Chapter 1

Introduction

1.1 Introduction

Waste water from different chemical processes such as petrochemical units, dye and dye intermediate manufacturing industries and textile units contain toxic organic compounds such as nitrophenols, dyes, pigments, insecticides, polychlorinated biphenyls, chlorinated solvents, etc. Their discharge into the environment pollutes the water as these compounds are hazardous to microorganisms as well as have carcinogenic effects on human beings. Dyes have become one of the main sources of severe water pollution as a result of the rapid development ofthe textile industries. Inefficacy in delivering dyes onto textile fibers can cause the residual dye which contains harmful substances, being released along with the effluents. The textile waste water effluent contains high amounts of agents that can cause damage to the environment and human health including suspended and dissolved solids, biological oxygen demand (BOD), chemical oxygen demand (COD), chemicals, odour and colour causing a major concern on the human health as well as marine lives. The characteristics of textile effluents vary and depend on the type of textile manufactured and the chemicals used. The textile industry uses massive amount of water during the "wet processes" (Table 1), such as, dyeing, printing and finishing operations [1, 2]. The possible pollutants and the nature of effluents released from each step of the wet process are listed in Table 2.

Table 1 Total water consumed during wet process [3]

Process	Water Utilised (%)
Bleaching	38
Dyeing	16
Printing	8
Boiler	14
Other uses	24

Table 2 Sources of water pollution at various stages of textile processing [4]

Process	**Possible Pollutants**	**Nature of Effluent**
Desizing	Starch, glucose, PVA (polyvinyl alcoholic resins), fats and waxes	Very small volume, high BOD (30-50% of total), PVA
Kiering	Caustic soda, waxes, soda ash, sodium silicate and fragments of cloth.	Very small volume, strongly alkaline, dark colour, high BOD values (30% of total)
Bleaching	Hypochlorite, chlorine, caustic soda, hydrogen peroxide, acids	Small volume, strongly alkaline, low BOD (5% of total)
Mercerizing	Caustic soda	Small volume, strongly alkaline, low BOD (less than 1% of total)
Dyeing	Dye stuff, mordant and reducing agents like sulphides, acetic acids and soap.	Large volume, strongly coloured, fairly high BOD (6% of total)
Printing	Dye, starch, gum oil, china clay, mordants, acids and metallic salts	Very small volume, oily appearances, fairly high BOD.
Finishing	Traces of starch, tallow, salts, special finishes, etc.	Very small volume, less alkaline, low BOD

BOD - Biological Oxygen Demand; COD - Chemical Oxygen Demand

Hydrogen peroxide is usually used for bleaching of cotton fabrics. The bleaching chemicals have to be removed, generally either through rinsing or by the addition of a reducing agent to neutralise the bleach. In the both cases, large volume of wastewater is generated.

The dyes used in various industries can be mainly classified intwo ways: (a) On the basis of the nature of chromophore group and (b) On the basis of its mode of application.

1.2 Classification of dyes On the basis of their applications

Dyes can be classified as follows [5]

(I) Reactive Dyes

These are dyes with reactive groups that readily form covalent bonds with OH, NH_2^-, or –SHgroups in fibers and have different chromophores. Monoazo dyes have only one N-N double bond, while diazo and triazo dyes contain two and three N-N double bonds, respectively. The azo groups are generally connected to benzene and naphthalene rings, but can also be attached to aromatic heterocycles or enolizable aliphatic groups [6]. These side groups are necessary for imparting the color to the dye, with many different shades and intensities being possible [6] Fiber-reactive azo dyes exhibit high wet- fastness, due to their ability to covalently bond to substrates. The bridging group serves to combine the chromogen with the reactive group of the dye molecule. The bridging group must be stable, soluble in water, and exhibit a certain degree of flexibility. Amino and alkylamino groups are generally used for this purpose. The reactive group serves to bond the dye molecule to a substrate via nucleophilic substitution or addition. Mono-, di-, and trichlorotriazinyl are all examples of reactive functional groups. Reactive dyes are thus extensively used in the textile industry because of their availabity in a wide spectrum of color, ease of application and minimal energy consumption. However, the degree of fixation is reduced due to the hydrolysis of the reactive groups. Thus, it is estimated that 10-50% of the applied dye will not react with fabric and would remain hydrolyzed in the water phase which is undesirable. The problem of colored effluents is therefore often identified mainly with use of reactive dyes.

(II) Acid Dyes

Acid dyes are anionic compounds which are mainly used for dyeing fabrics like wool, polyamide, silk and modified acryl which contain basic groups. Application is generally made under acidic conditions which cause protonation of basic groups. The dyeing process is reversible and dyes aregenerally removed from fabrics during washing. Most of the acid dyes contain azo, anthraquinone or triarylmethane type of chromophore groups.

(III) Direct Dyes

They are large, flat linear molecules which bind to the fiber through Van der Waals forces. They have high affinity for cellulose fibers. NaClor Glauber’s salt is often used with direct dye during dyeing, because the presence of excess sodium ions favors establishment of equilibrium with minimal amount of dye. The dyeing process with direct dyes is reversible similar to acid dyes and exhibit poor wash fastness. A typical exampleof direct dye is Congo red.

(IV) Basic Dyes

They are cationic compounds and are used for dyeing synthetic fibers containing acidic groups, like modified polyacryl. They generally give intense and brilliant shades but have poor light fastness. They are used for dyeing silk and wool directly. Methyl Violet, Crystal Violet, Rhodamine, Magenta etc. fall into the category of basic dyes.

