1. INTRODUCTION

1.1. Environmental Pollution:

Environment is interconnected with human life. It is common for all. The physical, chemical and biological components of living and non-living things are present in it. The detriment caused to land, water, air and other natural resource is termed environmental pollution. Conditions on the land and in the waters are determined by the complex bio-system. Rivers nurtured early civilization and life in full harmony with nature and without disturbing the ecosystems. However, modernization has reversed the trend. Cities and villages grew along rivers and valleys discharging huge quantities of sewage into water bodies virtually turning them into open sewers. When industries were set up in urban and sub-urban areas, discharge of industrial wastewater treatment plants, toxins and oil fills from offshore drilling platforms overloaded water streams and oceans. Probably, the most serious cause of environmental degradation is overpopulation. The total area of land available for cultivation is shrinking due to desertification, excessive lumbering, soil erosion, changes in the weather, rapid growth of road systems and decline in water irrigation.

Nature does not produce anything that it cannot decompose and return to the pool of fresh resources. Nature returns organic wastes in the soil as manure and inorganic waste as fertilizers. Man often dumps such wastes in the oceans, and thus treats nature as a commodity; land, oceans and atmosphere as free dumps. It is necessary for us to be aware that dimensions of the biosphere are fixed and its ability to withstand and absorb pollutants is limited. Socio-economic development is the key to water security in an increasing water-stressed situation where more and more wastes are being produced as an
inseparable part of human activities. Effective management administrative and technical progresses are important factors to achieve water security but it is not possible to produce them without economic resources.

1.2. Water Pollution:

Saving water to save the planet and to make the future of mankind safe is an emergent need now. With the growth of mankind, society, science and technology, our world is reaching new high horizons, but the cost which we are paying or will pay in the near future is surely going to be too high. Environmental disorder is one among the consequences of the rapid growth. United Nations World Water Development Report, UNESCO reported that agricultural, industrial and domestic sectors are consuming 70, 22 and 8% of the available fresh water respectively, and this has resulted in the generation of large amounts of wastewater [1].

Water pollution is the contamination of water bodies such lakes, rivers, oceans and ground water. It occurs due to release of pollutants directly or indirectly into water bodies without adequate treatment. It causes deaths and diseases. Water pollution is caused by the discharge wastewater from commercial and industrial waste, discharges of untreated domestic sewage and chemical contaminants such as chlorine fertilizers, pesticides, waste disposal and leaching into groundwater.

One of the most important classes of the pollutants is dyes and heavy metal ions. It is important to recall that water pollution by both heavy metals and dyes is considered as a serious environmental problem because these pollutants modify the chemical properties of water and are toxic to aquatic flora, animals and human beings [2-3].
1.3. Heavy Metal Ion as Pollutants:

Heavy metals in surface and groundwater supplies have been prioritized as major inorganic contaminants of the environment, particularly because of their mobility in aquatic ecosystems, and their toxicity towards higher forms of life. Their presence even in low concentrations or undetectable quantities, leads to their recalcitrant and consequent persistence in water bodies, exhibiting toxic characteristics. These metals can either be detected in their elemental state, showing that they are not subjected to further biodegradative processes, or can be found in the form of various salt complexes. In either instance, metal ions cannot be mineralized. Apart from environmental issues, the technological aspects of metal recovery and reuse from industrial wastewater must also be considered.

1.4. Sources and Toxic Effects of Heavy Metals on Human Beings:

Heavy metal ions have lethal effects on all forms of life and these enter the food chain through the disposal of wastes in water channels. Among the various metal ions, lead, mercury, cadmium and chromium (VI) top of the toxicity list [4]. Due to non-biodegradability, metal ions accumulate and their amounts are increased along the food chain. Hence, their toxic effects are more pronounced in the animals at higher tropic levels.

1.4.1. Lead:

Source:

Lead occurs in water in the divalent state and arises from a number of industrial and mining sources. Lead is widely used in electroplating, manufacturing of batteries, pigments, ammunition, electrodes in electrochemistry and chemical industry.
Toxic Effect:

Lead being one of the essential minerals for the human and animals, more than 400 mg of lead in human body can cause brain damage, vomiting, loss of appetite, diminishing IQ, uncoordinated body movements, convulsions, anemia, anorexia and malaise. However, more than 10 mg per kg of body weight causes rapid respiration and pulse rates, congestion of blood vessels, hypertension and drowsiness [5-7].

1.4.2. Cadmium:

Source:

Cadmium is a heavy metal, which is regarded as an element of high toxicity, mainly used in electroplating, smelting, alloy manufacturing, pigments, plastics, mining and refining.

