile-processing wastewaters, typically with dye content in the range 10-200 mg L\(^{-1}\)[^28] are therefore usually highly colored and discharge in open waters presents an aesthetic problem. As dyes designed to be chemically and photolytically stable, they are highly persistent in natural environments. The majority of dyes pose a potential health hazard to all forms of life. These dyes may cause allergic responses, skin dermatoses, eczema (Su and Horton, 1998), and may affect the liver, the lungs, the vasco-circulatory system, the immune system and the reproductive system[^29] of experimental animals as well as human systems.

Dyes with azo bonds nitro-or amino-groups are carcinogenic, causing tumors of liver and urinary bladder in experimental animals[^30]. However, reduction of azo dyes, i.e. cleavage of the dye's azo linkage(s), leads to formation of aromatic amines and several aromatic amines are known mutagens and carcinogens. In mammals, metabolic activation (reduction) of azo dye is
mainly due to bacterial activity in the anaerobic parts of the lower gastrointestinal tract. Various other organs, especially the liver and the kidneys, can, however, also reduce azo \textsuperscript{[31]}. 

The toxicity of aromatic amines depends on the nature and location of other substituents. As an example the substitution with nitro, methyl or methoxy groups or halogen atoms may increase the toxicity; whereas substitution with carboxyl or sulphonate groups generally lower the toxicity\textsuperscript{[32]}.

1.3.1 Toxicological Aspect of dyes

Textile dyes are generally aromatic compounds and may consist of some heavy metals embodied in their structure. The complex aromatic frame work of dyes and presence of heavy metals induce toxicity in particular and they may be mutagenic, teratogenic or carcinogenic \textsuperscript{[33]}. Dyes were reported to cause chromosomai fractures and respiratory toxicity too.

McGeorge et al. \textsuperscript{[34]} reported the mutagenic activity of textile effluents using the Salmonalla/microsome assay. Costan et al.\textsuperscript{[35]} found that a textile effluent ranked second in toxicity, among eight industrial sectors represented by using a series of bio-assays assessing the acute, sub lethal and chronic toxicity at various tropic levels. The highest rates of toxicity were found amongst basic and diazo direct dyes \textsuperscript{[36]}. Sub-chronic exposure (13 weeks) to Benzedrine-based dyes resulted in hepatocellular carcinomas and hepatic neoplastic nodules in rats \textsuperscript{[37,38]}. Histopathological changes in the tests of rats exposed to textile waste water caused reduction in the number of germs and leydigcells, resulting in impaired spermatogenesis \textsuperscript{[39]}.

Epidemiology studies of workers in the dye industry have historically shown increased incidents of bladder tumors. For instance, as increase in bladder cancer has been shown to occur in Kimino painters who had the practice of licking their brushes \textsuperscript{[40]}. A study carried out by
Rajaguru et al.\textsuperscript{[41]} indicates that the ground water contaminated with dyeing effluents in Tirupur area is capable of inducing DNA damage in human cells.

1.4 Need for the water Treatment

Chemicals are discharged through effluents from industrial sources to surface water bodies and infiltrate into drinking water sources. The chemicals accumulate in the sediments of water bodies are flushed out in the event of high water flow. Many industrial chemicals are toxic even at relatively low concentration and water polluted by industrial activities often contains a number of different toxic chemicals. The extent to which chemicals can be removed before the water reaches the consumer will depend on the nature of the decontamination and type of treatment processes used.

1.4.1 Water treatment Technologies

A variety of methods have been developed for the removal of trace inorganics and organics from water and waste water. The methods include precipitation, evaporative and electrolytic recovery, solvent extraction, cementation, reverse osmosis, electro dialysis, ion exchange and adsorption.