(V) Mordant Dyes

Mordants are those compounds which when applied attach to the fiber and then combine with the dye to form an insoluble complex. Though the use of mordant dyes is reduced, they are still used for dyeing wool, leather, silk, paper and modified cellulose fibers. However, these dyes require a pre treatment of the fiber with mordants (usually metal salts such as chromium and iron salts) as by themselves have poor affinity for the fibre. Most mordant dyes are azo, oxazine or triarylmethane compounds.

(VI) Disperse Dyes

They are less soluble dyes and their application to the fiber requires swelling of the fiber, either by high temperature (>120˚C) or with the help of chemical softener, so that the dye can diffuse inside. They are used to color synthetic fibers like celluloseacetate, polyester, polyamide, acryl, etc. They are usually small azo or nitro-compounds (yellow to red), anthraquinones (blue and green) or metal complex azocompounds (wide range of colors).

(VII) Vat Dyes

These dyes are generally applied in their more soluble reduced forms which are obtained by treating the compound 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 and contain indigo and anthraquinone type of chromophoric groups.

(VIII) Sulfur Dyes

They are heterocyclic S-ring containing polymeric aromatic compounds. Similar to vat dyes dyeing withsulfur dyes involve reduction and oxidation process. The dyes are reduced with sodium sulfide to solubilise them and exhibit affinity for cellulose upon exposure to air they get oxidized to the original form of insoluble dye inside the fiber. They are mainly used for dyeing cellulose fibers.

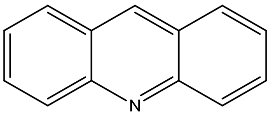
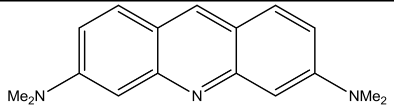
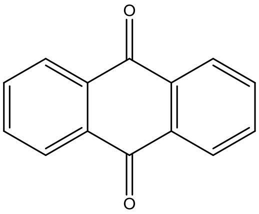
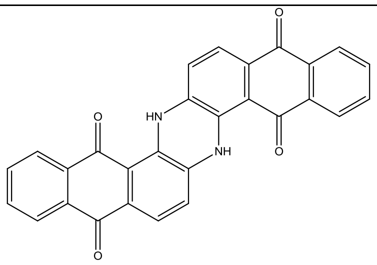
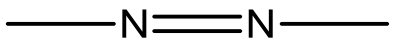
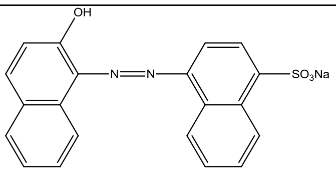
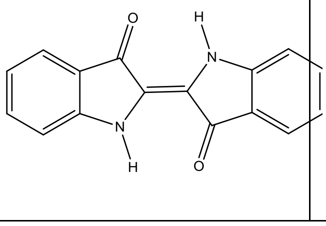
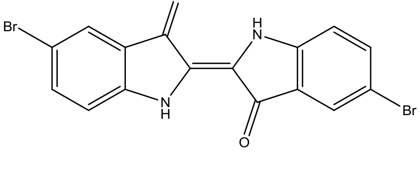
(IX) Solvent Dyes

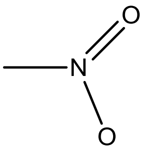
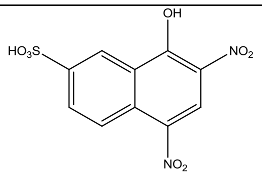
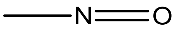
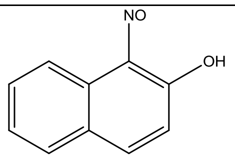
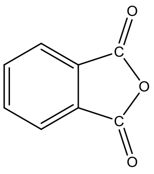
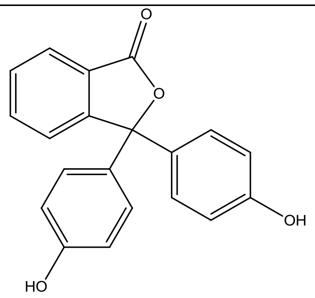
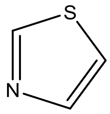
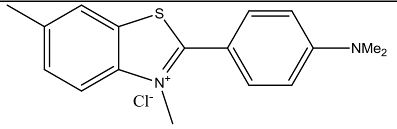
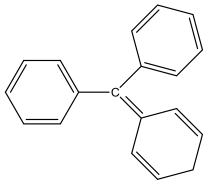
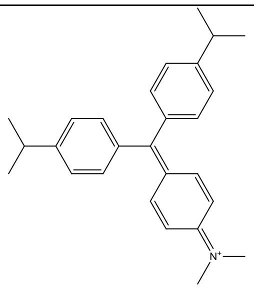
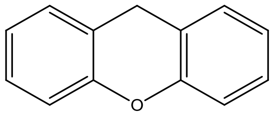
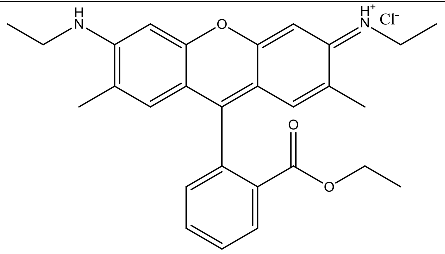
Solvent dyes (lysochromes) are non ionic dyes having diazo groups that are used for dyeing substrates inwhich they can dissolve, e.g., plastics, varnish, ink, waxes and fats and have very less application in textile industry.

1.3 Classification of dyes on the basis of Chromophore group

On the basis of their **chromophore groups** dyes can be classified as azo, anthraquinone, nitro, nitroso, xanthenes, acridine, indigoid, thiazole etc. as shown in Table 3.