Toxic Effect:

Cadmium ions are not biodegradable and can accumulate easily in living tissues and can get readily absorbed into the human body through the food chain. An excessive level of cadmium (50 mg) ions in water can cause carcinogenic, renal disturbances, lung insufficiency, bone lesions, cancer, hypertension, weight loss and Itai-Itai disease. It takes 5-10 years for chronic cadmium intoxication. During the first phase, discoloration of teeth, loss of sense of smell and mouth dryness occurs. Afterwards, it may cause decrease of red blood cells, impairment of bone marrow, lumber pains, disturbance in calcium metabolism, softening of bones, fractures, skeletal deformations, damage of kidney, hypertension, tumor formation, heart disease, impaired reproductive function, genetic mutation, etc [8-10].
1.4.3. Mercury:

**Source:**

It is discharged from weathering of mercuriferous areas, volcanic eruptions, naturally-caused forest fires, biogenic emissions, battery production, fossil fuel burning, mining and metallurgical processes, paint and chloralkali industries.

**Toxic Effect:**

Mercury is very toxic. Excess mercury in human body (more than 100 mg) may cause headache, abdominal pain, diarrhea, destruction of hemoglobin, neurological and renal disturbances, impairment of pulmonary function, corrosive to skin, eyes, kidney damage, muscles, and dermatitis [11-12].

1.4.4. Copper:

**Source:**

Copper is also one among the heavy metals and is widely used in many industries including printed circuit board manufacturing, electronics plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printed operations.

**Toxic Effect:**

A higher concentration of copper (more than 470 mg) can cause severe mucosal irritation, widespread capillary damage, hepatic and renal damage, reproductive and developmental toxicity, neurotoxicity and acute toxicity, dizziness and diarrhea [13-14].

1.4.5. Zinc:

**Source:**

Zinc is one of the most important heavy metals and it is released into the environment from various natural and anthropogenic activities, such as acid mine
drainage, galvanizing plants, ores and municipal wastewater treatments. Zinc ions are not biodegradable and can get accumulated easily in living tissues.

**Toxic Effect:**

Higher concentrations of zinc (165 mg) ions can cause hazardous effects in plants and animals. It also causes “metal-fume fever”, gastrointestinal distress, nausea and diarrhoea [15].

**1.4.6. Nickel:**

**Source:**

Nickel is one among the toxic pollutants, and it gets into water from non-ferrous metal, mineral processing, paint formulation, electroplating, porcelain enameling, copper sulphate manufacture and steam-electric power plants.

**Toxic Effect:**

Excessive amounts of nickel in water can affect biosystems and pose a threat to human beings. Toxicity due to nickel causes adverse health effects such as chronic bronchitis, reduced lung function and lung cancer [16-17].

**1.4.7. Chromium:**

**Source:**

An important consumer of chromium for many years has been the tanning industry. Other uses are pigment production and application, graphics industry and industries using chromium alloys or plated materials. Ferrochrome and chromium metals are the most important classes of chromium used in the alloy industry.
**Toxic Effect:**

Trivalent (chromic) and hexavalent (chromate) are the two species of chromium of prime interest for toxicity. The most biologically active species, chromates are particularly water soluble compounds readily taken up by living cells and reduced within the cell via reactive intermediate to stable Cr (III) species. Hexavalent chromium causes carcinogenic, mutagenic, teratogenic, epigastric pain nausea, vomiting, severe diarrhoea and producing lung tumors [18-19].

**1.5. Dye as Pollutants:**

Dyes are complex and sensitive chemicals. A dye is a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber. The dyes are obtained from animals, vegetables, mineral origin, plants, roots barriers, bark, leaves and wood.

Dye molecule comprises two key components: the chromophores, responsible for producing colour and the auxochromes, which not only can supplement the chromophores but also render the molecule to be soluble in water and give enhanced affinity (to attach) towards the fibers.
1.6. Types of Dyes:

Dyes exhibit considerable structural diversity and are classified in several ways. These can be classified [20] both by their chemical structure and their application to the fiber type. Dyes may also be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes. Besides this, either a major azo linkage or an anthraquinone unit also characterizes dyes chemically. It is worthwhile noting that the azo dyes are the one most widely used and accounts 65-70% of the total dyes produced. Though the classification of dyes on the basis of structure is an appropriate system and has many advantages, like it readily identifies dyes as belonging to a group and having characteristic properties, e.g., azo dyes (strong, good all-round properties, cost-effective) and anthraquinone dyes (weak, expensive) there are a manageable number of chemical groups.
Some properties of dyes classified on their usage [21] are discussed briefly here.

**Acid Dyes:**

Acid dyes are water soluble anionic dye that are used to nylon, wool, silk, modified acrylics and also to some extent for paper, leather, ink-jet printing, food and cosmetics. The principal chemical classes of these dyes are azo, anthraquinone, triphenylmethane, azine, xanthenes, nitro and nitroso.