**Precipitation** method is one of the oldest and most widely used methods for the removal of metals from waste water. Many reagents have been applied for precipitation purposes and these include caustic soda, hydrated lime, soda ash and sodium sulphide to precipitate the metal ions as insoluble hydroxides, carbonates and sulphides\textsuperscript{[42-48]}. However, problems can arise due to the incomplete removal of the precipitated metal form the treated effluent. As the sludge is disposed of as landfills, it could lead to contamination of ground water when conditions are favorable for their dissolution.
There are reported literature about utilizing evaporative recovery method for the removal of copper\textsuperscript{[49]}, cadmium\textsuperscript{[50]}, nickel\textsuperscript{[51]} and zinc \textsuperscript{[52]}. However, there is a possibility of retaining all the non-volatile constituents of the waste water which is considered a major drawback. Solvent extraction involves equilibrium distribution of an analyte between a liquid phase and a solid phase. However, this method is not commercially viable. Cementation process involves percolation of wastewater containing copper, through a bed of scrap iron and as a result copper cements onto iron\textsuperscript{[53,54]} cementation is suitable only for small waste water flow because of long contact time required. The main disadvantage of the process is the consumption of the solid metals as reducing agents and the redox potentials \textsuperscript{[55]}.

The direct electrolytic process is successfully followed to recover copper from copper pickling and brass pickling bath.\textsuperscript{[56]} This process consumes high electrical power and hence cannot be adopted for the treatment of dilute wastes. In addition, a pre concentration step, ion-exchange or evaporative recovery prior to this process is needed\textsuperscript{[57]}. The major advantage of this process is the creation of a large surface area per unit volume and the major disadvantage is the development of a low current density on the electrode surface.

**Electro dialysis** is an economically feasible treatment process for metal recovery from rinsed waters of plating and metal finishing operations\textsuperscript{[58]}. But its usage is limited, due to the requirement of pretreatment, primarily for the removal of suspended solids. Membranes are susceptible to fouling and must be replaced \textsuperscript{[59]}.

**Ion exchange method** is a reversible process that facilitates the removal of anionic and cationic constituents present in water by exchange with the ions of the resin \textsuperscript{[60-66]}. When the resin bed becomes saturated it is regenerated using acid or alkali. The economic limitations of the process come from the initial investment cost. The presence of complex forming species,
however, can interfere with the exchange process. In addition, the fouling of resin bed with wetting agents and organic brighteners used in plating, clogging due to precipitated hardness of water and oxidation of resin by oxidizing agents, if present, are some of the frequent problems associated with ion exchange method.

**Nano filtration** is a relatively recent membrane filtration process used most often with water containing low total dissolved solids such as surface water and fresh groundwater, with the purpose of softening (poly valent cation removal) and removal of disinfection by-product precursors such as natural organic matter and synthetic organic matter \[^{67,68}\]. Filtration is more widely used in food processing applications. It is used in the removal of contaminants from a water source, it is also commonly used for desalination but leaves the water devoid of essential nutrients like (calcium, magnesium ions, etc.), placing the nutrient levels below that of the required WHO standards and the researchers had to go back and add nutrients to bring solute levels to the standard levels for drinking water consumption. Further it is a very inexpensive method compared to conventional treatment systems \[^{69}\].

**Ultra filtration** is a variety of membrane filtration in which hydrostatic pressure forces a liquid against a semi permeable membrane. Suspended solids and solutes of high molecular weight are retained, while water and low molecular weight solutes pass through the membrane. This separation process is used in industry and research for purifying and concentrating macro molecular (103 - 106 Da) solutions, especially protein solutions. Ultrafiltration is not fundamentally different from microfiltration or nanofiltration, except in terms of the size of the molecules it retains. Ultra filtration is not effective in separating organic streams. It is very prone to membrane fouling caused by increased solute concentration at the membrane surface (either by macromolecular adsorption to internal pore structure of membrane, or aggregation of protein
deposit on the surface of membrane), which leads to concentration polarization which is the major culprit in decreasing permeate flux \[70\].

**Reverse osmosis** is a filtration process that is often used for water. It works by using pressure to force a solution through a membrane, retaining the waste water on one side and allowing the pure solvent to pass to the other side. This is the reverse of the normal osmosis process. The main limitations of Reverse Osmosis are the effects of physical conditions such as pH and temperature and chemical properties such as membrane-chemicals interaction and fouling. High capital costs, incomplete treatment of the effluent, presence of all impurities of the effluent in the concentrate and need for alternate technology for effective purification of the concentrate are some of the disadvantages of Reverse Osmosis.

**Adsorption** is the accumulation of atoms or molecules on the surface of a material. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the adsorbent's surface. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both the processes, while desorption is only the reverse process. Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins, and water purification. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption.
(characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding) [71].