Table 3 Classification of Dyes

Class	Chromophore	Example
Acridine dyes		 Acridine Orange
Anthraquinone dyes		 Indanthrone
Azo dyes		 Acid Red 88
Indigoid dyes		 6,6'-Dibromoindigo

Nitro dyes		 Naphthol Yellow
Nitroso dyes		 1-Nitroso-2-naphthol
Phthalein dyes		 Phenolphthalein
Thiazole dyes		 Thioflavin
Triphenyl methane dyes		 Crystal Violet
Xanthene dyes		 Rhodamine 6G

The pollution due to dyes is characterized by effluents containing biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, bad smell, toxicity and especially color [7]. Dyes can cause acute and/or chronic toxic effects as well as carcinogenic effects on exposed organisms depending on the exposure time and dye concentration; cause color to aquatic bodies at concentrations as low as 0.005 ppm [7-12] absorb and reflect sunlight entering water, hindering photosynthesis in aquatic plants and also affect other aquatic life [13] Among the aquatic life the growth of bacteria is also affected, limiting them to levels insufficient to biologically degrade impurities in the water resulting in high BOD. The reactive dyes which are mostly azo compounds, the largest class of dyes used in textile processing industries are designed to be chemically and photolytically stable; they exhibit a high resistance to microbialdegradation and are highly persistent in natural environment. Because they are highly colored, azo dyes are readily visible in effluent water. These compounds are also of concern because some of the dyes, dye precursors or their biotransformation products, such as aromatic amines, have been shown to be carcinogenic [14]. Reactive Red 141 (RR-141) belongs to the class of azo dyes and is known for its toxicity [15].

Another class of dyes that deserves attention is the group of reactive dyes that have phthalocyanine chromophore (complexes containingcopper, nickel or other metals). An example of a dye in this class is Reactive Blue 21 (RB-21), which contains copper phthalocyaninechromophore and vinyl-sulfonic acid [16]. The dyes in this class are potentially harmful and carcinogenic [17].

The Triphenylmethane and Xanthene group of dyes are the most used versatile class of dyes [18]. For instance, hazardous xanthene dye, Rhodamine 6G (Rh6G), is widely used as a dye for silk, cotton, wool, bast fibers, paper, leather and plastics [19]. The carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity of this dye to humans and animals have been experimentally proven [20].

In addition to dyes, nitroaromatic compounds are the largest and another important group of industrial chemicals in use today. They are xenobiotics used in the manufacturing of dyes, plasticizers, pesticides, fungicides and explosives. These anthropogenic compounds are highlyhazardous on release in the environment. Particularly, 4-nitrophenol (4-NP) has been listed as ‘‘priority pollutant’’ by US Environmental Protection Agency (EPA) because of its higher solubility and stability in water and resistance to degradation [21]. The nitro group (–NO_2) present in 4-NP is relatively more stable in biological systems and can cause several blood disorders, hormonal imbalance, central nervous system poisoning, kidney and liver damage and eye irritation and is known as a persistent pollutant and endocrine disrupting compound.

It is evident therefore, that removal of dyes and nitrophenols from aqueous effluents is of significant environmental importance. Various physicochemical and biological techniques can be employed to remove these compounds from wastewaters. Figure 1 shows the most common techniques used to remove dyes from waste water.

1.4 Dye Removal techniques

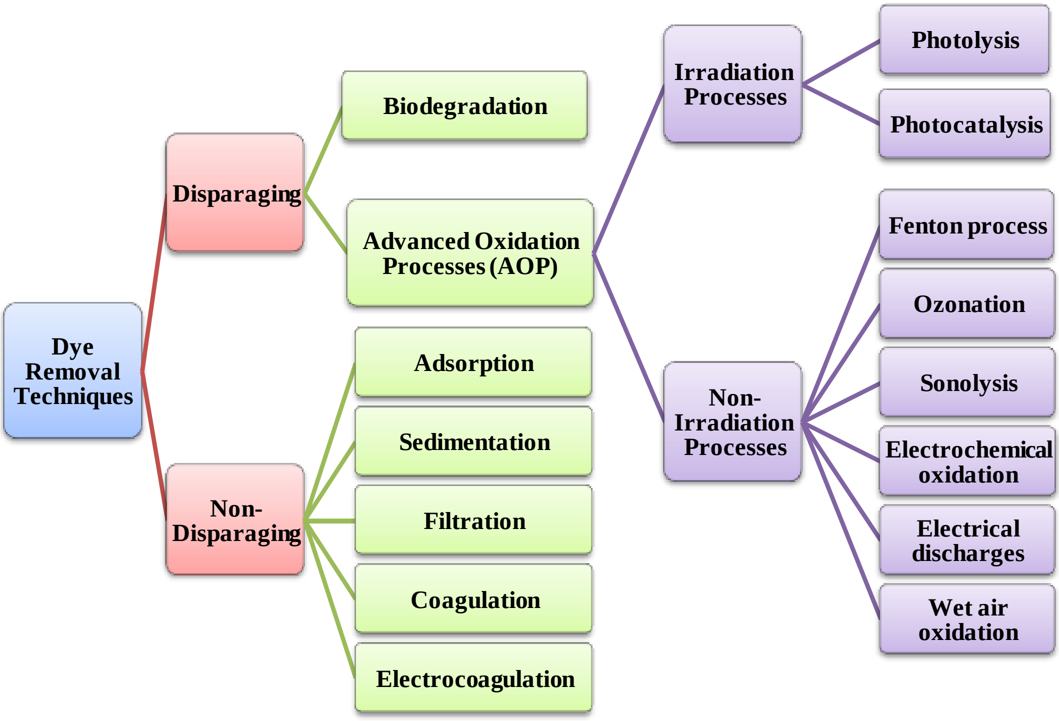


Figure 1.1 Dye removal techniques

Conventional methods of removing dyes from wastewater such as coagulation and flocculation [22], reverse osmosis [23], activated sludge [24], bacterial action [25], chemical oxidation [26], ozonation [27] and physical methods like membrane filtration [28], ion exchange [29] and electrochemical techniques [30] are either expensive or ineffective [31]. The methods which are widely used are as follows:

1.4.1 Biodegradation

In this technique, as the name indicates, removal occurs by means of living microorganisms (e.g., bacteriaor fungi) [32-42]. The first step involves anaerobic treatment that cleaves the azo linkages of the dyes and removes the coloration of the wastewater. Hazardous aromatic amines are formed during this step, which in the second step are mineralized completely by aerobic treatment [43]. It has been demonstrated that immobilized microbial systems decrease the generation of biological sludge [44]. Since these techniques involve living organisms, the process is affected by drastic conditions (e.g., pH and temperature). Futhermore, since these dyes are toxic to the organisms used in the process these techniques cannot be applied to most textile wastewaters [45]. However, the main advantage is that dyes can be removed from large volumes of waste water at alow cost using this technique [46].

1.4.2 Adsorption

In comparision with other techniques adsorption is superior in simplicity of design, being economic, and ease of operation and in being insensitive to toxic substances. Adsorption is one of the most effective physical processes for colour removal and is effective with all types of dyes [8, 9, and 47]. The dyes can be removed using different kinds of adsorbents. Some widely used adsorbents are:

1.4.2.1 Activated Carbon

Activated carbon (powdered or granular) is the most widely used adsorbent because it has excellent adsorption potential for both organic and inorganic compounds. However commercially available activated carbon is very expensive [48]. Nowadays a number of low cost materials are used as precursors to economically prepare activated carbon. For instance agricultural wastes [49], corn cob [50] and plum kernels [51] have been used as precursors of carbon for the removal of acid blue 25. The adsorption of acid violet 1, acid blue 264 and acid yellow 36 has been studied on carbon from cassavashell [52], pine wood [53] and saw dust [54] as well as rice husk [56], respectively. Cherry stones [57] have also been used as precursors for the preparation of activated carbon [55]. Finger citron-based activated carbons were used for the removal of MB and MO [58].

1.4.2.2 Carbon Nano Tubes

Due to their large specific surface area, small pore size, hollow and layered structures, carbon nanotubes have been proven to possess a great potential as adsorbents for removing many kinds of organic and inorganic contaminants from aqueous solution [59]. Wu studied adsorption equilibrium, kinetics and thermodynamics of a reactive dye, Procion Red MX-5B, on carbon nanotubes [60]. Kuo et al. investigatedthe adsorption of two direct dyes, C.I. Direct Yellow 86 and

C.I. Direct Red 224, on carbon nanotubes and evaluated the effects of various parameters like pH, temperature etc affecting the adsorption of the direct dyes by CNTs [61]. Gong et al. reported removal of cationic dyes, methylene blue, neutral red and brilliant cresylblue, from aqueous solution by a magnetic multiwalled carbon nanotube nanocomposite. Colloidal carbon nanospheres (CNS) with rich surface functional groups of −OH and $-COO^-$ were prepared from glucose solution via hydrothermal reaction and activated by NaOH solution and were used as adsorbents toward basic dyes [62].

1.4.2.3 Graphene

Graphene, a two-dimensional one atom thick nanomaterial consisting of sp^2-hybridized carbon, has attracted great interest among scientists due to its unique properties. Graphene exhibits novel electronic property as a zero-band gap semiconductor and is highly electronically conductive for storing and transporting electrons. Liu et al. 2012 reported that graphene prepared by a modified Hummers' method (using $KMnO_4$, $NaNO_3$, H_2SO_4) had the maximum adsorption capacity for methylene blue. Zhang et al. 2013 prepared polyethersulfone enwrapped GO, which was porous inside and dense outside, and demonstrated its selective adsorbability towards cationic dyes such as methylene blue and methyl violet. Yongfang Yang et.al had improved the adsorption property of Methylene blue by grafting Polyacrylamide chains with reduced Graphene oxide.

Graphene can be functionalized with polymers containing heteroatoms to increase the adsorption capacity of graphene. 3D graphene sponges or foams have attracted extensive attention due to the high porosity for the practical application of being a high-efficient adsorbent. For example, Sun et al. 2013, made ultra-light weight and multifunctional carbon aerogels by freeze-drying aqueous solution of CNTs and giant grapheme oxide sheets. It exhibited super-high adsorption capacity and ultra-fast adsorption rate for oil and organic solvents [63-64].

1.4.2.4 Low cost Adsorbents:

I) Non carbonized agro waste

Cellulosic and lignocellulosic biomasses have attracted increasing worldwide interest as abundant, inexpensive and environmentally benign biopolymers and researchers have attempted to expand their domains of application as a bio-filter for remediation of water, contaminated with different hazardous pollutants due to the possibility of their regeneration and reusability [65]. Recently some non-carbonized low cost adsorbents such as: avocado kernel [66], banana peel [67], coconut shell [65], orange peel [66], peanut hulls [67-68]. Shells of bittim [69], sugar cane bagasse [70] and wastes of maize [71-73] have been studied for the adsorption of acid dyes.Wheat shell [74] and canola hull [75-76]; materials such as egg shell, peanut hull and microorganisms have been used as adsorbents for the removalof reactive dyes from effluents [77-81]. Despite possessing various advantages, like renewability, reusability and low-cost, the non-conventional cellulosic/lignocellulosic bioadsorbents in their native form are not comparable in their adsorption capacity towards varius pollutants to commercial adsorbents (e.g., activated carbon or zeolite) [82].