**Cationic (Basic) Dyes:**

Basic dyes are water soluble cationic dyes that are mainly applied to paper, polyacrylonitrile, modified nylons, modified polyesters, cations dyeable polyethylene terephthalate and to some extent in medicine too. Originally they were used for silk, wool and tannin-mordant cotton. These water soluble dyes yield colored cations in solution and hence are called as cationic dyes. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine.

**Disperse Dyes:**

Disperse dyes used mainly on polyester and to some extent on nylon, cellulose, cellulose acetate and acrylic fibers. These are substantially water insoluble nonionic dyes used for hydrophobic fiber from aqueous dispersion. They generally contain azo, anthraquinone, styryl, nitro and benzodifuranone groups.

**Direct Dyes:**

Direct dye is normally carried out in a neutral or slightly alkaline dye bath, with addition of either sodium chloride or sodium sulfate. Direct dyes are used on dyeing of cotton and rayon, paper, leather and to some extend to nylon. They are water soluble
anionic dyes and when dyed from aqueous solution in the presence of electrolytes have affinity for cellulosic fibers. Generally the dyes in this class are polyazo compounds along with some stilbenes, phthalocyanines and oxazines.

**Reactive Dyes:**

These are generally used for cotton and other cellulosic’s but are also used to a small extend on wool and nylon. These dyes form covalent bond with the fiber and contain chromophoric groups such as azo, anthraquinone, triarylmethane, phthalocyanines, formazan, oxazine, etc. Their chemical structures are simpler, absorption spectra show narrower absorption bands and the dyeing is brighter making them advantageous over direct dyes.

**Solvent Dyes:**

Solvent dyes are used for plastics, gasoline, lubricants, oils and waxes. These dyes are solvent soluble (water insoluble) and generally nonpolar or little polar, i.e., lacking polar solubilizing groups such as sulfonic acid, carboxylic acid or quaternary ammonium. The principal chemical classes are predominantly azo and anthraquinone but phthalocyanines and triarylmethane are also used.

**Sulfur Dyes:**

Sulfur dyes are used for cotton and rayon and have limited use with polyamide fibers, silk, leather, paper and wood. They have intermediate structures and though they form a relatively small group of dyes, the low cost and good wash fastness properties make this class an important form in economic point of view.
Vat Dyes:

Vat dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye and subsequent oxidation reforms the original insoluble dye.

Food Dyes:

Food dyes are food additives, which are manufactured to a higher standard than some industrial dyes. Food dyes can be direct, mordant and vat dyes and their use is strictly controlled by legislation. Many are azo dyes, although anthraquinone and triphenylmethane compounds are used for colors such as green and blue. Some naturally occurring dyes are also used.

Other Important Dyes:

Besides these, some other classes like azoic having azo groups are used for cotton and other cellulosic materials; fluorescent brighteners having stilbenes, pyrazoles, coumarine and napthalimides used for soaps and detergents, fibers, oils, paints and plastics and mordant having azo and anthraquinone used for wool, leather, natural fibers after pretreating with metals and anodized aluminium.

1.7. Conventional Methods for Removal of Metal Ion and Dye:

Various methods are developed to remove the heavy metal ions as well as the dyes from the aqueous solutions and waste water [22]. These include ion-exchange, electro-dialysis, evaporation, reverse osmosis, precipitation, chemical treatment, oxidation, biological treatment and adsorption, etc.
1.7.1. Ion-exchange method:

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 [23-24]. 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.

1.7.2. Electro-dialysis method:

The direct electrolytic process is successfully followed to recover copper from copper pickling and brass pickling bath [25]. 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 [26]. 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 [27]. 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.
1.7.3. Evaporation method:

There is reported literature about utilizing evaporative recovery method for the removal of copper [28], cadmium [29], nickel [30] and zinc [31]. However there is a possibility of retaining all the non-volatile constituents of the wastewater which is considered a major drawback.

1.7.4. Reverse osmosis method:

This is essentially a process in which a semi permeable membrane allows water molecules through and retains [32]. The concentrated solutions are subjected to high pressure as a result of which the solvent is forced out through a semi permeable membrane to the dilute solution region. The concentrated solution becomes more concentrated and can therefore be removed. The three membranes most commonly used are cellulose acetate, aromatic polyamide and NS-100. The application of this process for the treatment of cadmium plating and zinc plating solutions and iron from acid mine drainage has been reported. The serious drawback of this method is being its high initial and capital and operating cost. This method is not adequate for the treatment of effluents containing high concentration of metallic ions and preliminary filtration of suspended particles is necessary for the protection of membrane.

1.7.5. Precipitation method:

The most popular process for the decontamination of industrial effluents is the precipitation process which is widely used when metal ion concentration is high followed by filtration. This method is used to remove hexavalent chromium from waste water. Here, hexavalent chromium is reduced to trivalent chromium using a suitable reducing
agent and it is precipitated as chromic hydroxide \[33\] with lime, soda ash, sodium hydroxide or barium carbonate as the precipitating agent. The presence of any complexing agent such as cyanide in the waste water inhibits chromic hydroxide precipitation. Sodium bisulphate and hydrogen sulphide are normally used as reducing agents. Cadmium can be precipitated as its hydroxide, sulphide or its carbonate. The use of coagulant normally increases the efficiency of precipitation. It has been reported that lime cannot be used to precipitate cadmium because this process needs high pH. The removal of cadmium as its sulphide has been the common process in industry.

