Chapter 1:
General Introduction
1. Introduction

The industrialization, population and pollution in the world are increasing hand in hand. Though technological advancement is the cause for all of them but at the same time it is a hope for the solutions of crises of pollution. The pollution has created the serious environmental crisis and threat to life on the earth. “Pollution is the introduction of contaminants into the natural environment that causes the antagonistic changes”. Both physical system and living organisms i.e. ecosystem are affected by the introduction of pollutants into the environment. The chemical, biological and physical substances also cause pollution. Pollutants are the elements of pollution which occurs in the form of foreign or natural substances. Such substances occurring at natural levels are considered as contaminants and not pollutants [1].

Pollution may be natural or man-made. Natural pollution is produced naturally which cannot harm to environment because it has the ability to regenerate, while the man-made pollution is extreme harm to environment and difficult to eliminate which is caused by human activities. Human population and technology are the backbones of man-made pollution where in new technologies might attract more side effects than their advantages [2].

2. Classification of pollution

Pollution is broadly classified into main six types but our discussion will focus on the water pollution.
2.1. Water Pollution

Water is the only naturally occurring inorganic liquid which covers one third of the earth. There is no life without water. But large number of environmental issues such as domestic, agricultural, industrial activities etc. makes water polluted day by day. Pollution makes water physically impure, foul or filthy, changing its natural qualities and making it unsuitable for use. Polluted water contains substances which cannot be easily degraded by the natural ecosystem. These substances may be of diverse nature and may have varied life span. They include petroleum products, minerals, industrial organic effluents, dyes, fertilizers and pesticides etc. [3].

Table 1.1: Water pollution can be defined as point source and non-point source

<table>
<thead>
<tr>
<th>Point Source</th>
<th>Non-point Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>• It is a pollution caused by discharge of effluents at one point known source.</td>
<td>• It is a pollution caused by discharge of pollutants over a wide area undefined source.</td>
</tr>
<tr>
<td>• Pollutants enter the water in high concentrations and slowly dilute into the ecosystem.</td>
<td>• Pollutant sources are widespread, not from one single source of input.</td>
</tr>
<tr>
<td>• Point of entry at high concentration has more severe effects than further away in diluted areas.</td>
<td>• Rarely have a single area of severe damage and are often variable (changing) and repeating over time.</td>
</tr>
<tr>
<td>Examples</td>
<td>Examples</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>➢ Leaking septic-tank.</td>
<td>➢ Chemicals added to road surfaces (salt and other de-icing agents).</td>
</tr>
<tr>
<td>➢ Leaking storage lagoons for polluted waste.</td>
<td>➢ Water runoff from city and suburban streets that may contain oil, gasoline, animal feces, and liter.</td>
</tr>
<tr>
<td>➢ Unlined landfills.</td>
<td>➢ Pesticides, herbicides, and fertilizer from residential lawns, golf courses, and farmland.</td>
</tr>
<tr>
<td>➢ Leaking underground storage tanks that contain chemicals or fuels such as gasoline.</td>
<td>➢ Feces and agricultural chemicals from livestock feedlots.</td>
</tr>
<tr>
<td>➢ Polluted water from abandoned and active mines.</td>
<td>➢ Precipitation containing air pollutants.</td>
</tr>
<tr>
<td>➢ Public and industrial wastewater treatment plants.</td>
<td>➢ Soil runoff from farms and construction sites.</td>
</tr>
<tr>
<td></td>
<td>➢ Oil and gasoline from personal watercraft.</td>
</tr>
</tbody>
</table>
2.2. Water pollutants can be broadly classified into the following three major groups are as chemical, physical and biological pollutants. **Chemical pollutants** are sub divided into four sub pollutants which are as under follows

1. Organic Pollutants
2. Inorganic Pollutants
3. Suspended solids and sediments
4. Radioactive materials

2.2.1. Organic Pollutants

Organic pollutants can be divided further are as follows:

2.2.1.1. Oxygen Demanding wastes

The colloidal, dissolved or suspended form of pollutants are found in considerable amount in biodegradable organic compounds which includes domestic, municipal sewage, paper and pulp mills, slaughter houses, breweries and distilleries. It is caused by the waste materials degradation and decomposition through bacterial activity. The aerobic oxidation of such organic matter consumes the dissolved oxygen present in the water body. Therefore, there is depletion in the dissolved oxygen below 4.0 mg L$^{-1}$ that affects the aquatic living organisms.

2.2.1.2. Synthetic Organic Compounds

The synthetic organic compounds like Synthetic detergents, pesticides, insecticides, food additives, pharmaceuticals, paints, synthetic fibers, plastics and volatile organic compounds (VOCs) etc. pollute the water through various man made activities. These compounds are toxic and remain unaffected by the microbial degradation [4]. For example Phenothiazine, Dimethylacridan etc. are used as insecticides, since 1930s, polychlorinated biphenyls (PCBs) are used in the industries, which are the complex mixtures of chlorobiphenyls. These compounds are fat solvable and enter into the tissues or cells due to exposure to the polluted atmosphere. Also they have long life in the environment. If hosted in the biological system they are extremely tenacious and there is high stability and drug resistance.
2.2.1.3. Petroleum Oil

The Petroleum Oil is a natural product which results from the plant remains fossilized, under marine conditions over millions of years. It is a complex mixture of hydrocarbons and degradable due to bacterial activity. In water, oil enters due to leak from oil pipes, oil spills and wastewater from production and refineries. Oil (ρ = 890 kg/m³) is spread over the surface of water (ρ = 1000 kg/m³) due to its lighter density, due to which contact of water with air doesn’t occurs, which result in the reduction of dissolved oxygen and the light transmission. This affects the water birds and coastal plants and also reduces the photosynthetic activities of the marine plants. Oil also contains carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAH) [5].

2.2.2. Inorganic Pollutants

In the inorganic pollutants, the high concentration of heavy metals found through sewage and industrial wastes which pollute the water. These compounds are non-biodegradable in the environment. The mineral acids, trace elements, inorganic salts, metals compounds, complexes of metals with organics are included in these pollutants. The metal-organic interactions involve natural organic species [6] like redox reactions, acid-base reactions, colloid formation and reaction involving microorganisms in water.

- The buildup of heavy metals may have opposing effect on aquatic flora and fauna and it may establish public health problems. They became part of the body through food chain, where infected organisms are used for food.
- Excess of nitrogen and phosphorous compound helps in Algal growth which reduces the amount of dissolved oxygen as well as penetration of light on the surface of water.
- High concentration of metals can be toxic to assemblage e.g. Hg, As, Cd, Pb, Se and Cu. Copper is toxic to microbes at a concentration greater than 0.1 mg L⁻¹ [7].
2.2.3. Suspended soils and sediments

- The causes of sediments include soil erosion, strip mining, construction activities and agricultural development.
- A suspended solid in water contains silt, sand and minerals, wind-swept from the land.

In tropical countries like India, quantitative and qualitative degradation of soil in land area i.e. water, wind and other natural forces causes in soil erosion. Thus, soil removed from agricultural fields to the other areas especially water bodies and enhances the suspended solids in water [8-10]. “Siltation” is a process in which soil particles find their way to reservoirs and dams. Water storage capacity of the dams and reservoirs are reduced and therefore shortens their life. The sunlight penetration in the water, required for the photosynthesis of bottom vegetation [e.g. Smother shellfish, corals and other bottom life] are blocked by the presence of suspended solids in the reservoirs and harbors. The stream or ocean bottom can damage and disturb the normal and diversity of aquatic system due to the deposition of solid sludge’s. The development of anaerobic conditions and formation of poisonous gases through decomposition will happen, if the deposited solids are organic in nature. The terrific problem of soil erosion can be controlled by proper cultivation practices and efficient soil and forest management techniques. The surrounding aquatic medium exchange cations with both suspended and sediment particles which act as sources for trace metals such as Mn, Mo, Co, Cu, Ni and Cr [11]. The suspended finer particles of silts and dust also injure and stiffer the gills of fishes and thus destroys the aquatic system.