II) Modified biosorbents

With the aim of enhancing the adsorption potential, the researchers chemically modified the original biomaterials, using diverse solvents under different synthetic conditions, by introducing new functional groups, such as, esters [83-84] amine [85], amino-terminated hydrocarbons [65], triethylenetetramine schiff bases [86] anhydride [87-88] aspartic acid [89], poly(methacrylic acid) [90] thiol [91] phosphates, oxides [92] etc. In another study [93], it was reported that untreated jute fiber (JF) possesses a significant potential toward dye absorption. The JF was chemically modified with polyphenolic tannin in aqueous medium via epoxy-activation under mild condition and applied as a potential adsorbent for the removal of Congo red.

1.4.2.5 Biopolymers

Various approaches have been investigated for the development of cheaper and more effective adsorbents. Amongst these, natural polysaccharides, biopolymers are of particular interest. These materials have proved to be better alternatives compared to their synthetic counterparts because of their structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards aromatic compounds, metals and other contaminants that cause water pollution. Some of them are Chitin, Chitosan, Alginates, Guargum, etc [94-95].

Amongst all the biopolymers, **chitosan** has excellent adsorption properties for the anionicdyes, due to the presence of protonated amino groups which interact with dyes insolution by ion exchange, at an appropriate pH. The high content of amino groups also facilitates various chemical modifications in the polymer, for the purpose of improving its adsorbent properties and adsorption capacity. Literature is abundant on the usage of chitosan for adsorption of dyes [95a]. Young et.al, Courtie

Mahamadi, and Epias Mawere had used alginates for adsorption of dyes. Niyaz Mohammad Mahmoodi had used magnetic alginate composite for adsorption of basic blue and red dyes [96-110].

1.4.2.6 Layered materials

Inorganic layered materials possess confined inter layer spaces in nanometer level and lateral size in micrometer level, high surface area, and high accessibility thus making them ideal candidates as adsorbents. For instance, clay, hydrotalcites, etc.

1.4.2.6.1 Clay

Clay has emerged as potential natural adsorbents due to their abundant reserve, low cost, high chemical and mechanical stabilities as well as high adsorptive properties. The applications of clay-based adsorbents for the removal of dye shave received increasing attention in the last decade [111-114]. Clay minerals represent a cheap and environmentally safe source of raw material for the preparation of low-cost adsorbents that may be useful in environmental remediation [114a].

1.4.2.6.2 Layered Double Hydroxides

Layered Double Hydroxides (LDHs), also known as hydrotalcite like compounds or anionic clay, have attracted considerable attention in recent years due to the presence of large interlayer spaces, positively charged layers and exchangeable anionsin the interlayers [115]. The chemical composition of LDHs can be expressed bythe general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}\ (OH)_2]_x{+}[Ax/n^{-}]_x{\cdot}mH_2O.]$ [116]. The divalent cations M^{2+} (Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc.) are partially substituted by trivalent ones M^{3+} (Al^{3+}, Fe^{3+}, Co^{3+}, Mn^{3+}, Ni^{3+}, Cr^{3+}, etc.), for generation of a positively charged layer [116, 117]. As a consequence, anions can be intercalated into the interlayer space of the LDHs to maintain charge neutrality [116]. Nowadays, LDHs are the focus of research for removing dyes from aqueous solutions. Ahmed and Gasser [117] synthesized an Mg–Fe-LDH as the adsorbent of Congo red. They found that Mg–Fe-LDH was particularly efficient for removing Congo red. $NiFeCO_3$ hydrotalcites were synthesized by Saiah et al [118]. They concluded that Ni-Fe LDH can be used effectively for removing Evans blue from aqueous solutions. Extremera et al [119] found that calcined Mg–Al LDHs can be used effectively for the removal of acid orange (AO10) from aqueous solutions. Auxilio et al. [120] synthesized Mg-Al LDH and only used it to adsorb Acid Blue 9 efficiently. R Shan et al investigated the feasibility of using Mg-Al LDH as adsorbent for red dyes (RR, CR and AR1). Gupta et al constructed a hydro phobic environment in the interlayer space of the hydrotalcite by its modification with anionic surfactants (dodecyl sulfate and dodecyl benzene sulfonate) into which lipophilic β-carotene and annatto dye were successfully incorporated and the incorporated dyes exhibited improved photo stability under visible irradiation [121].

1.4.2.6.3 Zeolites

Zeolites are crystalline, microporous, hydrated alumino silicates that are built from an infinitely extending three-dimensional network of $[SiO_4]^{4-}$ and $[AlO_4]^{4-}$ tetra hedral linked to each other by the sharing of oxygen atom. The general formulae for Zeolites is $M_{x/n}[(AlO_{2x}(SiO_2)_y]\bullet wH_2O$, where M is an alkali or alkaline earth cation, n is the valence of the cation, w is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and the ratio y/x usually has values of 1 to 5, though for the silica zeolite, y/x can range from 10 to 100. Wang et al had discussed the role of physical and chemical regeneration of zeolitic adsorbents for dye removal in wastewater treatment [122].

1.4.2.6.4 Zirconium phosphate

Zirconium phosphate is a layered inorganic ion exchanger of the class of tetravalent metal acid (TMA) salts. It has been recently demonstrated as an excellent adsorbent for heavy metals due to itshigh selectivity, thermal stability and absolute insolubility inwater [123]. In recent years, layered zirconium phosphate has received considerable attention as a multi-functional material [124-125]. The stable nature and strong resistance of acid and alkali broaden its application scope [126]. Special organic groups can be inserted or grafted through ionic bonds, van der Waals force and hydrogen bond, which allows modifying interlayer distances, introduces selectivity, adsorption capacity and reactivity [127-128].

