INTRODUCTION

“The earth provides enough to satisfy every person’s need but not every person’s greed” – Mahatma Gandhi.

The human life has adapted to the natural variation of the earth’s system and its climate. The earth consists of plants, animals, human beings, air, water, soil and land. It has certain conditions for development of our life. If the conditions are unlimited, it produces some of the problems. The earth has provided as great heights in arts, science and technology. Human activities are now so pervasive and profound in their consequences that they too affect the earth.

Scientific and engineering researches are also playing an increasing role in protecting in the environment. Research has demonstrated the importance of the environment to human health economic, social and aesthetic harm. Scientific and engineering research has provided to reduce the pollution in air and water in the world. As result in some respects we have conquered nature but we are directing our own evolution

An environment, which is hygienically safe and aesthetically acceptable, should provide us sufficient clean water, soil and natural resources necessary for our modern man. Initially man relied on inexhaustible resources as the planet appeared to be without limits and the laws of nature directed our evolution. Later we started to supplement our muscle power with exhaustible energy sources, coal, oil and uranium and to substitute the routine functions of our brains by machines. As a result, in some respects, we have conquered nature but we are directing our own evolution.
ENVIRONMENTAL POLLUTION

Nature is the gift from God. One should not interfere or destroy its beauty. If we do so, we will have to face the consequences. We should take care of nature, because it is the basis of all life. Now pollution is the major problem in our country.

Environment is interconnected with human life. It is common for all. The Physical, Chemical and Biologicals presence of living and non-living things are present in it. They caused to land, water, air and other natural resources is termed environmental pollution. According to ISO 14001, Environment can be defined as surroundings in which an organisation operates including air, water, land and natural resources. The life supporting environment of planet, earth is also composed of air, water and land. Holdgate defined pollution as the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to resources and ecological damage or interface with legitimate use of the environment depending on the activity responsible for the release of pollutants.

The environment is mainly contaminated by industrial wastes. Increasing population, industrialisation, modern civilisation and automobiles alter the natural environment. Toxic substances are mixed with air, water and land which produces pollution in the affect the human health, plants and animals.

Pollution is the introduction of contaminants into a natural environment that causes instability, disorder, harm or discomfort to the ecosystem i.e. physical systems or living organisms. Pollution can take the form of chemical substances or energy, such as noise, heat, or light.
The major forms of pollution are listed below:

**AIR POLLUTION**

The release of chemicals and particulates from chemical industries mixed into the atmosphere. Common gaseous air pollutants include carbon monoxide, sulfur dioxide, chlorofluorocarbons (CFCs) and nitrogen oxides produced by industry and motor vehicles.

**LIGHT POLLUTION**

Includes light trespass, over-illumination and astronomical interference.

**NOISE POLLUTION**

Which encompasses roadway noise, aircraft noise, industrial noise as well as high-intensity sonar. One who is exposed to these noise becomes tensed. The sick can not take rest.

**SOIL POLLUTION**

Soil contamination occurs when chemicals are released intentionally, by spill or underground leakage. Among the most significant soil contaminants are hydrocarbons, heavy metals, MTBE, herbicides, pesticides and chlorinated hydrocarbons.
RADIOACTIVE POLLUTION

Radioactive contamination resulting from 20th century activities in atomic physics, such as nuclear power generation and nuclear weapons research, manufacture and deployment. It induces cancer, abnormal births and mutation in man.

THERMAL POLLUTION

Thermal pollution is the rise or fall in the temperature of a natural body of water caused by human influence. A common cause of thermal pollution is the use of water as a coolant by power plants and industrial manufacturers.

Thermal pollution can also be caused by the release of very cold water from the base of reservoirs into warmer rivers. With the realization of the need to control environmental pollution in terms of both effluent treatment and remediation of polluted environment, has come a whole industry, one dedicated to environmental cleanup. The application of the new technologies is the way to solve the environmental problems today. The technologies have been divided into techniques, which result in destruction or phase shift, concentration and immobilization of the pollutants. They are further classified as physical, chemical, thermal, or biological techniques. Waste management and waste site remediation involve consideration of various criteria like protection of human health and environment, compliance with environmental statues, long-term effectiveness and permanence, reduction of toxicity, mobility and volume, short-term effectiveness, technical feasibility, cost, state acceptance as well as community acceptance.
Among the various kinds of environmental pollutions, water pollution forms the most formidable since water is the most crucial component of the environment. There is little question about the harmful effects of ozone depletion acid rain or greenhouse effect. At the millennium shift, the modern civilized world faces an alarming stress on water security. Water represents a profound need of both organism and society. About 97% of earth’s water is found in the ocean 2% is frozen as ice in polar regions and the remaining 1% is available to us in the form of fresh water in rivers, streams, lakes and groundwater and which human beings want for their daily needs, irrigation and in factories. The demand for water has tripled since 1950. While the demand for water continues to raise, the basic amount of freshwater supply of stress; the rivers are running dry and the water table continues to fall. 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 progress is important factors to achieve water security; but they are not possible to produce without economic resource.

WATER POLLUTION

Water Pollution is the condemnation of water bodies such lakes, rivers, oceans and ground water. It occurs directly or indirectly into water bodies without adequate treatment to remove harmful introduction. It causes deaths and diseases. Water pollution is occurred by the discharge of 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.

Water pollution is a major global problem. It has been suggested that it is the leading worldwide cause of deaths and diseases. Daily more than 14,000 people are death. An estimated 700 million Indians have no access to a proper toilet, and 1,000 Indian children die of diarrheal sickness every day. The 90% of China's cities suffer from some degree of water pollution and nearly 500 million people lack access to safe drinking water. In addition to the acute problems of water pollution in developing countries, industrialized countries continue to struggle with pollution problems.

Contaminants may include organic and inorganic substances.

Organic water pollutants includes Detergents, chloroform, food processing waste, which can include oxygen-demanding substances, fats and grease, insecticides, herbicides, a huge range of organo halides, Petroleum hydrocarbons, including fuels (gasoline, diesel fuel, jet fuels, and fuel oil) and lubricants (motor oil), Volatile organic compounds (VOCs).

Inorganic water pollutants includes, Acidity caused by industrial discharges especially sulfur dioxide from power plants, Ammonia from food processing waste, Chemical waste as industrial by-products, Fertilizers containing nutrients such as nitrates, phosphates, heavy metals from motor vehicles, acid mine drainage and Silt.
All kinds of pollutions are health hazards. Therefore, today’s need is to preserve the environment and guard it against all kinds of pollution. It is the duty of every human being to preserve the environment for the future generations.

**Metal ions as pollutants**

Waste water contains organic, inorganic and toxic pollutants. Most of the metals (Cd, Cr, Co, Cu, Zn, Pd, Hg, Ni and Ag) and metalloids (Se, As and Sb) causes hazard. Inorganic Pollutants consists of metal compounds and mineral acids. They may toxic and disturb the bio-chemical processes. In the 20th century large quantities of various metals have been required. So the usage of metals increased and the pollution will be also increased.

Metal pollutants are primarily disturbed in the atmosphere, water, soil and sediments. Atmospheric metal pollution arises mainly from the mining, smelting and refining of metal ores. High metal concentrations have rendered 9.5% of Japanese rice paddies incapable of producing consumable products. Some of the major metal pollutants include Lead, Mercury, Cadmium, Arsenic, Copper, Chromium and Iron

<table>
<thead>
<tr>
<th>METAL</th>
<th>SOURCE</th>
<th>DISEASES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>Industries from Glass, Ceramic and Lead storage batteries,</td>
<td>Hypertension, reproductive disorders, neurological and metabolic problems.</td>
</tr>
<tr>
<td>Mercury</td>
<td>Mining and Refining Industries, Fungicides</td>
<td>Central Nervous System damage and kidney failure.</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Burning of fossilE fuels and industrial waste`</td>
<td>Kidney damage and hypertension</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Insecticides ,Pesticides, coal Combustion, Metal Smelling and roasting</td>
<td>Cancer</td>
</tr>
<tr>
<td>Copper</td>
<td>Alloys, Paints, Ceramics, Industrial wastes and Pesticides</td>
<td>Coma and Ferver</td>
</tr>
<tr>
<td>Chromium</td>
<td>Industries from wool and Silk</td>
<td>Ulcer, convulsions, Kidney and Liver damage</td>
</tr>
<tr>
<td>Iron</td>
<td>Iron Tablets and industrial wastes</td>
<td>Kidney and Liver damage</td>
</tr>
</tbody>
</table>
Chromium Pollution

Chromium and its compounds form a large and varied group of chemicals which present a variety of risks to workers’ health. They are known by the terms, chromium metal (0) chromium (II), chromium (III) (known as trivalent compounds), chromium (IV) and chromium (V1) (known as hexavalent) compounds.

Chromium is a hard, silver metal which is used for chrome plating and in the manufacture of stainless steel. It is not usually considered a health hazard. However, some chromium compounds such as hexavalent compounds are toxic. They include chromium trioxide and chromic acid. Other compounds called trivalent compounds include chromic oxide and chromic sulphate are non toxic. Chromium compounds are used in dying textiles like silk and wool, in pigments for paint and pottery, in wood preservatives and in catalysts in the chemical manufacturing industry.