2.2.4. Radioactive materials

The radioactive pollution may also be defined as discharge of radioactive or high energy substances into the water or on the earth through human activities, either accident or design [12-15]. The origins of the radioactive materials are as following:

- In research works Medical, Industrial and Agricultural activities uses such as $^{131}$I, $^{32}$P, $^{60}$Co, $^{45}$Ca, $^{35}$S, $^{14}$C, etc. in their radioactive materials.
- Nuclear power plants and nuclear reactors discharge radioactive elements e.g. $^{90}$Sr, $^{137}$Cs, $^{248}$Pu, $^{238}$U, $^{235}$U.
• In the processing of ores and mining.
• In the testing and uses of nuclear weapons.

In the living being these radioactive isotopes can cause serious disorders and they also accumulate in the bones and teeth. The concentration limit is $1 \times 10^{-7}$ microcuries per ml for lifetime consumption.

Water pollution due to heavy metals and organic pollutants has been a major apprehension. Heavy metals are non-biodegradable and are the cause for many terrible disorders due to their accumulation in different parts of body. On the other hand many organic pollutants are carcinogenic in nature.

2.3. Effects of Water Pollution

Effects of various types of water pollutants are as follows:

2.3.1. Oxygen demanding wastes: The micro-organisms present in the water help in the decomposition of organic matter.

2.3.2. Nitrogen and phosphorus compounds: The growth of algae and other plants are consumed by nitrogen and phosphorous compounds and when these organisms will die and decay then it can consume oxygen of water. Thus, many physico-chemical characteristic of water will change in the form of pH, dissolved oxygen and temperature.

2.3.3. Pathogens: Wastewaters sewage contains many pathogenic, non-pathogenic micro-organisms and viruses. Cholera, typhoid, jaundice etc. are water borne diseases.

2.3.4. Toxic Compounds: Aquatic organisms are effects by pollutants such as dyes, heavy metals, pesticides, cyanides and organic and inorganic compounds. “Bioaccumulation” is the process in which substances tend to accumulate in the body of the organisms. The successive levels of concentration of these toxic substances are built by the food chains.

2.4. Control of water pollution

1. Minimum usage of agrochemicals (like pesticides and fertilizers) which will decrease their leaching and surface run-off.
2. The uses of fertilizers are supplemented by nitrogen fixing plants.
3. The prevention run-off manure.
4. Prevent overflow of sewage with rainwater by the separating the sewage and rainwater drainage system.
5. Prevent soil erosion and reduction of pollution by sediments through planting trees.
6. Reduce the BOD, COD levels for discharge by using primary and secondary treatments of wastewater.

3. Water Pollution by dyes and Heavy metals

3.1. Heavy metals

Heavy metal includes metals with atomic number higher than 20, having specific gravity greater than 5 g cm$^{-3}$, excluding alkali metals, alkaline earth metals, lanthanides and actinides. Both industrial and developing countries face significant environmental problems due to increasing pollution of industrial wastewater or groundwater by heavy metal ions. Numerous developments to control pollution of heavy metal ions have been reported [16].

Heavy metals are used for various purposes in industries. They are used-

1. To make batteries.
2. To make pigments.
3. Used as catalysts in petroleum refining.
4. To prevent corrosion/rusting by applying coating on the other metals.
5. Used as stabilizers in plastics.
6. Used in chemical synthesis and metallurgical processes.

Heavy metals enter the air, water and soil due to human activities and natural processes causing serious health hazards due to their acute toxicity to terrestrial and aquatic life [17-18]. The heavy metals are non-biodegradable and some of them are highly toxic when present even in trace amount. They are probable carcinogenic in nature [19]. On the other hand, trace amount of some heavy metals is essential for living beings. Mercury, lead and cadmium are known to be ‘big three’ heavy metal poisons [20].
3.1.1. Effects of heavy metals on Environment

From Environmental point of view, the heavy metals are of larger concern than other metals as they cause toxic or inhibitory effect on living things. Industrial waste, automobiles, atmospheric deposition, landfill runoff and acid mine drainage (AMD) contains metals like cadmium, chromium, copper, zinc, nickel, lead and mercury. Heavy metal pollutants cause direct toxicity to living beings, due to their absence of specific limits. Sources and health effects of some heavy metals are shown in Table 1.2 below:

**Table 1.2: Sources and health effects of some heavy metals**

<table>
<thead>
<tr>
<th>Heavy Metals</th>
<th><strong>Drinking water standard (MCL) mgL⁻¹</strong></th>
<th>Sources</th>
<th>Health Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>1.3</td>
<td>Pulp and paper, electrical goods, utensils, chemicals etc.</td>
<td>Caner (Suspected).</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.1</td>
<td>Cooling tower, dyes, electroplating, ink, anodizing, paints, tanning etc.</td>
<td>Cancer.</td>
</tr>
<tr>
<td>Lead</td>
<td>0.015</td>
<td>Battery industry, paints etc.</td>
<td>Affects nervous and renal system, headache, constipation, cancer etc.</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.002</td>
<td>Coal combustion, electrical batteries, Chlor-alkali industry.</td>
<td>Nerves damage, death, Kidney and brain damage.</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.005</td>
<td>Coal combustion, metal plating, water pipe, phosphate fertilizers etc.</td>
<td>Cardiovascular disease, cancer kidney damage, hypertension</td>
</tr>
<tr>
<td>Nickel</td>
<td>-</td>
<td>Diesel Oil, coal, steel &amp; non-ferrous alloys, tobacco smoke etc.</td>
<td>Lung cancer, respiratory symptoms, hemorrhages</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.05</td>
<td>Metal alloys, power plants, gasoline.</td>
<td>Nervous system damage.</td>
</tr>
<tr>
<td>Cobalt</td>
<td>-</td>
<td>Alloys, steel, electroplating glass, enamel etc.</td>
<td>Cancer.</td>
</tr>
</tbody>
</table>
3.1.1.1. Copper

Copper is most common industrial metal. Copper is an essential element for humans and the level of homeostatically can regulate through body, although fatal effects occurs due to acute doses. Extremely low copper concentration affects genes expression profile of human beings [21], while “Wilson’s diseases” is due to excess amount of copper absorbed by body. Copper is accumulated in the brain, skin, liver, pancreas and myocardium. In addition, copper is phototoxic and indeed has been used as algaecide to control algal blooms. It also damages the plants.

3.1.1.2. Chromium

Chromium occurs both as Cr (III) and Cr (VI) in aqueous state. Cr (VI) is highly toxic, mutagenic and carcinogenic than Cr (III) [22]. In processes of electroplating, cooling water of power plants, tanning, as a biocide, it is consistently being discharged from the effluents. Cr (III) becomes more or less immobilized inside the body, and therefore, tends to accumulate.

3.1.1.3. Lead

Annually lead consumption is 3 million tons, in which 60% is used in the production of batteries and electric accumulators, 12% in construction of building, 6% in cable coating, 5% in ammunition and remaining 17% for other usage. The permissible limit of Pb (II) in drinking water is 0.01 mg L⁻¹ [23]. Lead also exists in Pb (IV) form and there is evidence that bacteria can methylate inorganic lead. Lead which is partially immobilized in soils or sediments can be re-dispersed into environment in the form which is more toxic than inorganic lead. Hyper- tension, brain damage and cancer in children are the effects of lead toxicity [24].