1.5 Adsorbents

Adsorbents are used usually in the form of spherical pellets, rods, mouldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapours.

Most industrial adsorbents fall into one of the three classes:

- Oxygen-containing compounds – are typically hydrophilic and polar, including materials such as silica gel and zeolites.
- Carbon-based compounds – are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.
- Polymer-based compounds - are polar or non-polar functional groups in a porous polymer matrix.

Activated carbon is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the adsorbing properties of the material [72].

Activated carbon is produced from carbonaceous source materials like nutshells, wood and coal. It can be produced in one of the following processes:

**Physical reactivation**: The precursor is developed into activated carbons using one or a combination of the following processes:
✓ Carbonization: Material with carbon content is pyrolyzed at temperatures in the range 600-900 °C, in absence of air (usually in inert atmosphere with gases like argon or nitrogen)

✓ Activation/Oxidation: Raw material or carbonised material is exposed to carbon dioxide, oxygen, or steam at temperatures above 250 °C, usually in the temperature range of 600-1200 °C.

Chemical activation: Prior to carbonization, the raw material is impregnated with certain chemicals. The chemical is typically a strong acid, strong base, or an salt (phosphoric acid, potassium hydroxide, sodium hydroxide, zinc chloride, respectively). Then, the raw material is carbonized at lower temperatures (450-900 °C). It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. This technique can be problematic in some cases, because, for example, zinc trace residues may remain in the end product. However, chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material.

1.5.1 Applications

Activated carbon is used in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and filter masks, filters in compressed air and many other applications.

One major industrial application involves the use of activated carbon in metal finishing field. It is very widely employed for the purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions.
Environmental applications Carbon as adsorbent has numerous applications in removing pollutants from air or water streams both in the field and in industrial processes such as: Spill cleanup, Groundwater remediation, Drinking water filtration, Air purification, Volatile organic compounds capture from painting, dry cleaning, gasoline dispensing operations, and other processes. Activated charcoal is also used for the measurement of radon concentration in air.

**Medical applications:** Activated carbon is used to treat poisonings and overdoses following oral administration \(^{[73]}\).

**Fuel Storage:** Research is being done in testing the ability of various activated carbons to store natural gas and hydrogen gas.

**Gas purification:** Filters with activated carbon are usually used in compressed air and gas purification to remove oil vapours, odours, and other hydrocarbons from the air.

**Distilled alcoholic beverage purification:** Activated carbon filters can be used to filter vodka and whisky of organic impurities which can affect color, taste, and odours.
1.6. Review of Literature

Commercial activated carbon is a preferred adsorbent for the removal of micro pollutants from the aqueous phase; however, its widespread use is restricted because of high cost. To decrease treatment costs, attempts have been made to find inexpensive alternative activated carbon (AC) precursors, such as waste materials from plant biomass, animal kingdom, industrial wastes and natural sources like ores, minerals etc., Considerable work has been carried out on the use of both natural materials and their modifications.

Dias et al.\cite{74} reviewed the preparation of activated carbons by recycling different types of waste materials and also their application in various aqueous-phase treatments and found that conventional (from agriculture and wood industry) and non-conventional (from municipal and industrial activities) wastes can be used to prepare activated carbons, that can be applied in various aqueous treatment processes, namely to remove organic pollutants, dyes, volatile organic compounds, and heavy metals.

David William O'Connell et al.\cite{75} reviewed the current state of research on the use of the naturally occurring material cellulose, its modified forms and their efficacy as adsorbents for the removal of heavy metals from waste streams. Adsorbents based on direct modification of cellulose were evaluated initially and subsequently modifications resulting from the grafting of selected monomers to the cellulose backbone with subsequent functionalization were also assessed. The heavy metal adsorption capacities for those modified cellulose materials were found to be significant and levels of uptake were comparable, in many instances, between other naturally occurring adsorbent materials and commercial ion exchange type resins.
Jonathan Febriantoa and co-workers\textsuperscript{[76]} reviewed the biosorption of heavy metals, summarized the essential issues and reported that most studies on the biosorption of heavy metal ions by miscellaneous biosorbent types have been directed toward the uptake of single metal ion in preference to multi component systems. In particular, Langmuir and Freundlich models were the most common isotherms for correlating biosorption experimental data though other isotherms, which were initially established for gas phase applications, can also be extended onto biosorption system. In kinetic modeling, the pseudo-first and pseudo-second order equations were considered.