1.7.6. Chemical treatment:

Chemical treatment of dye wastewater with a coagulating/flocculating agent \[34\] is one of the robust ways to remove colour. The process involves adding agents, such as aluminum (\(\text{Al}^{3+}\)), calcium (\(\text{Ca}^{2+}\)) or ferric (\(\text{Fe}^{3+}\)) ions, to the dye effluent and induces flocculation. Besides these, other agents \[35\] have also been used for the process. Sometimes combination of two may also be added to enhance the process. Generally, the process is economically feasible with satisfactory removal of disperse, sulfur and vat dyes. However the main drawback of the process is that the final product is a concentrated sludge produced in large quantities. Besides, this the removal is pH dependent. This process is not good for highly soluble dyes and the results with azo, reactive, acid and especially the basic dyes are generally not good.

1.7.7. Oxidation:

Oxidation is a method by which wastewater is treated by using oxidizing agents. Generally two forms viz. chemical oxidation and UV assisted oxidation using chlorine,
hydrogen peroxide, Fenton’s reagent, ozone or potassium permanganate are used for treating the effluents, especially those obtained from primary treatment (sedimentation). They are among the most commonly used methods for decolourisation processes since they require low quantities and short reaction times. They are used partially or completely to degrade the dyes. However, a complete oxidation of dye can theoretically reduce the complex molecules to carbon dioxide and water. It is worth noting that pH and catalysts play an important role in oxidation process.

Chlorine is a strong oxidizing agent used and may also be applied as calcium hypochlorite and sodium hypochlorite. In addition to being the most widely used disinfectant for water treatment, it is extensively used for reduction of colour like pulp and textile bleaching. Reactive, acid, direct and metal complex dyes, which are soluble, are decolorized readily by hypochlorite but water insoluble disperses and vat dyes are resistant to decolourisation in this process [36]. It has been reported that decolourisation of reactive dyes generally require long reaction times, while metal complex dye solution remains partially colored even after an extended period of treatment.

1.7.8. Biological treatment:

It is the most common and widespread technique used in dye wastewater treatment [37]. A large number of species have been used for decolouration and mineralization of various dyes. The methodology offers considerable advantages like being relatively inexpensive, having low running costs and the end products of complete mineralization not being toxic. The process can be aerobic (in presence of oxygen), anaerobic (without oxygen) or combined.
Aerobic treatment:

Bacteria and fungi are the two microorganism groups that have been most widely studied for their ability to treat dye wastewaters. In aerobic conditions, enzymes secreted by bacteria present in the wastewater break down the organic compounds. Studies to identify and isolate aerobic bacteria capable of degrading various dyes have been going on for more than two decades. A number of triphenylmethane dyes, such as magenta, crystal violet have been found to be efficiently decolorized (92-100%) by the strain Kurthia sp [38]. It was reported by the workers that after biotransformation, the extent of COD reduction of the cell free extracts of triphenylmethane dyes was more than 88% in all dyes except in the case of ethyl violet (70%). Nevertheless, it is susceptible to decomposition by activated sludge in a conventional aerobic process. Various factors like concentration of pollutants, dyestuff concentration, initial pH and temperature of the effluent affect the decolourisation process. It has been suggested that after the fungal treatment an improvement in the treatability of the effluent by other microorganisms can be observed. Although the treatments are suitable for some dyes, most of them are recalcitrant to biological breakdown or non-transformable under aerobic conditions.

Anaerobic treatment:

The potential of anaerobic treatment applications for the degradation of a wide variety of synthetic dyes has been well demonstrated and established by [39]. Though some efforts in the recent past to decolorize dyes under aerobic conditions have met with success, the general perception of non-biodegradability of most azo dyes in conventional aerobic systems still persists.
1.7.9. Adsorption:

The stringent discharge requirements of wastewater coupled with rising cost in the treatment of it with the convergence of diminishing supply of fresh water have prompted many researchers to examine new avenues for treating it. Among the methods, adsorption is the best and the most attractive because it is well established and a powerful technique for treating domestic and industrial effluents. Adsorption is one of the processes, which besides being widely used for dye removal, also has wide applicability in wastewater treatment [40]. The term adsorption refers to a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings. The history of carbon adsorption in the purification of water dates back to ancient times.