3.1.1.4. Mercury

The average annual consumption of mercury in the world is about 10,000 tons, out of which half is used in the manufacture of paper pulp which is bleached by the chlorine. Mercury is highly toxic than other heavy metals, so studied more widely. In aquatic environment it is found in two forms, i.e. inorganic and organic form. Inorganic form is the divalent ions that can be hydrated or complexed whereas organic ion is mercury methyl. The toxic methyl mercury freely passes from the bloodstream into the
Chapter 1

cerebellum and cortex. Its damage is symphonized by numbness, awkwardness of posture, and blurred vision. Monomethyl form of mercury is found in fishes and around 90% of methyl mercury is absorbed by the human body on consuming the contaminated fish food. Minamata disease was caused by eating mercury contaminated fish [25].

3.1.1.5. Cadmium

The production of cadmium is about 20,000 tons annually. The electroplating industry’s discharge of cadmium into natural waters and about 50% annual consumption of cadmium in the U.S. Anthropogenic sources of Cd (II) are nickel-cadmium battery industry, fertilizers, manure, metallurgical industries, sewage sludge [26]. The effect of Cd (II) poisoning includes kidney damage, bones, liver and blood constitution [27].

3.1.1.6. Nickel

The permissible limit of Ni (II) in drinking water is 0.07 mg L\(^{-1}\) [28]. Long life batteries and electroplating processes contain nickel which is discharged through the effluents by industrial wastewater. The environment is harmful by the evidence of nickel carcinogenicity and its elevated levels [29].

The toxicity of all these heavy metals is summarized in Table 1.3[30].

Table 1.3: Toxicity data for heavy metals

<table>
<thead>
<tr>
<th>Metal (Soluble Salt)</th>
<th>Acute Toxicity (μg L(^{-1})) (CMC)a</th>
<th>Acute Toxicity (μg L(^{-1})) (CCC)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium III</td>
<td>570</td>
<td>74</td>
</tr>
<tr>
<td>Chromium VI</td>
<td>16</td>
<td>11</td>
</tr>
<tr>
<td>Copper</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>Cadmium</td>
<td>4.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Lead</td>
<td>82</td>
<td>3.2</td>
</tr>
<tr>
<td>Zinc</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Nickel</td>
<td>470</td>
<td>52</td>
</tr>
<tr>
<td>Mercury</td>
<td>1.7</td>
<td>0.91</td>
</tr>
</tbody>
</table>

(CMC)\(a\) = criterion maximum concentration which is the U.S. acute water quality criterion [30].

(CCC)\(b\) = Criterion continuous concentration which is the U.S. chronic water quality criterion [30].

3.2. Dyes

Dyes have suitable colour and affinity to the substrate to which it is being applied and resistance to water, light, dilutes acids, alkalies, detergents and organic solvents [31].

Nowadays, starting materials of dye are aniline, benzene, and phenol. William Henry Perkin in 1856 was first coined synthetic organic dye “mauveine” containing N-phenyl phenosafranine.

In 1876 Otto N. Witt suggested that dye molecule should contain two groups:

- **Chromophore**: The colour of a compound is responsible by the presence of an atom or functional group.

- **Auxochrome**: The chromophore is attached to atoms which contain functional group, which changes the ability of the chromophore to absorb light, shifting the wavelength or intensity of the absorption. In auxochromes molecule the fibers are enhanced by soluble affinity.

Nitroso, nitro, azo, azoxy, azomethine, ethyl, azo amine, carbonyl, o-quinonoid, p-quinonoid etc. auxochromes are unable to produce colour themselves, but can deepen the colour produced by chromophore. Auxochrome are certain acidic or basic groups e.g. –COOH, -SO\(_3\)H, -OH, -NH\(_2\), -NHR etc.

3.2.1. Classification of dyes

There are different ways for classification of dyes. Each class of dye has a unique chemistry, particular way of bonding and structure. Dyes can react chemically with the substrates to form strong bonds while other in the process of physical forces. Dyes are classified according various standards as shown below:
1. Classification based on the source of materials [32].
2. Chemical classification of the Dyes- based on the nature of their respective chromophores [33].
3. Dyes according to the nuclear structure [34, 35].
4. Industrial Classification of the Dyes [33].

3.2.1.1. Classification based on the source of materials

The materials which are based on the source of the dyestuff are classified as-

3.2.1.1.1. Natural Dyes

Natural dyes are simply dye substances which are extracted from the natural sources. In the early time, natural dyes were the main source of dyes but nowadays it is replaced by synthetic dyes because it is cheaper, more reliable and can be supplied more easily. Haematoxylin, carmine, orcein are the natural dyes which are still being used in colorings. Leather, cloth, food, pottery and housing have been modified through dye. The Colour Index used for classification of natural dyes-

Natural + Base color + number

Usually the anion is the colored part of molecules. In structural formula molecular charge on a specific atom, the whole molecule will charge.

3.2.1.1.2. Synthetic Dyes

Synthetic dyes are derived from the organic or inorganic compound. Vat dye, Sulphure dye, Disperse dye Acid, Basic, reactive, mordant, metal complex etc. are the example of synthetic dyes. However, textile dyestuffs are grouped into following 14 categories or classes:
Table 1.4:

<table>
<thead>
<tr>
<th>Group</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>Cotton, Cellulosic and Blends</td>
</tr>
<tr>
<td>Vat dyes</td>
<td>Cotton, Cellulosic and Blends</td>
</tr>
<tr>
<td>Sulphur</td>
<td>Cotton, Cellulosic fibers</td>
</tr>
<tr>
<td>Organic pigments</td>
<td>Cotton, Cellulosic, Blended Fabrics, paper</td>
</tr>
<tr>
<td>Reactive</td>
<td>Cellulosic fibers and fabric</td>
</tr>
<tr>
<td>Dispersed dyes</td>
<td>Synthetic fibers</td>
</tr>
<tr>
<td>Acid Dyes</td>
<td>Wool, Silk, Synthetic fibers, leather</td>
</tr>
<tr>
<td>Azoic</td>
<td>Printing inks and pigments</td>
</tr>
<tr>
<td>Basic</td>
<td>Silk, wool, cotton</td>
</tr>
<tr>
<td>Developed Dyes</td>
<td>Cellulosic fibers and Fabric</td>
</tr>
<tr>
<td>Oxidation dyes</td>
<td>Cellulosic fibers and Fabric</td>
</tr>
<tr>
<td>Mordant dyes</td>
<td>Cellulosic fibers and Fabric, Silk, Wool</td>
</tr>
<tr>
<td>Optical/Fluorescent Brighteners</td>
<td>Synthetic fibers, leather. Cotton. Sports goods</td>
</tr>
<tr>
<td>Solvent dyes</td>
<td>Wood Staining, solvent inks, waxes, colouring oils</td>
</tr>
</tbody>
</table>

3.2.1.2. Chemical classification of the Dyes-based on the nature of their respective chromophores in Table 1.5 below:

<table>
<thead>
<tr>
<th>Class of Dyes</th>
<th>Functional groups</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroso</td>
<td>Nitro group as chromophores, phenolic as auxochrome in o-position</td>
<td>Fast green, Naphtol green Y</td>
</tr>
<tr>
<td>Nitro</td>
<td>Nitro group as chromophore</td>
<td>Martius yellow, Naphtol yellow S</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>Presence of chromophore =C=O and =C=C arranged in anthraquinone complex</td>
<td>Alizarin red S, Alizarin blue</td>
</tr>
<tr>
<td>Triphenylmethane</td>
<td>Quinonoid group as chromophore and acidic –OH and basic –NH₂, -NHR, etc. group as auxochrome</td>
<td>Malachite green, Methyl violet</td>
</tr>
<tr>
<td>Diphenylmethane</td>
<td>NH=C= group as chromophore, also contain a diphenylmethane nucleus</td>
<td>Auraine-O</td>
</tr>
</tbody>
</table>
3.2.1.3. Dyes according to the nuclear structure

3.2.1.3.1. Cationic Dyes

Cationic dyes are also called basic dyes because these basic dye molecules contain a positive charge on the chromophore. The basic side of the isoelectric points reacts by the basic dyes. They are salts, usually chlorides, in which the dyestuff is the basic or positive radical. Cationic dyes are powerful coloring agents. The cationic dyes are applied to wool, silk, cotton and acrylic fibers. Usually acetic acid is added to the dye baths which assemble the dye onto the fiber. Basic dyes are also used in the coloration of paper.

