

Chapter I

Introduction

Water is life's matter and matrix, mother and medium. There is no life without water.

- Albert Szent-Gyorgyi

1.1 Importance of Water

Five most essential elements for the existence of human life are air, water, food, heat and light, of which next to air, water is one of the prime necessities of life. Living organisms can hardly live without water for a few days¹. It is one of the most distributed and abundant materials in the world, covering 75% of the world's surface, therefore, the name 'blue planet', for earth. The importance of water for the living beings may be judged from the fact that it is a part of life itself, since the protoplasm of most living cells contains about 80% water and any substantial reduction in this percentage of water is disastrous. Most of the biochemical reactions that occur in the metabolism and growth of living cells involve water, which is often been referred as the universal solvent. Further, it has been estimated that almost two-thirds of the human body constitutes water which is required for the satisfactory performance of physiological organisms, as a circulatory fluid, as a carrier of nourishing food and for removal of the waste products from the body².

However, man uses water not only for drinking and culinary purposes but also for bathing, washing, laundering, heating and air conditioning; for agriculture, stock raising and gardens; for industrial processes and cooling; for water power and steam generation; for fire protection; for recreational purposes; for fish and wild life propagation; and for navigation.

Water is supplied with different qualities viz., good, bad and few outrightly dangerous which insist the need of water quality, being more important than water itself.

1.2 Drinking Water Quality

In general, water is considered to be fit for drinking, only when it possesses the following characteristics³

- ❖ Colourless, odourless and tasteless in nature
- ❖ Free from turbidity and suspended impurities
- ❖ Free from pathogens and microorganisms

- ❖ pH values between 7 - 8.5
- ❖ Anticorrosive and free from hazardous substances
- ❖ Satisfaction of all water quality parameters within the prescribed limits

Today, varied water resources are polluted with hundreds of toxins and impurities. Reports are available from various authorities only for a limited number of them. Pollution of drinking water results in the decline of man's health, vitality and longevity. Drinking water today, far from being pure, contains some two hundred deadly commercial chemicals. Added to that, prevalence of bacteria, viruses, inorganic minerals (making the water hard) pose a chemical cocktail that is unsuitable for human consumption⁴.

1.3 Water Pollution

Water pollution may be defined as, “the alteration in physical, chemical and biological characteristics of water which may cause harmful effects on humans and aquatic life.” Life is indispensable without water and its requirements are enormous extending to agricultural sectors and industrial processes. With the fast pace of its need in our civilization, the demand for water is increasing tremendously day-by-day. The problems related are population increase, sewage disposal, dumping industrial waste etc. have polluted water resources much considerably. About 10% of rivers and streams not only in India, but of almost in all the countries contain polluted waters¹. The industrial effluents and trade wastes of pulp and paper, textile, distillery, fertilizer, electroplating, asbestos, silt, alcohol, detergents, steel, tannery, cane sugar, oils contribute a major role in contaminating water bodies. These effluents pollute discharges by 16% through their streams, ponds, lakes⁵ etc. Textile industries generally consume a large amount of water of high purity. Most of the effluent treatment plants (ETP) perform their physical and chemical processes satisfactorily due to the imposed regulations under commercial scales.

1.4 Textile Industries

Indian textile industry is one of the oldest and largest industries in the world and employs many people directly or indirectly. The textile industry has a \$1 trillion worldwide business. Consumer demand for textiles is ever increasing in the domestic and

international market. Textiles are not only used just for apparels, but also in homes, hospitals, workplaces and vehicles, in the form of cleaning materials, leisure equipments and so on. Textile industry consists of spinning, weaving, chemical processing and apparel manufacturing, out of which the chemical processing division is the most polluting one as it is chemically intensive. The textile chemical processing industry uses large quantities of water in each of its processes namely desizing, scouring, bleaching, dyeing and finishing. On an average, to process 1kg of finished fabric, 200-400 litres of water are required⁶.

Desizing is the first step which involves the removal of sizing materials present in the greige cloth to make it suitable for further processing. Starch, PVA and CMC are the major pollutants in desizing process and its effluent possess exceeding BOD and COD levels than prescribed limits. Scouring process is done mainly for cotton and wool to improve the absorbency, the possible pollutants being caustic soda, waxes, surfactants, suspended and dissolved solids. Scouring effluents have high pH, COD and BOD. Bleaching is done to remove the natural colour present in the fibres, the effluent contents having high caustic soda, chlorine and hydrogen peroxide along with high pH and BOD values. Dyeing is the process of imparting colour to the fabric which utilizes various dyes and auxiliaries. The dyeing wastewater emits volatile organic compounds into air and contains high amounts of metals, salt, surfactants, organic processing assistants, cationic materials, colour, BOD, sulphide, acidity or alkalinity and spent solvents. Finishing imparts the required feel to the fabric like anti-crease, anti-shrink, anti-pill, etc. which employs chemicals as per the end use⁷. In total, the textile wastewaters generated are brownish to black in colour, pH range around 8.5, Total suspended solids of around 270 mg/L, Total dissolved solid of 2300 mg/L, BOD 350mg/L and COD of 770 mg/L and an unpleasant odour⁸. Most of the chemicals used in the above processes result in harmful effects to the ecosystem.

The pollution control boards in various countries have formulated various norms for the discharge of effluent into the environment. The textile wastewater needs treatment prior to discharge into the environment. The norms suggested by Pollution Control Board of India are as follows: It allows a pH range of 6-9, Total suspended solids of 100 mg/L, Total dissolved solids of 2100 mg/L, BOD 30 mg/L and COD of 250 mg/L.

These standards are frequently not met by the actual parametric values in the textile wastewaters as they are usually alarmingly high.

Depending upon the quantity of the clothes produced and various manufacturing processes employed, volumes of composite effluents discharged from the textile mills vary from 1 to 10 million litres per day. These when evaporate, they cause air pollution and when discharged directly into streams lead to water pollution, creating health hazards.

Approximately, 40,000 different dyes and pigments are utilized in industries and over 7×10^5 tons of these dyes are produced annually worldwide⁹. Textile industries consume substantial volumes of water and chemicals in wet processing. It was estimated that 10-15 % of the dyes used in textile processing were lost in the effluents during the dyeing processes¹⁰. These dyes include several structural varieties, such as acidic, reactive, basic, direct, disperse, azo, diazo, anthraquinone based and metal complex dyes.

1.5 Dyes

Dyes are coloured organic compounds that are applied to impart colour to various substrates including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials. The sources of natural dyes are obtained from plants (e.g., alizarin, catechu, indigo and logwood), from animals (e.g., cochineal kermes and tyriapurple) and from certain naturally occurring minerals (e.g., ocher and prussian blue). They have now almost been replaced by synthetic dyes.