Chromium poisoning may occur at work in the industry if the necessary protective clothing is not used. Exposure can occur by breathing in dust, by skin contact with solutions or solids or by eating, drinking or smoking in areas where chromium is used. Members of the public could be exposed to it due to a spillage or inadequate safety measures during disposal. All Chromium compounds may cause dermatitis and some may cause occupational asthma. They can also cause chrome ulcers which form little holes in the skin. Chromium compounds Produces irritation and inflammation of the nose and upper respiratory tract. The inhalation of a large concentration of hexavalent compounds may lead to coughing, wheezing, inspiratory pain, fever and loss of weight.

8
Chromium (V1) compounds are more dangerous than other compound. They are irritants, corrosive and inhaled. They can cause lung irritation, obstruction and lung cancer. Prolonged skin contact may lead to irritation and, if skin damage is extensive, sufficient of the compound may be absorbed to cause renal damage and death.

**Treatment and Prevention**

The exposure must stop immediately. The symptoms can then be managed. The body normally removes chromium rapidly. Acute chromium poisoning may result in death as there is no proven antidote. In these cases, supportive measures may include mechanical ventilation, cardiovascular support and monitoring of kidney and liver functioning. For chromium (V1) compounds, exposure must be kept within the maximum exposure limit (MEL) of 0.05mg/m³ averaged over an 8 hour working day. For other chromium compounds, exposure must be lower than the occupational exposure standard (OES) of 0.5mg/m³ averaged over an 8 hour day. Protective measures may include the use of extraction equipment, chemical / mechanical spray suppressants at plating baths, protective clothing and equipment, adequate washing facilities, skin creams and proper training.

Chromium(III) is an essential nutrient that helps the body use sugar, protein, and fat. An intake of 50–200 µg of Chromium (III) per day is recommended for adults. On the average, adults in the United States take in an estimated 60–80 µg of Chromium per day in food. Therefore, many people's diets may not provide enough
Chromium (III). Without Chromium (III) in the diet, the body loses its ability to use sugars, proteins, and fat properly, which may result in weight loss or decreased growth, improper function of the nervous system, and a diabetic-like condition. Therefore, Chromium (III) compounds have been used as dietary supplements and are beneficial if taken in recommended dosages. Chromium (VI) is more toxic than chromium (III). Breathing in high levels (greater than 2 µg/m³) of Chromium (VI) such as in a compound known as chromic acid or chromium (VI) trioxide can cause irritation to the nose, such as runny nose, sneezing, itching, nosebleeds, ulcers and holes in the nasal septum. Large amounts of chromium can cause stomach upsets, ulcers, convulsions, kidney, liver damage, and even death. The metal chromium (0) is less common and does not occur naturally and does not cause any serious health risk. The maximum permissible level of chromium is 2.0 mg/l.

**Iron Pollution**

Iron is the fourth most abundant element in the earth’s crust and the most abundant heavy metal. It is present in the environment mainly as Fe (II) or Fe (III). The most important commercial iron ores are magnetite, siderite, limonite and hematite. The main use of iron ores in India is steel production, which consumed more than 14 millions tones, one-half of which was supplied by iron and steel scrap metal recycling. Iron is also used in the production of paint pigments, polishing agents and electrical materials.

Iron is an essential element in human nutrition and it is an integral component of cytochromes, porphyrins and metalloenzymes. Dietary iron requirements vary
according to sex and age, infants, children and women of menstrual age are most vulnerable to iron deficiency. The effects of iron deficiency can include impaired mental development and performance in children elevated catecholamine and restlessness in children, reduced work performance in adults and, in severe cases, anemia and impaired oxygen delivery\textsuperscript{5}.

In the bloodstream, iron binds to transferrin and is transported to the spleen, bone marrow and liver, which are the main storage sites for endogenous iron. The reticuloendothelial cells of the liver, iron are bound to haemosiderin; in the parenchyma cells, it is bound to ferritin. Because absorption is low and because iron is recycled in the body, the amount of faecal iron is similar to the amount of dietary iron. Less than 1 mg/d of endogenous iron is lost by the skin, faces and urine.

The ingestion of large quantities of iron results in haemochromatosis. It is a condition in which normal regulatory mechanisms do not operate effectively, leading to tissue damage as a result of the accumulation of iron. This condition rarely develops from simple dietary overloading. Tissue damage has occurred, however, in association with excessive intake of iron from alcoholic beverages in some cases of alcoholism. Tissue damage has also resulted from prolonged consumption of acidic foodstuffs cooked in iron kitchenware.

Poisoning of small children has occurred following ingestion of large quantities of iron tablets. As adult iron tablets can contain considerably more elemental iron than children’s tablets, children who accidentally ingest iron supplements destined for adults risk being poisoned. Three grams of Fe (II) sulphate is regarded as the lethal dose of two-year-olds. Between 14 and 17.5 g is the lethal
dose for an adult male. Iron supplements are commonly used (14% of premenopausal women in one study) without reported toxic effects, except for gastrointestinal upset.

Iron is generally present in surface waters as salts containing Fe (III) when the pH is above 7. Most of those salts are insoluble and settle out or are adsorbed onto surface; therefore, the concentration of iron in well-aerated waters is seldom high. Under reducing conditions, which may exist in some groundwater, lakes or reservoirs and in the absence of sulphide and carbonate high concentrations of soluble Fe(II) may be found. The presence of iron in natural waters can be attributed to the weathering of rocks and minerals; acidic mine water drainage, landfill leakages, sewage effluents and iron-related industries.

There is no evidence of dietary iron toxicity in the general population. Because absorption is regulate, body tissues are generally not exposed to high iron concentrations. Pharmaceutical sources and disease states, such as idiopathic haemochromatosis and thalassaemia major (which requires many blood transfusions), will result in elevated iron concentration. Those individuals who do develop an iron overload are reported to be at greater risk of developing neoplasm’s. The maximum permissible limit of iron is 0.30 mg/L.$^6$
Copper pollution

Copper is one of the earliest known metals. It is present in all land and main organism. In 1827, copper was shown to be present in combined form with the blood proteins of snails. Later, it was established that copper in addition to iron is necessary for blood formation. Soon after this discovery, several reports appeared regarding disorders of grazing sheep and cattle due to deficiencies of copper and their recovery after providing copper supplements. Several enzymes such as tyrosinase, cytochrome oxides, uricase, ascorbic acid oxidase, and monoamine oxidase and B-aminolevulinic acid dehydratase contain copper. Many of the manifestations of copper deficiency in animals seem to be related to the decreased tissue concentrations of some of these enzymes.

Copper is a chalcopile element, which is mostly found in sulfide deposits along with lead, cadmium and zinc. It is used in the manufacture of alloys, paints, ceramics and pesticides. Laboratory studies have shown several physiological functions involving copper. Those are defects in pigmentation, bone formation, reproduction, spinal cord, cardiac function and connective tissue formation because of copper content increases.

Workers involved in use of fungicides containing copper sulphate develop a respiratory disorder called vineyard sprayer’s lung, which is characterized by the development of interstitial pulmonary lesions and nodular fibro-hyaline scars. This may lead to even lung cancer. Copper poisoning can occur as an industrial hazard in
workers engaged in copper mining or processing. Soluble copper levels in water lie in the range 0.5 to 2.0 mg/L. The maximum permissible limit of copper in drinking water is 1.5 mg/L.

**DYES POLLUTION**

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, berries, bark, leaves and wood.

Both dyes and pigments appear to be colored because they absorb some wavelengths of light more than others. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Buts Dyes are soluble, Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments.

**TYPES OF DYES**

The first human-made (synthetic) organic dye, mauveine, was discovered by William Henry Perkin in 1856. Many thousands of synthetic dyes have since been prepared. Synthetic dyes quickly replaced by traditional natural dyes. Dyes are now classified according to how they are used in the dyeing process.
**ACID DYSES**

Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Acid dyes are not substantive to cellulosic fibers.

**BASIC DYSES**

Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, for wool and silk. Usually acetic acid is added to the dyebath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.

**DIRECT OR SUBSTANTIVE DYE**

Direct or substantive dye is normally carried out in a neutral or slightly alkaline dyebath, with the addition of either sodium chloride (NaCl) or sodium sulfate (Na₂SO₄). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

**MORDANT DYSES**

Mordant dyes require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes or chrome dyes. They are applied to wool. Many mordant dyes contain heavy metal that can cause hazardous to health and extreme care must be taken in using them.
VAT DYES

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

REACTIVE DYES

Reactive dyes utilize a chromophore attached to a substituent that is capable of directly reacting with the fibre substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. Cold reactive dyes, such as Procion MX, Cibacron F, and Drimarene K, are very easy to use because the dye can be applied at room temperature. Reactive dyes are the best choice for dyeing cotton, cellulose fibers and art studio.