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. Adsorption arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Thus, when a solid surface is brought into contact with a liquid or gas, there is an interaction between the fields of forces of the surface and that of the liquid or the gas. The solid surface tends to satisfy these residual forces by attracting and retaining on its surface the molecules atoms or ions of the gas or liquid. This results in a greater concentration of the gas or liquid in the vicinity of the solid surface than in the bulk gas or vapor phase, despite the nature of the gas or vapor.
1.8. Types of adsorption:

Adsorption can be classified into two types:

1) Physical adsorption (Physisorption)

2) Chemical adsorption (Chemisorption)

1.8.1. Physical adsorption:

If the physical forces of attraction hold the adsorbate to the surface of the adsorbent, the adsorption is called physical adsorption or physisorption [41]. Forces associated with interactions between the dipole moments of adsorbate and adsorbent molecules commonly fall under physical adsorption processes. Interactions between polar molecules and non-polar molecules in which dipole moments are thereby induced represent one class of physical adsorption. The heat evolved in physical adsorption is usually less than 20 kJ mol$^{-1}$.

1.8.2. Chemical adsorption:

If the chemical forces hold the adsorbate molecules to the surface of the adsorbent, the adsorption is called chemical adsorption or chemisorptions [42]. This type of sorption has all of the characteristics of true chemical bonds and is characterized by relatively large heats of sorption. The reactions may involve substantial activation energies and be favored by high temperature.

1.8.3. Sorption, Occlusion:

In many examples of adsorption process, the initial rapid adsorption is followed by a slow process of absorption of the substances into the interior of the solid. In this case, the effects of sorption cannot be distinguished from those of adsorption. Hence a
new term called sorption had been introduced. Sorption is a process in which both adsorption and absorption take place simultaneously. Sorption of gases on metals is called as **Occlusion**.

Adsorption technology is currently used extensively for the removal of organic and inorganic micro-pollutants from aqueous solution. Adsorption phenomenon is mainly related with two terms-adsorbent and adsorbate.

**Adsorbent**: The substance which adsorbs another substance on its surface is called as adsorbent. e.g. charcoal, polymer composites, etc.

**Adsorbate**: The substance which itself gets adsorbed on the surface of another substance is called adsorbate. e.g. heavy metal ions, dyes, etc.

**1.9. 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** - contains compounds that 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.

1.9.1. Activated carbon:

Activated carbon is the oldest adsorbent known and is usually prepared from coal, coconut shells, lignite and waste plant materials, etc, using one of the two basic activation methods: physical and chemical [43].

1.9.2. Physical activation:

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 the absence of air (usually in inert atmosphere with gases like argon or nitrogen)

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

1.9.3. Chemical activation:

Prior to carbonization, the raw material is impregnated with certain chemicals. The chemical is typically a strong acid, strong base or a salt (sulfuric acid, potassium hydroxide, sodium hydroxide, and zinc chloride respectively). Then the raw material is carbonized at lower temperatures (450 °C - 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.

1.9.4. Applications of activated carbon:

Activated carbon finds numerous applications such as decolourisation of sugar and sweeteners, drinking water treatment, gold recovery, production of pharmaceuticals and fine chemicals, catalytic processes, off-gas treatment of waste incinerators, automotive vapors filters, colour / odour correction in wines and fruit juices, additive in liquorices and biosensors, etc. Activated carbon, because of its large surface area, a micro porous structure and a high degree of surface reactivity, has been considered to be very good adsorbent for the adsorption of organic and inorganic from waste water.

1.10. Maranta arundinacea:

![Maranta arundinacea](image)

**Fig. 1.2. Maranta arundinacea (Arurutukkilangu)**

Family: Marantaceae

Genus: Maranta

Species: arundinacea
Maranta arundinacea (In Vernacular name: Aruruttukkilangu) is an herbaceous rhizomatous plant cultivated widely in tropical countries for its starchy roots. The West Indian Arrowroot (Maranta arundinacea), a native of tropical America, is widely cultivated in countries like India, Srilanka, Indonesia, Australia and Philippines. The edible tuberous rhizomes are rich in starch and are also a commercial source of fine grade starch used often in weaned foods and biscuits. The starch is also reported to have medicinal uses and is an important ingredient in the preparation of barium meals and tablets. The plant which grows under shade is resistant to many insects and pathogen attack. Traditionally the tuberous rhizomes are used in the treatment of diarrhea. The objective of this research was to evaluate its potential in dye decolorization.

1.11. Coscinium fenestratum:

![Coscinium fenestratum](image1.png)

**Fig. 1.3. Coscinium fenestratum (Maramanjal)**

**Family**: Menispermaceae

**Genus**: Coscinium

**Species**: fenestratum
Coscinium fenestratum (tree turmeric, maramanjal), is widely used in folk and ayurvedic systems of medicine. The chemical constituents reported from C. fenestratum belongs to different classes of alkaloids, some minor alkaloid as well as ceryl-alcohol, saponin, hentriacontane, sitosterol glucoside, palmitic acid, oleic acid isolated from stem and roots of this plant. Among these, berberine has been reported to be the major and active constituent having numerous biological activities. The remarkable medicinal properties are wound healing, anti fungal, anti bacterial, hypertensive, anti hyperglycemic activity, anti proliferative, antihepatotoxic, antipyretic, antiulcer, antioxidant, and neurotoxin activities.