All colorants were of natural origin upto middle of the 19th century. In 1856, an English chemist W.H. Perkin synthesized a bluish substance viz. Aniline purple and Tyrian purple with excellent dyeing properties. This invention and Kekule's discovery of benzene structure strongly stimulated the production of various synthetic dyes. Thus, in the beginning of 20th century, the natural dyestuffs were replaced by synthetic dyestuffs.

1.5.1 Classification of Dyes

The compounds which absorb electromagnetic energy in the visible range (~350-700 nm) are coloured. Dyes contain chromophores (delocalised electron systems with conjugated double bonds) and auxochromes (electron-withdrawing or electron donating substituents). The chromophore imparts colour to the dye molecule and

auxochrome intensifies the colour of the former by altering the overall energy of the electron system. Usual chromophores contain C=C, C=N, C=O, N=N, -NO₂ groups and quinoid rings. Auxochromes¹⁰ include -NH₂, -COOH, -SO₃H and -OH.

In 1924, the Society of Dyers and Colourists and the American Association of Textile Chemists and Colourists classified the dyes on the basis of colour, structure and application method in the Colour Index (C.I.) which is further revised every three months. These dyes are classified as: azo (monoazo, disazo, triazo, polyazo), anthraquinone, phthalocyanine, triarylmethane, diarylmethane, indigoid, azine, oxazine, thiazine, xanthene, nitro, nitroso, methine, thiazole, indamine, indophenol, lactone, aminoketone, hydroxyketone, stilbene and sulphur dyes. Each dye was given a C.I. generic name on the basis of its application, characteristics and its colour. The Colour Index discriminate 15 different application classes:

(i) Acid Dyes

They are the largest class of dyes in the colour index and is referred to as Acid dyes. Acid dyes are anionic compounds that are mainly used for the dyeing nitrogen-containing fabrics like wool, polyamide, silk and modified acryl. They bind to the cationic NH₄⁺ ions of those fibres. Most of the acid dyes are azo, anthraquinone or triarylmethane compounds. The adjective 'acid' refers to the requirement of acidic condition for dyeing these dyes to fibers (cotton, wool, silk and nylon).

(ii) Reactive Dyes

According to the Colour Index, reactive dyes are the second largest class of dyes, introduced in 1956. Reactive dye is a type of water soluble anionic dye having good affinity for cellulose fibres. In the presence of alkali, they react with hydroxyl groups present in the cellulose and thus are linked with the fibre by means of a covalent bond. Fibre reactive dyes are relatively new dyes and are used extensively on cellulosic when bright shades are desired. Reactive dyes, particularly those used for dyeing cotton, have become one of the major classes of dye because of their good washing fastness, ability to produce bright shades and versatility in application either by batch or continuous dyeing methods.

(iii) Metal Complex Dyes

Many metal complex dyes are classified under acid and reactive dyes. Metal complex dyes are the strong complexes of one metal atom (usually chromium, copper, cobalt or nickel) and one or two dye molecules (1:1 and 1:2 metal complex dyes respectively). About 16% of the azo dyes listed in the colour index are metal complexes. The phthalocyanine metal complex dyes are also being used.

(iv) Direct Dyes

Direct dyes are one of the largest dye class in the colour index with respect to the amount of dyes. Direct cotton dyes have inherent substantivity for cotton and for other cellulosic fibres. Chemically, direct dyes are sodium salt of aromatic sulphonic acids and most of them contain an 'azo' group as the main chromophore. Vander Waals forces make them bind to the fibre. These classes of dyestuffs are applied directly to the substrate in a neutral or alkaline bath. The bath is then gradually heated, usually to the boiling conditions and additions of salt promote dyeing. Direct dyes give bright shades but exhibit poor wet fastness property.

(v) Basic Dyes

Basic dyes represent 5% of all dyes listed in the colour index. They are cationic compounds and used for the dyeing acid-group containing synthetic fibres like modified polyacryl. They bind to the acid groups of the fibres. Most of the basic dyes are diarylmethane, triarylmethane, anthraquinone or azo compounds.

(vi) Mordant Dyes

The dyes which required the mordant for dyeing it to fibres is called as mordant dyes. They are used for dyeing wool, leather, silk, paper and modified cellulose fibres. Most mordant dyes are azo, oxazine or triarylmethane compounds. The mordants are usually dichromates or chromium complexes.

(vii) Disperse Dyes

Disperse dyes form the third largest group of dyes under colour index. Disperse dyes are scarcely soluble dyes, thus it required high temperature or chemical softeners for dyeing to synthetic fibers viz. cellulose acetate, polyester, polyamide, acryl, etc. Dyeing

takes place in dye baths with fine disperse solutions of these dyes. They are usually small azo or nitro compounds, anthraquinones or metal complex azo compounds.

(viii) Pigment Dyes

These are insoluble non-ionic compounds or insoluble salts which retain their crystalline or particulate structure throughout their application. Pigment dyes (i.e. organic pigments) represent a small but increasing fraction of the pigments, the most widely applied group of colorants. About 25% of all the commercial dyes listed in the colour index are pigment dyes. Pigment dyeing requires the use of dispersing agents. Pigments are usually used together with thickeners in print pastes for printing diverse fabrics. Most of them are azo compounds/ metal complex phthalocyanines/ anthraquinones/ quinacridones.

(ix) Vat Dyes

Vat dyes are water insoluble that are widely used for dyeing cellulose fibres. They refer to the vats that are used for the reduction of indigo plants through fermentation. The dyeing method is based on the solubility of these dyes in their reduced (leuco) form. Alternate reduction and oxidation processes are used in this form of dyeing with sodium dithionite as reducing agent. Almost all vat dyes are anthraquinones or indigoids.

(x) Anionic Dyes and Ingrain Dyes

Azoic and ingrain dyes (naphthol dyes) are insoluble products resulting from the reaction between a coupling component, including naphthols, phenols or acetoacetyl amides and a diazotised aromatic amine. This reaction is carried out in the fibre. All naphthol dyes are azo compounds.

(xi) Sulphur Dyes

Sulphur dyes are complex polymeric aromatics with heterocyclic S-containing rings. This dye group represents about 15% of the global dye production. Dyeing with sulphur dyes involves reduction and oxidation comparable to vat dyeing. They are mainly used for dyeing cellulose fibres.

(xii) Solvent Dyes

Solvent dyes are non-ionic dyes that are used for dyeing substrates in which they can dissolve, e.g. plastics, varnish, ink, waxes and fats. They are not often used for textile processing but have increased applications. Most solvent dyes are diazo compounds that undergo few molecular rearrangements. Also triarylmethane, anthraquinone and phthalocyanine solvent dyes are applied.