Disperse dyes

Disperse dyes are water insoluble. They were originally developed for the dyeing of cellulose acetate. Their main use is in dye polyester but they can also be used to dye nylon, cellulose triacetate, and acrylic fibres. They have fine particle size which gives a large surface area that aids dissolution to allow uptake by the fibre. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.
AZOIC DYES

Azoic dye is an insoluble azo dye is produced directly onto or within the fibre. This is achieved by treating a fibre with both diazoic and coupling components. This dye is applied on cotton.

SULFUR DYES

Sulfur dyes are two part developed dyes used to dye cotton with dark colors. The initial bath imparts a yellow or pale chartreuse color. This is after treated with a sulfur compound in place to produce the dark black Sulfur Black 1 is the largest selling dye.

FOOD DYES

Food dyes are food additives, they 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

A number of other classes have also been established including Oxidation bases, Laser dyes, Leather dyes, Fluorescent brighteners, Solvent dyes, Carbene dyes, Contrast dyes.
MALACHITE GREEN

Malachite green is an organic compound and related to tri aryl methane dye that is used as a dyestuff and has emerged as a controversial agent in aquaculture. Malachite green is traditionally used as a dye for materials such as silk, leather and paper.

STRUCTURES AND PROPERTIES

Malachite Green refers to the chloride salt \([\text{C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_2]\text{Cl}\), although the term Malachite Green is used loosely and often just refers to the coloured cation. The oxalate salt is also marketed. The chloride and oxalate anions have no effect on the color. The intense green color of the cation results from a strong absorption band at 621 nm (extinction coefficient of \(10^5 \text{ M}^{-1}\text{cm}^{-1}\)).

Malachite green is prepared by the condensation of benzaldehyde and dimethylaniline to give leuco malachite green (LMG):

\[
\text{C}_6\text{H}_5\text{CHO} + 2 \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 \rightarrow \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_2 + \text{H}_2\text{O}
\]

This colourless leuco compound is oxidized in the presence of manganese dioxoide gives MG

\[
\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_2 + \text{HCl} + 1/2 \text{O}_2 \rightarrow [\text{C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_2]\text{Cl} + \text{H}_2\text{O}
\]
The carbinol derivative of MG is derived from LMG by replacement of the unique C-H by C-OH.

Hydrolysis of MG gives the carbinol form $^9$

$$[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl + H_2O \rightarrow C_6H_5C(OH)(C_6H_4N(CH_3)_2)_2 + HCl$$

MG is deeply coloured and absorbs visible light, whereas the LMG and carbinol derivatives are not. This difference arises because only the cationic form has extended pi-delocalization, which allows the molecule to absorb visible light.

**USES**

Malachite green is traditionally used as a dye. Millions of kilograms of MG and related triarylmethane dyes are produced annually for this purpose. MG is active against the oomycete Saprolegnia, which infects fish eggs in commercial aquaculture. It is also a very popular treatment against ichthyophthirius in freshwater aquaria. The principal metabolite, LMG, is found in fish treated with malachite green, and this finding is the basis of controversy and government regulation $^{10}$.

Malachite green can also be used as a saturable absorber in dye lasers, or as a pH indicator between pH 0.2 - 1.8. Leuco-malachite green (LMG) is used as a detection method for latent blood in forensic science. Hemoglobin catalyzes the reaction between LMG and hydrogen peroxide, converting the colorless LMG into malachite green. Therefore, the appearance of a green color indicates the presence of blood $^{11}$. It causes carcinogenic $^{12}$ symptoms and liver tumor.
Rhodamine B

It is a fluorone dye. It is often used as a tracer dye within water to determine the rate, direction of flow and transport. Rhodamine dyes fluoresce and can thus be detected easily and inexpensively with instruments called fluorometers. Rhodamine dyes are used extensively in biotechnology applications such as fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy and ELISA. It absorbs to plastics and should be kept in glass.

Rhodamine B is used in biology as a staining fluorescent dye, sometimes in combination with auramine O, as the auramine-rhodamine stain to demonstrate acid-fast organisms, notably *Mycobacterium*. It is tunable around 610 nm when used as a laser dye. Its luminescence quantum yield is 0.65 in basic ethanol, 0.49 in ethanol, 1.0 and 0.68 in 94%.

**STRUCTURE**

![Rhodamine B](image)

**IUPAC name**

[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride
Properties

Molecular formula  \( \text{C}_{28}\text{H}_{31}\text{ClN}_{2}\text{O}_{3} \)

Molar mass  479.02

Appearance  red to violet powder

Melting point  210 – 211 °C  (Decomposes)

Solubility in water  ~50 g/l

USES

Rhodamine B is used as a biomarker in oral rabies vaccines for wildlife, such as raccoons, to identify animals that have eaten a vaccine bait. The rhodamine is incorporated into the animal's whiskers and teeth. It is also often mixed with herbicides to show where they have been used.\(^\text{18}\). It is suspected to be carcinogenic, cancer, phototoxic and photoallergic.

Dyes are an important class of pollutants, and can be identified by the human eye. Disposal of dyes in precious water resources must be avoided, and for that various treatment technologies are in use. Among various methods adsorption occupies a prominent place in dye removal. The growing demand for efficient and low-cost treatment methods and the importance of adsorption has given rise to low-cost alternative adsorbents (LCAs).
<table>
<thead>
<tr>
<th>Example Applications</th>
<th>Description</th>
<th>Economics</th>
<th>Types of Wastes</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-Exchange</td>
<td>Waste stream pass through resin bed where ionic materials are selectively removed</td>
<td>Relatively high costs</td>
<td>Heavy metal aqueous solutions</td>
<td>Metal plating solutions</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>Separation of molecules by size using membranes</td>
<td>Relatively high costs</td>
<td>Heavy metal aqueous solutions</td>
<td>Metal coating applications</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>Separation of dissolved materials from liquid through a membrane</td>
<td>Relatively high costs</td>
<td>Heavy metals; organics, Inorganic aqueous solutions</td>
<td>Seldom used industrially</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>Separation of positively charged materials by application of electric current</td>
<td>Dependent on concentrations</td>
<td>Heavy metals; ions from aqueous solutions; copper recovery</td>
<td>Metal plating</td>
</tr>
<tr>
<td>Precipitation</td>
<td>Chemical reaction caused formation of solids which settle</td>
<td>Relatively high costs</td>
<td>Lime slurries</td>
<td>Metal plating, wastewater treatment</td>
</tr>
<tr>
<td>Evaporation</td>
<td>Solvent recovery by boiling off the solvent</td>
<td>Energy intensive</td>
<td>Organic/Inorganic aqueous streams</td>
<td>Rinse waters from metal platingwaste</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>Separation based on differential rates of diffusion through membranes</td>
<td>Moderately expensive</td>
<td>Separation/concentration of ions from aqueous streams</td>
<td>Separation of acids and metallic solutions</td>
</tr>
<tr>
<td>Reduction</td>
<td>Oxidative state of chemical changed through chemical reaction</td>
<td>Inexpensive</td>
<td>Metals, mercury in dilute streams</td>
<td>Chrome plating solutions and tanning operations</td>
</tr>
<tr>
<td>Flocculation</td>
<td>Agent added to aggregate solids together to facilitate separation</td>
<td>Relatively inexpensive</td>
<td>Aqueous solutions with finely divided solids</td>
<td>Refinery oil-water mixtures, paper wastes; mineral industry</td>
</tr>
</tbody>
</table>
A detailed survey of literature reveals that the works related to the removal of metal ions as pollutants. Hence the silent features of the most recent works only are listed below.

Som Shankar Dubey and Co-workers investigated the mechanism of Cr (III) and Cu(II) ions removal by local clay. Adsorptive concentration (10^{-4}–10^{-6} mol dm^{-3}), pH (ca 2.0-9.0) and temperature (303-333 k) were examined for assessing optimum conditions for removal of these ions. The adsorption phenomenon was highly dependent on the amount of the adsorbent concentrations. The uptake of ions fitted well for Freundlich isotherm, increased with increase in the temperature and no significant desorption took place in the studied temperature range. The energy of adsorption process for the both cations indicates that the adsorption phenomenon is of chemisorption type. The rate kinetics of the adsorption followed the first order kinetics.

Sathyanarayana and Sessaiah examined the sorption of manganese (II) and nickel(II) onto two adsorbents, kaolinite and bentonite. Effect of pH, contact time, adsorbent dose, and initial metal ion concentration on adsorption was investigated. The adsorbents exhibit good sorption potential for manganese and nickel with a peak value at pH 5 and pH 6 respectively. More than 70% sorption occurred within 20 min for manganese and nickel and equilibrium was attained at 90 min for manganese and 120 min for nickel. Freundlich and Langmuir’s mathematical models were used to describe batch adsorption. The adsorption data was found to be favourable with respect to both the isotherms. The adsorption of the
two metal ions from an aqueous solution onto two adsorbents followed pseudo-second order kinetics.

