

Applications of Adsorption and Ion Exchange Chromatography in Waste Water Treatment



Edited by
Inamuddin
Amir Al-Ahmed

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The ion-exchange process is a natural phenomenon and mankind has been using this technique since the early days of civilisation. With the progress of technologies and concepts, we got a better understanding of this technique and increased its application horizon. Like in other research areas, nanotechnology has also penetrated heavily into this field, and has helped develop smart materials with better properties for application in adsorption and ion-exchange chromatography. A large amount of research was carried out in this field in the last few decades, showing the importance of these materials and technologies.

Water treatment is receiving great attention worldwide, due to the increasing demand of drinking water and hence the need to recycle polluted water sources. Keeping this importance in mind, this book “*Applications of Adsorption and Ion Exchange Chromatography in Waste Water Treatment*” has been edited with contributions from well know experts in the field, who have been working on different ion-exchange materials and technologies for many years.

Applications of Adsorption and Ion Exchange Chromatography in Waste Water Treatment

Edited by

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Preface

The ion-exchange process is a natural phenomenon and mankind has been using this technique since the early days of civilisation. For example, ancient societies were using some soils, sands, natural zeolites and plants as tools for improving the quality of drinking water by way of desalting or softening. However, they may have not been aware of the actual phenomenon occurring in the process. With the progress of technologies and concepts, we got a better understanding of this technique and increased its application horizon. The development of newer materials also helped this progress. Like in other research areas, nanotechnology has also penetrated heavily into this field, and has helped develop smart materials with better properties for application in adsorption and ion-exchange chromatography. A large amount of research was carried out in this field in the last few decades, sighting importance of these materials and technologies. At a glance, ion-exchange techniques and materials have their applications in various fields, such as water treatment, separation and preconcentration of metal ions, nuclear separations, nuclear medicine, synthesis of organic pharmaceutical compounds, catalysis, redox systems, electro-dialysis, hydrometallurgy, effluent treatment, ion-exchange membranes, chemical and biosensors, ion memory effect, ion-exchange fibers, ion-selective electrodes, proton conductors and so on.

Among all these application *water treatments* is receiving great attention worldwide, due to the increasing demand of drinking water and the need to recycle polluted water sources. Keeping this importance in mind, this book “*Applications of Adsorption and Ion Exchange Chromatography in Waste Water Treatment*” has been edited with contributions from well know experts in the field, who have been working on different ion-exchange materials and technologies for many years. These scientists agreed to share their research expertise as well as visions for future developments. We, the editors, would like to express our gratitude to all contributing authors, publishers, and other research groups for granting us the copyright permissions to use their illustrations.

One of the editors, Dr. Amir Al-Ahmed is thankful to the director of Centre of Research Excellence in Renewable Energy at King Fahd University of Petroleum & Minerals, Saudi Arabia for his continuous support. Finally, we would like to acknowledge the sincere support of Mr. Thomas Wohlbier of Materials Research Forum LLC in evolving this book into its final shape.

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Chapter 1

Remediation of dyes from industrial wastewater using low-cost adsorbents

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Abstract

Water pollution is one of the leading environmental issue triggering serious problems for living organisms. Various toxic substances are being introduced into the water bodies from various human activities and the removal of such substances from the water and wastewater has become a core interest for scientists and researchers around the globe over the past few decades. Dyes are an important class of water pollutants having various negative impacts on the living organisms. The removal of color from dye-bearing effluents is a major problem due to the difficulty in treating such wastewaters by conventional treatment methods. Although a number of successful physical, chemical, and biological processes have been applied, however, the cost-effective removal of color from effluents remains a challenge for wastewater treatment.

Keywords

Environmental Pollution, Water Pollution, Wastewater Treatment, Dyes, Adsorption, Low-cost Adsorbent

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1. Introduction

Since the middle of the 19th century, things have started happening in quite disproportions putting the ecological system out of balance. The population explosion, prosperous society with an aspiration for a vast array of products, automobiles, greater

energy use leading to increased radiations, increase in food production needs, etc. are some of the potent factors responsible for creating this imbalance. Science and technology brought in this revolutionary change for human life. Modernization made man's life more and more comfortable. Today one can travel faster, speak or send a message to distant places through our modern means of communication. Villages have become growing cities as a result of industrialisation. It was the industrial revolution that gave birth to environmental pollution as we know it today.

One of the greatest problems that the world is facing today is the environmental pollution which is increasing with every passing year and causing severe damage to our earth. Today, environmental pollution is occurring on a vast and unprecedented scale globally. The word "Pollution" is derived from a Latin word "Polluere" which means "to defile" or "to make dirty". Pollution is an undesirable change in the physical, chemical or biological characteristics of air, land and water that makes the environment unhealthy to live and creates potential health hazards to living organisms.

The Royal Commission on Environmental Pollution in U.K. in its third report [1] defined the term "Pollution" as "Introduction by man into the environment of substance or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structure or amenity or interference with legitimate uses of the environment."

In fact, environmental pollutants are the executing agents of environmental pollution. A pollutant is a substance or energy introduced into the environment that has undesirable effects or adversely affects the usefulness of a resource. Environmental pollutants can be classified into two types – *Biodegradable pollutants* and *non-biodegradable pollutants*.

Biodegradable Pollutants: Biodegradable pollutants are the ones that can be broken down into simpler, harmless substances in due course of time by the action of microorganisms (like bacteria). For example, domestic wastes, faecal matter, vegetable waste, etc.

Non-biodegradable Pollutants: Non-biodegradable pollutants cannot be broken down into simple and harmless substances by the action of microorganisms. For example, plastics, polythene bags, pesticides, glass, heavy metals, etc.

2. Forms of environmental pollution

The environmental pollution may be classified into different major forms such as air, water, soil, noise pollutions, etc.

2.1 Air pollution

Air pollution is the introduction of particulates, biological fragments and other harmful materials into the earth's atmosphere resulting in diseases, allergies and damage to the natural environment. Sources of air pollution can be natural or anthropogenic. Air pollutants can be classified as *primary* and *secondary*.

Primary air pollutants are introduced into the environment by natural sources and human activities as well. Some common examples of primary pollutants are given below.

Carbon monoxide (CO): It is produced by the incomplete combustion of fuels such as natural gas, wood or coal, vehicular emission, cigarette smoking, etc. It is also generated naturally by the plants during the oxidation of methane (swamps, bogs, rice paddies, etc.) and decomposition of chlorophyll.

Sulphur oxides (SO_x): Sulphur compounds are commonly emitted into the atmosphere during volcanic eruptions. Sulphur oxides are sprayed out as aerosols from the sea during rough weather. These oxides are also produced during the biogenic decomposition of sulphur-containing organic compounds on land and in sea. Anthropogenic sources of SO_x are burning of fossil fuels (coal, petroleum and its products), smelting of sulphide ores, manufacture of sulphuric acid, etc.

Nitrogen oxides (NO_x): They are produced during thunderstorms and by soil microorganisms. These are also formed by fossil-fuel based power plants and vehicles.

Toxic metals: Arsenic, cadmium, lead, mercury, chromium, etc. and their compounds are released into the air by industrial and other activities.

Volatile organic compounds (VOC): Xylene, toluene, methane, 1,3-butadiene, benzene, formaldehyde, etc. are examples of VOC. Sources of VOC include paints, varnishes, air fresheners, fuel oil, cleaning products, etc.

Particulates: These are the tiny particles of solid or liquid suspended in air. They originate from agricultural operations, dust storms, forest and grassland fires, volcanoes, burning of fossil fuels, construction and demolition activities, vehicles and aerosols.

Ammonia: Major source of ammonia in the atmosphere is the decay of organic matter and fertilisers.

Chlorofluorocarbons (CFCs): These are released into the atmosphere from air conditioners, refrigerators, aerosol, etc.

Secondary air pollutants: These pollutants are not emitted directly into the atmosphere. They are formed in the air when primary air pollutants interact with each other.

Ground-level ozone: Ground level ozone is formed due to the reaction of NO_x , carbon monoxide and VOC in the presence of sunlight.

Smog: The term ‘smog’ is derived from two words, namely, smoke and fog. Two different types of smog are caused by the low-pressure gradient weather patterns depending on the kind of emissions and the intensity of radiation. The **London smog** is formed in winters consisting of a mixture of gaseous and solid aerosols and natural fog. It results from the accumulation of smoke from coal burning having high sulphur content leading to the production of high concentrations of sulphuric acid in fog droplets. On the other hand, the **Los Angeles smog** is formed during sunny summer days in regions where automobile emission is very high. It is formed as a result of interactions among nitrogen oxides, reactive hydrocarbons and sunlight.

2.2 Water pollution

Water pollution is the contamination of water bodies by the release of industrial wastes, domestic sewage, chemical contaminants, urban and agricultural runoff containing fertilisers and pesticides, eutrophication, littering, etc. Water pollution will be discussed in detail in Section 3.

2.3 Soil pollution

Soil pollution is the degradation of land in the presence of xenobiotic chemicals or alteration in the natural environment of the soil. It is typically caused by domestic, agricultural and industrial activities and improper disposal of wastes. Some common and harmful soil pollutants are pesticides (herbicides, fungicides, insecticides, etc.), heavy metals (lead, arsenic, mercury, copper, cadmium, etc.), petroleum hydrocarbons, organic solvents and polynuclear aromatic hydrocarbons (naphthalene, benzopyrene, etc.). Crops and plants are grown on polluted soil act as media for the transportation of the pollutants to living organisms. Long-term exposure of living bodies to such soil can affect their genetic make-up, causing congenital illnesses and chronic health problems that cannot be cured easily. Fungi and bacteria (found in the soil binding it together) begin to decline to create additional problem of soil erosion. The fertility of soil slowly diminishes, making land unsuitable for agriculture and any local vegetation to survive. The death of many soil organisms (e.g. earthworms) in the soil leads to an alteration in soil structure.

2.4 Noise pollution

Noise pollution refers to the presence of such levels of noise or sound in the environment that are disturbing, irritating and annoying to living beings. Noise is measured in decibels (dBA). In daily life, people are generally exposed to noise levels ranging from 30–80

dBA. Exposure to noise level greater than 80 dBA leads to stress [2]. Major sources of noise pollution are industries, transport vehicles, household (televisions, domestic gadgets, air conditioners, vacuum cleaners, etc.), public addressing systems (loudspeakers), agricultural machines (tractors, thrashers, tube wells, etc.), defense equipment (artillery, tanks, explosives, etc.), construction works, etc. Noise pollution causes uneasiness and harm living being's mental and physical health. It is one of the major causes of deafness. Noise pollution also leads to cardiac disturbance, sleeplessness, headache, irregular blood pressure psychological imbalance, etc.

3. Water pollution

Water is one of the world's most precious resources without which life is not possible on earth. As stated by philosopher Thales from Miletus, "*Hydor (Water) is the beginning of everything*". Thales understood that water is life and living organisms cannot survive without it. Over two-thirds of earth's surface is covered with water and less than one-third is taken up by land. As the earth's population is growing day by day, people are putting ever increasing pressure on the earth's water resources. In a sense, our oceans, rivers and other water resources are being squeezed by human activities and also reducing its quality. Today contamination of freshwater systems with a wide variety of pollutants is a subject of great concern.

Water pollution can be defined as the alteration of the physical, chemical or biological characteristics of water which makes it harmful for living organisms and unsuitable for the desired usage. Water pollution is a major global problem. It may be caused by natural sources or human activities and can have detrimental effects on aquatic ecosystems as well as other living organisms.

4. Wastewater treatment

Before the industrial revolution, the natural purification phenomenon was sufficient to provide water of high purity. However, excessive human interference with the environment has pushed the natural purification processes beyond their limits. Hence, a series of purification operations are required to restore the natural qualities of water. Various water treatment plants are developed and used to purify the water before it is discharged from the industries into the freshwater systems. Water is purified in following four successive stages: preliminary, primary, secondary and tertiary treatments [3, 4].

4.1 Preliminary treatment

The objective of the preliminary treatment is the removal of suspended coarse solids and other large floating materials often found in wastewater. Removal of these materials is necessary to reduce the maintenance and treatment cost of subsequent treatment units. Suspended matter is removed by *screening* whereas the floating matter is eliminated by *skimming*.

In screening, impure water is allowed to pass through screens made of rows of iron bars with a spacing of 1–2 inches. Materials like rags, sticks, polyethene bags, wood pieces, papers, etc. are held back by the spacing in the iron bars. Impurities which are lighter than water such as oil, grease, etc. rise to the surface of the water and can be removed by mechanical skimming. Skimming technique can also be used to remove grit particles by blowing compressed air in polluted water. The air bubbles that are formed attach themselves to grit particles and lift them to the surface from where they can be skimmed off easily.

4.2 Primary treatment

In this stage, colloidal and suspended matters are allowed to settle down as *sludge*. It involves two methods – *sedimentation* and *flocculation*.

Some solids suspended in water are either too fine to be screened out or too heavy to be skimmed off. Such impurities are removed by allowing them to settle down under the influence of gravity. This technique is called *sedimentation* and is carried out in sedimentation tanks. Polluted water is allowed to remain in tanks for 1–3 hours. The sludge thus formed undergoes putrefaction and hence should not be left in the sedimentation tanks for too long. The tanks have mechanical gears to remove sludge at regular intervals.

To get rid of extremely fine particles, the *flocculation* method is used. Such fine particles take a very long time to settle down and hence cannot be removed by sedimentation. However, their rate of settlement can be enhanced up to a considerable extent by adding some flocculating agents such as potash alum, ferrous sulphate, ferric chloride, etc. These fine suspended particles in polluted water bear either positive or negative charge. When flocculating agents are added, positive charges are neutralised by sulphate or chloride ions whereas negative charges are neutralised by Al^{3+} , Fe^{2+} or Fe^{3+} ions. Once the charges are nullified, the particles come in contact with each other, coalesce and rapidly settle down.

4.3 Secondary treatment

Secondary treatment involves the oxidation of dissolved and colloidal organic compounds in the presence of microorganisms. The organic compounds are biodegraded into simpler and harmless compounds with the consumption of oxygen. The aerated conditions are obtained by *trickling filters*, *activated sludge tanks* or by *oxidation ponds*.

Trickling filters consist of circular or rectangular beds packed with stones, gravel, etc. which serve as a habitat for bacteria, fungi and other microorganisms. A part of the sludge from the primary settling tank is applied to the bed from above and polluted water is allowed to pass over these beds. Gradually with time, a biotic community is established as a gelatinous layer on the surface of the bed. This layer contains bacteria, fungi, algae, etc. When water trickles through this biological layer, the organic impurities are broken down in the presence of dissolved oxygen into simpler compounds. Also, the microorganisms already present in water are retained on the beds and supplement the purification phenomenon.

In *activated sludge method*, water containing organic pollutants is aerated and some amount of sludge settles down. Soon microorganisms start inhabiting the sludge. Next, when a fresh batch of polluted water is aerated over this sludge, it gets purified more efficiently than the previous one. More and more sludge accumulates and a greater density of microorganisms settles on it. Hence, after each purification slot, the sludge becomes more activated. After each slot, the aeration time is reduced because the purification is achieved in shorter duration.

Oxidation ponds are used in warmer climates to purify polluted water through an interaction between bacteria and algae. Polluted water is made to flow through the ponds (shallow lagoons with an average depth of 1 meter) at a slow speed. The bacteria in the pond decompose the biodegradable organic matter with the consumption of dissolved oxygen generating carbon dioxide, nitrates and phosphates. These nitrates and phosphates are consumed by algae and carbon dioxide is utilised in photosynthesis liberating oxygen. Thus, the dissolved oxygen which was consumed by bacteria is restored and a fresh cycle can be again started.

4.4 Tertiary treatment

Tertiary treatment of water removes the impurities that remain after the first three stages of purification. These impurities are mainly the soluble inorganic impurities. Different techniques are used in this stage depending on the nature of pollutants.

Chlorination refers to the addition of gaseous chlorine or compounds containing active chlorine such as bleaching powder. It disinfects the pathogenic bacteria by inactivating

the enzymes that are essential for the life processes of bacteria. It controls the growth of undesirable algae in water treatment plants. It also eliminates the odours associated with the anaerobic decomposition of organic matter in water.

The impurities present in water are oxidised to harmless materials using suitable oxidising agents such as hydrogen peroxide. The hydroxyl radical generated by the action of ultraviolet light on H_2O_2 attacks the inorganic and organic pollutants. The sulphur compounds are oxidised to sulphates, phosphorus compounds to phosphates, cyanides to cyanates and halogen compounds to halides. This method is known as *wet oxidation*.

In *reverse osmosis*, impure water is placed above a semi-permeable membrane and is subjected to high pressure. As a result, pure water flows down the semi-permeable membrane and the solute molecules having larger diameters than the pores of the semi-permeable membrane are retained by the membrane.

The *Electrodialysis* technique is used to purify brackish water (water containing a higher concentration of ionic impurities). The equipment consists of an electrolytic cell divided into three compartments by two semi-permeable membranes. The orifices on the membrane near the cathode are coated with negatively charged ions. This membrane repels anions but attracts cations. Similarly, the orifices of the membrane near anode are coated with positively charged ions which repel cations but attract anions. When current is induced, cations present in impure water pass through the cation-permeable membrane and discharge at the cathode. Similarly, anions present in impure water pass through the anion-permeable membrane and discharge at the anode. The central compartment is devoid of any impurity and contains pure water.

During the tertiary stage of water purification, about 1 ppm of fluoride is added, either in the form of sodium fluoride or as sodium hexafluorosilicate (IV). This process is called *fluoridation*. Fluoride is essential to protect teeth against dental decay.

The *ion-exchange technique* is also used for the purification of brackish water. The equipment consists of a cation exchanger coupled with an anion exchanger. Each ion-exchanger contains a resin (high molecular weight polymeric material with ionic functional groups). As water containing ionic impurities is passed over these ion exchangers, the functional groups can exchange ions. Impure water is first passed through cation exchanger. The cations present in impure water are exchanged with the H^+ ions of the resin (cation exchanger contains ionic sulphonc acid group). When water is passed through an anion exchanger (containing quaternary ammonium hydroxide group), the anions present in the impure water are exchanged with the hydroxide ions of the resin. The H^+ ions and OH^- ions combine to form water.

Several compounds which are resistant to biodegradation may persist in water even after primary and secondary treatment. *Adsorption* technique is used for the elimination such impurities (heavy metals and dyes) from water by passing the water over a bed of granulated active charcoal. When the charcoal becomes saturated with impurities, it is heated at about 1800 K in vacuum to remove impurities from the used adsorbent so that it can be used again.

5. Dyes

A dye is a coloured substance that has an affinity for the substrate to which it is being applied. The phenomenon of absorption of light is important for the sensation of colour. However, it was recognised in 1870 that unsaturation is essential for the light absorption and hence colour sensation. Otto Witt, a German chemist, put forward his theory of colour and constitution and is known as a *chromophore-auxochromes theory*. The main points of this theory are:

1. The colour of an organic compound is mainly due to the presence of unsaturated groups known as *chromophores* (German: *Chroma* means colour and *protein* means to bear). The compound bearing the chromophoric group is called *chromogen* [5, 6]. For example, azo ($-\text{N}=\text{N}-$), carbonyl ($\text{C}=\text{O}$), methine ($-\text{CH}=\text{}$), and nitro ($-\text{NO}_2$) groups, etc.
2. The greater the number of chromophores, the greater is the intensity of colour.
3. Certain substituents fail to produce colour by themselves but they deepen the colour due to the chromophoric group already present. Such groups are called *auxochromes* (German: *auxanein* means to increase). Common auxochrome groups include hydroxyl ($-\text{OH}$), amino ($-\text{NR}_2$, $-\text{NHR}$, $-\text{NH}_2$) groups, halogens, etc.

5.1 Classification of dyes

Dyes can be classified in several ways. Some bases of classification are given below:

- On the basis of source of dyes
- On the basis of nature of chromophore
- On the basis of application of dyes

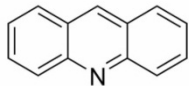
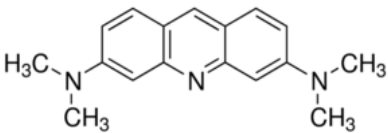

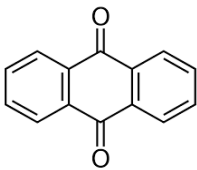
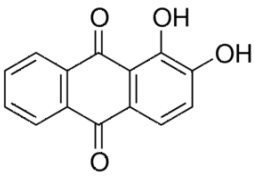

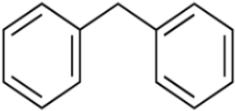
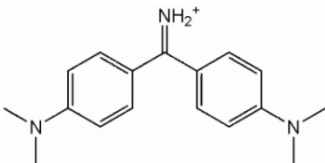

(a) Classification based on source of dye

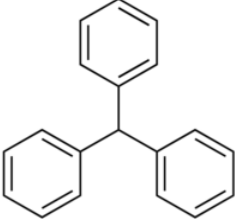
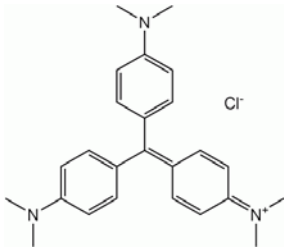

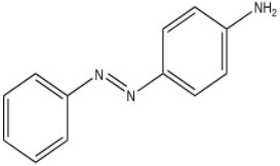
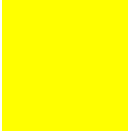
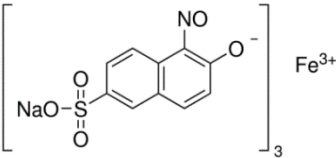
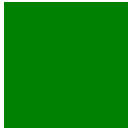
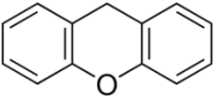
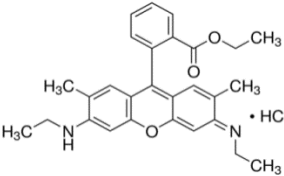

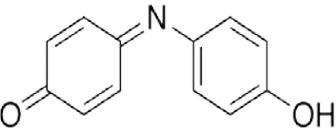
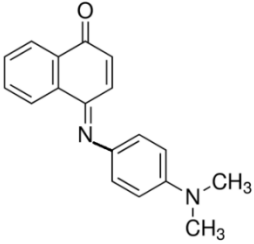

On the basis of the source from which the dye is obtained, dyes can be classified as *natural* and *synthetic*.

Natural dyes: These dyes are obtained from natural sources. Most of the natural dyes have plant origin (extracted from leaves, flowers, roots, berries, roots, bark, etc.). Some natural dyes are also obtained from insects and mineral compounds. For example, indigo, madder, saffron, osage orange, safflower, madder, etc. Natural dyes are of two types- *additive* and *substantive* dyes. Additive dyes require a mordant to fix to the fiber (for example, madder). Substantive dye does not require the use of any mordant (for example, cochineal and safflower).

Synthetic dyes: Dyes prepared from organic or inorganic compounds are known as synthetic dyes. While searching for a remedy for malaria, William Henry Perkin, an English chemist, serendipitously discovered the first synthetic dye, Mauveine. Since then thousands of different synthetic dyes were manufactured and used due to their low cost and colour fastness. Based on this classification, textile dyes can be categorised into various groups, namely, direct, vat, sulphur, organic pigments, reactive, dispersed, acidic, azoic, basic, oxidative, developed, mordant, and solvents dyes.

Table 1. Classification of dyes based on chromophoric group

Dye category	Chromophoric group	Representative example	Colour
Acridine dyes		 Acridine orange	 Orange
Anthraquinone dyes		 Alizarin	 Crimson
Arylmethane dyes		 Auramine O	 Yellow

		 Crystal violet	 Violet
Azo dyes	--N=N--	 Aniline yellow	 Yellow
Nitroso dyes	--N=O	 Naphthol green B	 Green
Xanthene dyes		 Rhodamin 6G	 Yellow fluorescent
Indophenol dyes		 Indophenol blue	 Blue

(b) Classification based on the nature of chromophore

On the basis of the nature of the chromophoric group present in the dye molecule structure, they can be classified into various categories which are listed in Table 1.

(c) Classification based on the application of dyes

On the basis of application, dyes can be classified into 9 categories:

Reactive dyes: These dyes have reactive groups which form covalent bonds with $-OH$, $-NH_2$ or $-SH$ groups on the fiber. Reactive dyes are extensively used in the textile industry because of a wide variety of colour shades and ease of application. The hydrolysis of the reactive groups in the side reaction lowers the degree of fixation. It is estimated 10–50% does not react with fabric and remain hydrolysed in the water phase. The problem of coloured effluents is, therefore, identified to be mainly because of the use of reactive dyes. For example, Reactive yellow HE6G, Reactive red, Reactive violet C2R, Reactive golden yellow MR, Reactive yellow MGR, etc.

Acid dyes: These are anionic compounds and used for dyeing basic group-containing fabrics like wool, polyamide and silk. These are applied to the fabric under acidic conditions which cause protonation of basic groups. The process is reversible and dyes are removed from fabrics during washing. For example, Acid black, Acid blue S5R, Acid green 20, Acid red 119, etc.

Basic dyes: These are cationic compound that are used for dyeing acid group-containing fibers, usually synthetic fibers like modified polyacrylate. They generally give intense shades but have poor light fastness. They are used for dyeing silk and wool directly. For example, Crystal violet, methylene blue, safranin, basic fuschin, etc.

Direct dyes: They dyes have a high affinity for cellulose fibers and bind to them through Vander Waals forces. The common salt or Glauber's salt is often used with direct dye to promote dyeing process because the presence of excess sodium ions favours the establishment of equilibrium with the minimum amount of dye. In this case, the dyeing process is reversible and exhibit poor wash fastness. For example, Direct orange 39, Direct blue 86, Direct red 10, etc.

Mordant dyes: These dyes have poor affinity for the fiber and require pre-treatment of the fiber with the mordant usually metal salts (such as chromium and iron salts). They are used for dyeing wool, leather, silk, paper and modified cellulose fibers. For example, Chrome blue 2K, Alizarin red S, Celestine blue B, Eriochrome cyanine R, etc.

Disperse dyes: They are specifically used to dye synthetic fibers like cellulose acetate, polyester, polyamide, acryl, etc. They are insoluble in water but in the actual fibres themselves. Its diffusion requires swelling of the fiber, either by high temperature ($>120^{\circ}\text{C}$) or with the help of chemical softener so that the finely ground particles can penetrate. For example, Disperse red, disperse blue, Disperse violet, Disperse yellow, Disperse green, etc.

Vat dyes: They dyes are insoluble in water but their reduced forms are soluble. These dyes are, therefore, applied in their reduced forms (reduced forms are obtained by treating the dye with some reducing agent such as alkaline sodium dithionite). When the reduced dye is adsorbed on the fiber, the original insoluble dye is reformed upon oxidation with air or chemicals. Vat dyes offer excellent fastness but they are quite expensive. For example, Vat blue 1, Vat orange 3, Vat yellow 1, etc.

Sulphur dyes: These are polymeric aromatic compounds containing heterocyclic S-ring. They are mainly used for dyeing cellulose fibers. Dyeing process involves reduction and oxidation of the dye. They become soluble when reduced to sodium sulphide and exhibit affinity for cellulose. But on exposure to air, they get oxidised to insoluble dye inside the fiber. For example, sulphur black 1, Sulphur red 1, Sulphur orange 1, Sulphur brown 21, Sulphur green 12, etc.

Solvent dyes: These dyes are non-ionic compounds soluble in organic solvents. They are used as a solution in an organic solvent. For examples, Solvent red 24, Solvent yellow 124, solvent blue 35, Solvent orange 5, Solvent black 3, etc.

5.2 Dyes as a source of colour contaminant in water

The discovery of the first synthetic dye, *Mauveine*, in 1856 by William Henry Perkin led the way to the synthesis of a wide variety of dyes to be used for various purposes. There are more than 10,000 commercially available dyes with over 7×10^5 tonnes of dyestuff produced annually [7]. Dyes are widely used in a variety of industries such as textiles, rubber, paper, plastics, printing, leather, cosmetics, pharmaceuticals, food, etc., to colour their products. The textile industry is one of the largest sectors globally consuming substantial amounts of water in its manufacturing processes. As a result, a large amount of coloured wastewater is generated which is discharged into the freshwater systems without sufficient treatment. It is estimated that 2% of dyes produced annually is discharged in effluents from associated industries [8]. Discharge of dye-bearing wastewater into natural streams and rivers poses severe problems to the aquatic life, food web and causes damage to the aesthetic nature of the environment.

5.3 Harmful effects of dyes

Colour is the first contaminant to be recognised in wastewater. The presence of an even very small amount of dyes in water is highly visible and hence undesirable. Also, dyes have harmful effects on living organisms. Dyes absorb and reflect sunlight entering the water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants. The problems become grave due to the fact that the complex aromatic structures of the dyes render them ineffective in the presence of heat, light, microbes and even oxidising agents and degradation of the dyes become difficult [7]. Dyes can cause allergic dermatitis, skin irritation, cancer, mutation, etc. Hence, these pose a serious threat to human health and water quality, thereby becoming a matter of vital concern.

Keeping the essentiality of colour removal, concerned industries are required to treat the dye-bearing effluents before dumping it into the water bodies. Thus, the scientific community shoulders the responsibility of contributing to the waste treatment by developing effective dye removal technique.

6. Techniques available for the removal of dyes from wastewater

In this section, the available treatment methods will be discussed with special emphasis on dye removal. These techniques can be broadly classified into three categories: Biological, chemical and physical [9].

6.1 Biological treatment

In this method, microorganisms such as bacteria, yeasts, fungi and algae are used to degrade different pollutants [10]. Biological methods can be broadly classified into two types- *aerobic* and *anaerobic treatment method*. The aerobic method involves the usage of free or dissolved oxygen by microorganisms to decompose the organic matter whereas, in the anaerobic method, decomposition of the organic wastes occurs in the absence of oxygen. However, the application of biological treatment methods is restricted due to methodological limitations such as the requirement of a large land area, sensitivity towards diurnal variations, the toxicity of some chemicals, less flexibility in design and unsatisfactory colour elimination [11].

6.2 Chemical treatment

Chemical methods include coagulation, flocculation, precipitation–flocculation with Fe(II)/Ca(OH)_2 , electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidising agents (ozone), electrochemical processes, advanced oxidative processes, etc. The chemical techniques are often expensive, create disposal problems

due to the accumulation of concentrated sludge and require a high input of electrical energy [12,13].

6.3 Physical treatment

Different physical methods such as membrane filtration (nanofiltration, reverse osmosis, electrodialysis, etc.) and adsorption techniques are widely used for the removal of dyes from wastewater. The main disadvantage associated with membrane filtration is the limited lifetime of the membrane. Fouling of the membrane occurs after a certain period of time and requires periodic replacement and thereby, reduces the economic viability of the process [14]. To overcome these limitations the adsorption method has been very commonly used. In fact, it is one of the preferred methods used for the removal of dyes from wastewater because of the various advantages such as ease of operation, the simplicity of design, avoidance of secondary pollution, insensitivity to toxic pollutants, low cost and, therefore, economic feasibility. [15, 16].

7. Adsorption

Adsorption is a surface phenomenon and may be defined as the “phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into a higher concentration of the molecules on the surface”. The adsorption process involves two components adsorbent and adsorbate. The adsorbent is the substance on the surface of which adsorption takes place while adsorbate is the substance which is being adsorbed on the surface of the adsorbent.

The process of adsorption arises due to the presence of unbalanced or residual forces at the surface of the liquid or solid phase. In a bulk of the material, every molecule is equally attracted from all sides and hence the net force experienced by each molecule in the bulk is zero. However, molecules present on the surface are not wholly surrounded by other molecules and therefore experience a net inward force towards the bulk.

7.1 Types of adsorption

There are two types of adsorption processes, namely, *physisorption* and *chemisorption*.

(a) Physisorption

It involves the attraction between the adsorbate molecules and the adsorbent surface via weak van der Waals forces. Physical adsorption occurs with the formation of a multilayer of adsorbate on adsorbent [17, 18].

Characteristics of physisorption

- It occurs at very low temperatures and its magnitude decreases with the rise in temperature
- Heat evolved in physisorption is low, varying between 4–40 kJ/mol
- In case of physisorption of gases over solids, the extent of adsorption increases with increase in pressure
- It is reversible
- It is not specific with respect to adsorbent
- The extent of adsorption increases with the increase in surface area of the adsorbent

(b) Chemisorption

Chemisorption is said to have taken place when the affinity between adsorbate and adsorbent is a chemical force or chemical bond. Chemisorption occurs with the formation of a monolayer of adsorbate on adsorbent [19].

Characteristics of chemisorption

- Chemisorption occurs at low as well as high temperatures and its magnitude increases with the rise in temperature
- Heat of adsorption is very high, varying between 40–400 kJ/mol
- The chemisorption is not appreciably affected by small changes in pressure
- Chemisorption is irreversible in nature
- It is highly specific and occurs only if there is some possibility of chemical bonding between adsorbent and adsorbate
- Like physisorption, chemisorption also increases with increase of surface area of the adsorbent

7.2 Factors affecting adsorption

Adsorption on a solid surface depends on a number of factors such as [20]:

- Surface area
- Nature of the adsorbate
- pH of the solution
- Temperature
- Nature of adsorbent

Surface Area: Adsorption is a surface phenomenon and the extent of adsorption is proportional to a specific surface area. The specific surface area can be defined as that portion of the total surface area that is available for adsorption. Thus, if the solid is more finely divided and more porous, the extent of adsorption accomplished per unit weight of solid adsorbent is greater.

Nature of adsorbate: The adsorption is also influenced by the solubility of the adsorbate in the solvent. Generally, the extent of adsorption increases with a decrease in solubility due to respective increase in solute-solvent interaction.

pH of the solution: The pH of a solution from which adsorption occurs influences the extent of adsorption. Since in most cases, the adsorption occurs via the association of hydronium or hydroxide ions, the process is greatly affected by pH of the medium. Alkaline medium offers favourable condition for the adsorption of cationic dye while anionic dye can be best adsorbed in acidic medium.

Temperature: Since adsorption is accompanied by evolution or absorption of heat depending upon the nature of the adsorbent-dye interaction, the magnitude of adsorption is also dependent on temperature.

Nature of adsorbent: The physiochemical nature of the adsorbent imparts profound effects on both rate and capacity for adsorption. Adsorption is affected by the presence of functional groups and other structural characteristics. Different adsorbents adsorb a dye in a different way because of their different characteristic intrinsic nature.

8. Selection of adsorbent

Activated carbon has been used as a most conventional adsorbent for the treatment of wastewater because of its excellent adsorption ability [21]. However, widespread use of activated carbon is restricted due to its high cost, difficulties in its regeneration and loss of adsorbent during regeneration. Ultimately these factors reduce its economic feasibility [22]. Literature survey reveals that a number of low-cost substitutes have successfully been developed and used for the treatment of dyes from aqueous solutions. Materials like chitin, chitosan, modified cotton, keratin, fly ash, oil cakes, fruit peels, barks, seeds, fruit wastes and much more have been used extensively as adsorbents for the removal of dyes from wastewater. Some typical examples [23-106] of such materials are presented in Table 2.

Table 2. Summary of the adsorbents used for the removal of dyes from wastewater.

Adsorbent	Dye	Reference
Acid-treated pine cone powder	Congo red	[23]
Aleurites Moluccana seeds	Rhodamine B	[24]
Aleurites Moluccana	Methylene blue	[24]
Avocado seed powder	Crystal violet	[25]
Bamboo leaves	Methylene blue	[26]
Banana fibre	Methylene blue	[27]
Biochar-palm bark	Methylene blue	[28]
Biochar-eucalyptus	Methylene blue	[28]
Blast furnace slag	Acid red 138	[29]
Blast furnace slag	Acid green 27	[29]
Bottom ash	Carmoisine A	[30]
	Fast Green FCF	[31]
Breadnut peel	Malachite green	[32]
Canola residues	Methylene blue	[33]
Carbon slurry	Methylene blue	[34]
	Crystal violet	[34]
	Meldola blue	[34]
	Chrysoidine G	[34]
	Ethyl orange	[34]
Carbon slurry	Metanil yellow	[34]
	Acid blue 113	[34]

Cerastoderma lamarcki shell	Malachite green	[35]
Citrus limetta peel	Eriochrome black T	[36]
Clay	Reactive Red 120	[37]
Coconut fibre	Methylene blue	[27]
Coconut husk-based activated carbon	2,4,6-trichlorophenol	[38]
Cotton stalk	Methylene blue	[39]
Curcuma angustifolia scales	Basic violet 14	[40]
De-oiled soya	Eosin yellow	[41]
	Carmoisine A	[30]
De-oiled soya	Fast Green FCF	[31]
Dicentrarchus labrax scales	Acid Blue 121	[42]
Eucalyptus sawdust	Brilliant green	[43]
Eucalyptus sheathiana bark	Methylene blue	[44]
Fly ash	Direct black	[45]
Giombo persimmon seed	Toluidine Blue	[46]
Hectorite	Congo red	[47]
Hen feather	Amido black 10B	[48]
	Congo red	[49]
Hen feather	Brilliant yellow	[50]
Hevea brasiliensis seed shell	Crystal violet	[51]
Illitic clay	Methylene blue	[52]
Jatropha curcas pods	Remazol brilliant blue R	[53]
Jujuba seeds	Congo red	[54]

Kaolin-Bentonite mixture	Congo red	[55]
Kaolin	Congo red	[55]
Kenaf fibre	Methylene blue	[56]
Lemna minor biomass	Acid blue 113	[57]
Longan shell	Methylene blue	[58]
Lotus leaf	Methylene blue	[59]
Melaleuca diosmifolia	Methylene blue	[60]
Melaleuca diosmifolia	Acridine orange	[60]
	Malachite green	[60]
Melon peel	Methylene blue	[61]
Mineral waste from coal mining	Aztrazon blue	[62]
Modified natural bentonite	Congo red	[63]
Modified sphagnum peat moss	Malachite green	[64]
Montmorillonite	Crystal violet	[65]
	Basic red 18	[66]
Moroccan clay	Malachite green	[67]
	Methylene blue	[67]
	Basic red 46	[67]
	Methylene blue	[68]
	Malachite green	[68]
	Methyl orange	[68]
NaOH-modified rice husk	Crystal violet	[69]
Natural Clay	Methylene blue	[70]

Neem sawdust	Malachite green	[71]
Olive pomace	Basic green 4	[72]
Orange peel	Methylene blue	[73]
Palm kernel fibre	Methylene blue	[74]
	Crystal violet	[74]
Peanut husk	Methylene blue	[75]
Perlite	Maxilon Blue 5G	[76]
Pine cone	Acid Black 26	[77]
	Acid Green 25	[77]
	Acid Blue 7	[77]
	Congo red	[23]
Pine tree leaves	Basic red 46	[78]
Pinus radiata	Methylene blue	[79]
Pistachio hull waste	Methylene blue	[80]
Red mud	Acid Blue 15	[81]
Rejected tea	Methylene blue	[82]
Rice husk	Direct Red 31	[83]
	Direct Orange 26	[83]
River sand	Methylene blue	[84]
Rosa canina galls	Methylene blue	[85]
	Crystal violet	[85]
Saklıkent mud	Brilliant green	[86]
Sawdust	Methylene blue	[27]

Sepiolite	Maxilon red GRL	[87]
Sesame hull	Methylene blue	[88]
Simarouba glauca seed shell	Malachite green	[89]
Soybean hull	Safranin	[90]
Spent tea leaves	Crystal violet	[91]
Tea dust	Crystal violet	[92]
Water chestnut	Rhodamine B	[93]
Water hyacinth	Methylene blue	[94]
Water hyacinth root	Dark blue-GL	[95]
Wheat bran	Reactive red 180	[96]
	Reactive orange 16	[96]
	Reactive black 5	[96]
	Direct red 80	[96]
	Acid red 42	[96]
Wheat bran	Acid yellow 199	[96]
Zeolite	Reactive Red 239	[97]
	Reactive Blue 250	[97]

9. Conclusion

Water pollution has become a plague in our modern society. Rapid increase in industrialisation has resulted in the generation of a variety of toxic pollutants such as detergents, acids, agro-chemicals, heavy metals, dyes, etc. Dyes are an important class of pollutants which are extensively used in various industries like textiles, leather, paper and pulp, pharmaceuticals, paint, cosmetics, plastic, etc. The presence of dyes in water even in trace amounts can be easily recognised and is aesthetically undesirable. Dyes largely