(xiii) Other Dye Classes

These include food dyes and natural dyes. Food dyes are not used as textile dyes. Natural dyes viz. anthraquinone, indigoid, flavanol, flavone or chroman compounds employed as mordant, vat, direct, acid or solvent dyes in textile processing are very limited.

1.5.2 Dye-Fibre interactions

Fibres can take up dyes as a result of Vander Waals forces, hydrogen bonds and hydrophobic interactions. The uptake of the dye in fibres depends on the dye nature and its chemical constituents. The strongest dye- fibre attachment is a result of a covalent bond with an additional electrostatic interaction where the dye ion and fibre have opposite charges, this process is called as the degree of fixation¹¹, and the unfixed dyes are lost to the effluent. The percentage of fixation varies based on dye and fibre types, which is maximum for basic dyes and minimum for reactive dyes. The estimated degree of fixation for different dye-fibre combinations are given in Table 1.1^{12,13}

Table 1.1 Fixation Degree of Different Dye Classes on Textile Materials

Dye Class	Fibre	Degree of Fixation %	Loss to Effluent %
Acid	Wool, cotton and nylon	80-90	5-20
Basic	Acrylic fibres, polyester, wool and silk	90-100	0-5
Direct	Cotton	70-95	5-30
Disperse	Polyester	90-100	0-10
Metal-complex	Wool	90-98	2-10
Reactive	Cellulose, nylon, silk and wool	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Vat	Cellulose	80-95	5-20

1.5.3 Dye Pollution

The effluents from dyeing industries are highly coloured / toxic to the aquatic life. It is estimated that 10–15% of the dyes employed in the textile processing, enter the effluent streams^{14,15}. Dyes usually are of synthetic origin and possess complex aromatic molecular structures. Generally, they are synthesized from known carcinogens, such as benzidine or their aromatic compounds. Even minute amounts of dyes can cause health hazards like nausea, haemorrhage, cancer, ulceration of skin and mucous membranes which may pose severe damages to kidneys, liver, brain and central nervous system when present in water bodies. Some specific properties, applications and toxicities of various dyes are listed in Table 1.2.

Dyes employed in the textile industries viz., acidic, reactive, basic, disperse, azo, diazo, anthraquinone based and metal complex dyes put up to have more or less harmful effects¹⁶. Intense exposure to these dyes lead to increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans¹⁷. Dyes like methanil yellow contain a tumour producing effect¹⁸ and can produce enzyme disorders in the human body¹⁹. However, it is not mutagenic but can

alter the gene expression²⁰. On oral consumption, it causes toxic methaemoglobinaemia and cyanosis. In humans, skin contact results in allergic dermatitis. Oral feeding or intraperitoneal and intratesticular administration of dyes in animals produce testicular lesions due to which the seminiferous tubules suffer damage and the rate of spermatogenesis produced is reduced²¹. Dyes are to be annihilated from these wastewaters before being expelled into the environment to prevent the ecosystem from being polluted.

Table 1.2 Dyes- Specific Properties, Applications and Toxicities

Acidic	Water soluble, anionic	Nylon, wool, silk, paper, leather, ink-jet printing	
Cationic	Water-soluble, releasing coloured cations in solution. Some dyes show biological activity	Paper, polyacrylonitrile, modified nylons, modified polyesters, used in medicine as antiseptics	Carcinogenic (benign and malignant tumors)
Disperse	Water-insoluble, non-ionic; for hydrophobic aqueous dispersion	Polyester, nylon, cellulose, cellulose acetate, acrylic fibers	Allergenic (skin), Carcinogenic
Direct	Water soluble, anionic, improves wash fastness by chelating with metal salts	Cotton, regenerated cellulose, paper, leather	Bladder cancer
Reactive	Extremely high wash fastness due to covalent bond formation brighter than direct dyes	Cotton, wool, nylon, ink-jet printing of textiles	Dermatitis, allergic conjunctivitis, rhinitis, Asthma
Vat	Use soluble leuco salts after reduction in an alkaline bath	Cellulosic fibers	-

1.6 Heavy Metals

In small quantities, certain heavy metals are nutritionally essential for a healthy life. But many of them are potentially toxic even at low concentrations. Metals such as arsenic, lead, copper, cadmium, nickel, mercury, chromium, cobalt, zinc and selenium are highly toxic even at minor quantities.

Environmental pollution due to heavy metals discharge have been accelerated dramatically during the last two decades as a result of mining, fertilizers, pesticides, traffic emission, smelting, municipal wastes, industrial effluents and chemicals. The textile industries play a vital role to deteriorate the surrounding ground water quality extensively. The effluents discharged from these units consist of high concentrations of heavy metals, organic pollutants and toxic colours, which may alter the surface water quality of the surrounding environment. Toxic pollutants may percolate down via the soil profile, affecting the crop production through irrigation, ultimately, reaching the groundwater table.

1.6.1 Heavy Metal: Sources, Toxicity and its Implications

Heavy metal ions are discharged into water system through various industrial activities such as electroplating industries, electronic equipment manufacturing and chemical processing plants. Due to rapid development of industrial activities, the concentrations of heavy metals in water systems have substantially increased. They can easily enter the food chain because of their high solubility in water. Sources and health disorders of few heavy metals are listed in Table 1.3.

The international community has recognized the adverse health effects of heavy metals²². Heavy metal toxicity may result in damaged/reduced mental, central nervous function, lowering energy levels and damaging blood composition further affecting lungs, kidneys, liver and other vital organs. Long-term exposure may result in slow progressing of physical, muscular and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals (or their compounds) may cause cancer. It is the need of the hour to treat heavy metal contaminations and take protective measures against excessive exposures²³.

Table 1.3 Heavy Metals - Sources and Implications

Heavy Metals	Sources	Implications
Chromium	Cooling tower, dyes, electroplating, ink, anodizing, paints, tanning etc.	Cancer
Cadmium	Coal combustion, metal plating, water pipe, phosphate fertilizers etc.	Cardiovascular disease,
Lead	Battery industry, paints etc.	Affects nervous and renal headache, constipation, cancer etc.
Copper	Pulp and paper ,electrical goods, utensils, chemicals etc.	Caner (Suspected).
Nickel	Diesel Oil, coal, steel & non-ferrous alloys, tobacco smoke etc.	Lung cancer, respiratory symptoms, hemorrhages.
Zinc	Galvanizing alloys, rayon, paper etc.	Cancer
Mercury	Coal combustion, electrical batteries, Chlor-alkali industry.	Nerves damage, death,
Cobalt	Alloys ,steel, electroplating glass, enamels etc	Cancer
Manganese	Metal alloys, power plants, gasoline.	Nervous system damage.