Sarabjeet Singh et al.\textsuperscript{[77]} reviewed the utilization of microbial and plant derived biomass and explored the possibility of exploiting them for heavy metal remediation and reported that biomass of Aspergillus niger, Penicillium chrysogenum, Rhizopusnigricans, Ascophyllum nodosum, Sargassummatans, Chlorella fusca, Oscillatoria angustissima, Bacillus firmus and Streptomyces sp. have highest metal adsorption capacities ranging from 5 to 641 mg/ g mainly for Pb, Zn, Cd, Cr, Cu and Ni ions.

Chun Yang Yin et al. \textsuperscript{[78]} reviewed a comprehensive list of literatures on chemical, physical and biological modification techniques of activated carbon pertaining to enhancement of contaminant removal from aqueous solutions. The precursors used for the preparation of activated carbons are numerous and it is not possible to go into the details of each adsorbent and their efficiency but the author discussed it briefly.

Shalini Srivastava et. al.\textsuperscript{[79]} explored sorption properties of the plant Moringa oleifera Lam, for decontamination of Cd. The adsorption data accurately fitted in a Freundlich isotherm.
Fourier transform infrared (FTIR) spectrometry highlighted amino acid–Cd interactions responsible for sorption phenomenon.

Contreras et al.\textsuperscript{[80]} studied the effect of another biosource (silica) on the removal to remove lead using the continuous flow column experiment. He found that the binding capacity of the adsorbent has shown considerable advantage where the results of this study showed that the new biosource is an inexpensive adsorbent for Pb removal from contaminated water even in the presence of other hard cations like Ca and Mg.

Biosorption equilibrium and kinetics of Cd\textsuperscript{2+} and Cu\textsuperscript{2+} ions on wheat straw Triticum aestivum, in an aqueous system were investigated by Dang et al.\textsuperscript{[81]} Among the models tested, namely Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms, the biosorption equilibrium for both Cd\textsuperscript{2+} and Cu\textsuperscript{2+} was best described by Langmuir model. The Langmuir biosorption capacity for Cd\textsuperscript{2+} was about 27\% higher than that for Cu\textsuperscript{2+}. It was also found that biosorption of Cd\textsuperscript{2+} and Cu\textsuperscript{2+} by wheat straw followed second- order kinetics. The equilibrium amount of metal ions adsorbed onto the wheat straw increased with the increase of pH from 4.0 to 7.0, and the effect was more pronounced for Cd\textsuperscript{2+} than for Cu\textsuperscript{2+}. Increase of temperature from 25 to 30°C enhanced the biosorption of Cd\textsuperscript{2+} and Cu\textsuperscript{2+} slightly. The above facts indicated the biosorption of Cd\textsuperscript{2+} and Cu\textsuperscript{2+} by wheat straw might follow a chemisorption mechanism.

The rate of removal of Cu (II) ions from aqueous solution by mercaptoacetic acid modified cassava wastes (0.5MCF and 1.0MCF) was studied by Augustine et al.\textsuperscript{[82]} in batch conditions. The rate of sorption of copper ion was rapid initially within 5-15 minutes and reached a maximum in 30 minutes. Kinetic modeling analysis showed that the pseudo-second order
equation was the most appropriate model for the description of Cu (II) transport with chemical sorption as its rate-limiting step.

Stephen Inbaraj et al.\textsuperscript{[83]} investigated the adsorption of mercury (II) by an extra cellular biopolymer, poly (γ-glutamic acid) (γ-PGA) and reported that an appreciable adsorption occurred at pH > 3 and reached a maximum at pH 6. Isotherms were well predicted by Redlich–Peterson model with a dominating Freundlich behaviour, implying the heterogeneous nature of mercury (II) adsorption. The adsorption followed an exothermic and spontaneous process with increased orderliness at solid/solution interface. The adsorption was rapid with 90% being attained within 5 min for 80 mg/L mercury (II) solution, and the kinetic data were precisely described by pseudo second order model. Ionic strength due to added sodium salts reduced the mercury (II) binding with the coordinating ligands following the order: Cl\textsuperscript{−} > SO4\textsuperscript{2−} > NO3.\textsuperscript{−}

Both light and heavy metal ions decreased mercury (II) binding by γ-PGA, with calcium (II) ions showing a more pronounced effect than monovalent sodium and potassium ions, while the interfering heavy metal ions followed the order: Cu\textsuperscript{2+} > Cd\textsuperscript{2+} > Zn\textsuperscript{2+}.