1.4.2.7 Nanoparticles

Nanoparticles have proven themselves as excellent adsorbents due to their unique features such as small size, catalytic potential, high reactivity, large surface area, ease of separation [128a] and large number of active sites for interaction with different contaminants. The commonly used nanoparticles for water treatment are made of alumina, anatase, cadmium sulphide, cobalt ferrite, copper oxide, gold, maghemite, iron, iron oxide, iron hydroxide, nickel oxide, silica, stannous oxide, titanium oxide, titanium oxide, zinc sulfide, zinc oxide, and zirconia. Belessi et al synthesized TiO_2 nanoparticles and used for the removal of reactive red 195 azo dye

[129]. Moussavi and Mahmoudi synthesized nanoparticles of MgO (38-44) nm (with surface area 153.7 m^2 /g) and used for the removal of azo and anthraquinone reactive dyes from water [130]. Yan et al and Kiani et al had used hexadecyl functionalized magnetic silica and halloysite nanotubesfor the remval of Rh6G and Malchite green respectively [131, 132] Anujit et.al had investigated adsorption of Methylene blue and methyl orange using Nickel nanostructures [133]. Bedabrata Saha et al had investigated the adsorption property of iron oxide nanoparticles [134].

1.4.2.8 Metal Organic Frame works

Recently metal–organic frameworks (MOFs) have drawn growing interest amongst the scientific community owing to their high porosity and tunability. These inorganic–organic hybrid compounds have been receiving attention for their diverse structures and many potential applications [134a]. Research studies say that MOFs of chromium have greater adsorption capacity for dyes compared to activated carbon. The metal–organic framework (MOF) compounds exhibit many properties such as gas adsorption, and photocatalysis. Mahata et al [135] had investigated decomposition of organic dyes using bipyridine (bpy) bridged MOF. There are a few drawbacks with MOFs; i.e., selected MOFs exhibit poor stability in humid conditions and also weak dispersive forces owing to the large amount of void spaces. Furthermore, the open frame works of MOFs are not able to provide strong, non specific adsorption forces to retain small molecules at ambientconditions. These drawbacks have been overcome by combining MOF materials with other substrates. Ling Li et al [136] had investigated the MOF/graphite oxide hybrid (MOF: HKUST-1) material for the adsorption of methylene blue from aqueous solution. Tian Wen, et al [137] had investigated degradation of dyes using Copper(I) Coordination Polymer Materials as photo catalysts. Rumei Cheng et al [138] had investigated anionic dye adsorption onto Copper(II) Complex of Dithiocarbamate-Modified Starch. A comparison of adsorption capacities with various adsorbents onto dyes have been summarized in Table 3.

Table 3 Comparison of adsorbents used for adsorption of various dyes

No.	**Adsorbent**	**Dye**	**Qmax mg/g**	**Reference**
1.	γ-Fe_2O_3/SiO_2/chitosan composite	Methyl orange	34.29	[139]
2.	Magnetic ferrite nanoparticle–alginatecomposite	Basic blue 9, Basic blue 41,Basic red 18,	106,25,56	[140]
3.	Magnetic Maghemite/Chitosan Nanocomposite	Methyl orange	28.94	[141]
4.	Chitosan/Montmorellonite	Congo red	53.42	[142]
5.	Chitosan/ Polyurethane	Acid violet 48	30	[143]
6.	Chitosan/ Activated clay	Methylene blue	330	[144]
7.	Chitosan /Activated clay	Reactive dye RR222	1912	
8.	Chitosan/bentonite	Tartrazine	294.1	[145]
9.	Chitosan/bentonite	Malachite green	435	
10.	Chitosan/maghemite composite	Methyl Orange	779	[146]
11.	chitosan/graphene oxide	Methylene blue	180.83	[147]
12.	Carbon/Cobalt Ferrite/Alginate Composite Beads	Methylene blue	0.105 (mol.Kg^{-1})	[148]
13.	TiO_2	red 195 azo	87	[129]
14.	Fe_3O_4	orange G and acid green	1883 and1471 mg/g for orange G and acid green dyes	[149]
15.	cross-linked chitosan	Acidicmetanilyellow and reactive blue 15	1334 mg/g for metanil yellow and 722 mg/g for dye reactive	[150]

			blue 15	
16.	Chitosan	eosin Y	3.333 mg/g	[151]
17.	Chitosan	Acid green 25	645.1	[152]
18.	Chitosan	Acid orange 10	922.9	
19.	Chitosan	Acid orange 12	973.3	
20.	Chitosan	Acid red 18	693.2	
21.	Chitosan	Acid red 73	728.2	
22.	ZrO2	methylene blue	0.5 mg/g	[153]
23.	Poly (N-Isopropylacrylamide) Microgels	Orange II	139.9 μmol/g	[154]
24.	Cellulose-Based Multicarboxyl Adsorbent	Malachite green	458.72	[155]
25.	Cellulose-Based Multicarboxyl Adsorbent	basic fuchsine	1375.52	
26.	chitosan/oil palm ash composite	Reactive blue 19	416.7	[108]
27.	Multiwall Carbon Nanotubes	Acid red 183	37.4	[156]
28.	Multiwall Carbon Nanotubes	Reactive blue 4	53	
29.	Dithiol-Protected Ag Quantum Cluster	Rhodamine 6G	17.2	[157]
30.	Dithiol-Protected Ag Quantum Cluster	Methylene blue	16.4	
31.	Dithiol-Protected Ag Quantum Cluster	Methyl orange	3.2	
32.	Dithiol-Protected Ag Quantum Cluster	Methyl red	0.2	
33.	Chitosan–clay composite	Methylene blue	142	[158]
34.	PVA/Chitosan foam	Malchite green	380.65	[159]