Chromium (Cr)

Chromium is a silvery, lustrous hard metal, occurring in the oxidation states of Cr(III) and Cr(VI). The most stable state of chromium is found to be Cr(III) being less toxic than Cr(VI)²⁴. The metal is discharged into the environment from industries such as electroplating, metal finishing, leather tanning, dyes, pigments and wood preservatives in the form of effluents²⁵. Cr(VI) is a carcinogenic element, causing acute and chronic health effects in humans which include ulceration, dermatitis, damage to nerve tissues, liver and kidney and even death at higher doses²⁶.

Nickel (Ni)

Nickel is a silvery white hard divalent metal. Ni(II) is used in nickel plating and battery manufacturing²⁷ and its presence above the permissible limit results in several health effects including gastrointestinal distress, lung and kidney damage, pulmonary fibrosis and dermatitis^{28,29}.

Copper (Cu)

Copper is a reddish brown metal. Regular availability of Copper in human beings is observed to be between 1.4 to 2.1 mg approximately per kilogram of body mass. Extremely low copper concentration affect gene expression profiles of human beings as it is required in minimum quantity, but is toxic at larger amounts³⁰. It is widely used in many industries including metal cleaning and plating baths, paints and pigments, fertilizer, paper board, wood pulp, printed circuit board production, etc. The effluents from these industries usually contain considerable quantity of copper, which spreads into the environment through soil and water streams, and finally gets accumulated along the food chain causing health hazards. Absorption of excess copper by man results in “Wilson’s disease” in which excess copper is deposited in the brain, skin, liver, pancreas and myocardium. A higher concentration of copper will also cause severe mucosal irritation, widespread capillary damage, hepatic and renal damage and irritation of the central nervous system followed by depression.

Cadmium (Cd)

Cadmium is regarded as an element of high toxicity. Cadmium ions are not biodegradable and can be accumulated easily in the living tissues, through absorption via food chain. The adverse health effects are bone lesions, cancer, pulmonary insufficiency and hypertension.

Lead (Pb)

Lead is a bluish-white soft metal. It occurs in nature in oxidation states of Pb(II) and Pb(IV) but stable state is found to be Pb(II)²⁴. High concentrations of Pb(II) ions are present in wastewaters discharged from battery and paint industries²⁵. Human health effects include damage of central nervous system, kidney, liver and reproductive system.

Toxic symptoms are anaemia, insomnia, headache, dizziness, irritability, weakness of muscles and renal damage²⁹. The regulatory limits for heavy metals in drinking water and discharge from industrial wastewaters are shown in Table 1.4.

Table 1.4 Permissible Limits for Heavy Metals in Drinking / Industrial Wastewaters

Metal	Permissible limits in drinking water	Industrial effluent discharge (mg/L) (Indian standards) ³¹		Industrial effluents as per International standards (µg/L)	
		Inland Surface water	Into public Sewers	WHO ³²	USEPA ³²
Nickel	0.10	3.00	3.00	2	-
Mercury	0.001	0.01	0.01	1	2
Arsenic	0.05	0.20	0.20	10	50
Cobalt	1.07	0.25	0.60	-	-
Lead	0.05	0.10	1.00	10	5
Chromium	0.05	0.10	2.00	50	100
Zinc	5.00	5.00	15.00	-	-
Copper	0.06	3.00	3.00	-	1300
Iron	2.00	0.01	0.01	-	-

1.7 Physico-Chemical Treatment of Textile Effluents

Conventionally, industrial wastewaters are treated by the following methods:

- ❖ Primary treatment
- ❖ Secondary or Biological treatment
- ❖ Tertiary treatment

1.7.1 Primary Treatment

This treatment is carried out to remove the suspended solids and to some extent, the colour and odour. This process includes screening, neutralization, coagulation, sedimentation etc., Screening process focuses on the removal of the floating materials such as yarn, rags etc., Equalization process is done mainly to maintain the pH and ensure uniform flow throughout the process. Coagulation is done to remove the suspended particles using alum, ferric chloride, ferrous sulphate and calcium chloride.

1.7.2 Secondary Treatment

Secondary treatment is done to break the complex organic molecules to simpler substances. The biological treatment is also known as the secondary treatment. This process involves aerobic and anaerobic treatment. In aerobic treatment, the destruction takes place mainly in the presence of oxygen and in the anaerobic treatment, in the absence of oxygen. This treatment includes: activated sludge process, trickling filtration, aerated lagoons and oxidation ponds. In the trickling filtration process, the wastewater is brought in contact with that of the microbial population in the form of a film of slime attached to the solid surface as the supporting medium. The slimes formed on the stones oxidize the waste during its passage. Aerated lagoons are activated sludge units operated with the sludge return. In this aerated lagoon treatment, the effluent from the primary treatment process is passed onto a tank and it is mechanically aerated. An oxidation pond is a shallow pond in which the waste is added at one end and the effluent is removed at the other end. Among all the above processes, the activated sludge process is employed widely.

1.7.3 Tertiary Treatment

Tertiary treatment is also termed as the advanced wastewater treatment. The main purpose of this treatment is the reclamation of water for reuse resulting from the primary and biological treatments. This process includes chemical coagulation/flocculation, membrane process, electrochemical method, photolysis, ozonation and adsorption.

(i) Coagulation/Flocculation

The chemical coagulation/flocculation process is used to remove colour, to reduce COD and suspended solids with the help of the chemicals such as $\text{Fe}^{3+}/\text{Cr}^{3+}$, alum with lime etc., 50% reduction of COD and 57% reduction of suspended solids were achieved in wool dyeing effluents using 100 mg/L of flocculants Zetas 92³³. Lime and alum mixture in dosage between 200 and 300 mg/L was the best coagulant mixture to remove 80% of colour and 65% of BOD³⁴. The main disadvantage of this method is the additional chemical load on the effluent. (normally increases salt concentration) which increases the sludge production and leads to the incomplete removal of metals and dyes.

(ii) Reverse Osmosis

In reverse osmosis process, water is forced to move from stronger saline solution to weaker solution through semipermeable membrane. Because molecules of salt are physically larger than water molecules, membrane blocks the passage of salt particles. The end result is desalinated water on one side and highly concentrated saline solution of water on the other side of membrane³⁵.