Satarug\textsuperscript{[84]} has stated the health effects of chronic exposure to low-level cadmium in foods and cigarette smoke as a result of bioaccumulation in the human body. The levels of Cd in organs such as liver and kidney increase with age. Cd persists in kidneys of humans for many years where the half life time could be estimated to be 30 years. This has been associated with occurrence of Cd toxicity, and increase in mortality risk by 40-100%. Besides, an excess amount of Cd may tend to pathologies such as renal failure, diabetics, and osteoporosis.

Wan Ngah and Hanafiah\textsuperscript{[85]} listed the advantages of using untreated plant wastes vs. chemically modified biosorbents as low-cost, selective for metals, simplicity of process, and easy
regeneration, and the disadvantages as mediocre adsorption capacities and release of some soluble organic compounds presented in the plant, which may affect the COD or BOD of the treated water.

Kadirvelu [86] stated that parameters such as agitation time, metal ion concentration, adsorbent dose and pH will affect the adsorption of lead from aqueous solution to the adsorbent. He also found that the adsorption equilibrium was reached in 100 min for a solution containing 15 mgdm$^{-3}$ and 125 min for a solution containing 20 and 25 mgdm$^{-3}$ Pb(II) respectively. Moreover, he noted that the lead removal increases from pH 2 to 4 while it remains constant up to pH 10.0.

Adsorption behaviour of natural (clinoptilolite) zeolites with respect to Co$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$ was studied by Erdem et al. [87] to consider its application to purity metal finishing waste waters. The batch method was employed, using metal concentrations in solution ranging from 100 to 400 mg/L. The percentage adsorption and distribution coefficients (Kd) were determined for the adsorption system as a function of sorbate concentration. It was found that the adsorption phenomena depended on charge density and hydrated ion diameter.

Some granular activated carbons (GACs) were prepared by Jaramillo et al. [88] from cherry stones (CS), an agricultural waste by thermal methods following pyrolysis in nitrogen and subsequent activation (with air, carbon dioxide and steam) or single-step activation in steam. A GAC prepared by activation with carbon dioxide was further treated with several oxidizing agents (air, air–ozone mixture, nitric acid and hydrogen peroxide). Both the non-oxidized and the oxidized GACs were used as adsorbent to study the adsorption of Cu (II) from aqueous solution. Adsorption isotherms data were well fitted to Langmuir equation and the adsorption capacity for
Cu (II) was greatly enhanced by GAC oxidation, especially with nitric acid and ozone treatments. The larger adsorption capacity of the oxidized GACs was attributed to oxygen functionalities (mainly carboxylic) fixed on the GAC surface, which can remove Cu (II) species from water by both ion-exchange and surface complexation mechanisms.

The removal of Pb(II) and Pb(II)-citric acid (Pb (II)-CA) from aqueous solutions by sawdust activated carbon (SDAC) was investigated by Sreejalekshmi et al.\textsuperscript{[89]} The higher adsorptive removal of Pb (II) from aqueous solutions containing Pb (II)-CA than Pb (II) only was observed. The adsorption was maximum for the initial pH in the range of 6.5–8.0 and 2.0–5.0 for Pb (II) and Pb (II)-CA, respectively. The solution pH, zero point charge (pHzpc) and species distribution of Pb(II) and Pb(II)-CA were found to play an important role in the adsorption process. The kinetic and equilibrium adsorption data were well modelled using pseudo-first-order kinetics and Langmuir isotherm model respectively.