1.12. Chitosan: (β-(1-4)-2-acetoamido-2-deoxy-D-glucose)

Other names: Poly-(D)glucosamine, LPoliglusam

Chitosan is a type of natural polyaminosaccharide, synthesized from the deacetylation of chitin, which is a polysaccharide consisting predominantly of unbranched chains of β-(1-4)-2-acetoamido-2-deoxy-D-glucose. Chitin is the second most abundant polymer in nature after cellulose. It can be extracted from crustacean shell such as prawns, crabs, fungi, insects and other crustaceans [44]. Chitosan is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption, etc.
[45]. Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups, which can serve as the active sites. To improve chitosan’s performance as an adsorbent, cross-linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrine, ethylene glycol diglycidyl ether and isocyanates have been used. Cross-linking agents do not only stabilize Chitosan in acid solutions so that it becomes insoluble, but also enhance its mechanical properties. Their use for the treatment of wastewater from another industry could be helpful not only to the environment in solving the solid waste disposal problem, but also to the economy.

1.13. Titanium dioxide: (TiO$_2$)

Titanium dioxide, also known as titanium (IV) oxide or Titania, is the naturally occurring oxide of titanium. It has a wide range of applications, from paints and varnishes as well as paper and plastics. The rest is used in other applications, for instance the production of technical pure titanium, glass and glass ceramics, electrical ceramics, catalysts, electric conductors and chemical intermediates. Titanium dioxide occurs in nature as well-known minerals rutile, anatase and brookite. In addition to these phase
three metastable phases can be produced synthetically (monoclinic, tetragonal and orthorhombic).

1.14. Adsorbate:

1.14.1. Congo red:

Congo red, is an anionic azo dye having IUPAC name as 1-napthalenesulfonic acid, 3,3-(4,4-biphenylenebis(azo))bis(4-aminodisodium). Congo red is a water soluble diazo dye with a solubility of 1g/30 mL. It exists as brownish-red crystal and is stable in the air. It is an anionic acidic dye, used in diagnosis of amyloidosis and in medicine as a biological stain. It acts as an indicator by changing to red-brown color in alkaline medium and to blue color in acidic medium. It is also used as gamma-ray dosimeter since its coloration decays with the intensity.

**Structure:** (Molecular Formula: \( \text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2 \))

![Fig. 1.6. Structure of Congo red](image)

**Application:**

Congo red is widely used in textiles, paper, rubber and plastic industries.
Toxic effect:

Congo red can cause irritation, changes in blood pressure, nausea, vomiting, stomach pain, difficulty breathing, irregular heartbeat, headache, drowsiness, dizziness, disorientation, hallucinations, loss of coordination, internal bleeding, kidney damage, unconsciousness, etc.

1.14.2. Rhodamine-B:

Rhodamine-B (RB) is one of the water soluble xanthenes class dyes, a basic red cationic dye which is a common water tracer fluorescent. The IUPAC name of RB is [9-(2-carboxyphenyl)-6-ethylamino-3-xanthenylidene]-diethylammonium chloride.

Structure: (Molecular Formula: $C_{28}H_{31}ClN_2O_3$)

![Fig. 1.7. Structure of Rhodamine-B](image)

Source:

Rhodamine-B is a water-soluble organic dye widely used in textile industries for dyeing cotton, wool and silk.
Toxic effect:

It is potentially harmful to human as it can cause dehydration, malabsorption, protein-losing gastroenteropathy, anorexia, weight loss, polydipsia, polyuria, cardiac arrhythmias, muscle weakness, kidney and central nervous system disturbance may be due to electrolyte imbalance.

1.14.3. Malachite Green:

Malachite Green is a basic dye and water soluble. It dissociates into anion and colored cations. It belongs to triphenyl methane class and it contains two amino groups.

Structure: (Molecular Formula: $[C_6H_5C(C_6H_4N(CH_3)_2)Cl]$)

![Structure of Malachite Green]

Fig. 1.8. Structure of Malachite Green

Source:

Malachite green is commonly used for dyeing wool, silk, leather, cotton, jute and as fungicide, ectoparasiticide in aquaculture, fisheries and also in manufacturing of paints and printing inks.
Toxic effect:

Though it effectively controls the infection of bacteria, protozoan’s, cestodes, trematodes, nematodes and crustaceans in aquaculture, MG was found to cause muscle glycogenolysis, impairs protein synthesis, severe damage to gills and degenerative changes in fishes.

1.14.4. Methylene blue:

The methylene blue is a basic cationic dye, heterocyclic aromatic chemical compound.