Baskaran et al.\textsuperscript{21} investigated the removal of ferrous ion using low cost adsorbents such as zea mays dust carbon (zdc) under different experimental conditions. The parameters such as agitation time, initial metal ion concentration, carbon dose, pH and temperature were studied. The adsorption followed first order reaction equation and the rate is mainly controlled by intraparticle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity (Qm) obtained from the Langmuir isotherm plot were found to 37.17, 38.31, 39.37 and 40.48 mg/g. The temperature variation study showed that the ferrous ions adsorption is endothermic and spontaneous. Significant effect on adsorption was observed on varying the pH of the ferrous ion solutions. The Langmuir and Freundlich adsorption isotherms obtained positive $\Delta H^0$ value. pH dependent results and desorption of metal ions in mineral acid suggest that the adsorption of ferrous ion on zdc involves physisorption mechanism.

Joseph Brady and John. Tobin\textsuperscript{1} were studied the adsorption capacity of rhizopus arrhizus was found to remove heavy metal ions such as $\text{Sr}^{2+}$, $\text{Cd}^{2+}$, and $\text{Cu}^{2+}$ efficiently from aqueous solution by using the pH range 4–6. Metal uptake values for each biomass type were found to increase in the order of $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Sr}^{2+}$. Freeze-dried biomass proved the most efficient biomass type for metal adsorption followed in order by oven-dried and live biomass for $\text{Sr}^{2+}$ systems, and live and oven-dried biomass for $\text{Cd}^{2+}$ and $\text{Cu}^{2+}$ systems. Each test ion displaced constant levels of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ ions from the three biomass types, indicating that
biomass pretreatment had no apparent effect on the ion-exchange capacity of Rhizopus arrhizus. Similarly, the levels of H⁺ displacement resulting from test ion adsorption were unaffected by pretreatment but were found to increase in the order Cu²⁺ > Cd²⁺ > Sr²⁺. Linear reciprocal Langmuir and Scatchard transformation plots reflected the predominantly ion-exchange mechanism of Sr²⁺ and Cd²⁺ adsorption and a curved Scatchard transformation plot reflected the more covalent nature of Cu²⁺ Sadsorption²².

Adebowale et al²³ studied the adsorption of four metal ions (Pb²⁺, Cd²⁺, Zn²⁺, and Cu²⁺) as a function of metal ion concentration. The metal ions showed stronger affinity for the phosphate-modified adsorbent with Pb²⁺, Cu²⁺, Zn²⁺, and Cd²⁺ giving an average of 93.28%, 80.94%, 68.99% and 61.44%. The order of the various adsorbents were Pb²⁺ > Cu²⁺ > Zn²⁺ > Cd²⁺. Desorption studies showed that the phosphate-modified adsorbent has the highest affinity for the metal ions than unmodified clay. The experimental data were confirmed well to both the Langmuir and Freundlich models.

Katsutoshi Inoue et al tested the adsorption for different metal ions such as Cr (VI), Cr(III), Fe(III), Zn(II), Cd(II) and Pb (II) from an aqueous solution of persimmon waste at pH (1 to 5). The Cr (VI) was to be selectively adsorbed on the cross-linked gel over the other metal ions studied. The adsorption isotherm of Cr (VI) followed the Langmuir type of adsorption and exhibited a maximum loading capacity of 7.18 mol kg⁻¹ at pH 1. The removal of Cr (VI) from Zn (ii) was successfully demonstrated²⁴.
Yuan tian and Co-workers\textsuperscript{25} investigated the absorption mechanism of gh-t-p for Au(III), Hg(II), Cu(II), Pb(II), Co(II), Zn(II), Ni(II), Cr(III) and Cd(II). And the results revealed that gh-t-p has the best adsorption capacity for Au(III). Gh-t-p could reach to the saturation adsorption capacity within 2 hours and it is an excellent adsorption capacity. For Au (III) was 266.49 mg/g when the initial solution concentration was 2.0 mmol/l at 35 °C. The adsorption kinetics can be modelled by pseudo-second-order rate equation gh-t-p is favourable and useful for the uptake of Au (III). So the adsorption capacity was good.

Srivastava Co- workers\textsuperscript{26} studied the adsorption potential for chromium, mercury and lead by the waste slurry generated from fertilizer plants. The adsorption potential for chromium, mercury and lead were good. Copper and molybdenum was poor scavenger for cadmium, nickel, cobalt and zinc. Isotherms have been used to obtain the thermodynamic parameters of the process.

Pandey and Co-workers investigated the mechanism of Cr (VI), Pb(II) and Cu(II) removal by calcium alginate. Calcium alginate beads were found to remove heavy metal ions efficiently from aqueous solution with selectivity in the order of and Cr (VI)>Cu(II)>Pb(II). The biosorption of metal ions by calcium alginate beads decreased as the initial concentration of metal ions increased in the medium. The maximum uptake of metal ions was obtained at pH 2.0. Above pH 2.0, biosorption of metal ions by calcium alginate beads was found to be relatively constant for Pb (II) efficiency. At temperature 35°C, the biosorption of metal ions was found to be relatively constant for Pb (II) and Cu(II) ions, biosorption of Cr(VI) still increased upto pH 3.0 having 86% removal efficiency. At temperature 35°C, the
biosorption of metal ions was found to be highest, with increase or decrease in temperature resulted in a decrease in the metal ions uptake capacity. The sorption data of all three metal ions conformed well to the Langmuir isotherm.  

Karamanis and Assimakopoulos tested the potential of aluminum-pillared-layered montmorillonites for the removal of copper and cesium from aqueous solutions by varying the initial conditions. The sorption kinetics and capacity of adsorbents were determined in relation to the effects of factors such as the initial metal concentrations initial pH of the solution and in the presence of competitive cations. Kinetic studies showed that an equilibrium time of few minutes was needed for the adsorption of metal ions on adsorbents. A pseudo-first-order equation was range for the removal of copper and calcium was found to be 4.0-6.0 and 3.0-8.0, respectively. Cesium and copper sorption isotherms were best represented by Langmuir model.  

Kaikake et al. investigated the feasibility of using dripped the degreased coffee beans as an adsorbent for removal of Cu(II), Zn(II), Pb(II), Fe(III) and Cd(II). The compositions of the adsorbents were characterized by FT-IR spectroscopy, scanning electronic micrograph and fluorescent X-ray. Batch adsorption experiments were carried out at various pH values in order to elucidate the selectivity of metal ions. All metals were adsorbed at low pH region (3.0-5.0). The adsorption isotherm for Cd (II) at pH 8 fitted with Langmuir equation.

Kurniawan et al. studied technical applicability of a various physico-chemical treatments for the removal of heavy metals such as Cd(II), Cr(III), Cr(IV), Cu(II), Ni(II) and Zn(II) form contaminated wastewater. A particular focus is given
to chemical precipitation, coagulation-flocculation, floatation, ion exchange and membrane filtration. Their advantage and limitations in application are evaluated. Their operating conditions such as pH dose required, initial metal concentration and treatment performance are presented. It is evident from the survey that ion exchange and membrane filtration are the most frequently studied and widely applied for treatment of metal-contaminated wastewater.

Nigmananda Das and Jana\textsuperscript{37} studied the batch isothermal adsorption experiments to evaluate the effectiveness of the water-washed leached residue for removal of different bivalent metal ions from aqueous synthetic solutions. The effects of pH, initial metal ions concentration, amount of adsorbent, interfering ions, and heat treatment were also investigated. The uptake of metal ions increased with increasing pH. Under identical conditions the adsorption capacity increased in the order Cd(II)<Cu(II)<Pb(II). The adsorption kinetics was found to follow a first-order rate expression and the experimental equilibrium adsorption data fitted reasonably well to both Langmuir and Freundlich isotherm models.

Raul Munoz and Co-workers\textsuperscript{38} examined the residual algal-bacterial biomass from photosynthetically supported organic pollutant biodegradation processes, in enclosed photo bioreactors. It was tested for its ability to accumulate Cu (II), Ni(II), Cd(II), and Zn(II). The algal –bacterial biomass combined the high adsorption capacity of micro algae with the low cost of the residual biomass, which makes it an attractive biosorbents for environmental applications. There was no observed competition for adsorption sites, which suggested that Cu(II), Ni(II), Cd(II) and
Zn(II) bind to different sites and that active Ni(II), Cd(II), and Zn(II) binding groups were present at very low concentrations.

Isabel Villaescusa et al. revealed the sorption of Pb (II), Ni(II), Cu(II) and Cd(II). The kinetic studies show that the initial uptake was rapid and equilibrium was established in one hour for all the studied metals and that the data followed the pseudo-second order reaction. The Langmuir and Freundlich isotherm models described the equilibrium sorption data for single metal system at initial pH 5.5. However the non-competitive Freundlich model has been found to provide the best correlation.