The adsorption of Cu (II) ions from aqueous solutions by hazel nut shell activated carbon (HSAC) was studied by Demirbas et al.\textsuperscript{[90]} The adsorption process was relatively fast and equilibrium was established in about 90 min. Maximum adsorption of Cu (II) ions occurred at around adsorption system was best described by the pseudo second-order kinetics. Desorption efficiencies in four cycles were found to be in the range 74–79%. The calculated thermodynamic parameters showed that the adsorption was endothermic and physical in nature.

Ong-Yung Wang et al.\textsuperscript{[91]} investigated the effects of manufacturing conditions on the adsorption capacity of heavy metal ions by Makino bamboo charcoal. Results showed that the specific surface area and iodine number of bamboo charcoal activated at 900 °C were larger than those of bamboo charcoal activated at 800 °C. The specific surface area of bamboo charcoal
activated at 800 °C by carbon dioxide was larger than that of charcoal activated by steam. However a contrary result was observed when the activation temperature was 900 °C.

The adsorption by activated carbons was investigated as a method to recover metal ions from acid mine drainage by Mohan and S. Chander [92] studied the adsorption of ferrous, manganese, zinc and calcium in single, binary, ternary, and quaternary systems. Concerned adsorption capacities were compared in single, binary, ternary and multi-component systems for different types of activated carbons. The adsorption data fitted Freundlich and Langmuir isotherms in most of the cases. The results indicated that Langmuir isotherm fits the data better in single component systems whereas the Freundlich is better in multi-component systems.

Cadmium sorption behaviour of granular activated carbon oxidized with nitric acid was systematically studied by Xin Huang et al. [93] The cadmium adsorption capacity of oxidized granular activated carbon increased with an increase in pH, and reduced with an increase in ionic strength. Adsorption processes were found to follow pseudo-second order rate equation. Adsorption isotherms correlated well with Langmuir isotherm model and Equilibrium constant Kd was evaluated. The values ∆H0 and ∆G0 values indicated the adsorption process was exothermic and spontaneous. The standard entropy ∆S0 was also negative, which suggested a decrease in the freedom of the system.

The effect of temperature on the adsorption of Mn (II), Ni(II), Co(II) and Ni(II) from aqueous solution by modified carrot residues (MCR) was investigated by Fuat Güzel et al. [94] Kinetic data obtained for each heavy metal by MCR at different temperatures were applied to Lagergren equation, adsorption rate constants (kad) at these temperatures and activation energies (Ea) were determined. Isothermal data were applied to linear forms of isotherm
equations that they fitted Langmuir adsorption isotherm, thermodynamic parameters were calculated and the values showed that the adsorption of heavy metal on MCR was endothermic.

Sulayman et al. [95] has investigated the removal of copper form aqueous solution using granular activated carbon in a fixed bed volume. The granular activated carbon was found to be suitable adsorbent for the removal of Pb, Cu, Cr and Co from aqueous solution. The study showed that as the flow rate and the initial metal ion concentration increase, and the bed height decreases, the time of the breakthrough point decreases.

Low-cost activated carbon prepared from Ceiba pentandra hulls, an agricultural waste material, for the removal of lead and zinc from aqueous solutions was investigated by Madhava Rao et al. [96] the adsorbent exhibited a good sorption potential at pH 6.0.

Xue-Fei Sun et al. [97] Studied the biosorption characteristics of a cationic dye, Malachite Green (MG), onto aerobic granules. Results showed that alkaline pH was favorable for the biosorption of MG and chemisorption seemed to play a major role in the biosorption process. Kinetic studies indicated in the system followed the pseudo-second order kinetics. The equilibrium time was 60 min for both 50 and 60 mg/L and 120 min for both 70 and 80 mg/L MG concentrations respectively. Langmuir isotherm was found to provide the best theoretical correlation of the experimental data for the biosorption of MG.

Hameed and El-Khaiary [98] studied the potential feasibility of rice straw-derived char (RSC) for removal of C.I. Basic Green 4 (malachite green (MG)), from aqueous solution. Equilibrium process was described well by Langmuir isotherm model. The kinetics of MG sorption on RSC followed the Lagergren's pseudo-first-order model and the overall rate of dye
uptake was found to be controlled by external mass transfer at the beginning of adsorption, while intra particle diffusion controlled the overall rate of adsorption at a later stage.