35.	Bentonite	Basic red 2	274	[160]
36.	Rattle-type Carbon−Alumina Core−Shell Spheres (CAL-2,CAL-5,CAL-10)	Orange -II	86,131,209	[161]
37.	Ferric chloride and organo zeolite modified with CTAB	Reactive blue 4,	13.22	[162]
38.	Ferric chloride and organo zeolite modified with CTAB	Reactive yellow	5.11	
39.	MOF/graphite oxide hybrid	Methylene blue	183.49	[136]

1.4.2.9 Composites

Integration of an adsorbent with other materials through methods such as grafting, impregnation, chelation and crosslinking has better adsorption properties than the individual components effects [144]. The synergy of adsorbent materials as composites have been tailored for gas, metals, pharmaceutical wastes, dyes and pesticide remediation. Composite adsorbents are known to possess enhanced selectivity, capacity for regeneration, increased surface area, mechanical strength and improved surface chemistry [163]. When the dispersed particles in the composites have at least one dimension in the nanometer range (nanofillers) they are termed nanocomposites.

1.4.2.10 Bionanocomposites

During the last few years, “bionanocomposite” has become a common term to designate those nanocomposites involving a naturally occurring polymer (biopolymer) in combination with an inorganic moiety, and showing at least one dimension on the nanometer scale [165, 166]. Because of their functional properties, bionanocomposites based on layered inorganic materials mentioned above are of singular importance, as described in a review [166]. Since the advent of nanocomposites, materials scientists are making huge efforts in this direction because of the excellent features of these nanohybrids as structural or functional materials, with interesting applications as components in, amongst others, heterogeneous catalysts and optical, magnetic, and electrochemical devices [167-172].

Bionanocomposites show improved mechanical properties, higher thermal stability and gas-barrier properties as shown by synthetic polymer composites as well as the remarkable advantage of exhibiting biocompatibility, biodegradability and in some cases, functional properties provided by either the biological or inorganic moieties. Living organisms are known to produce natural nanocomposites that show an amazing hierarchical arrangement of their organicand inorganic components from the nanoscale to the macroscopic scale. Nacre in pearls and shells [173, 174] and enamel and dentine in teeth [174] are well known examples of bionanocomposites found in nature. Mann's group has reviewed how the understanding of biomineralization processes has helped researchers to develop new hybrid nanostructured materials [175-177].

New synthetic methods inspired by nature are also being explored. For instance, Deville et al. [178] had replicated the nacre structure by mimicking a process that takes place in nature, giving rise to ultra-lightweight materials of high strength by directional freezing of an aqueous hydroxyapatite (HAP) suspension forcing the arrangement of HAP into well-defined layers similar to the freezing of seawater inducing a layered structure of crystals of pure ice, forcing salts and microorganisms to concentrate in the space between the ice crystals. The result was a porous HAP scaffold with a multilayered structure that resembles nacre. Other inorganic solids, including layered and fibrous clay minerals, show similar arrangements when using freezing techniques. There are many natural biomacromolecules such as starch, cellulose (and its derivatives) and poly (lactic acid) (PLA) that can be used in the preparation of these green bionanocomposites [179-182].

Their combination with natural layered materials, such as clays, provides reinforced bioplastics that offer the advantages of nanocomposites as well as biocompatibility and biodegradability.

Biopolymers bearing functional groups or biomacromolecules showing highly specific catalytic properties, such as enzymes, have been involved in the development of bionanocomposites with the aim of preparing hybrid nanostructured materials with a desired functionality, usually applied for sensing or biosensing purposes. Recently, a wide number of charged polysaccharides have been combined with natural clays and synthetic layered double hydroxides (LDHs), resulting in tough bionanocomposites with ion-recognition ability, thereby opening a new field of application in electroanalysis [183-185].

However, when they were used to treat colored effluents, new secondary waste was generated, requiring potentially expensive post-treatment techniques [186].

1.4.3 Reduction Process

In this decade, nano/micro zero-valent iron (ZVI) particles have emerged as new materials that can be applied in environmental treatment. The nano/micro zero-valent iron (ZVI) particles with large surface area per unit mass have been found to be highly efficient reducing agents capable ofenvironmental remediation. The advantages of these materials are low-cost, low toxicity, small footprint and ease of availability [187]. The decolorization of dyes by ZVI is of importance, not only for its potential utilization in the reduction of dye wastewater, but also because it could be applied as a pretreatment method prior to biological treatment. Thus, ZVI can serve as a promising alternative technique to decolorize dye wastewater. Most studies dealing with the decolorization of textile wastewater have been conducted with azo dyes [188-191] and fewer studies the degradation of anthraquinone [192,193].

1.4.4 Advanced oxidation processes

In recent years newer technologies have been developed for more efficient treatment of industrial effluents. Among them, Advanced Oxidation Processes (AOPs) appear to be a promising technology for the destruction of target pollutants.

The various AOPs include the following:

1.4.4.1 AOP without iradiation

These are based on the principle that strong oxygen-based oxidizers (e.g., $OH^{\bullet}$, $HO_2^{\bullet}$ and $O_2^{-\bullet}$) were formed from the water and O_2 present in the reaction medium in the presence of an oxidant source. These radicals were used to degrade dye molecules completely. Oxidant radicals were obtained commonly through: electrochemical oxidation [194-196] Fenton’s reagent [197-202] and ozone [203-215].