Structure: (Molecular Formula: $C_{16}H_{18}ClN_3S$)

![Methylene blue structure](image)

Fig. 1.9. Structure of Methylene blue

Source:

Methylene blue dye has wide applications, which include paper coloring, cotton or wool dyeing and coating for paper stock.

Toxic effect:

In case of methylene dye, the colored effluents have various harmful effects on living things. Once inhaled, it can cause an increase in heart-beat rate, nausea and vomiting. If the amount of intake is large, severe symptoms such as difficulties in breathing, mental confusion and methemoglobinemia like syndromes may take place.
1.15. Characterization techniques:

Characterization of adsorbent is done using a variety of techniques, mainly drawn from materials science. The common techniques used to characterize the adsorbents are given below:

- B.E.T analysis- Surface area
- Scanning electron microscopy (SEM)- Morphology
- Energy dispersive spectroscopy (EDS)- elemental investigation
- Powder X-ray diffraction (XRD)- To determine crystalline and crystal structure
- Thermo gravimetric analysis (TGA)- To proximate analysis of activated carbon sample
- Fourier Transform Infrared spectra (FTIR) - surface functional groups before and after adsorption sample.
- Ultraviolet-visible spectroscopy (UV-vis)- Optical properties

1.16. Equilibrium models

The equilibrium models are extensively used to investigate the amounts of metal ions and dyes adsorbed by certain biomass. The distribution of metal ions/dyes between solution and biomass is a measure of the position of equilibrium (Table 1.1) and can be expressed by one or more isotherms. Langmuir model, Freundlich model, Temkin model, Dubinin-Radushkevich (D-R) model and Jovanoic model are some examples and among these most common are the monolayer adsorption developed by Langmuir and the multi-layer adsorption Freundlich models.
### Table 1.1. Adsorption isotherm equations with parameters

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>Linear form</th>
<th>Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td>$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$</td>
<td>$C_e = \frac{1}{C_{e}} + \frac{C_e}{q_m}$</td>
<td>$q_m, K_L$</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td>$q_e = K_F C_e^{1/n}$</td>
<td>$\log q_e = \log K_F + 1/n \log C_e$</td>
<td>$K_F, n$</td>
<td>[47]</td>
</tr>
<tr>
<td><strong>Temkin</strong></td>
<td>$q_e = \frac{RT}{b \ln(K_T C_e)}$</td>
<td>$q_e = B_1 \ln K_T + B_1 \ln C_e$</td>
<td>$B_1, K_T$</td>
<td>[48]</td>
</tr>
<tr>
<td><strong>D-R</strong></td>
<td>$q_e = q_m \exp(-\beta C_e^2)$</td>
<td>$\ln q_e = \ln q_m - \beta C_e^2$</td>
<td>$q_m, \beta$</td>
<td>[49]</td>
</tr>
<tr>
<td><strong>Jovanoic</strong></td>
<td>$\ln q_e = \ln q_m + K_J C_e$</td>
<td></td>
<td>$q_m, K_J$</td>
<td>[50]</td>
</tr>
</tbody>
</table>

- **Langmuir** - The sorption occurs at the surface of the sorbent in a homogeneous way and the atoms/ions form a monolayer, having no mutual interactions, on the sorbent surface. Although it gives no information about the mechanism, it is still used to obtain the uptake capacities of the sorbents.

- **Freundlich isotherm** model considers the non-ideal sorption on heterogeneous surfaces in a multilayer way.

- **Temkin isotherm** contains a factor that explicitly takes into the account adsorbing species adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies up to some maximum binding energy.

- **D-R isotherm** predicts the nature of adsorption—whether physical or chemical adsorption. The value of mean free energy will decide the nature of adsorption.
The adsorption process will be a physical adsorption for $E < 8 \text{kJ/mol}$ and it will be a chemical adsorption or chemisorptions for $8 < E < 16 \text{kJ/mol}$.

- **Jovanoic isotherm** suggests the possibility of some mechanical contacts between the adsorbing and desorbing molecules on the homogeneous surface.

### 1.17. Kinetic modeling

An ideal adsorbent for wastewater pollution control must have not only a large adsorbate capacity but also a fast adsorption rate. Therefore, the adsorption rate is another important factor for the selection of the material and adsorption kinetics must be taken into account since they explain how fast the chemical reaction occurs and also provides information on the factors affecting the reaction rate.

Three kinetic models (Table 1.2) have been widely used in the literature for adsorption processes: (i) pseudo-first-order kinetic model (Lagrgren model) [51]; (ii) pseudo-second-order kinetic model (Ho and McKay model) [52]; (iii) and intraparticle diffusion model (Webber and Morris model) [53]. These kinetic models are used to examine the controlling mechanism of adsorption process such as adsorption surface, chemical reaction and/or diffusion mechanism.