![Cationic dye](image)

Figure 1.1: Cationic dye

3.2.1.3.2. Anionic Dyes

Acid dye is water soluble anionic dyes, which contains salt of a carboxylic, phenolic, sulfuric organic acid. The salts are often ammonium or sodium salts. Acid dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Fiber salt formation is partially attached in between the dye anionic groups and fiber cationic. Acid dyes are essential to food colour but not to cellulosic fibers.
3.2.1.4. Industrial Classification of the Dyes

Textile industry primarily consumes the majority of dyestuff. The classification of performances in the dying process is given below. About 60% of the dyestuff worldwide is based on azo dye that is used in the processing of textiles industry. It is categorized as:

3.2.1.4.1. Cellulose Textile Dyes

3.2.1.4.1.1. Direct dyes

The requirements of direct dyes are not fixed. Direct dyes are almost as azo dyes but have some similarities with acid dyes. They have sulphonate functionality which improves solubility. In Figure 1.3, sulphonate groups present uniformly in the molecule along which the molecule on the opposite side form hydrogen bonding through –OH groups, to reduce any repulsive effects.

The direct dyes have lack of fastness during washing. However, they are cheap and it popular for items which are less likely to require fastness during washing. Dyes contain –NH₂ as well as sulphonate functional groups. In this process, dyed fabric is treated with sodium nitrite, which causes the dye convert to a diazo salt. The resultant is larger azo molecule which has more affinity for the fibers and is less soluble.
3.2.1.4.1.2. Vat Dyes

It is the cross-over between dyes and pigments. Vat dyes are insoluble in water whereas its reduced form is soluble in an alkali solution whereby leuco vat is obtained. The leuco compound is adsorbed on fiber and the dye remains fixed to the cloth due to oxidization. Indigo and anthraquinone are the examples.

![Vat dyes](attachment:Vat_dyes.png)

**Figure 1.4: Vat dyes**

3.2.1.4.1.3. Basic dye

These are either hydrochloride or zinc chloride complexes of colour bases which are directly used for silk or wool in basic medium. \(NR^3+\) or \(=NR^2+\) are the cationic functional groups of basic dyes. It is better on the natural fibers, but works well on acrylics.

![Basic Dye](attachment:Basic_Dye.png)

**Figure 1.5: Basic Dye**
3.2.1.4.1.4. Fiber reactive Dyes

The first fiber-reactive dyes contain 1,3-5- triazinyl group which reacts with cellulose in mild alkaline solution was shown by Rattee and Stephen. ICI launched a range of dyes based on this chemistry, called procion dyes. This is applied to every way to vat and direct dyes, having excellent wash fortification and wide range of brilliant colors.

![Schematic diagram of fiber-reactive dye](image)

**Figure 1.6: Schematic diagram of fiber-reactive dye**

3.2.1.4.2. Protein Textile Dyes

3.2.1.4.2.1. Acid dyes

Acid dyes are the sodium salts of colour acids containing sulfonic and phenolic groups. These are always used in an acidic solution. They dye silk and wool directly. Maritus yellow, Orange II, napthol yellow etc. are the examples of such dyes.

3.2.1.4.2.2. Mordent dye

Mordent is a Latin word which means “to bite”. Mordents act as “fixing agents” to improve the colour fortification of some acid dyes which have ability to form complexes with metal ions. Fiber attached by mordent like tannin or tannic acid and then these acids combines with dye to form an insoluble coloured complex. Examples are Alizarin, anthraquinone and azo dyes.
3.2.1.4.3. Synthetic Textile Dyes

3.2.1.4.3.1. Disperse Dyes

Nylon, Dacron, acetate rayons and other synthetic fiber are dyed by this dye. The fiber to be dyed is dipped in a dispersion of finely divided dye in some solubilizing agent such as phenol, cresol or benzoic acid which is present in a soap solution. In adsorption of the dye onto the fiber the high temperature, pressure and time play an important role e.g. Fast pink B.

3.2.1.4.3.2. Solvent or sprit soluble Dyes

These are simple azo or triarylmethane bases or anthraquinone which are used to colour oils, waxes, varnishes, lipsticks, dressings and gasoline etc.

Table 1.6: Other important dyes and their application are shown below

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leather Dyes</td>
<td>Used for leather</td>
</tr>
<tr>
<td>Oxidation Dyes</td>
<td>Used mainly for hair</td>
</tr>
<tr>
<td>Optical Brighteners</td>
<td>Used primarily for textile fibers and paper</td>
</tr>
<tr>
<td>Solvent Dyes</td>
<td>For application in wood staining and production of coloured lacquers, solvent inks, waxes, and colouring oils etc.</td>
</tr>
<tr>
<td>Fluorescent Dyes</td>
<td>Innovative dye, used for application in sports good etc.</td>
</tr>
<tr>
<td>Fuel Dyes</td>
<td>Used in fuel</td>
</tr>
<tr>
<td>Smoke Dyes</td>
<td>Used in military activities</td>
</tr>
<tr>
<td>Sublimation Dyes</td>
<td>Textile printing</td>
</tr>
<tr>
<td>Inkjet Dyes</td>
<td>Writing industry including the inkjet printers</td>
</tr>
<tr>
<td>Leuco Dyes</td>
<td>Electronic industries and papers</td>
</tr>
<tr>
<td>Food Dyes</td>
<td>Colouring food, candles, confectionaries and cosmetics</td>
</tr>
</tbody>
</table>

3.2.2. Dye pollution sources and their hazardous effects

There are more than 10,000 synthetic dyes available commercially and more than $7 \times 10^5$ tones are produced and consumed annually [36, 37] because these dyes are widely
used in paper, cosmetics, rubber, plastics, pharmaceuticals, leather, textiles and food industries. Thus they have gradually rising demand and production. The disposal of synthetic dyes are of abundant great because synthetic dyes contain complex aromatic molecular structure which includes ring like benzene, anthracene, naphthalene, toluene, xylene etc. [38, 39]. Dyes pollution affects the aquatic life because they reduce the sunlight penetration and less availability of oxygen for photosynthesis process. Furthermore, some dyes are considered toxic even carcinogenic for human beings [40, 41]. The following Table 1.7 lists the harmful effects of few dyes.