Sona and D’souza reported the possibility of low grade phosphate for the removal of lead, copper, zinc and cobalt ions from aqueous solutions. Effects of contact time, amount of adsorbent and initial concentration of metal ions were studied. Adsorption of heavy metal ions was found to follow the order of Pb (II)>Cu (II)>Zn(II)>Co(II). Similarly Chockalingam and Subramanian reported the utility of rice husk as an adsorbent for metal ions such as iron, zinc and copper from acid mine water. The adsorption isotherms exhibited Langmuir behavior and were endothermic in nature. The free energy values for adsorption of the chosen metal ions onto rice husk were found to be highly negative attesting to favorable interaction. Over 99% Fe(III), 98% of Fe(II) and Zn (II) and 95% Cu(II) uptake was achieved from acid mine water, with a concomitant increase in the pH value by two units using rice husk indicated successful growth of *Desulfotomaculum nigrificans*(D.nigrificans). The possible mechanism of metal ion adsorption onto rice husk is discussed.
Shukla and Co-workers\textsuperscript{42} investigated the potential of cheap lignocelluloses fiber, coir, for the removal of heavy metal ions like Ni (II), Zn(II) and Fe(II) from their aqueous solutions. The adsorbent was oxidized with hydrogen peroxide to form the chemically modified fiber. Langmuir type adsorption was followed by the coir fibers. The modified coir fibers gave higher metal ion uptake as 4.33, 7.88 and 7.49 mg/g for Ni (II), Zn (II) and Fe(II) respectively, against 2.51, 1.83 and 2.84 mg/g for the unmodified coir fibers. The metal ion uptake values decreased with lowering of pH.

Shaobin Wang et al\textsuperscript{43} tested the hydro thermally treated fly ash for adsorption of heavy metal ions and dyes in aqueous solution. It was shown that fly ash and the modified forms could effectively absorb heavy metals and methylene blue but not effectively adsorb Rhodamine B. Namasivayam and Sangeetha\textsuperscript{44} examined the ZnCl$_2$ activated lignocelluloses agricultural waste, coir pith carbon for the removal of toxic anions, heavy metals, organic compounds and dyes from water. Sorption of inorganic anions such as nitrate, thiocyanate, selenite, sulfate, molybdate, phosphate and heavy metals such as Ni (II) and Hg(II) have been studied. Removal of organics such as resorcinol, 4-nitrophenol, catechol, bisphenol A, 2-aminophenol, quinol, o-cresol, phenol and 2-chlorophenol have also been investigated. Uptake of acidic dyes such as acid brilliant blue, acid violet, basic dyes such as methylene blue, rhodamine B, direct dyes such as direct red 12B, Congo red and reactive dyes such as procion red, procion orange were also examined to assess the possible use of the adsorbent for the treatment of contaminated ground water. Favorable conditions for maximum removal of all adsorbents at the adsorbate concentration of 20 mg/L were
used. Results show the ZnCl₂ activated coir pith carbon is effective for the removal of toxic pollutants from water.

Kobya and Co-workers⁴⁵ examined the acid activated carbonized apricot stones for the removal of Ni(II), Co(II), Cu(II), Pb(II), Cr(III) and Cr(VI) ions from aqueous solutions by adsorption. Batch adsorption experiments were conducted to observe the effect of pH (1-6) on the activated carbon. The adsorption of these metals was found to be dependent on solution pH. Highest adsorption occurred at 1-2 for Cr(VI) and 3-6 for the rest of the metals ions, respectively. Adsorption capacities for the metal ions were obtained in the descending order of Cr(VI)>Cd(II)>Co(II)>Cr(III)>Ni(II)>Cu(II)>Pb(II) for the activated carbon prepared from apricot stone.

Ramesh and his research team⁴⁶ revisit the literature for evaluating the thermodynamic parameters of adsorption equilibrium uptakes of heavy metals and dyes from water and wastewater streams using low-cost adsorbents derived from agricultural waste, industrial wastes and some natural product. They highlighted the possible flaws in some adsorption studies when their thermodynamic parameters were assessed since compensation effects during enthalpy and entropy evaluation were assessed since compensation effects during enthalpy and entropy evaluation were possibly overlooked.

Machida and Co-workers⁴⁷ evaluated the removal of Cu (II) and Pb(II) by adsorption onto activated carbon in single and binary component solutions. Reversibility of adsorption of the heavy metals by the carbon was evaluated by desorption experiments. The number of the maximum adsorption sites and
adsorption equilibrium constants of Cu (II) and Pb(II) was estimated by the results of single component systems assuming the Langmuir adsorption model. The adsorption sites per gram of activated carbon resulted in similar values for Cu (II) and Pb (II) from the isotherms. Competitive adsorption of Cu (II) and Pb (II) on the same adsorption sites was confirmed by both experimental and predicted results of adsorption in the binary mixture.

Vijayaraghavan et al.[48] investigated the ability of Turbinaria ornata, a brown marine alga to remove Cu (II) from aqueous solution. Batch equilibrium test shows the maximum copper uptake at pH6, according to the Langmuir model. A solution of 0.1 M HCl performed well in eluting copper from copper loaded biomass and caused no damage to the biosorbent. The ability of T. ornata to biosorb copper in a packed column was investigated as well. The experiments were conducted to study the effect of important design parameters such as bed height and flow rate.

The biosorption of Zn (II), Cu(II) and Co(II) onto O. angustissima biomass from single binary and ternary metal solutions, as a function of PH and metal concentrations Via Central Composite Design generated by statistical software package Design Expert 6.0revealed that metal interactions could be best studied at lower pH range that is 4-5, which facilitates adequate availability of all the metal ions. The sorption capacities for single metal decreased in the order Zn(II)>Co(II)>Cu(II)[49]. Singh and Hasan[50] reported the removal of Cu (II) from wastewater by rice polish successfully. The maximum removal of Cu (II) has been found to be 97.5% at PH 8.0.
Chojnacka and Co-workers\textsuperscript{51} examined the process of biosorption of heavy metal ions by blue green algae spirulina so., spirulina sp. Which was found to be a very efficient biosorbent the kinetic experiments showed that the process equilibrium was reached quickly, In less than 5-10 min. It was found that the equilibrium dependence between biosorption capacity and bulk metal ion concentration could be desired with Langmuir equation. This suggests that the mechanism of biosorption is rather chemisorptions than physical adsorption and was further confirmed by the low surface area associated with physical adsorption and by the presence of cations that appeared in the solution after biosorption.

Shukla and Pai studied of a lignocellulosic fibre, jute for adsorption of heavy metal ions like Cu(II), Ni(11) and Zn(II) from their aqueous solutions. The fiber was also used as adsorbent after chemically modifying it by two different techniques, viz, loading of a dye with specific structure, Reactive Orange 13, and oxidizing with hydrogen peroxide. Both the modified jute fibers gave higher metal ion adsorption. Adsorption isotherm models indicated best fit for Langmuir model for the modified adsorbents were also assessed for the successive adsorption and desorption cycles\textsuperscript{52}.

Jang et al.\textsuperscript{53} assessed the ability of three mulches to remove several of the heavy metal ions typically encountered in urban runoff. Three types of mulch, cypress bark(C), hardwood bark (H), and pine bark nugget (p) selected as potential sorbent to capture heavy metals in urban runoff. The hardwood bark (H) mulch had the best capacity for all the heavy metal ions. It was concluded that the H mulch is the best of the three adsorbents for treatment of urban runoff containing trace amounts of heavy metals. In order to investigate the sorption isotherm equilibrium
models, the Freundlich and Langmuir isotherms were analyzed. The sorption of these metals on H mulch conformed to the linear form of the Langmuir adsorption equation.

Chuah and his team\textsuperscript{54} reported the removal of heavy metals and dyes by rice husk, a low-value agricultural by-product. It has been investigated as a replacement for currently employed expensive methods of heavy metal removal from solutions. The heavy metals being studied are As, Au, Cr, Cu, Pb, Fe, Mn, Zn, Cu and Cd. Rice husk is also being used to treat textile dyes such as like malachite green and acid yellow 36. The treatment and preparation of rice husk activated carbon are of importance and become a subject of study.

Chojnacka\textsuperscript{55} analyzed the sorption of Cr (III) ions from aqueous solutions by animal bones. Animal bones were found to be an efficient sorbent with the Maximum experimentally determined sorption capacity in the range of 29-194 mg/g that depended on pH and temperature. The maximum experimentally determined sorption capacity was obtained at 50\textdegree C at pH 5. Batch kinetics and equilibrium experiments were performed in order to investigate the influence of contact time, initial concentration of adsorbate and sorbent, temperature and pH. Mathematical models describing kinetics and static’s of sorption were proposed. It was found that process kinetics followed the pseudo-second-order pattern.

Harshala and co-workers\textsuperscript{56} investigated uranium adsorption by coir pith. The influence of different experimental parameters such as final solution pH, adsorbent dosage, sorption time, temperature and various concentrations of uranium of uptake were evaluated. Maximum uranium adsorption was observed in the pH range 4.0-
6.0. The Freundlich and Langmuir adsorption models were used for the mathematical descriptions of the adsorption equilibrium. The equilibrium data fitted well to both the equilibrium models in the studied concentration range of uranium (200-800 mg/L) and temperatures (305-336K).

The utility of recent technology to remove heavy metal ions from aqueous solutions was reported by Osman Gulnaz et al. The biosorption of copper ions from aqueous solution by dried activated sludge was investigated in batch systems. Effect of solution pH, initial metal concentration and particle size range were determined. The suitable pH and temperature for studied conditions were determined 4.0 and 20°C, respectively. The equilibrium data fitted very well to both Langmuir and Freundlich isotherm models. The pseudo first and second-order kinetic models were used to describe the kinetic data.