Dizge, et al.\cite{99} studied the adsorption kinetics of three reactive dyes namely, Remazol Brilliant Blue (RB), Remazol Red 133 (RR) and Rifacion Yellow HED (RY) from aqueous solutions on fly ash (FA). Adsorption of RB reactive dye was found to be pH dependent but both RR and RY reactive dyes were not. The values of Langmuir and Freundlich constants were found to increase with the increasing temperature and found that the reaction was spontaneous and endothermic in nature.

Shaobin Wang and Eko Ariyanto \cite{100} employed a natural zeolite as adsorbent for the removal of malachite green and Pb$^{2+}$ ions from aqueous solution. Single and binary systems were carried out. The single component system followed the first-order kinetics and the adsorption was diffusion process with single-stage for Pb$^{2+}$ and two-stages for malachite green. For the single component system, malachite green adsorption isotherm followed Langmuir model while Pb$^{2+}$ adsorption followed the Freundlich isotherm. In the binary system, Pb$^{2+}$ exhibited higher affinity and selectivity to be adsorbed on zeolite. The dynamics adsorption of malachite green and Pb$^{2+}$ followed the first-order kinetics.

Y. Önal et al.\cite{101} prepared activated carbon (T3K618) from Lignite by chemical activation with KOH. Adsorption capacity of malachite green (MG) onto T3K618 activated carbon was investigated and found that the adsorption process was relatively fast and equilibrium was reached after about 20 min. for 100, 150 mg/L at all adsorption temperature. Equilibrium time for 200 mg/L was determined as 20 min. and 40 min. at 298, 313 and 323 K, respectively. Pseudo second-order model was found to explain the kinetics of MG
adsorption most effectively. The activation energy (Ea) was determined as 48.56, 63.16, 67.93 kJ/mol for 100, 150, 200 mg/L, respectively. The adsorption process was found to be endothermic.

K.Porkodi and K.Vasanth Kumar [102] investigated the sorption of eosin yellow, malachite green and crystal violet onto jute fiber carbon (JFC). Langmuir isotherm was found to be the optimum isotherm for eosin yellow/JFC system and Freundlich isotherm was found to be the optimum isotherm for malachite green/JFC and crystal violet/JFC systems at equilibrium conditions. A pseudo second order kinetic model well represented the kinetic uptake of dyes studied onto JFC.

B.H.Hameed, A.T.M.Din and A.L.Ahmad [103] carried out adsorption of methylene blue by bamboo-based activated carbon. Bamboo was used to make activated carbon by physiochemical activation with potassium hydroxide and carbon dioxide. Adsorption models and kinetic studies were also conducted and it was found that pseudo second-order model best described the process.

R.A.Shawabkeh and E.S.M. Abu-Nameh [104] performed study of adsorption of phenol and Methylene Blue by activated carbon from pecan shells. Activated carbon was prepared from pecan shells by chemical activation with phosphoric acid. Then it was treated with sodium dodecyl sulfate to prepare the surface for adsorption. The results indicated good removal of phenol and Methylene Blue dye by pecan shells.

The removal of methylene blue using treated and untreated activated carbon was investigated by Yasin, Hussein and Ahmad [105]. The effects of various experimental parameters like contact time, pH of the solution and adsorbent dosage were studied. It was found
that the amount of methylene blue removal increased with the increase in contact time, solution pH and amount of adsorbent used. The data obtained best fitted the Langmuir isotherm plot.

Gregorio Crini, et al. [106] carried out Batch sorption experiments for the removal of C.I. Basic Green 4 (Malachite Green) from its aqueous solution using cyclodextrin-based material (CD/CMC material) as adsorbent. Sorption of dye reached equilibrium in 120 min. and found that the adsorption kinetics followed a pseudo-second-order suggesting that the rate-limiting step may be chemisorption.

Renmin Gong et al. [107] investigated the effect of chemical modification of rice straw on the cationic dye sorption. They modified the rice straw thermo chemically with citric acid (CA) as esterifying agent. The sorption equilibriums were reached at about 10 hr. The sorption processes followed the pseudo-first-order rate kinetics. After chemical modification, the intra particle diffusion rate constant (kid) was obviously increased.