**Table 1.7: Harmful effects of dyes**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Harmful Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malachite green</td>
<td>Accumulates in the tissues, liver, thyroid gland and bladder</td>
</tr>
<tr>
<td>Congo red</td>
<td>Mutagenic, hazardous in skin contact, eye irritant</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>Toxic to blood, reproductive system, liver, upper respiratory tract, skin and eye contact, central nervous system</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>Skin irritation, eye irritation, toxic if swallowed, respiratory tract irritation</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>Causes respiratory tract irritation, eye and skin irritation, digestive tract irritation, adverse reproductive and fetal effects in animals, vomiting and diarrhea</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>Mutagen and mitotic poison</td>
</tr>
<tr>
<td>Amido Black 10 B</td>
<td>Skin corrosion/ irritation, serious eye damage, specific target organ toxicity, respiratory irritation</td>
</tr>
<tr>
<td>Alizarine Red S</td>
<td>Chronic health effects, skin irritation</td>
</tr>
</tbody>
</table>

Choy et al., [42] reported that the effluent of the textile industries contains 10-20% of the dyes in residual liquors through incomplete exhaustion and washing operations, due to which surface and ground water is polluted. Before discharge, treatment is done to the effluents which contain complex aromatic substances. This has resulted in a demand for environment friendly technologies to remove the dyes from effluents. Easton [43] predicts the degree of fixation for different dye/fiber combinations which are listed in Table 1.8.
Table 1.8: Predicted degree of fixation for different dye/fiber combinations

<table>
<thead>
<tr>
<th>Dye Class</th>
<th>Fiber</th>
<th>Degree of fixation (%)</th>
<th>Recovery of the dye from the effluent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Polyamide</td>
<td>80-95</td>
<td>5-20</td>
</tr>
<tr>
<td>Basic</td>
<td>Acrylic</td>
<td>95-100</td>
<td>0-5</td>
</tr>
<tr>
<td>Direct</td>
<td>Cellulose</td>
<td>70-95</td>
<td>5-30</td>
</tr>
<tr>
<td>Disperse</td>
<td>Polyester</td>
<td>90-100</td>
<td>0-10</td>
</tr>
<tr>
<td>Metal-complex</td>
<td>Wool</td>
<td>90-98</td>
<td>2-10</td>
</tr>
<tr>
<td>Reactive</td>
<td>Cellulose</td>
<td>50-90</td>
<td>10-50</td>
</tr>
<tr>
<td>Sulphur</td>
<td>Cellulose</td>
<td>60-90</td>
<td>10-40</td>
</tr>
<tr>
<td>Vat</td>
<td>Cellulose</td>
<td>80-95</td>
<td>5-20</td>
</tr>
</tbody>
</table>

3.2.2.1. Amido Black 10 B

Amido Black 10 B is a synthetic diazo dye which is also known as Naphthol Blue Black. The dye is used for staining of proteins in biochemical research, mainly to stain for total proteins on transferred membrane blots [44, 45]. The dye is applicable to all kind of natural fibers like wool, cotton, and silk, as well as to synthetic fibers like polyesters, acrylic and rayon. It is also used in paints, inks, plastics, and leather industries.

Hazardous effects of Amido Black 10 B

Irritation and damage to respiratory track are caused due to dye inhalation. Ingestion of dyes also causes toxicity. Amido Black 10 B symptoms includes as coughing and shortness of breath. Skin and eye irritation and rashes with redness and pain with the repetition of this dye [46]. Several health problem to mankind as well as animals are due to the toxic nature of dye present in the living system.

3.2.2.2 Alizarin red S

Alizarin red S is also named as Turkey Red. It is a staining representative in biological research. It stains free calcium and calcium compounds into red or light purple color [47]. Alizarin is commercially used as a red textile dye. It is also used for rat’s embryonic bones or osteogenesis study.
Hazardous effect of Alizarin red S

It is toxic by ingestion. Inhalation of dye causes irritation to the respiratory tract. Symptoms include coughing and shortness of breath etc. [48]. It causes skin irritation such as redness, itching and pain.

4. Wastewater Treatments

Treatment of wastewater includes preliminary, primary, secondary and tertiary treatments.

4.1. Preliminary Treatment

In this treatment Gross solids such as large floating and suspended solid matter, grit, oil and grease are removed. Large quantities of floating rubbish such as cans, cloth, wood and other objects present in wastewater are usually removed under preliminary treatment.

4.2. Primary Treatment

Primary treatment is the removal of settle able organic and inorganic solids by sedimentation, and the removal of materials that will float by skimming. Gross solids, excessive quantities of oil and grease and gritty materials are removed by using primary treatment. Some organic nitrogen, organic phosphorus, and heavy metals associated with solids are also removed during primary sedimentation but colloidal and dissolved constituents are not affected. This is amid which reducing the strength of the wastewater and also ease to secondary treatment.

4.3. Secondary Treatment

Dissolved and colloidal organic particles are removed from wastewater by using aerobic or anaerobic bacteria and other microorganism. Coagulation and flocculation are also done by adding chemicals like alum for secondary treatment. This secondary treatment reduces BOD; it also eliminates significant amounts of oil and phenol. However, secondary treatment systems are expensive for wastewater treatment.
4.4. Tertiary Treatment

Final or Tertiary wastewater treatment is done when specific wastewater constituents which cannot be removed by secondary treatment must be removed. In this treatment individual treatment processes are necessary to remove nitrogen, phosphorous, additional suspended solids, refractory organics, heavy metals and dissolved solids. However, final treatment processes are sometimes combined with primary or secondary treatment or used in place of secondary treatment. In Figure 1.7 schematic representation of wastewater treatment shown.

![Schematic representation of wastewater treatment](image)

Figure 1.7: Schematic representation of wastewater treatment

5. Appropriate routes for the treatment of Dyes and heavy metals from aqueous solution

The metals as well as dyes are removed from precipitation aqueous solutions and waste water by using various methods such as chemical and electrochemical precipitation, reverse osmosis, ion-floatation, cationic and anionic ion-exchange resins, membrane filtration, evaporation, adsorption etc.
5.1. Chemical Precipitation

The removal of inorganic metal ions from waste water by precipitation as insoluble hydroxides, carbonates and sulphides is done by using reagents such as caustic soda, hydrated lime, soda ash and sodium sulphide. Generally lime is used for the precipitation of the heavy metals due to their low price and ease of pH control.

\[ M^{2+} + 2(OH)^{-} \leftrightarrow M(OH)_2 \]

However problems can ascend due to partial removal of the precipitated metal ions from the treated wastewater. If we disposed off sludge as landfills, it may contaminate the ground water, when conditions are favorable for their dissolution [49- 51].

5.2. Coagulation/Flocculation

In the process of the treatment of water and wastewater in which ferric chloride or polymers are added to wastewater which destabilizes the colloidal materials that turns the small particles to agglomerate into larger flocs [52, 53]. First of all coagulant is added to the wastewater, by which colloidal particles are destabilizes and continue in the suspension leading to their agglomeration. In Flocculation the destabilized particles combine to make large flocs which are more easily removed from the wastewater solution. Advantage of this process is to decolorize the dye wastewater and separate many kinds of particles from water and enhanced the filtration process. On the other hand, drawback of this technique includes the transfer of toxic compounds into solid phase and production of large quantity of sludge [54].

5.3. Filtration Method

Reuse of water and chemical recovery was done by filtration methods like ultrafiltration, nanofiltration and reverse osmosis. These methods help to separate dye constantly from the effluent [55, 56]. Membrane filtrations are resistance to temperature, chemical environment and microbial attack. According to the temperature and chemical composition of the wastewater proper sieve size of filter [57] for efficient filtration. The main disadvantage of membrane technology is its high cost, potential membrane fouling and production of a concentrated dye bath which needs to be treated [58, 59].
Chapter 1

5.4. Photochemical treatment

Photochemical treatment is degradation of molecule caused by the absorption of photons, particularly in visible and UV light. In photochemical methods such as UV/H₂O₂, UV/Fenton’s reagent, UV/O₃ etc. free radicals are formed due to UV irradiation. The UV-based methods in presence of a catalyst such as ZnO and TiO₂ have been used for the removal of colour [60, 61]. Intensity of the UV radiation, dye structure, pH and dye bath composition play major role in the degradation of dye [62]. Advantages of this process are dye containing effluents are that no sludge is produced, and foul smells are reduced. The main disadvantage of this method is production of secondary pollutant due to degradation of dyes.

5.5. Ion exchange method:

Ion exchange is the reversible process, in which cationic and anionic constituents exchange ions from water and resin. A variety of synthetic organic resins, inorganic gels, and liquid ion exchangers are used for removal of heavy metal ions from dilute aqueous solutions. Though Ion exchangers can be regenerated by using acid or alkali when resins become saturated but the limitation of ion exchange processes are clogging of the resin due to precipitated water hardness and oxidation of resin by oxidizing agents, organic brighteners used in plating, fouling of resin bed with wetting agents etc. [63, 64].