Reverse osmosis membranes are susceptible to fouling due to the presence of organics, colloids and microorganisms. Scale causing constituents like hardness, carbonate, silica, heavy metals, oil etc have to be removed from the feed. As the membranes are sensitive to oxidizing agents like chlorine or ozone, their absence are to be ensured. Ultra-filtration process is similar to reverse osmosis. The difference between the two lies primarily in the retention properties of the membranes. Reverse osmosis membranes retain all solutes including salts, while ultra filtration membranes retain only macro molecules and suspended solids. Thus salts, solvents and low molecular weight organic solutes pass through ultra filtration membrane in the presence of permeate water.

Nanofiltration can be positioned between reverse osmosis and ultra filtration. It is essentially a lower pressure version membrane, where the purity to permeate water is less important. This process is used where the high salt rejection of reverse osmosis is not necessary. The nanofiltration is capable of removing hardness causing elements such as calcium or magnesium together with bacteria, viruses and colour. This process is operated at lower pressure than reverse osmosis and as such the treatment cost is lesser

than reverse osmosis treatment (CPCB 2007). Membrane separation process is a new separation technology, with high separation efficiency, low energy consumption, easy operation, no pollution and so on. However, this technology is still not promoted on a large scale because it has the limitations of special equipments, skilled man power, high investment, membrane fouling etc³⁶.

(iii) Ion Exchange

The process involves usage of resins for targeted ions of electrolytes. Uptake of these ions by the resins, prohibits reversibility and promotes exchange of similar ions, unaffected the resin structures³⁷. In addition, pre-treatment, such as the removal of suspended solids from wastewaters, is required before employing operating procedures. Consequently, capital and operational costs are high in ion exchange processes³⁸.

1.7.4 Electrochemical Treatment Techniques

(i) Electrochemical Precipitation

This technique concentrates on the potentiality of electrical charges against regular chemical precipitation, which mostly favours the heavy metal removal from discharges³⁹.

(ii) Electrodialysis

Electrodialysis is a membrane separation in the electro process where ionic solutions move from one compartment to another with the help of ion exchange membrane. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations towards the cathode, crossing the anion exchange and cation exchange membranes⁴⁰. Tzanetakis⁴¹ et al., evaluated the performance of the ion exchange membranes for the electrodialysis of Ni(II) and Co(II) ions from a synthetic solution. Essential requirements of this technique include: neat feed, meticulous operation, consistent maintenance to avoid discrepancies in the mould⁴².

1.7.5 Membrane Electrolysis

Membrane electrolysis, a chemical process driven by an electrolytic potential, applied to remove metallic impurities from metal finishing wastewaters. There are two

types of cathodes used: a conventional metal cathode and a high surface area cathode. When an electrical potential is applied across an ion exchange membrane, reduction–oxidation reaction takes place in electrodes⁴³. Energy consumption is the primary shortcoming of this method.

1.7.6 Photocatalysis

Photocatalysis refers to the acceleration of a photoreaction in the presence of a catalyst. Photochemical oxidation has many advantages of the mild reaction conditions (ambient temperature and pressure), powerful oxidation ability, fast kinetics etc. Dye decomposition in presence of UV/sun light, photoactivate oxidation, optical excitation and photocatalysis oxidation constitute the types of photocatalysis. This technology can effectively destroy a lot of organic pollutants whose structures are stable and difficult to degrade biologically. The obvious advantages of this technology are significant energy efficiency and complete degradation of pollutants. Almost, all of the organic matter can be completely oxidized to CO₂, H₂O and other simple inorganic substances under the light catalyst. However, photocatalysis oxidation process is not ideal for highly concentrated wastewaters⁴⁴.

1.7.7 Ozonation

Ozone is one of the strongest oxidizers commercially available and popular for disinfection of potable water. Besides this, it has multiple applications. Large, complex organic molecules, detergents, phenols etc. can be broken into simpler compounds by ozonation. Among the industrial applications, oxidation of organics and inorganics, deodorization, and decolourisation are the main usages. For most industrial applications, ozone has to be produced at insitu. Although, there are several methods by which ozone can be generated, the corona discharge method is a widely used procedure. An ozone generation unit incorporates a series of electrodes fitted with cooling arrangements mounted in a gas tight container. When the source gas (air or oxygen) is passed through narrow gap separating electrodes, the oxygen gets converted into ozone. Ozone is applied by means of diffuser tubes or turbine mixers. A dose of 2 mg/L has been reported to result in virtually complete removal of colour and hard pollutants such as detergents. The treated water after sand filtration becomes clean and sparkling (CPCB 2007). In

textile effluent it initiates and accelerates azo bond cleavage. Even though this method sounds advantageous, its drawback lies in the release of carcinogenic aromatic amines, toxic molecules and hence is less preferred⁴⁵.

1.7.8 Adsorption

Adsorption has emerged as a promising technique for the removal of heavy metals and dyes. The processes can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, or liquid-solid interfaces⁴⁶. Moreover, adsorption is a practically feasible separation method for purification or bulk separation in newly developed material production process, for example, high-tech materials and biochemical and biomedical products. Surface characteristics and pore structures of adsorbents are the main properties in determining adsorption equilibrium and rate properties which are needed for plant design. New adsorbents are continuously being developed, introducing new applications for adsorption technology. The adsorption processes takes place in different steps (1) bulk solution transfer (2) film diffusion transfer (3) pore transport and (4) adsorption. Bulk solution transfer involves the movement of the material to be adsorbed through the bulk liquid to the boundary layer of fixed film of liquid surrounding the adsorbent. Film diffusion transport involves the transport by diffusion of the material to be adsorbed through the stagnant liquid film to the entrance of the pores of the adsorbent. Pore transport involves the transport of material to be adsorbed through the pores by a combination of molecular diffusion through the pore liquid/ or by diffusion along the surface of the adsorbent. Adsorption involves the attachment of the material to be adsorbed onto adsorbent at all available adsorption sites⁴⁷.

Advantages of adsorption:

- ❖ Selective removal of dyes/metals at lesser concentrations
- ❖ Effluent discharge concentrations under Govt. Regulations
- ❖ Operation of broad pH ranges (2-9)
- ❖ Effective temperature ranges (4-900°C)
- ❖ Low capital investment / operation cost
- ❖ Metal pollutant conversion to metal product
- ❖ Simple design, easy operation

1.7.9 Types of Adsorption

There are two types of adsorption phenomena, physical adsorption and chemical adsorption⁴⁸.

(i) *Physical adsorption*

It is the result of intermolecular forces of attraction between molecules of the solid adsorbent and the substance adsorbed. It is a readily reversible phenomenon. In industrial adsorption operations, this reversibility is used for the recovery of adsorbent/adsorbed substance.