Ngah and Co-workers studied the batch adsorption system for the adsorption of Fe (II) and Fe (III) ions from aqueous by chitosan and cross linked chitosan beads. Chitosan beads were cross-linked with glutaraldehyde (GLA), epichlorohydrin ECH) and ethylene glycol diglycidyl ether (EGDE) in order to enhance the chemical resistance and mechanical strength of chitosan beads. Experiments were carried out as function of pH, agitation period, agitation rate and concentration of Fe (II) and Fe (III) ions. Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm constants. The kinetic experimental data correlated well with the second-order kinetic model, indicating that the chemical sorption was the rate limiting step.
Badruzzaman et al\textsuperscript{59} evaluated arsenic removal in potable water systems by granular ferric hydroxide ion adsorbent which is commercially available. GFH is a highly porous adsorbent with a BET surface area of $235 \pm 8 \text{ m}^2/\text{g}$. The purpose of this work is to quantify arsenate adsorption kinetics on GFH and to determine if intraparticle diffusion is a rate-limiting step for arsenic removal in packed-bed treatment systems. Data from bottle-point isotherm and differential column batch reactor (DCBR) experiments were used to estimate Freundlich isotherm parameters ($K$ and $1/n$) as well as kinetic parameters describing mass transfer resistance surface diffusion.

Bhattacharya and Arunima\textsuperscript{60} investigated the adsorbent developed from the mature leaves of the Neem tree for removing Pb (II) from water. Adsorption was carried out in a batch process with several different concentrations of Pb(II) by varying amount of adsorbent, pH, agitation time and temperature. The uptake of the metal was very fast initially but gradually slowed down indicating penetration into the interior of the adsorbent particles. Both first-order and second-order kinetics were tested and it was found that the latter gave a better explanation. The experimental data closely followed both Langmuir and Freundlich isotherms. The adsorption continuously increased in the pH range of 2.0-7. The adsorption was exothermic at ambient temperature and the computation of the parameters $H$, $S$ and $G$ indicated the interactions to be thermodynamically favorable.

Kadirvelu and Co-workers\textsuperscript{61} examined the sago industrial waste activated with sulphuric acid for Hg II) removal. Adsorptive removal of Hg (II) from aqueous solution onto Ac prepared from sago industry waste has been studied under varying
conditions to assess the Kinetic and equilibrium parameters. The Langmuir and Freundlich equilibrium isotherm models were found to provide an excellent fitting of the adsorption data. The adsorption capacity obtained from the Langmuir equilibrium isotherm model was found to be 5.56 mg/g at pH 5.0 for the particle size range of 125-250 um. The percent removal increased with an increase in pH from 2 to 10.

During the past three decades extensive studies on the equilibrium kinetic and thermodynamic aspects of the adsorption of metal ions using variety of adsorbents have been carried out. The salient features of the most recent endeavors in this area were explained in the foregoing pages. In addition to the adsorbents mentioned above, different other material have been scanned for their ability to abate metal ions from aqueous solution and the they include cross linked amphoteric starch\textsuperscript{62}, humic umbrisols\textsuperscript{63}, aminated and protonated mesoporous aluminas\textsuperscript{64}, activated carbons prepared from various materials\textsuperscript{65-72}, minerals\textsuperscript{73-79}, coconut coirpith\textsuperscript{80}, natural organic matter\textsuperscript{81}, tree fern\textsuperscript{82}, modified pinus radiate bark\textsuperscript{83}, mango seed powder\textsuperscript{84}, salicylaldoxime immobilized silica gel\textsuperscript{85}, poly acrylamide grafted iron(III) oxide\textsuperscript{86},iron bearing industrial sludges\textsuperscript{87}, peat\textsuperscript{88}, chitosan\textsuperscript{89}, polyacrylamide grafted used tea leaves\textsuperscript{90}, alumina\textsuperscript{91}, flyash\textsuperscript{92-93}, peanut hull pellets\textsuperscript{94}, citric acid modified agricultural by products\textsuperscript{95}, ion exchange resins\textsuperscript{96}, stannic-titanic mixed-oxide gel\textsuperscript{97}, biomaterials\textsuperscript{98-103}, industrial wastes\textsuperscript{104-105} and agro wastes\textsuperscript{106-107}.\textsuperscript{99}
1.5 REVIEW OF LITERATURE ON ADSORPTION OF DYSES

This section gives an overview of previous investigation on the removal of dyes from an aqueous solutions. The salient features of the most recent works related to the equilibrium kinetic, and thermodynamic aspects of the adsorption of dyes are listed below.

Mohammed and Co-workers studied the removal of two dyes sulphanilic azo antipyrine and sulphanilic azo imidazole from an aqueous solution on charcoal. The experiments were undertaken in a batch adsorption technique to access the effect of the variables such as contact time, initial dye concentration, initial pH, adsorbent dose and temperature. Adsorbent dosage (0.1 g) was higher value for both dyes. The equilibrium in the solution was observed within (35 min) of two sulphanilic dyes on charcoal. The equilibrium isotherms for both dyes were determined to describe the adsorption process. The results showed that the equilibrium data was fitted with Freundlich isotherm.

Jayaraj et al analyzed the adsorption of malachite green onto activated enteromorpha carbon by using batch adsorption method. Adsorption kinetics and equilibrium were investigated as a function of initial dye concentration, pH, contact time and adsorbent dosage. Kinetics studies indicated that the adsorption was pseudo second order reaction. Equilibrium data was analyzed using Langmuir and Freundlich isotherm models. On the basis of experimental results and the parameters, the adsorption capacity of enteromorpha was found to be 94.74%. It can be inferred that the carbonaceous enteromorpha is effective for the removal of malachite green from an aqueous solution.
Natesan Buvaneswari and Chellapandian Kannan investigated the mechanism of cationic malachite green (mg) and anionic methyl orange (mo) on brinjal plant root powder (cellulose). The effect of organic dyes were poisoning or non-poisoning was identified. The recovery of both dyes have been studied in water at 80 °c on bpr surface and observed that the mo recovery is 95% and mg is 10%. The poor desorption of mg is due to the strong chemisorption on bpr (cellulose) surface proves its plant poisoning nature. The high recovery of mo due to physisorption mechanism proves that mo is not poisoning the plant.

Alok Mittal Co workers tested the removal of triphenylmethane dye - Methyl Violet, from wastewaters of power plant and waste agricultural material of De-Oiled Soya. The characterization of each adsorbent has been carried out by IR and DTA curves. The effects of pH, sieve size, amount of adsorbent, contact time, temperature, concentration of the adsorbate solution were measured. Kinetic studies have been used to determine the nature of rate was first order. Various thermodynamic parameters have also been calculated by using the Langmuir and Freundlich adsorption isotherms. Boyd and Reichenberg's expressions were verified. For both adsorbents, column operations have been carried out for the bulk removal of the dye. The adsorbed dye has been recovered by eluting hydrochloric acid of pH 3 through exhausted columns. The methyl Violet dye was successfully removed.

Santhy and Selvapathy explained the removal efficiency of activated carbon prepared from coir pith towards three highly used reactive dyes in textile industry. Batch experiments showed that the adsorption of dyes increased with contact time.
and carbon dose. Maximum decolourisation of all the dyes were observed at acidic pH. Adsorption of dyes were found to follow the Freundlich model. Kinetic studies indicated that the adsorption followed first order and the values of the Lagergren rate constants of the dyes were in the range of $1.77 \times 10^{-2} - 2.69 \times 10^{-2} \text{min}^{-1}$. The column experiments using granular form of the carbon (obtained by agglomeration with polyvinyl acetate) showed that adsorption efficiency increased with an increase in bed depth and decrease of flow rate. The Bed Depth Service Time (BDST) analysis carried out for the dyes indicated a linear relationship between bed depth and service time. The exhausted carbon could be completely regenerated and put to repeated use by elution with 1.0 M NaOH. The coir pith activated carbon was not only effective in removal of colour but also significantly reduced COD levels of the textile wastewater.

Gültén Atun and Co-workers investigated the adsorption characteristics of two basic dyes, thionine (TH) and safranine T (ST), onto fly ash (FA) and its three zeolitized products prepared at different hydrothermal conditions. Typical two-step isotherms were observed for TH adsorption onto four adsorbents, whereas the isotherms of the larger ST molecules were S-shaped. The adsorption capacities of the zeolitized fly ash (ZFA) estimated from the first plateau region of the TH isotherms was nearly twice the FA capacity. The capacities increased by up to five times in the second plateau region. The adsorption capacity of FA for ST is equivalent that of TH, whereas the capacities of ZFA are lower than those found for TH. The equilibrium results were well-described by the Freundlich isotherm.
model. The kinetic data obtained in the temperature range of 298–318 K was analyzed using Paterson's and Nernst Plank's approximations based on the homogeneous surface diffusion model (HSDM). The thermodynamic functions for the transition state were evaluated from the temperature-dependence of the surface diffusion coefficients by applying the Eyring model.