5.6. Adsorption

The term adsorption is given by Kayser. Adsorption occurs when unsaturated and unbalanced molecular forces contact on the solid surface, this solid surface (adsorbent) when comes in contact with a liquid or gas there is contact between surface with that of the liquid or the gas and their dissolved substances (adsorbates) get adsorbed on the solid surface. Thus Adsorption is a surface phenomenon in which accumulation of substance on the surface of the solid from liquid or gas takes place. Adsorption is the physicochemical process in which dissolved molecules are attached to the surface of an adsorbent by physical forces. If it occurs via chemical forces then it is called chemisorption. Organic and inorganic micro-pollutants are removed from aqueous solutions through adsorption [65]. Furthermore, the nature of adsorbent and adsorbate plays a vital role in the process of adsorption.
**Adsorbent:** The substance which adsorbs another substance on its surface is called as adsorbent. E.g. Charcoal, biomass, synthetic materials

**Adsorbate:** The substance which itself get adsorbed on the surface of another substance is called adsorbate. E.g. Organic and inorganic species

Adsorption is an efficient method for the elimination of colour, odour, inorganic and organic pollutants from municipal and industrial effluents. Adsorption process has the advantages such as convenience, ease of operation, high efficiency and simplicity of design which make it unique for the treatment of water. High adsorption capacities of activated carbon and polymeric adsorbents in water due to low adsorption potential [66] make them ideal adsorbents. In adsorption processes following important mechanisms are involved:

1. **Film diffusion** - The adsorbate molecule must be shifted from the bulk solution to the surface of the adsorbent particle through solvent film that surrounds the adsorbent particles.

2. **Pore diffusion** - The adsorbate molecule passes to an adsorption site through inside the pores of the adsorbent that control its movement.

3. The adsorbent particle must be attached to the surface of the solute for proper adsorption and removal.

There are many factors that influence the rate of adsorption and the range to which a particular solute can be adsorbed. The general effects of some important factors like nature of adsorbent and adsorbate, concentration, pH, extent of agitation, contact time, temperature, size and shape of adsorbent particles, solubility of the solute etc. are shown in Table 1.9.
Table 1.9: Effects of various parameters on adsorption

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact time</td>
<td>Adsorption increases with increase in contact time until equilibrium achieved.</td>
</tr>
<tr>
<td>Adsorbent characteristics</td>
<td>Adsorption is surface phenomenon. Adsorption rate increases with decreasing particle size of adsorbent and presence of surface charges.</td>
</tr>
<tr>
<td>Size and shape of adsorbate</td>
<td>Adsorption usually decreases, as the size of the molecules becomes large due to steric effect.</td>
</tr>
<tr>
<td>Concentration</td>
<td>Rate of adsorption increases with increase in concentration. Rate constant is directly proportional to concentration.</td>
</tr>
<tr>
<td>pH</td>
<td>Change in ionic concentrations of water and solutes help in strong influence on adsorption.</td>
</tr>
<tr>
<td>Temperature</td>
<td>Adsorption capacity and rate affects.</td>
</tr>
</tbody>
</table>

The adsorption capacity for an adsorbate adsorbed per gram of adsorbent (mg g\(^{-1}\)) and removal rate (R %) was calculated using the following equation.

\[
q = \frac{(C_0 - C_e)V}{w} \quad (1)
\]

\[
% R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)
\]

where,

\(C_0 = \) initial concentration (mg L\(^{-1}\)) of adsorbate

\(C_e = \) equilibrium concentration at time \(t\)

\(w = \) dry weight of adsorbent

\(V = \) volume of the adsorbate solution (L)
6. Adsorption Isotherm models

In adsorption process, the point of equilibrium is obtained by the relation of concentration of adsorbate in the bulk and amount adsorbed at the interface that can be conveyed by a series of isotherm models. In experimental data process, isotherms accuracy varies and is considerably affected by the specific interfaces between the adsorbate and adsorbent. For the quantitative calculation of the adsorption capacity or the amount of adsorbent vital to eliminate the unit mass of pollutant from water and wastewater by using the adsorption data through theoretical or empirical equations. The different models tried for the dyes and metal ions adsorptions are given below:

6.1. Langmuir isotherm model

The Langmuir isotherm model assumes the formation of a monolayer that occurs on a homogeneous adsorbent surface of finite number of uniform active energetically adsorption sites. After saturation, no further adsorption occurred on these vacant adsorption sites. The linear form of Langmuir isotherm is given by the following equation [67]

\[
\frac{C_e}{q_e} = \frac{1}{b q_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

(3)

Where,

\( C_e \) = equilibrium concentration of dye or metal ion in mg L\(^{-1}\)

\( q_e \) = equilibrium adsorption capacity in mg g\(^{-1}\)

\( q_{\text{max}} \) = maximum adsorption capacity of dye or metal ion in mg g\(^{-1}\)

\( b \) = Langmuir constant

6.2. Freundlich isotherm model

According to the Freundlich isotherm model, a heterogeneous adsorption surface exist that exhibits unequal available sites with different energies of adsorption is involved in the adsorption process. The Freundlich adsorption isotherm model is represented by equation below:

\[
\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e
\]

(4)
where

\[ q_e = \text{amount of adsorbed solute} \]

\[ C_e = \text{equilibrium concentration of solute in solution} \]

\[ K_F = \text{Freundlich constant (the adsorption or distribution related to the bond energy)} \]

\[ n = \text{intensity of the adsorbents} \]

6.3. Temkin isotherm model

The Temkin isotherm, similar to Freundlich isotherm, is one of the first conveyed isotherms and assumes that when the coverage increases then the heat of adsorption decreases linearly.

\[ q_e = B \ln A + B \ln C_e \] (5)

Where

\[ q_e = \text{Adsorbed amount of solute} \]

\[ C_e = \text{Concentration of solute in solution at equilibrium} \]

\[ A = \text{Equilibrium binding constant (1 mg\(^{-1}\))} \]

\[ B = \text{Heat of adsorption.} \]

Assumption in this model, heat of adsorption as a function of temperature of all molecules in the layer decreases linearly rather than logarithmic with coverage on ignoring the extremely low and high value of concentration [70].

6.4. Dubinin–Radushkevich isotherm

Dubinin–Radushkevich isotherm deals with the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [71-72]. This model has well fitted to high solute activities and the intermediate range of concentrations data, but has insufficient asymptotic properties and does not predict the Henry’s law at low pressure [73]. Application of this model is done to differentiate the physical and chemical adsorption. The D–R isotherm in linear form [74] is represented as:
\[ \ln Q_e = \ln Q_{D-R} - \beta \varepsilon^2 \]  \hspace{1cm} (6)

where

\( Q_{D-R} \) = Theoretical saturation capacity of adsorbent (µg g\(^{-1}\))

\( \beta \) = constant that is related to mean free energy of adsorption per mole of the adsorbate (mol\(^2\) k\(^{-1}\)J\(^{-2}\))

\( \varepsilon \) = Polanyi potential, a function of adsorbate concentration that is represented by the relationship

\[ \varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \]  \hspace{1cm} (7)

The change in free energy involved for the transfer of one mole of metal ions from infinity in the solution to the surface of solid was calculated from \( \beta \) value using the following relationship:

\[ \varepsilon = \frac{1}{\sqrt{(-2\beta)}} \]  \hspace{1cm} (8)

7. Adsorption kinetics models

The kinetics of adsorption plays a very important role in water and wastewater treatment which helps to find out the pathways of reaction, and the mechanism of sorption process. The rate of solute uptake that controls the residual time of solute at the solid-solution phase is the most important factor in the designing of a suitable water and waste water treatment plant. There are various kinetic models which are proposed by different researchers and are given below:

7.1. Pseudo-first order kinetic model

Lagergren’s pseudo-first order is the rate equation to describe the adsorption of an adsorbate from the liquid phase [75]. The linear equation of pseudo-first-order is given below [76].

\[ \log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \]  \hspace{1cm} (9)
where,

\[ q_t = \text{amount of adsorbate adsorbed at time } t \text{ (mg g}^{-1}) \]

\[ k_1 = \text{pseudo-first-order rate constant (min}^{-1}) \]

### 7.2. Pseudo-second order kinetic model

The widely used linear form of pseudo-second-order model is given by the equation [77]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(10)

Where, \( q_e \) and \( q_t \) are the adsorption capacity at equilibrium and at time \( t \) in (mg g\(^{-1}\)).