(ii) *Chemisorption*

Chemisorption is the result of chemical interaction between the solid adsorbent and the adsorbed substance. The adhesive force and the heat liberated are much greater than those observed in physical adsorption. The process is frequently irreversible. Some substances undergo only physical adsorption substantially at low temperatures. But they exhibit chemisorption at high temperatures and sometimes both the phenomena may occur at the same time. Chemisorption is of particular importance in catalysis.

1.8 Activated carbon

Activated carbon is broadly defined to include a wide range of amorphous carbon based materials prepared in such a way which exhibit a high degree of porosity and an extended surface area. For many centuries, the activated carbon had been used in the form of carbonized wood. The earliest activated carbon prepared from wood chars was utilized by the Egyptians and Sumerians in 3750 BC, for the reduction of ores in the manufacturing of bronze, domestic smokeless fuel and medicinal applications. In 1500 BC, Egyptian papyrus was used as adsorbent for odorous vapours from putrefying wounds and from within the abdominal tract. The wrecks of Phoenician trading ships suggest that drinking water was stored in charred wooden barrels. This practise was certainly still in use in the 18th century for extending the use of potable water on long sea voyages. The ancient Hindus in India of the same period (450 BC) used sand and charcoal filters for purifying drinking water. In 157 AD, Claudius Galvan referred the use of carbons of both vegetable and animal origin for the treatment of a

wide range of diseases. The specific adsorptive capacity of charcoal was recognized by Scheele at 1773 AD, who measured the volumes of gases that could be adsorbed by carbons derived from different sources. In 1785, Lowitz reviewed the abilities of charcoals to adsorb odours and vapours from a range of organic chemicals. He also studied the effectiveness of charcoal in decolourizing tartaric acid. In 1794, wood charcoal was used to decolourize the sugarcane syrups. In 1811, Figuier evaluated the decolourizing capacity of bone char and wood char, also during 1815, most of the sugar refining industry had switched to the use of granulated bone char as a decolourant. Joseph de Cavaillon patented a method for regenerating used bone chars in 1817. Bussy (1822) demonstrated that the decolorizing properties of carbons were inherent to the source material and also depended on the thermal processing and the particle size of the finished product. Kayser (1881) first used the term adsorption to describe the uptake of gases by carbons. The basis for the industrial production of 'activated carbon' from coal was established in 1900, in order to replace the bone char in the sugar refining process. The first powdered commercial activated carbon, eponite was produced in Europe in 1909. During the First World War (1914), steam activation of coconut shell and almond shell char was developed in the United States for use in gas masks. It has been used subsequently for water treatment, solvent recovery and air purification. This type of activated carbon mainly contains fine pore structures suited for gas phase adsorption applications. In Czechoslovakia two varieties of pelletized carbons were produced from sawdust through zinc chloride activation, for the recovery of volatile solvents and for the removal of benzene from town gas. Nowadays, zinc chloride process of chemical activation has been largely superseded by the use of phosphoric acid. The use of carbon molecular sieves in gas separation, in particular oxygen and nitrogen, has grown steadily in the past years⁴⁹.

Activated carbons are useful adsorbents due to their porous structures, the presence of various oxygenated functional surface groups depending on the precursor's nature and the procedures used in their preparation, and thus activated carbons show differences in their adsorptive behaviour. To produce these carbons, chemical, physical and mixture of both as activating agents are used and a number of activation procedures have been reported in

the literature⁵⁰ using the above said activating agents. In general, it can be classified either as single stage or two-stage process.

Activated carbon also called activated charcoal, is a form of carbon that has been processed with oxygen to create millions of tiny pores between the carbon atoms. Commercial activated carbons have internal surface area ranging from 500 to 1500 m²/g. Activated carbon can also be prepared from feed stock with high carbon and low inorganic content. The most common feed stocks used for the production of activated carbons are wood, coconut shell, bituminous coal, peat etc. The chars obtained from them could be activated easily to produce reasonably high quality activated carbons. During the activation process, the unique internal pore structure is created, which provides the activated carbon its outstanding adsorptive properties.

They possess a number of unique characteristics such as large internal surface area, chemical properties and good accessibility of internal pores. According to IUPAC definitions, three groups of pores can be identified.

Macropores (above 50nm diameter)

Mesopores (2-50 nm diameter)

Micropores (Under 2 nm diameter)

Micropores generally contribute to a major part of the internal surface area. Macro and micropores can generally be regarded as the highways into the carbon particle, and are crucial for kinetics. The desirous pore structure of an activated carbon product is attained by combining the right raw material and suitable activation procedure.

1.8.1 Preparation of activated carbon

Most carbonaceous substances can be converted into activated carbon, the final properties of the carbon will depend significantly on the nature of the starting material. A large number of processes for making activated carbons have been developed over the past century. However, most processes consist of the pyrolysis of the starting material, followed by a stage of controlled oxidation or vice versa. The purpose of the oxidation stage is to activate the carbon.

(i) Pyrolysis

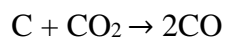
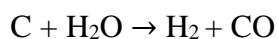
Pyrolysis step (or also called as Carbonization) involves heating the source materials to temperatures ranging between 600 to 900°C in the absence of air⁵¹. This process is to eliminate most of the non-carbon elements such as hydrogen, nitrogen, oxygen and sulphur as volatile gaseous products. Low molecular weight volatiles are first released, followed by light aromatics and finally the hydrogen gas, the resultant product produced being a fixed carbonaceous char. The residual carbon atoms are grouped into condensed sheets of aromatic ring with a cross-linked structure in a random manner. The mutual arrangement of these aromatic sheets is irregular and leaves free interstices between the sheets, which may be filled with the tarry materials. To remove these tarry materials, activation process is carried out. It also enlarges the diameters of the pores, created during the carbonization process with inclined porosity⁵².

(ii) Activation

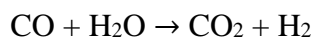
The basic characteristic of carbon is established during the pyrolysis, and the ensuing oxidation step must be designed to complement the pyrolysis step. During this step, the oxidising agent increasingly erodes the internal surfaces of the carbon, develops an extensive and fine network of pores in the carbon and brings about changes for those atoms lying on the surface to specific chemical forms leading to selective adsorption capabilities. This activation step is done by two methods either physical activation or chemical activation.