Alok Mittal [108] Studied the utilization of hen feather as potential adsorbent to remove a hazardous triphenylmethane dye, Malachite Green from waste water by adsorption process and first order adsorption kinetics was found to be operative during the adsorption. The specific rate constants at different temperatures were found to be dependent upon the concentration of the dye. The adsorption was found to operate via film and particle diffusion process in the higher and lower concentration ranges, respectively.

K.Vasanth Kumar et al. [109] conducted sorption experiments for the removal of malachite green from its aqueous solution using Pithophora sp., fresh water algae as biosorbent. Maximum uptake was observed at a pH of 6. Kinetic studies showed that the biosorption process followed first order rate kinetics with an average rate constant of 0.9213 min⁻¹.
The adsorption of Malachite Green (MG) from aqueous solution by two different adsorbents (CZn5, PETNa8) was studied by Akmil-Başar et al.[110] Adsorbents were prepared from pine sawdust and poly ethylene terephatalate (PET) by chemical activation with ZnCl2 and NaOH respectively. The pH of dye solution in the range of 6–10, was found to be favorable for the removal of MG by using the two adsorbents at high concentrations. Equilibrium times were 120 and 90 min for CZN5 and PETNa8 respectively. Kinetics of removal MG was studied using Lagergren equation and diffusion phenomena was analyzed using Weber and Morris intraparticle diffusion plots. It also showed that the adsorption isotherm followed Langmuir model.

Adsorption of malachite green (MG) was studied by Indra Deo Mall et al.[111] using three adsorbents namely, bagasse fly ash (BFA), a sugar industry waste, activated carbon commercial grade (ACC) and activated carbon laboratory grade (ACL). The effective pH was 7.0 for adsorption of MG by the three adsorbents. Equilibrium reached in 4 hr. contact time.

Alok Mittal et al.[112] utilized de-oiled Soya as waste material and low cost adsorbent for the removal of toxic textile dye malachite green. The kinetic measurements confirmed the applicability of the first-order rate expression.

Rajeev Jain et al.[113] reported the photo catalytic and adsorptive treatment of a hazardous xanthene dye, Rohdamine B, in wastewater. On the basis of adsorption data, the Langmuir and Freundlich adsorption isotherm models were confirmed. The adsorption isotherm constants thus obtained were employed to calculate thermodynamic parameters like Gibb’s free energy, change in enthalpy and entropy. A significant decrease in the COD values was observed, which clearly
indicated that both photo catalytic and adsorption methods offered good potential to remove Rhodamine B from industrial effluents.

Activated carbon was prepared by Kadirvelu et al.\textsuperscript{[114]} using industrial solid waste called sago waste and studied its physico-chemical properties and the effectiveness to adsorb Rhodamine B from aqueous solution. The adsorption of Rhodamine B onto the carbon followed second order kinetic model. Adsorption data were modeled using both Langmuir and Freundlich classical adsorption isotherms. The equilibrium time was found to be 150 min. for 10, 20 mg l\textsuperscript{–1} and 210 min for 30, 40 mg l\textsuperscript{–1} dye concentrations respectively. 100% removal was achieved when the pH was increased to 7 for an adsorbent dose of 275 mg/50 ml of 20 mg /L dye concentration. Desorption studies were carried out in water medium by varying the pH from 2 to 10. Desorption studies were performed with dilute HCl and showed that ion exchange was predominant in dye adsorption mechanism.

The effect of acidic treatments of activated carbons on dye adsorption was investigated by Shaobin et al.\textsuperscript{[115]} the study revealed that HNO\textsubscript{3} treatment produced more active acidic surface groups such as carboxyl and lactone, resulting in a reduction in the adsorption of basic dyes. However, HCl treatment decreased the active acidic groups and thus enhanced the adsorption of larger molecules on activated carbons. For methylene blue, the adsorption showed an order of AC > AC-HCl > AC-HNO\textsubscript{3} while for crystal violet and Rhodamine B, the adsorption order was AC-HCl > AC > AC-HNO\textsubscript{3}. It was also found that solution pH showed a significant influence on adsorption of methylene blue but little effect on Rhodamine B. Kinetic studies indicated that the adsorption of dyes followed the pseudo-second-order model and the adsorption was endothermic.