Chatterjee et al investigated the physico-chemical adsorption of congo red by chitosan hydrobeads. Adsorption process has been found to be dependant on temperature with optimum activity at 30⁰ C. Both ionic interaction as well as physical forces is responsible for binding of congo red with chitosan theoretical correlation of the experimental equilibrium adsorption data for congo red-chitosan hydrobeads system would be best explained by linear form of Langmuir isotherm model. The kinetic results follow pseudo second–order rate equation 108

Kumari and Emilia109 studied the biosorption of textile dyes using nonviable biomass of aspergillus niger, aspergillus japonica, rhizopus nigricans, rhizopus arrhizus and saccharomyces cerevisiae. The selected anionic reactive dyes were C.I reactive black 8, C.I reactive Blue 3. The effect of initial dye concentration, dose of biosorbent loading, temperature and pH on adsorption kinetics were studied. The data showed an optimal fit to the Langmuir and Freundlich isotherms. The maximum uptake capacity for the selected dyes was in the range 112-204 mg/g biomass.

Aravindhan et al.110 studied the potential use of calcium alginate beads for removal of dyes from colored effluent in dynamic batch mode. Basic black dye, which is one of the most commonly used dyes in leather industry, has been chosen
for the study. Maximum adsorption capacity of 57.70 mg/g has been achieved at an initial concentration of 300 mg/L with 4 g/L of alginate dosage, at pH 4.0 and at room temperature. Adsorption isotherm studies clearly indicate that the Langmuir isotherm shows a better fit for adsorption of the dye by alginate beads, implying a homogeneous and monolayer binding surface. The thermodynamic parameter such as ΔG, ΔH and ΔS has been determined, which indicate a spontaneous endothermic adsorption process.

Bulut and co-workers investigated the application of wheat shells for the removal of direct blue 71 from aqueous solutions. The extent of dye removal decreased with increasing adsorbent dosage and also increased with increasing contact time, temperature, in solution concentration. It was found that the Langmuir equation fit better than the Freundlich equation. The adsorption data obtained at different temperatures were applied to pseudo first-order, pseudo second-order and Weber Morris equations, and the rate constant of first-order adsorption, the rate constant were calculated, respectively. The rates of adsorption were found to conform to pseudo second-order kinetics with good correlation.

Ghasemi and Asadpour investigated the adsorption of methylene blue onto activated carbon by means of UV-Visible spectroscopy. In this work, the effects of various experimental parameters such as temperature and ionic strength have been investigated, using a batch adsorption technique to obtain information on treating effluents from the dye industry.

Renmin Gong et al. studied effect of chemical modification on the cationic dye sorption of rice straw. The removal capacities of native and modified rice straw
sorbing malachite green from aqueous solution were completed. The effects of various experimental parameters such as initial pH, sorbent does, dye concentration, contact time were investigated. For modified rice straw (MRS), the dye removal percentage came up to the maximum value beyond pH 4. The sorption isotherms fitted the Langmuir or Freundlich models. The sorption process followed the pseudo-first-order rate kinetics.

Jeremias de Souza and Co workers\textsuperscript{114} investigated the mechanism of the adsorption of dyes onto mesoporous active carbon prepared from coconut coir dust. The methylene blue (MP) and remazol yellow (RY) molecules were chosen for study of the adsorption capacity. The adsorption kinetics was studied with the Lagergren first and pseudo-second-order kinetic models as the system dyes/adsorbent follow pseudo-second-order kinetics with a significant contribution of intraparticle diffusion. Colorimetric studies reveal that dyes/adsorption interaction forces are correlated with the pH of the solution, which can be related to the charge distribution on the adsorbent surface.

Tahir and Naseem rauf\textsuperscript{115} studied the ability of bentonite to remove malachite green from aqueous solutions for different adsorbate concentrations by varying the amount of adsorbent, temperature, pH and shaking time. Maximum adsorption of the dye has been achieved in aqueous solutions using 0.05g of bentonite at a pH of 9. Thermodynamic parameters such as $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ were calculated for the sorption processes. Analysis of adsorption results showed that the adsorption pattern on bentonite seems to follow the Langmuir and Freundlich isotherms.
Rajagopal et al\textsuperscript{116} studied the removal of malachite green using activated carbon prepared from rubber wood saw dust by steam and chemical treatment with phosphoric acid. The adsorption capacity was determined by using iodine number and methylene blue number and surface area by ethylene glycol mono ethyl ether (EGME) method. Langmuir, Freundlich and Temkin adsorption isotherms were analyzed and Langmuir isotherm shows satisfactory fit to experimental data. The adsorption capacity was found to decrease in the order; stem activated carbon>acid+steam activated carbon> commercial activated carbon > acid activated carbon.

Maurya and coworkers\textsuperscript{117} reported that the biosorbents prepared from dead macro fungi, namely \textit{fomes fomentarius} and \textit{Phellinus igniarius} can uptake methylene blue (M|B) and rhodamine B (RB). Equilibrium isotherm data was well described by the langmuir and Freundlich models. Methylene blue was found to be more adsorbable than rhodamine B. Molecular structure and ionic radius of dyes were found to be responsible for differences in their uptakes. Results showed that sorption of MB increased while that of RB decreased as pH of respective dye solutions changed from 3 to 11.

Messina and Schulz\textsuperscript{118} reported that the adsorption of two basic dyes, methylene blue (MB) and rhodamine B(RB), from aqueous solution onto mesoporous silica-titania materials. They studied the effect of dye structure, adsorbent particle size, TiO\textsubscript{2} presence and temperature on adsorption. The presence of TiO\textsubscript{2} augmented the adsorption capacity. This would be due to possible degradation of the dye molecule in contact with the TiO\textsubscript{2} particles in the adsorbent
interior. The adsorption enthalpy was relatively high indicating that interaction between the sorbent and the adsorbate molecules was not only physical but chemical. Both Langmuir and Freundlich isotherm equations were applied to the experimental data. It was found that the adsorption kinetics of methylene blue and rhodamine B on to the adsorbent under different operating conditions was best described by the first-order method.

Papinutti and coworkers\textsuperscript{119} studied the adsorption of malachite green (MG) on to wheat bran by using a batch technique. The effects of contact time, dye concentrations and pH were investigated. The equilibrium was attained after 40 min of contact time irrespective of MG concentration. The pH of MG aqueous solution greatly influenced the adsorption capacity and intensity, it was found that maximum adsorption of dye occurred at pH range 7-9, where the amount of dye removed was nearly 90%.

Vasantha kumar et al\textsuperscript{120} carried out the batch sorption experiments for the removal of malachite green from its aqueous solution using \textit{pithophora sp.}, a fresh water algae as a biosorbent. Dye uptake was found to increase with contact time and initial dye concentration. Equilibrium uptake was found to be pH dependent and maximum uptake was observed at pH of 6. The effect of algae concentration on equilibrium uptake was also estimated. The equilibrium data tend to fit Freundlich isotherm equation. Kinetic studies showed that the biosorption process follows first order rate kinetics.

Wang and Zhu\textsuperscript{121} employed an Australian natural zeolite for basic dye adsorption in aqueous solution. The natural zeolite is mainly composed of
clinoptiloite, quartz and mordonite and has cation-exchange capacity of 120 meq/100g. The natural zeolite presents high adsorption capacity of methylene blue than rhodamine B. kinetic studies indicated that the adsorption followed the pseudo second-order kinetics and could be described as two-stage diffusion process. The adsorption isotherm could be fitted by the Langmuir and Freundlich models. Thermodynamic calculations showed that the adsorption is an endothermic process.

Yunus Onal\textsuperscript{122} reported the adsorption of methylene blue (MB), Malachite green (MG), and crystal violet (CV) on to an activated carbon prepared by chemical activation with ZnCl\textsubscript{2}. The Kinetics of adsorption MB, MG and CV have been discussed using six kinetic models i.e., the pseudo-first-order, the pseudo-second-order, the Elovich equation, the intraparticle diffusion model, the Bangham equation, and the modified Freundlich equation. It was shown that the second-order kinetic equation could describe the adsorption kinetics for three dyes. The dyes uptake process was found to be controlled by external mass transfer at earlier stages and by intraparticle diffusion at later stages, the thermodynamics of dyes indicates endothermic process.

Bouberka et al\textsuperscript{123} investigated the removal of supranol yellow using different clays such as a clay exchanged with sodium (BNa\textsuperscript{+}) and hydroxyaluminic polycation pillared clays in the presence or absence of non-ionic surfactant. The study of the behavior of three clays with respected to coloring solutions allowed determining the equilibrium time and the rate-determining step of the dyes adsorption. Two simplified kinetic models were tested to investigate the adsorption mechanisms in terms of pseudo-first order and pseudo-second order equations. Besides, the
adsorption capacity data were fitted to Langmuir and Freundlich equations as well. A better fixation was obtained with an acidic pH. The effect of temperature on the adsorption of dye has also been studied and the thermodynamic parameters were determined.