Physical activation

Physical activation or partial gasification is generally carried out at elevated temperatures between 750 and 1100° C with oxidants such as steam, carbon dioxide, air or mixture of these gases. Chlorine, sulphur vapours, sulphur dioxide, ammonia and a number of other substances having activation effects are rarely used. Gasification of the carbonized material with steam and carbon dioxide occurs by the following endothermic reactions:



The reaction of steam with carbon is accompanied by the water gas formation reaction, which is catalyzed by the carbon surface as,



Since the reaction of carbon with steam and with carbon dioxide is both endothermic, external heating is required to drive the reactions and maintain the reaction temperature. The activation process can be manipulated to produce products of desired characteristics. Activation temperature, steam and CO₂ flow rates control the pore development, which in turn affect pore size distributions and the level of activity of the activated carbon.

Chemical activation

Chemical activation is usually carried out by impregnating the raw or pre-carbonized material with an activating agent and pyrolyzed between 400 and 800 C in the absence of oxygen. The most commonly used activating agents are phosphoric acid, hydrochloric acid, sulphuric acid, alkalis namely KOH and NaOH, zinc chloride and alkaline metal compounds. Phosphoric acid and zinc chloride are used for the activation of ligno cellulosic materials. Phosphoric acid is the most preferred activating agent because of its low environmental impact when compared to zinc chloride. The resultant activated carbon is washed, dried till constant weight is obtained and ground to required size. Activated carbons produced by chemical activation generally exhibit a very open structure ideal for the adsorption of large molecules.

1.8.2 Combination of physical and chemical activation

A combination of physical and chemical activation can be used to prepare granular activated carbons with a very high surface area and porosity adequate for certain specific applications such as gasoline vapour control, gas storage, etc. Activated carbons of these types have been reported using ligno cellulosic precursors chemically activated with phosphoric acid and zinc chloride and later activated under a flow of carbon dioxide. Uniform, medium-size microporosity and surface areas above 3600 m²/g are obtained with this mixed procedure⁵⁰.

1.8.3 Advantages of chemical activation over physical activation

An important advantage of chemical activation is that the process normally takes place at a lower temperature and for a shorter time than those used in physical activation. In addition, very high surface area activated carbons can be obtained with the yields of carbon through chemical activation being usually higher than those in physical activation because the chemical agents used are substances with dehydrogenation properties that inhibit the formation of tar and reduce the production of other volatile products. The activation of wood using H_3PO_4 could be carried out at temperature less than 500°C ⁵⁰, while ZnCl_2 activation was carried at between 600°C to 709°C . Consequently, the modification of chemical/precursor ratio permits the adjustment of the porosity in the final activated carbon. However, the most important disadvantage of chemical activation is the incorporation of impurities, coming from the activating agent, which may affect the chemical properties of the activated carbon. Another disadvantage is the investment needed for the unit in recovery of chemicals used for impregnation⁵³.

1.9 Review of Literature

Activated Carbon

Activated carbon is the most extensively employed as adsorbent for dye removal due to its salient characteristics: extended surface area, micro-pore structure, high adsorption capacity and degrees of surface reactivity. However, commercially available activated carbon is very expensive and pose high regeneration problem while exhausted. This has led to the search for alternate economically viable substances. Researchers have regularly attempted in developing more suitable, efficient and feasible materials.

Agricultural based materials being discarded as litter have little or no economic values. The utilization of these materials is of great significance⁵⁴. Many investigators have reported about the utility of materials like pearl millet husk, date pit, saw dust, buffing dust of leather industry, coir pith, crude oil residue, tropical grass, olive stone, almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of dyes and heavy metals from aqueous solutions at different operating conditions.

Tree barks are found to be an effective adsorbent owing to their high tannin contents. They are abundantly available in semi-arid areas. Satish Patil⁵⁵ et al., checked the utility of Teak tree bark powder for the removal of methylene blue, where the dye uptake registered maximum at alkaline pH.

Jia Li⁵⁶ et al., have formulated carbon fibres generated from silkworm cocoon waste through a combination of $(\text{NH}_4)_2\text{HPO}_4$ -pretreatment and KOH activation for the removal of congo red dye. The prepared sorbent exhibited high BET surface area, the sorption system being fitted well into the pseudo-second-order kinetic model.

A.Umar Isah⁵⁷ et al., explored coconut shell based activated carbon, where the equilibrium data of the system fitted well to Langmuir and Freundlich isotherm models along with best agreement for pseudo-second-order kinetic model.

NaOH pre-treated rice husks were carbonised using sulphuric acid and phosphoric acid by Yun Chen⁵⁸ et al., and employing in the removal of methylene blue, ensuring monolayer adsorption.

Mahogany sawdust carbon⁵⁹ evidenced with high surface area exhibited maximum uptake of direct dyes at pH 3.

Yuan Gao⁶⁰ et al., conceived crab shell-based activated carbon using various activating agents like KOH, NaOH, H_3PO_4 and $\text{H}_4\text{P}_2\text{O}_7$ and the results emphasized that AC-KOH possessed high BET surface area and large pore volume.

Activated carbon prepared by Mohammed Nabil Mahamad⁶¹ et al., from the pyrolysis (500°C , 1 hour) of pineapple waste biomass (leaves, stem, crown) impregnated with ZnCl_2 registered sufficient adsorption of methylene blue.

Removal of Direct N Blue-106 using activated carbon derived from orange peel⁶² exhibited a relevant adsorption capacity of the latter against optimized initial concentration.

Jagdish Singh⁶³ et al., evaluated the removal of malachite green from aqueous solutions using carbon generated from rice straw and reported that the system suits into first-order kinetics and the adsorption process to be a chemical one with spontaneity and exothermicity in nature.

Elephant Dung Activated Carbon (EDAC) prepared by Theivarasu C⁶⁴ et al., promoted, a noticeable removal of crystal violet (CV) under optimized conditions of 40 mg/L concentration, 300 minutes contact time, 100 mg dosage at pH 7.

The Reactive Yellow 84 dye sorption onto carbon derived from animal bone meal was verified by M. El Haddad⁶⁵ et al., where maximum uptake had occurred at pH 6.6 and an equilibrium attainment at an initial dye concentration of 40 mg/L.

Removal of Erichrome Black T from aqueous solutions by Mosambi peel modified activated carbon⁶⁶ revealed extended dye removal at experimentally specified doses. RL value was registered as 0.235 suggest favourable adsorption for the system.

Constant agitation of basic red 29 dye molecules by *Euphorbia antiquorum* activated carbon⁶⁷ attained equilibrium at 90 minutes of contact time. The kinetic data were illustrated by pseudo first-order, pseudo second-order, Elovich and intraparticle diffusion models.

Removal of Astrazon red dye from textile wastewaters using *Posidonia oceanic* activated carbon⁶⁸ recorded maximum adsorption capacity of the latter at room temperature itself.