**Table 1.2. Three kinetic model and their linear forms**

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>Linear form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lagrgren</td>
<td>$\log \left( \frac{q_e}{q_e - q_b} \right) = \frac{k_1}{2.303} t$</td>
<td>$\ln (q_e - q_t) = \ln q_e - k_1 t$</td>
</tr>
<tr>
<td>Ho and McKay</td>
<td>$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t$</td>
<td>$t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$</td>
</tr>
<tr>
<td>Webber and Morris</td>
<td>$q_t = k_{id} t^{0.5} + C$</td>
<td></td>
</tr>
</tbody>
</table>
When adsorption is preceded by diffusion through a boundary, the kinetics in most cases follow the \textit{pseudo-first-order rate} equation.

\textbf{Pseudo-second-order} is based on the adsorption capacity. It only predicts the behavior over the “whole” range of studies supporting the validity and is in agreement with chemisorptions being the rate-limiting step.

Above two-lumped kinetic pseudo-models cannot identify adsorption mechanism. Hence, several investigators proposed to use the diffusion mechanisms such as \textit{intraparticle diffusion} using the Weber and Morris equation.

\subsection*{1.18. Effect of Temperature – Thermodynamic control}

The most important features involved in the investigation of adsorption phenomenon are the adsorption isotherm and kinetics, the interface characteristics, the adsorbate – adsorbent interactions and also the thermochimistry of adsorption. In particular, the adsorption characteristics of a material can be expressed in thermodynamic parameters such as $\Delta G^\circ$ (Gibbs free energy change), $\Delta H^\circ$ (enthalpy change), and $\Delta S^\circ$ (entropy change). These parameters can be calculated (Table 1.3) by using thermodynamic equilibrium coefficient obtained at different temperatures. Evaluation of these parameters gives an insight into the possible mechanisms of adsorption [54].

The original concepts of thermodynamics assumed that in an isolated system where energy cannot be gained or lost, the entropy change is the driving force. In environment engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Thermodynamic considerations tell us that, at constant temperature and pressure, the $\Delta G^\circ$ value is the fundamental criterion
of spontaneity and a negative value for $\Delta G^*$ stands for the adsorption take place, indicating the spontaneity of the reaction.

**Table. 1.3. Thermodynamic equations and their parameters**

<table>
<thead>
<tr>
<th>Expression</th>
<th>Linear equation form</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbs</td>
<td>$\Delta G^* = -RT \ln K_L$</td>
<td>Free energy change ($\Delta G^*$)</td>
</tr>
<tr>
<td>van’t Hoff</td>
<td>$\ln K_L = \frac{\Delta S^<em>}{R} - \frac{\Delta H^</em>}{RT}$ with $K_L = \frac{q_e}{C_e}$</td>
<td>Enthalpy change ($\Delta H^*$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Entropy change ($\Delta S^*$)</td>
</tr>
</tbody>
</table>

A plot of $\ln K_L$ versus $1/T$ gives the straight line and $\Delta S^*$ and $\Delta H^*$ can be determined.

- The negative value of $\Delta G^*$ shows the process is feasible and spontaneous.
- $\Delta H^*$ shows the route of energy in the system. A positive value shows an endothermic process and negative value indicates an exothermic process.
- Negative values of $\Delta S^*$ showed a decreased randomness or increased orderliness at the metal-biomass interface. The positive value showed a change in biomass structure during the adsorption process, causing an increase in the disorderliness of the system.

**1.19. Scope of the present work**

In recent years removal of heavy metal/dyes using adsorption process has gained momentum as the means for reducing treatment costs.

The *present study is undertaken with the following objectives*:

- To identify the prospects of using low cost substance as raw materials for the production of adsorbents for removing heavy metals and dyes.
To prepare the activated carbon as adsorbents from *Maranta arundinacea* and *Coscinium fenestratum* by sulfuric acid treatment.

To prepare the polymer composite material as adsorbent from Chitosan and Titanium dioxide by condensation polymerization method.

To characterize adsorbents using B.E.T analysis, Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), Powder X-ray diffraction (XRD), Thermo gravimetric analysis (TGA), Fourier Transform Infrared spectra (FTIR) and Ultraviolet-visible spectroscopy (UV-vis).

To find out the effect of parameters like Initial metal/dye concentration, dose of the adsorbent, contact time and temperature by systematic batch mode studies.

To investigate various kinetic models like Lagergren pseudo-first-order, Ho and McKay’s pseudo-second-order and Webber and Morris intra particle diffusion.

To match the equilibrium data obtained at different initial concentration with various isotherm models like Langmuir model, Freundlich model, Temkin model, Dubinin-Radushkevich (D-R) model and Jovanoic model and to find out which one of these best fits the experimental data.

To calculate the thermodynamic parameters from temperature variation studies.

To study the recovery and reuse of adsorbents.

1.20. References:


