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A Review on Dye Removal from Aqueous Solution by using Alternative Low Cost Adsorbent.

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ABSTRACT
This review article provides extensive literature information about water pollutants dyes. Dyes, its classification, sources, toxicity, various treatment methods, dye adsorption and characteristics by various adsorbents. This review paper also includes the factors affective adsorption of dye such as solution pH, initial dye concentration, adsorbent dosage, and temperature. The one of the objective of this review article is to scattered available information on various aspects on a wide range of potentially effective adsorbents in the removal of dyes. Therefore, an extensive list of various adsorbents such as natural materials, waste materials from industry, agricultural by-products, and biomass based activated carbon in the removal of various dyes has been compiled here. Dye bearing waste treatment by adsorption using low cost alternative adsorbent is a demanding are double benefits i.e. water treatment and waste management. Further, activated carbon from biomass has the advantage of offering an effected low cost replacement form on-renewable coal based granular activated carbon provided that they have similar or better adsorption on efficiency.

1.1 INTRODUCTION:

Since the middle of the 19th century, things have started happening in quite disproportions putting the ecological system out of the balance. The population explosion, prosperous society with an aspiration for a vast array of products, the automobiles, greater energy use leading to increased radiations, increase in food production needs, etc. are some of the potent factors responsible for creating the imbalance. Science and technology brought in the revolutionary change in 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 the modern means of communication. Villages have become growing cities as a result of industrialization. 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 the 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**.

1) **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 stuff, etc.

2) **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.

1.2 Forms of Environmental pollution

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

1.2.1 Air pollution:

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

1.2.2 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 fertilizers and pesticides, eutrophication, littering, etc. Water pollution will be discussed in detail in Section 1.3.

1.2.3 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 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 creating 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.

1.2.4 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 (loud speakers), agricultural machines (tractors, thrashers, tube wells, etc.).

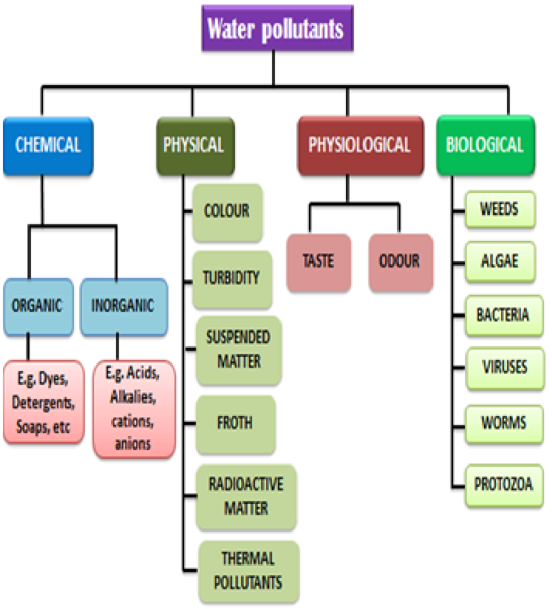
1.3 Water pollution:

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 in the physical, chemical or biological characteristics of water which makes it harmful for living organisms and unsuitable for 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.

1.3.1 Sources of water pollution

The sources of water pollution can be broadly classified into two categories:



(a) Point sources:

In this case, the pollutants are discharged from a single identifiable source. An example of this type is discharge from industries into water, sewage treatment plants, etc. The sources can be easily monitored

(b) Non-point sources:

It refers to the contamination which is spread over a wide area and is not ascribed to a single source. Rain water travelled through the agricultural regions contains mixed pollutants (pesticides, fertilisers, animal manure, etc.) is a most suitable example of this type of pollution. Such pollutants cannot be monitored easily.

However, there is no sharp line of differentiation between point and non-point sources of water pollution. The contamination of groundwater by the leakage of chemicals from the disposal tank of one factory may be a point source of pollution. But, in an industrial area, the leakage of chemicals from the disposal tanks of several factories contaminating the groundwater comes under the category of non-point source of water pollution.

1.3.2 Classification of water pollutants:

Water pollutants can be broadly classified into four categories, namely, chemical, physical, physiological and biological pollutants [3].

Schematic diagram showing the detailed classification of water pollutants is presented in Fig. 1.1.

(a) Chemical pollutants:

Chemical pollutants can be subdivided into two different types, organic and inorganic pollutants.

Organic pollutants: They include naturally occurring compounds like proteins, fats, carbohydrates, etc. as well as synthetic compounds such as dyes, soaps, detergents, pesticides, etc. Some common organic pollutants along with their source of origin are listed in Table 1.1. When an organic pollutant is discharged into a water body, it is gradually degraded by aerobic bacteria. Thus, complex, hazardous organic compounds are broken down into simple, harmless, inorganic components in the presence of dissolved oxygen. This phenomenon is known as *self-purification* of water. However, non-biodegradable organic pollutants such as detergents and their aromatic derivatives are resistant to microbial degradation. Their degradation occur extremely slow consuming large amounts of dissolved oxygen.

Table 1.1. Some important organic pollutants along with their sources of origin

Pollutants	Sources	Representative Example
Proteins	Food processing, cannery waste, slaughter house waste, tannery waste.	Gelatin, keratin, casein
Fats	Fat refining, wool scouring waste, edible oil waste	Glycerol palmitate, glycerol stearate
Carbohydrates	Paper and pulp industry, textile industry	Starch, cellulose
Resins	Paint manufacture, textile industry, lacquer industry	Amber, rosin
Soaps	Laundry waste, soap industry, textile waste, domestic waste	Sodium palmitate, potassium stearate, sodium stearate
Detergents	Laundry waste, textile waste, detergent industry, domestic waste	Sodium lauryl sulphate, sodium dodecyl benzene sulphonate, polyglycol ether
Dyes	Dyeing and printing industry, pulp and paper, leather, textile paint, pharmaceuticals, carpet, cosmetic industries, etc	Fluorescein, magenta, methylene blue, crystal violet, congo red, malachite green, rhodamine B, metanil yellow

Agro-chemicals	Agricultural runoff, chemical industry	Acephate, acetamiprid, tricyclazole, methomyl, carbaryl, atrazine, diuran, DDT

Inorganic pollutants: They generally originate from industrial wastes. Inorganic acids and alkalis can do extensive damage to a water body by altering its natural buffer system and its normal pH value. Change in pH has a profound effect on aquatic organisms, especially fishes. Some common classes of inorganic pollutants are listed in Table 1.2.

Table 1.2.: Some important inorganic pollutants along with their sources of origin

Pollutants	Sources	Representative examples
Acids	Iron pickle liquor, industrial by-products Mine runoff,	Hydrochloric acid Sulphuric acid, phosphoric acid, nitric acid
Alkalis	Tannery waste, cotton processing waste, various industries	Caustic soda, lime, magnesium hydroxide
Heavy metals	Industrial and domestic activities, Metallurgical operations, motor vehicles, etc	Mercury ,cobalt, arsenic, cadmium, chromium, nickel, thallium, lead

(b) Physical pollutants:

Natural qualities of water are also affected when the physical parameters of water are drastically changed. Physical pollutants originate as a secondary consequence of chemical pollution. Physical pollutants include colour, turbidity, suspended matter, froth, radioactivity, thermal pollutants, etc.

(c) Physiological pollutants:

Physiological pollution is a secondary phenomenon arising due to the presence of trace quantities of chemicals. As a result of this, natural water no longer remains tasteless or odorless.

(d) Biological pollutants:

The undesirable and harmful aquatic organisms, which may sometime multiply excessively, are classified as biological pollutants. These pollutants generally arise as a secondary result of pollution by sewage or industrial wastes. Biological pollutants include weeds, algae, bacteria, viruses, protozoa, worms, etc.

1.4 Wastewater Treatment

Before the industrial revolution, 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 [4, 5].

1.4.1 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 **s**creening 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, polythene 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 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.

1.4.2 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 **s**edimentation 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 interval of time.

To get rid of extremely fine particles, flocculation method is used. These particles take 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 neutralized by sulphate or chloride ions whereas negative charges are neutralized by Al^{3+}, Fe^{2+} or Fe^{3+} ions. Once the charges are nullified, the particles come in contact with each other and coalesce and rapidly settle down.

1.4.3 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 microoragnisms. 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 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. Nextly, when 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 utilized in photosynthesis liberating oxygen. Thus, the dissolved oxygen which was consumed by bacteria is restored and fresh cycle could be started again.

1.4.4 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 the water treatment plants. It also eliminates the odors associated with the anaerobic decomposition of organic matter in water.

The impurities present in water are oxidized to harmless materials using suitable oxidizing 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 oxidized 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.

Electrodialysis technique is used to purify brackish water (water containing 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 attract 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.

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 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 sulphonic acid group). When water is passed through anion exchanger (containing quaternary ammonium hydroxide group), the anions present in 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.

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1.5 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 recognized in 1870 that unsaturation is essential for light absorption and hence colour sensation. Otto Witt, a German chemist, put forward his theory of colour and constitution and is known as chromophore-auxochrome theory. The main points of this theory are:

(a) The colour of an organic compound is mainly due to the presence of unsaturated groups known as chromophores (German: *Chroma* means colour and *phorein* means to bear). The compound bearing the chromophoric group is called chromogen [6,7]. For example, azo (–N=N–), carbonyl (C=O), methine (–CH=), and nitro $(-NO_2)$ groups, etc.
(b) The greater the number of chromophores, the greater is the intensity of colour.
(c) 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 (–OH), amino $(-NR_2, -NHR, -NH_2)$ groups, halogens, etc.

1.5.1 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.

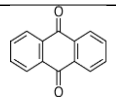
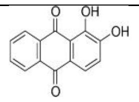
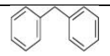
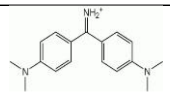
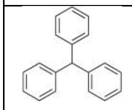
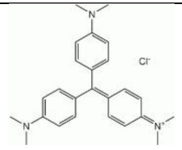
Natural dyes: These dyes are obtained from natural sources. Most of the natural dyes have plant origin (extracted from leaves, flowers, roots, berries, roots, bark, etc.). Some natural dyes are also obtained from insects and mineral compounds. For example, indigo, madder, saffron, osage orange, safflower, madder, etc. Natural dyes are of two types- **a**dditive and **s**ubstantive 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).

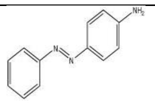
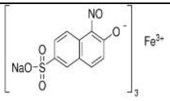
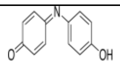
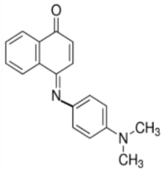
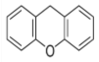
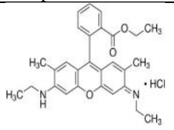
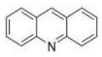
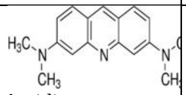
Synthetic dyes: Dyes prepared from organic or inorganic compounds are known as synthetic dyes. While searching for a remedy for malaria, William Henry Perkin, an English chemist, serendipitously discovered the first synthetic dye, Mauveine. Since then thousands of different synthetic dyes were manufactured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

b) Classification based on 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 1.3.

Table 1.3. Classification of dyes based on chromophoric group

Anthra quinone dyes		 Alizarin	🟥 Crimson
Arylme thane dyes		 Auramine O	🟨 *Yellow*
		 Crystal violet	🟪 Violet

Azo dyes	–N=N–	 Aniline yellow	🟨 Yellow
Nitroso dyes	–N=O	 Naphthol green B	🟩 Green
Indophenol dyes		 Indophenol blue	🟦 Blue
Xanthene dyes		 Rhodamin 6G	🟨 Yellow fluorescent
Acridine dyes		 Acridine orange	🟧 Orange

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 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 polyacryl. 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 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 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˚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 quiet expensive. For example, Vat blue 1, Vat orange 3, Vat yellow 1, 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.

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.

1.5.2 Dyes as a source of colour contaminant in water:

The discovery of 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 dye stuff produced annually[8]. Dyes are widely used in variety of industries such as textiles, rubber, paper, plastics, printing, leather, cosmetics, pharmaceuticals, food, etc., to colour their products. 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[9]. 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.

1.5.3 Harmful effects of dyes:

Colour is the first contaminant to be recognized in wastewater. The presence of 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 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[8]. 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 into the water bodies. Thus, the scientific community shoulders the responsibility of contributing to the waste treatment by developing effective dye removal technique.

1.6 Techniques available for removal of dyes from wastewater:

The wastewater treatment process has already been discussed in Section 1.4**.** 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].

1.6.1 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. Aerobic method involves the usage of free or dissolved oxygen by microorganisms to decompose the organic matter whereas in 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 requirement of large land area, sensitivity towards diurnal variations, toxicity of some chemicals, less flexibility in design and unsatisfactory colour elimination [11].

1.6.2 Chemical Treatment

Chemical methods include coagulation, flocculation, precipitation– flocculation with $Fe(II)/Ca(OH)_2$, electrofloatation, 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 accumulation of concentrated sludge and require high input of electrical energy [12, 13].

1.6.3 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 most preferred methods used for the removal of dyes from wastewater because of the various advantages such as ease of operation, simplicity of design, avoidance of secondary pollution, insensitivity to toxic pollutants, low cost and economic feasibility, etc.[15, 16].

1.7 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‖.

Adsorption process involves two components adsorbent and adsorbate. 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 adsorbent.

The process of adsorption arises due to presence of unbalanced or residual forces at the surface of liquid or solid phase. In a bulk of 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.

1.7.1 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 multilayer of adsorbate on adsorbent[17, 18].

(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 monolayer of adsorbate on adsorbent[19].

2. DESICCATION & RESULT:

2.1 Factors Affecting Adsorption of Dye:

There are many factors affecting dye adsorption such as solution pH, temperature, initial dye concentration, etc. Thus, the effects of these parameters are to be taken into account. Optimization of such conditions will greatly help in the development of industrial-scale dye removal treatment process. In this section, some of the factors affecting adsorption of dyes are discussed below:

Effect of solution pH:

One of the most important factors affecting the capacity of adsorbent in wastewater treatment is solution pH. The efficiency of adsorptions dependent on the solution pH, since variation in pH leads to the variation in the degree of ionization of the adsorptive molecule and the surface properties of adsorbent [20, 21] studied the effect of solution pH on the adsorption of Basic Green4dye by An anscomosus leaf powder and they noticed that at a pH range from 2 to 10, the dye removal ratio was maximum at a pH 10.[22] studied the effect of solution pH on the adsorption of Congo red by pine cone and they noticed that the adsorption was maximum at pH of 3.5.[23] studied the adsorption of RB4 dye by modified barley straw and they found that RB4 gives a complete removal of 100% at pH of 3 and decreased value below 50% as the pH was increased.[24] reported that adsorption of cationic dye MB onto raw pine leaves biomass was increased with increase In solution pH (Figure1).

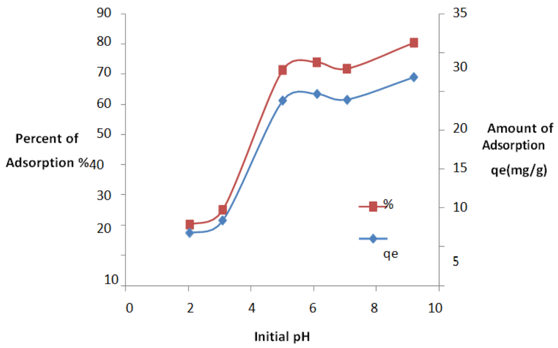


Fig.1 Effect of initial solution pH on the adsorption of Methylene Blue (MB) on pine leaves[24]

The adsorption ability of the surface and the type of surface active centers are indicated by the significant factor that is the point of zero charge (pH_{pzc}) [25]. The pH at which the surface charge is zero is called the point of zero charge (pzc) and is typically used to quantify or define the electro kinetic properties of a surface. The value of pH is used to describe pzc only for systems in which $H^+/OH^-$are the potential determining ions. Many researchers studied the point of zero charge (pH_{pzc}) of various adsorbents prepared from agricultural solid wastes; in order to underset and the adsorption mechanism. Due to presence of functional group such as OH^-group, cationic dye adsorption Is favoured at $pH > pH_{pzc}$, whereas, anionic dye adsorption is favoured at $pH < pH_{pzc}$ where the surface becomes positively charged[25].

Effect of initial dye concentration:

The amount of adsorption for dye removals highly dependent on the initial dye concentration. The effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface. In General, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. On the other hand the increase in initial dye concentration will cause an increase in the capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration[26,27] studied the adsorption of Methyl Orange by Chitosan/Alumina interface and it was found that when the Methyl Orange concentration increased from 20 mg/L to 400mg/L, the percentage of dye removal decreased from 99.53% to 83.55% with the same MB concentration range. [24] studied the effect of initial dye concentration on the adsorption of methylene blue (MB) by pine leaves and they noticed that as the initial dye concentration increase from10 to 90 mg/L ,the percentage removal of dye decreased from 96.5 to 40.9% on increasing the initial dye concentration from 10 to 90 mg/L after 240 minutes. Fig 2 showed that the amount of CR dye adsorption increased with increase initial dye concentration.