Coir pith Activated carbon prepared and characterized for the adsorption of toxic heavy metals by Kadirvelu⁶⁹ et.al., imposed a positive gradation in the removal process with pH ranging from 2 to 6, followed by an equilibrium reach at pH 10.

Broad bean peel was used by Hameed and El-Khaiary⁷⁰ after suitable activation for removal of cationic dye whose adsorption capacity was notable with a declining sorption at increased initial methylene blue concentration.

Beech wood sawdust⁷¹ carbon was employed to study the comparative adsorption of reactive, direct and basic dyes from aqueous solutions. The percentage removal for the above systems was in the order of: Basic Blue 86 < Direct Brown 2 < Direct Brown under suitable batch conditions.

Sulphuric acid activated sunflower seed hull⁷² was efficient on Acid violet 17 where a record of 116.27 mg/g sorption capacity was observed.

Methylene blue removal from aqueous solutions using Pumpkin seed hull activated carbon⁷³ recorded higher percentage at alkaline pH.

Adsorption of aqueous Cr(III) by groundnut shell activated carbon⁷⁴ revealed that the system exhibited a linear plots for Langmuir and Freundlich isotherms following first order kinetics.

Performance of rice husk activated carbon to effectively trap Pb(II) and Cu(II) was evaluated by K.K. Wong⁷⁵ et.al., who reported the potentiality of the material to be greater in trapping copper than lead from aqueous media.

Investigation on adsorption of Ni(II) and Cd(II) ions using rice straw⁷⁶ suggested that the ionic strength of the solutions highly influences the sorption rate.

Bengal gram husk⁷⁷ (*Cicer arietinum*) proved to be efficient in sequestering 99% of Cr(VI) ion under highly acidic conditions (pH 2).

Activated Carbon- Magnetic Nanocomposites

In recent years, metal nano particles have engrossed much research attention due to their unique electric, catalytic, and optical properties originating from the quantum-scale dimensions⁷⁸. Metal NPs have been of increasing interest in applications as biological and chemical nanosensors.

Magnetism is a unique physical property that can be exploited in reclamation of water contaminated by pollutants⁷⁹. In combination with other processes, these magnetic nanocomposites have a rapid adsorption rate and efficiency towards pollutants. These materials are readily recoverable and reusable by separating the adsorbed contaminants through a simple magnetic process, thereby facilitating an efficient purification of water/wastewaters.

Activated carbon/ iron oxide magnetic composites were prepared and characterized by Luiz C.A. Oliveira⁸⁰ et al., for the removal of contaminants in water. N₂ adsorption measurements showed that the presence of iron oxides did not significantly affect the surface area or the pore structure of the activated carbon.

The synthesized Activated carbon/CoFe₂O₄ composite⁸¹ was used for the removal of malachite green (MG) dye from aqueous solution. The composite exhibited a clearly

hysteretic behaviour under applied magnetic field, which promoting magnetic separation. The experimental data fitted well with the Langmuir model with a monolayer adsorption capacity of 89.29 mg g^{-1} .

V.Ranjith kumar⁸² et al., explored activated carbon- Fe_3O_4 composites for the trapping of acid yellow dye. Kinetics data of adsorption of dyes indicate that the adsorption follows pseudo-second order kinetic model.

Na Yang⁸³ et al., studied the sorption dynamics of Magnetic Fe_3O_4 -activated carbon nanocomposite derived from rice husk based activated carbon with large pore diameter and high surface area for the removal of methylene blue.

A comparison between the adsorption capacities of different MFe_2O_4 ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) ferrite nanocrystals implied that distribution of MFe_2O_4 is the most important factor to decide their adsorption capacity⁸⁴.

Acid yellow 17 dye was treated with activated carbon/ Fe_2O_3 nanocomposite⁸⁵ where the size of iron oxide nanoparticles was in the range of 5–17 nm. The adsorption data were found to fit well with Langmuir isotherm following pseudo-second order kinetic model.

Kamila Banu N⁸⁵ et al., prepared tri metal oxide composite (Zn-Mn-Fe-Nano Oxide metal) for the removal of Reactive yellow 15. Maximum adsorption capacity of prepared composite was reported as 22.73 mg g^{-1} .

Jing Hu⁸⁶ et al., synthesized various magnetic nanoparticles for the removal of Cr(VI) from synthetic electroplating wastewater and registered that the efficiency to follow the order: $\text{MnFe}_2\text{O}_4 > \text{MgFe}_2\text{O}_4 > \text{Zn Fe}_2\text{O}_4 > \text{Cu Fe}_2\text{O}_4 > \text{Ni Fe}_2\text{O}_4 > \text{Co Fe}_2\text{O}_4$.

Puja Rai⁸⁷ et al., investigated the effect of various parameters such as initial dye concentration, contact time, pH and temperature in the sorption of crystal violet by SnFe_2O_4 /activated carbon magnetic nanocomposite and observed the capacity to be as 158.73 mg/g at 323 K.

Activated Carbon- Photocatalytic Nanocomposites

A photocatalytic process is featured by the high reactive nature of hydroxyl radicals to complete elimination of pollutants. Despite its known potential, problems still

arise such as the limitations of the widely use catalyst TiO_2 and the cost prohibitive reaction medium associated with powder catalysts. The limitations of TiO_2 in photo catalysis include low surface area and adsorption capacity. Impregnation of AC with TiO_2 is one option to address the problem. The synergistic effect of combined TiO_2 and AC is known to enhance the efficiency of the catalyst for pollutant degradation⁸⁸.

Photocatalytic performance of TiO_2 films for degradation of Azorubine dye had been evaluated and compared by Jatinder Kumar⁸⁹ et al. The activated carbon had also been immobilized along with TiO_2 to examine the dual effect of photo degradation and adsorption in the removal of Azorubine which revealed better dye degradation capabilities.

Photocatalytic colour removal of Turquoise blue dye (TBD) using immobilized Titania-activated carbon (AC/ TiO_2) was studied by Jurex Gallo⁹⁰ et al. The results indicated that the initial dye concentration parameter was highly influential under the colour removal capability while the recirculating flow rate to be the least significant factor.

K.M.Joshi⁹¹ et.al compared the sorption ability of TiO_2 and ZnO photocatalysts against commercially activated carbon in the removal Acid blue 29 and Congo red dyes. From the experimental results, it was obvious that the removal efficiency increased with decreasing dye concentration and increasing dose of the respective sorbents.

Jolly Pal and Manas Kanti Deb⁹² investigated the removal of congo red (CR) dye using activated carbon coated with silver (AgNPs) and gold nanoparticles (AuNPs). Equilibrium data exhibited excellent sorption of congo red at room temperature.