\( k_2 \) (g min\(^{-1}\) mg\(^{-1}\)) is the pseudo-second order rate constant.

### 7.3. Elovich kinetic model

The Elovich model is employed to describe chemisorption and is given by the equation [78]

\[
q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln (t)
\]

(11)

Where,

\( \alpha \) = initial sorption rate (mg (g min\(^{-1}\))\)

\( \beta \) = Desorption constant (g mg\(^{-1}\)) which express the amount of surface coverage and the activation energy for chemisorption.

### 8. The adsorption thermodynamics

The nature of the adsorption process is evaluated by the thermodynamic data. The thermodynamic feasibility and the spontaneous nature of the adsorption process were determined by the calculation of free energy, enthalpy and entropy changes and thermodynamic constants. The thermodynamic parameters such as change in the entropy (\( \Delta H \)), change in the entropy (\( \Delta S \)) and change in the Gibb’s free energy (\( \Delta G \)) were calculated by using following equation:
\[ K_0 = \frac{q_e}{c_e} \] (12)

\[ \Delta G = -RT \ln K_0 \] (13)

\[ \ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \] (14)

where, \( K_0 \) is equilibrium constant, \( R \) is universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the absolute temperature (K).

The thermodynamic parameters (\( \Delta H \)) and (\( \Delta S \)) were calculated from the intercept and slope of the plot of \( \ln K_0 \) versus \( 1/T \) which is also known as Van’t Hoff plot.

The following conclusion can be made from the above equation and Van’t Hoff plot.

Table 1.10: Show thermodynamic parameters

<table>
<thead>
<tr>
<th>( \Delta H )</th>
<th>+ve</th>
<th>Endothermic process</th>
</tr>
</thead>
<tbody>
<tr>
<td>-ve</td>
<td></td>
<td>Exothermic process</td>
</tr>
<tr>
<td>( \Delta G )</td>
<td>+ve</td>
<td>Non-spontaneous process</td>
</tr>
<tr>
<td>-ve</td>
<td></td>
<td>Spontaneous process</td>
</tr>
<tr>
<td>( \Delta S )</td>
<td>+ve</td>
<td>Increase in randomness at solid/solution interface</td>
</tr>
<tr>
<td>-ve</td>
<td></td>
<td>Decrease in randomness at solid/solution interface</td>
</tr>
</tbody>
</table>

9. Nanotechnology and Nanomaterials:

“Nanotechnology literally means any technology performing at nanoscale and has applications in the real worlds”. Nanotechnology embraces the production, modification and application of physical, chemical, and biological systems at scales [Figure 1.8] ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems [80, 81]. They show unique physico-chemical properties which are different from those of their respective bulk counterparts of their small size [82, 83].
9.1. Classification of nanomaterials

Nanostructured materials based on the dimensions of their structural elements are classified as shown in [Figure 1.9]:

9.1.1. Zero dimensional (0D) materials

These nanomaterials have nano dimensions in all the three directions. Most of these nanoparticles are spherical in size and diameter of these particles will be in the range of 1-50 nm. Metallic nanoparticles such as gold and silver nanoparticles and semiconductor like quantum dots, cubes and polygons shapes are the examples of such materials.

9.1.2. One-dimensional (1D) materials

In these nanostructures, one dimension of the nanostructure will be outside the nanometer range. These materials are long but with diameter of only few nanometers. These include nanowires, nanotubes of metals, oxides and other materials.

9.1.3. Two-dimensional (2D) materials

In these nanomaterials, two dimensions are outside the nanometer range. The area of the nano films can be large but the thickness is always in nano scale range. Examples: nano films, plates, multilayers or networks.
9.1.4. Three-dimensional (3D) materials

All dimensions of these are outside the nanometer range. These include bulk materials composed of the individual blocks which are in the nanometer scale (1-100 nm).

![Classification of nanomaterials](image)

**Figure 1.9: Classification of nanomaterials**

9.2. Nanocomposites

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm, or structure having nano-scale repeat distance between the different phases that make up the material.

Nanocomposite may include porous media, colloids, gels and copolymers but usually solid combination of a bulk matrix and nano-dimensional phase differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of nanocomposite will differ markedly from that of the component materials.

Nanocomposites are found in nature, structure of the abalone shell and bones. The use of nanoparticle-rich materials long predates the understanding of physical and chemical nature of these materials. Surface to volume ratio of the reinforcing phase makes nanocomposites different from conventional composite material.
9.3. Classification of nanocomposite

There are three types of nanocomposite-

9.3.1 Ceramic-matrix nanocomposites
9.3.2 Metal-matrix nanocomposites
9.3.3 Polymer-matrix nanocomposite

9.3.1. Ceramic-matrix nanocomposite

This is subgroup of composite materials as well as subgroup of technical ceramics, i.e. chemical compound form the group of oxides, nitrides, borides, silicide etc. Ideally both components, the metallic one and ceramic one, finely dispersed in each other in order to elicit the particular nanoscopic properties. Nanocomposite from these combinations was demonstrated in improving their optical, electrical and magnetic properties as well as tribological, corrosion-resistance and other protective properties.

Examples: Fe-Cr/Al₂O₃, Ni/Al₂O₃, Co/Cr, Fe/MgO, Al/CNT, Mg/CNT.

9.3.2. Metal-matrix nanocomposites

It is also defined as reinforced metal matrix composites. These types of composites material have at least two constituent parts, one begins with metal necessarily and other part may be different metal or another material such as ceramic or organic compound. It was made by dispersing reinforcing material into metal matrix. The reinforcement surface can be coated to prevent a chemical reaction with the matrix.

Examples: Al₂O₃/SiO₂, SiO₂/Ni, Al₂O₃/TiO₂, Al₂O₃/SiC, Al₂O₃/CNT

9.3.3. Polymer-matrix nanocomposite:

It consists of polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix. These may be of different shape but at least one dimension must be in range of 1-50 nm. These PNC’s belong to the category of multi-phase systems, required controlled mixing/ compounding, stabilization of the achieved dispersion, orientation of the dispersed phase are similar.

Example: Thermoplastic/thermoset polymer/layered silicates, polyester/TiO₂, polymer/CNT, polymer/ layered double hydroxides.
10. Synthesis of nanomaterials

Nanomaterials are the chemical products (molecule, metal complex, cluster, etc.) whose attributes are different from their originators. The preparation of nanomaterials and assembling of the nanostructures into ordered arrays to make them to be functional and operational is crucial aspect of nanoscience and nanotechnology. The nanomaterials/nanostructures include nanoparticles, nanowires, nanoribbons, nanotubes, nanocapsules, nanostructured alloys and polymers nanoporous solids. Many of the chemists have synthesized molecular entities of nanometric dimensions mainly built up from their elemental constituents [84]. In principle, all the methods of synthesis can be broadly divided into two groups: top-down and bottom-up [85]. The principles of these two approaches are compared schematically and examples cited in Figure 1.10 and Figure 1.11 respectively.