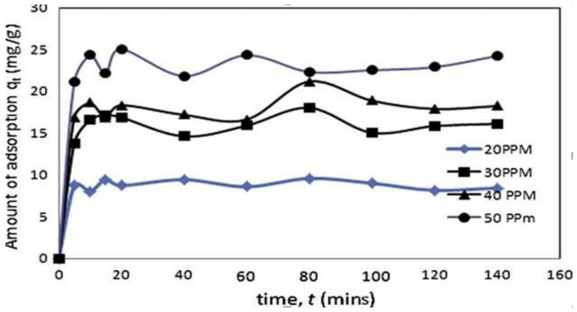


Fig.2 Effect of Initial Dye concertation (amount of CR dye adsorption increased with increase initial dye concentration.)

Effect of Temperature:

Effect of temperature is another significant physio-chemical process parameter because temperature will change the adsorption capacity of the adsorbent [28]. If the amount of adsorption increases with increasing temperature then the adsorption Is an endothermic process. This may be due to increasing mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature. Whereas the decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process. This may be due to increasing temperature decrease the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result of decreasing the amount of adsorption[29].

Effect of Amount of Adsorbent:

Adsorbent dosage is an important process parameter to determine the capacity of an adsorbent for a given amount of the adsorbent at the operating conditions. Generally the percentage of dye removal increases with increasing adsorbent dosage, where the quantity of sorption sites at the surface of adsorbent will increase by increasing the amount of the adsorbent. The effect of adsorbent dosage gives an idea for ability of a dye adsorption to be adsorbed with a smallest amount of adsorbent, so as to recognize the capability of a dye from an economical point of view [1] Fig 3 presented the effect of doses on the removal of acidic and basic dye by tea waste [30].

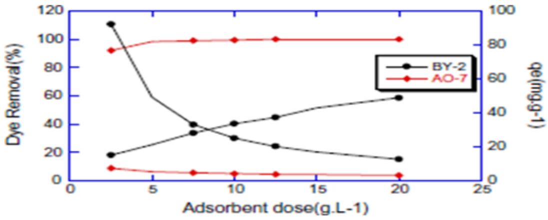


Fig 3 presented the effect of doses on the removal of acidic and basic dye by tea waste.

2.2 Various Adsorbents in the removal of Dyes from aqueous Solution:

Activated carbon:

Activated carbon is the most popular for the removal of pollutants from wastewater among allthe sorbent materials proposed[31, 32]. In particular, the effectiveness of adsorption on activated carbons for removal of a large variety of dyes from waste water such as made it an ideal alternative to the expensive treatment options[31].However, activated carbon possess several disadvantages, it is quite expensive ,problem in regeneration, non-selective and ineffective against disperse and vat dyes[32]. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications[33].This has led many researcher to search for alternative low cost adsorbents.

Low Cost Adsorbents for Dyes Removal:

Selection of the precursor for the development of low cost adsorbents depends on many factors. The precursor should be freely available, in-expensive and non-hazardous in nature. In recent times, attention has been focused on different natural solid, which are able to remove pollutants from contaminated water at low cost. Cost is an important parameter for comparing the sorbent materials. In general, a sorbent can be assumed to be “low cost” if It requires little processing and is abundant in nature, or waste material from another industry, which has lost its economic or is a by-product or further processing values. There are many low cost adsorbents that have been used for the removal of dyes. Also certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for dye removal. Waste treatment by adsorption using low cost adsorbent is a demanding area as it has double benefits i.e. water treatment and west management. Given below table shows example of absorption for removal of dye The use of agricultural waste helps tore duce the waste and produce a better waste minimization plan. Various cost effective adsorbents have been successfully used in the removal of dyes from.