Uzun and Guzel\textsuperscript{124} studied the effect of temperature on the adsorption on some dyestuffs such as orange II, crystal violet, reactive blue and p-nitrophenol by chitosan and by modified chitosan [monocarboxymethylated chitosan] from aqueous solution. Kinetic data applied to Lagergren and Weber-Morris equations, and adsorption rate constants ($k_{\text{ads}}$) and pore diffusion rate constants ($K_p$) were determined, respectively. In addition Langmuir isotherm constants with experimental data were related to the adsorptions.

Kadirvelu et al.\textsuperscript{125} studied the adsorption of rhodamine B using activated carbon prepared from industrial solid sago waste. The physico-chemical properties of carbon in were carried out to explore adsorption process. The effectiveness of the carbon in adsorbing rhodamine B from aqueous solution studied has been as a function of agitation time, adsorbent dosage, initial dye concentration, pH and desorption. Adsorption equilibrium studies were carried out in order to optimize the experimental conditions. The adsorption of rhodamine B onto carbon followed second order kinetic model. Adsorption data were modeled using both langmuir and Freundlich classical adsorptions isotherms.

Akmil-Basar and co-workers\textsuperscript{126} studied adsorption of malachite green (MG) from aqueous solutions by two different adsorbents prepared from pine sawdust and polyethyleneterephthalate by chemical activation with ZnCl\textsubscript{2} and NaOH,
respectively. Both the adsorbents were found to be very effective in removing the dye. The pH of dye solutions in the range of 6-10, was favorable for the removal of malachite green by using the two adsorbents at high concentrations kinetics of removal of MG was studied using Langmuir equation and diffusion phenomena was analyzed using Weber and Morris intraparticle diffusion plots.

Ozacar and Sengil\textsuperscript{127} attempted to alleviate the problem caused by the presence of metal complex dyes used in textile industries by using pine saw dust. The effects of adsorbent particle, pH, adsorbent dose, contact time initial dye concentrations on the adsorption of metal complex dyes by pine sawdust were investigated. Acidic pH was favorable for the adsorption of metal complex dyes. A contact time of 120 min was required to reach the equilibrium. The experimental isotherm data was analyzed using the Langmuir, Freundlich and Temkin equations. The equilibrium data fit well the Langmuir isotherm.

Mahir Alkan and co-worker\textsuperscript{128} analyzed the removal of reactive blue 221 and acid blue 62 anionic dyes onto sepiolite from aqueous solution using parameters such as calcinations temperature, pH, Ionic strength and temperature. After 200°C calcinations temperature, the specific surface area of sepiolite decreased with increasing calcinations temperature, the specific surface area of sepiolite decreased with increasing calcinations temperature. The amount of adsorbed of reactive blue 221 and acid blue 62 on sepiolite increased with increasing ionic strength and temperature, and decreasing pH. The sepiolite sample calcinated at 200°C has a maximum adsorption capacity. However, calcinations at high temperature caused a
decrease in the amount adsorbed of dye. It was found that the Freundlich isotherm appears to fit the isotherm data better than Langmuir isotherm.

Senthilkumar et al\textsuperscript{129} studied the feasibility of employing jute fiber activated carbon (JFC) for the removal of methylene blue (MB) from aqueous solution. The adsorption of MB on JFC has found to dependent on contact time, MB concentration and pH. Experimental result follows Langmuir isotherm model. The optimum pH for the MB removal was found to be 5-10. The kinetic data obtained at different concentrations have been analyzed using a pseudo-first-order, pseudo-second-order equation, intraparticle diffusion and Elovich equation. Among the kinetic models studied the intraparticle diffusion was the best applicable to describe the adsorption of MB onto JFC.

Namasivayam and Sumithra\textsuperscript{130} investigated the removal of direct red 12B and methylene blue by adsorption onto Fe(III)/Cr(III) hydroxide using various parameters. Equilibrium adsorption data followed both Langmuir and Freundlich isotherms. Adsorption data followed both Langmuir and Freundlich isotherms. Adsorption followed second-order kinetics. Acidic pH was favorable for the adsorption of direct red 12B and basic pH for methylene blue. Desorption studies showed that chemisorption seems to be the major mode of adsorption. Mall and coworkers reported the adsorption of malachite green (MG) using three adsorbents namely bagasse fly ash (BFA), and activated carbons commercial grade (ACC) and laboratory grade (ACL). Batch adsorption studies were conducted to evaluate the effect of various parameters. The initial pH of the dye solution strongly affected the Chemistry of both the dye molecules and adsorbents in an aqueous solution. The
effective pH was 7.0 for adsorption of MG by the three adsorbents. The adsorption followed pseudo-second-order kinetics. Equilibrium adsorption data were analyzed by Freundlich, Langmuir, Dubnin-Radushkevich, Redlich-Peterson and Temkin isotherm equations using regression analysis. Non-linear error analysis showed that the Freundlich isotherm best fits the equilibrium data for adsorptive removal of MG by BFA and ACC and Redlich-Peterson follows the equilibrium data for ACL.

Bhatnagar and Jain\textsuperscript{132} investigated the utility of four adsorbents prepared from industrial wastes to remove cationic dyes. Studies have shown that the adsorbents prepared from blast furnace sludge, dust, and slag have poor porosity and lower surface area, resulting in very low efficiency for the adsorption of dyes. On the other hand carbonaceous adsorbent prepared from carbon slurry waste obtained from the fertilizer industry was found to show good porosity and appreciable surface area and consequently dyes to an appreciable extent. The adsorption of two cationic dyes, viz. Rhodamine B and Bismarck brown R on carbonaceous adsorbent conforms to Langmuir equation is a first-order process and pore diffusion controlled. It was found that prepared carbonaceous adsorbent exhibits dye removal efficiency that is about 80-90\% of that observed with standard activated charcoal samples.

Yupeng Guo and co-workers\textsuperscript{133} investigated the adsorption of Rhodamine (RDB) by rice husk-based porous carbons and commercial carbons from aqueous medium. Three samples of carbons prepared by NaOH activation three samples prepared by KOH activation and two samples of commercial carbons have been used. The adsorption isotherms have been determined after modifying the carbon
surface by oxidation with nitric acid and hydrogen peroxide and after degassing at 800 C. The adsorption capacity of RB on oxidation carbons is increased and the adsorption capacities on carbons with heat treatment are larger than that on oxidation.

Yuh-Shan Ho et al\textsuperscript{134} reported the sorption of three dyes, namely basic violet 10, basic violet 1, and basic green 4 from aqueous solution onto sugarcane dust. The results revealed the potential of sugarcane dust, a waste material, to be a low- cost sorbent. Equilibrium isotherms were analyzed using the Langmuir, the Freundlich and the three parameter Redlich-Peterson isotherms. In order to determine the best fit isotherm for each system, two error analysis methods were used to evaluate the data by the linear coefficient of determination and the chi-square statistic test. Results indicated that the chi-square test provided a better determination for the three sets of experimental data.

Janos and Veronika\textsuperscript{135} investigated the sorption of basic dyes like methylene blue, malachite green, rhodamine B, and crystal violet onto non-conventional organomineral sorbent-iron humate. It was found that nonionic (Triton X-100) and cationic (cetyltrimethylammonium bromide) surfactants exhibited a relatively small effect on the dye sorption. Anionic surfactants (sodium dodecyl sulfate), on the other hand, affected (in most cases) dramatically the sorption of basic dyes. Typically the dye sorption was enhanced in the presence of low concentrations of anionic surfactants. At high surfactant concentrations, a steep decrease in the dye sorption was observed in some systems, probably due to the formation of micelles
that solubilize the dye molecules and prevent their sorption. Diffusion processes were identified as the main mechanisms controlling the rate of the dye sorption.

Bhattacharya and Arunima\textsuperscript{136} investigated the biosorption of Congo red from aqueous solution using leaves of azadirachta indica (locally known as the Neem tree) in the form of a powder as a biosorbent. The sorbent was made from mature Neem leaves and was investigated in a batch reactor under variable conditions. The interactions were tested with respect to both pseudo-first-order and second-order reaction kinetics. Of these the latter was found to be more suitable. Considerable intraparticle diffusion was found to occur simultaneously. The sorption process was in conformity with Langmuir and Freundlich isotherms. Thermodynamically, the sorption process was exothermic and spontaneous.

The foregoing pages have described the salient points related to the results of kinetic and thermodynamic studies on the adsorption of dyes onto various adsorbents reported in literature during recent past. However, such studies with an aim to identify easily available and economically viable materials for the removal of dyes from aqueous solutions are on. Apart from the adsorbents mentioned above lots of other materials have also been tried for the past several years to abate dyes from aqueous solutions which include acid activated bentonite\textsuperscript{137} Diatomite\textsuperscript{138} agricultural waste residues corn cob and barely husk\textsuperscript{139}, anionic resins\textsuperscript{140}, fungus aspergillus niger\textsuperscript{141} and Thelephora sp\textsuperscript{142}, yeast kluyveromyces marxianus\textsuperscript{143}, chitin\textsuperscript{144} and activated carbons prepared from various materials by chemical or thermal activation process\textsuperscript{141-151}, natural wastes\textsuperscript{152} and fly ash\textsuperscript{153}. 