Figure 1.10: Schematic comparison of top-down and bottom-up approaches
10.1. Top Down Approach

Top Down Approach starts from macroscopic structures which are subsequently structured by lithographical and etching techniques down to the nanometer scale [86]. In this approach nanoparticles can be built up by various dispersion and aggregation procedure. This approach includes different versions of mechanochemical dispersion, condensation from the gas phase, plasmochemical synthesis and certain other methods. Physical method involves in top-down approach. The dispersion of compact materials into nanosize particles will result in retainment of the original structure in nanoparticles [87].

10.2. Bottom Up Approach

Bottom up approach involves the self-organization of the basic building blocks of nature, i.e. atoms and molecules to build up nanostructures [86]. This approach combines method that allow preparation and studies of nanoparticles but does not involves the development of new materials. It includes processes like condensation at super low temperatures, certain types of chemical, photochemical, radiation reduction and laser induced evaporation. The bottom-up approach largely pertains to chemical
methods of preparation of nanomaterials. In this approach, knowledge of chemistry is needed for assembling and organizing of these nano-objects into nanomaterials. In nanoparticles formed by aggregation of atoms, the position of atoms can be different, which affects the electronic structure of these nanoparticles [87]. The approach from the “bottom”, aims to prepare materials with well-defined (optical, mechanical, chemical and magnetic) properties from smaller sized starting materials (molecules, metal complex, clusters etc.) [88].

There are many novel techniques for the preparation of nano materials and their numbers are growing with the evolution of nanotechnology [89]. Some of the common used processes are:

10.1.1. Sol-Gel Processing

The sol-gel process can be referred broadly as room temperature solution method for preparing oxide and sulphide materials. The process involves the hydrolysis and polymerization of metal alkoxide precursors of silica, ferrous, titania, zirconia as well as other oxides. The solutions of precursors are reacted to form irreversible gels that ultimately dry and shrink to rigid oxide forms [90]. The sol-gel process involves a combination of chemical reactions which turns a homogeneous solution of reactants into an infinite molecular weight oxide polymer. This polymeric unit is a 3-dimensional structural skeleton which consists of inter-connected pores. Ideally, this polymeric unit must be isotropic, homogeneous, and obviously uniform in the nano-domain [89]. Scientifically and technologically important aspects of gel are the structures and nanosized porosity of the gels. The various steps involved in sol-gel process are mixing, gelling, shape forming, drying and finally densification.

10.1.2. Electrochemical Deposition

Synthesis of composite nanomaterial’s routes involved electrochemical deposition process. To minimize the problem of chemical interaction and thermally induced stresses by the low processing temperature, through serious problems take place in the conventional methods like sintering, vapor-phase or liquid-metal processes, which are often used to fabricate numerous composite materials. This method involves a simple methodology in which particulate material is suspended in the plating electrolyte and co-deposited with the metallic matrix. This can be proficient both by electroplating
and by electrode less deposition. The method is commercially used for co-deposition of silicon carbide, alumina or diamond with a metal such as nickel. The most important challenge in this work is to inhibit the cluster of the sample particles anterior to co-deposition [89, 91-93].

10.1.3. Plasma-Enhanced Chemical Vapor Deposition

The Plasma-Enhanced Chemical Vapor Deposition (PECVD) is generally used for the production of thin films. The PECVD belongs to the family of deposition processes, which are broadly defined as “chemical vapor deposition”. In conventional CVD, ‘precursor gases’ are thermally decomposed by the temperature at about 500-1000°C [94]. However, in the PECVD processes, deposition is preceded at much lower temperatures, because the energetic electron gas of plasma is capable of highly dissociating the feed gas [89]. In PCEVD the feed gas and the substrate are kept at near room temperature, hence, it is very useful for deposition on sensitive substrates that can be damaged by high temperature, or in the case of semiconductor production, where dopant redistribution is of important concern [89].

10.1.4. Attrition Milling Process

The name ‘Attritor’ is very often referred to as “stirred ball mill”. The operation of an Attritor is very simple and effective. The material to be ground and the grinding media are placed in a stationary, jacketed tank. This tank is spherical, normally measuring about 2.4 to 9.5 mm in diameter. The common types of grinding media used are: carbon steel, stainless steel, chrome steel, tungsten carbide and ceramics like alumina or zirconia. The material and media are agitated by shaft with arms, which are rotating at high speed causing the media are agitated by a shaft with arms, which are rotating at high speed causing the media to exert both shearing and impact forces on the material, resulting in optimum size reduction and dispersion. Pre-mixing of the material and media is not necessary. The material can be fed directly into the jacketed grinding tank of the Attritor. The Attritors are equipped with specially designed motors which have high starting, electrically driven, two-speed torque. The batch Attritors are equipped with built-in pumping system that maintains the circulation during grinding operation for accelerated attrition and uniformity. This pump can also be used for material discharging. The final product of the grinding action is fine and even particle dispersion [89].
10.1.5. Chemical Precipitations Methods

Chemical precipitation in water and wastewater treatment is the change in form of materials dissolved in water into solid particles. Chemical precipitation is used to remove ionic constituents from water by the addition of counter-ions to reduce the sol-utility. It is used primarily for the removal of metallic cations, but also for removal of anions such as fluoride, cyanide, and phosphate as well as organic molecules such as the precipitation of phenols and aromatic amines by enzymes, detergents and oil emulsions by barium chloride. Major precipitation processes include water softening and stabilization, removal of heavy metals and phosphates. Water softening involves the removal of divalent cationic species, primarily calcium and magnesium ions. Removal of heavy metals are most widely practiced in the metal plating industry, where soluble salts of cadmium, chromium, copper, nickel, lead, zinc etc. need to be remove and possibly recovered [95].

11. Application of nanocomposite in water and wastewater

There are many applications for the treatment of water and wastewater by using carbon based nano-adsorbent, nanoscale metal oxide, nanofibers with core-shell structure, Photocatalysis, Disinfection and microbial control, membranes and membrane processes, sensing and monitoring etc. for the removal of organic and inorganic ions. In these nanocomposites, there are highly assessable adsorption sites, tunable surface chemistry, high specific surface area, reactive core degradation, easily reuse, short internal diffusion distance etc. [96].

12. Objectives of the research

• To synthesize new adsorbents and catalysts based on nanocomposites.

• To characterize the synthesized nanocomposite materials and to examine their applications.

• To optimize different parameters of adsorption, viz.; time of equilibration, concentration of adsorbate solution, dosages of adsorbents, pH and temperature.

• To study the thermodynamics of adsorption to understand the mechanism of adsorption.
• To study the kinetics of metal ion and dye adsorption.

• To study the adsorption isotherm of metal ion and dye adsorption.

• To study the catalytic behavior of the new synthesized catalysts.

13. Importance and Future Prospect of the Study

Adsorption, in the physicochemical treatment of water and wastewaters is the essential process. Nowadays, such treatments are highly needed to maintain the quality of water and to reuse of water economically. This study is of common interest to applications relating to solid/liquid interface and wastewater remediation. This study shall give an idea about the mechanism of adsorption of dye and other toxic metal ions on the surface of nanocomposite materials. It also has the scope of improving the basic understanding of the adsorption process under different conditions. In the physicochemical treatment of water and wastewater it is necessary for the application of adsorption operation and functioning design for complete estimated performance, in which systematic information required process, the interchange of control and response variables itself. When the thermodynamically and kinetically procedure was done, then the settings of particular operation were described, mathematical displaying techniques can be active for the accelerative estimate of adsorbent design and performance. The findings from this research have many potential applications such as it can be used to evaluate sorption performance and a reactor can be designed for wastewater purification at large scale. Furthermore, variations in the interaction force between surfaces of adsorbent and adsorbate due to sorption of charged species can be used to develop sensors. Synthetic organic/inorganic composites are potential materials for the water and wastewater decontamination. Such kind of materials helps to generate nanosheets as well as nanofilters for the cleansing of water and wastewater.
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