Adsorbents	**Dyes**	**Adsorption capacity (mg/g)**	**Reference**
Acid-treated pine cone powder	Congo red	40.19	[34]
Avocado seed powder	Crystal violet	95.9	[35]
Bamboo leaves	Methylene blue	333.33	[37]
Melon peel	Methylene blue	95.4	[38]
Orange peel	Methylene blue	95.4	[38]
Raw coffee residue	Basic blue 3G	251	[39]
Raw coffee residue	Remazol Blue	232	[39]
Coffee waste	Toluidine Blue	142.5	[40]
Pine tree leaves	Basicred46	71.9	[41]
Pinecone	Congo red	19.18	[42]
Acid treated pinecone	Congo red	40.19	[42]
Pinecone	AcidBlack26	62.9	[43]
Pinecone	AcidGreen25	43.3	[43]
Pinecone	AcidBlue7	37.4	[43]
Rice husk	Methylene blue	40.6	[44]
Pine tree leave	Methylene Blue	126.6	[45]
Pinecone	Methylene blue	109.9	[46]
Palm shell	Reactivered141	14	[47]
Palm shell	Reactiveblue21	24.7	[47]
Pine saw dust	Acid yellow132	398.8	[48]
Pine saw dust	Acidblue256	280.3	[48]
Pine sawdust	Acid yellow132	398.8	[48]
Organ attapulgite	Congo red	189.4	[49]
Coffee residues	BasicBlue3G	179	[50]
Swede rape straw	Methylene Blue	246.4	[51]
Grape fruit peel	Crystal violet	254.16	[52]
Wheat bran	Crystal violet	80.37	[53]
Japonica	Crystal violet	82.83	[53]
Coniferous pinus bark	Crystal violet	32.78	[54]
Citrus sinensis Bagasse	Methylene Blue	96.4	[55]
Peanut hull	Methylene Blue	68.06	[59]
Banana peel	Methylene Blue	20.8	[57]
Orange Peel	Methylene Blue	18.6	[57]
Pine apple stem	Methylene Blue	119.05	[58]
Garlic peel	Methylene Blue	82.64	[59]
Coconut bunch waste	Methylene Blue	70.92	[60]
Coffee husk	Methylene Blue	90.1	[61]
Rubber seed shell	Methylene Blue	82.64	[62]
Yellow passion fruit waste	Methylene Blue	44.7	[63]
Rice husk	Methylene Blue	40.59	[64]
Coconut coir	Methylene Blue	15.59	[65]
Neem leaf powder	Methylene Blue	3.67	[66]
Pine apple leaf powder	Crystal violet	78.22	[67]
Sawdust	Crystal violet	37.83	[68]
Rice husk	Crystal violet	44.87	[69]
Mango seed kernel	Methylene Blue	142.86	[70]
Pinecone	Basic Red 46	73.53	[71]
Canola hull	Basic Red 46	49.00	[72]
Princess tree leaf	Basic Red 46	43.1	[73]
Rice husk	Direct Red 23	4.35	[74]
Rhizophoraapiculata bark	Direct Red 23	21.55	[75]
Pea nut hull	Reactive Black 5	55.55	[76]
Ground hazel nutshells	Methylene Blue	76.9	[77]
Walnut sawdust	Methylene Blue	59.17	[77]
Cherry sawdust	Methylene Blue	39.84	[77]
Poplar leaf	Methylene Blue	135.35	[78]
Pine Tree Leaves	Basic Red 46	71.94	[79]
Rejected tea	Methylene blue	242.11	[80]
Spent tea leaves	Crystal violet	114.94	[81]
Tea dust	Crystal violet	175.4	[82]

3. CONCLUSION:

A review of various type of activated carbon as adsorbent has been presented. The use of these activated carbon as adsorbent is recommended since they show a good potential in eliminating dyes from industrial wastewater, easily available, low cost and renewable. This paper presented the potential of adsorption process using activated carbon from agricultural waste to remove dye from industrial wastewater. The factors effecting dye adsorption such as effect of Temperature, adsorbent dosage, pH and initial dye concentration has been discussed. . Solution of pH turn to be the most important condition in adsorption process as for anionic dye, a low pH value are preferable in contrast for cationic dye where the suitable pH value is high. Is was also highlighted that the contact time between adsorbent and dye affecting the efficiency of dye removal where strong attraction force will shortened the time. As for the effect of dye initial concentration, increasing the initial concentration, enhance the increment of adsorbent surface area to adsorb dyes. For the adsorbent dose, that the adsorption capacity increase along with the increment of adsorbent dosage due to the increase of available amount of sorption site. Extensive studies in literature show that industrial waste and biosorbent activated carbon are among the less selective compound in removing dye. Furthermore, agricultural waste activated carbon showed effectiveness in removing dye such as basic dye and direct dye yet often being test for other pollutant. However, the raw material of activated carbon to be used are depends on the local sources available at low cost. According to the literature reviewed, these adsorption method using agricultural waste activated carbon have potential to be applied at full-scale wastewater treatment. These low cost adsorbent can used to replace the expensive adsorbents in the market nowadays.

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