The catalytic wet air oxidation (CWAO) using air or oxygen as oxidant achieves high conversions, but high temperatures are needed for this process [216]. The use of H_2O_2 allows to perform oxidation reaction at ambient conditions, decreasing the investment costs. Hydrogen peroxide is known to be a powerful, non-specific oxidant adequate for degradation of pollutants that can be used incombination with a catalyst and/or UV light to produce free radical intermediates. For the generation of ${}^{\bullet}OH$ radicals from H_2O_2 and minimization of the side reaction of decomposition to water, catalytic activation is needed (this includes the H_2O_2 + UV, Fenton: H_2O_2 +Fe^{2+}/Fe^{3+}, Fenton-like reagents: H_2O_2 +Fe^{2+}-solid/Fe^{3+}- solid and photo-Fenton: H_2O_2 +Fe^{2+}/Fe^{3+} + UV).

1.4.4.1.1 Fenton

The oxidation using Fenton's reagent, a powerful source of oxidative HO radicals generated from H_2O_2 in the presence of Fe^{2+} ions, has proved to be an effective treatment method for the destruction of a large number of toxic pollutants [207]. The generated ${}^{\bullet}OH$ radicals are highly oxidative, non-selective and able to decompose many organic compounds including dyes. Fenton's reagent has been widely used for treatment of textile waste waters [208-212]. Fenton process is based on an electron transfer between hydrogen peroxide (H_2O_2) and a homogeneous metal catalyst (Fe^{2+}) resulting in the production of hydroxyl radicals as shown in Eq. (1)

$$\mathbf{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH} \qquad \text{......Eq. (1)}$$

This reaction is propagated by ferrous ion regeneration, which is mainly due to the reduction of the produced ferric species with hydrogen peroxide Eq. (2).

$$\mathbf{H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H_2O + H^+} \qquad \text{......Eq. (2)}$$

However in these reactions, the rate constant of Eq. (1) varies between 63 and 76 L mol^{-1} s^{-1}; whereas the rate constant of Eq. (2) is in the order of 0.01–0.02 L mol^{-1} s^{-1}. This indicates that the consumption of ferrous ions is more rapid than the regeneration. This results in the formation of large amount of ferric hydroxide sludge during the process, which results in separation and disposal problems [213]. Another added disadvantage is that the amount of iron used in homogeneous Fenton process is above European Union limits. Thus, wastewater cannot be discharged with the Fe used. In addition, treatment of the sludge containing iron is not economialc. Furthermore strict control of pH of around 2–3 is required. Other less studied mechanisms of AOPs include: ultrasound [202-207], electrical discharges (pulsed corona discharges) [216-218] and, use of an oxidant gas such as ozone in hydrothermal conditions (wet air oxidation) [219-221]. Use of ozoneincludes ozonation, photo-ozonation, ozonation + catalysis and O_3 + H_2O_2 and O_3 +Fe^{2+}/Fe^{3+}) Sonochemistry [222, 223] is a rapidly growing area and is an example of an AOP that deals with the destruction of organic species in aqueous solution. The chemical effects of high intensity ultrasound result primarily from acoustic cavitation: the formation, growth and impulsive collapse of bubbles in liquids [224]. In sonophotocatalysis, due to the generation of sites of high temperature and pressure by acoustic cavitation, overall water splitting was proposedto proceed by a two-step reaction as reported in literature [225]. Reports on heterogeneous sonophotocatalysis under differentexperimental conditions [226-228] are available in literature.

1.4.4.2 AOP with irradiation

Another category of AOP uses radiation treatment with ultraviolet (UV) light known as photolysis [229]. In this case, radicals are formed by irradiating an oxidant e.g., H_2O_2 (photolysis) [230-232] or using a heterogeneous catalyst usually TiO_2 or ZnO (photocatalysis) [233-234].

1.4.4.2.1 Photocatalysis

Aphotocatalyst absorbs a photon of energy equal to or greater than its band gap, causing an electron to be promoted from the valence band to the conduction band (e^-_{cb}) leaving behind an electron vacancy or a‘‘hole” in the valence band (h^+_{vb}). If the charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with adsorbed species. Titanium dioxide (TiO_2) is found to be the most efficient catalyst for photocatalytic degradation of pollutants due its ability to transfer electrons faster to molecular oxygen [235-237].

Zinc oxide is another promising photocatalyst for degradation of organic solutes in aqueous systems. The ZnO-mediated photocatalysis process has been successfully used to degrade dye pollutants by many researchers [238-244].

In dye photocatalysis, it can make use of the solar energy in a visible range [245]. During the process electrons can be stimulated from a photocatalyst for adsorbed dye decomposition. The major advantage of this process is that, compared to other advanced technologies, photocatalysts are self-regenerated and are recyclable or reusable. An ideal photocatalyst should be highly photoactive, stable and non-toxic and meet primary criteria for a higher H_2O/OH couple [246].

The photocatalytic discoloration of a dye is believed to take place according to the following mechanism.When a catalyst is exposed to UV radiation; electrons are promoted from the valence band to the conduction band. As a result of this, an electron–hole pair is produced [247].

$$\mathbf{catalyst + hv \rightarrow e^-_{cb} + h^+_{vb}}$$

where, e^{-}_{cb} and h^{+}_{vb} are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases h^{+}_{vb} can react easily with surface bound H_2O to produce •OH radicals, while, e^{-}_{cb} can react with O_2 to produce superoxide radical anion of oxygen [298].

$H_2O + h^{+}_{vb} \rightarrow \bullet\, OH + H^{+}$ ......Eq. (3)

$O_2 + e^{-}_{cb} \rightarrow O_2^{-\bullet}$ ......Eq. (4)

This reaction prevents the combination of the electron and the hole which are produced in the first step. The •OH and O_2• produced in the above manner can then react with the dye to form other species and is thus responsible for the discoloration of the dye.

$O_2^{-\bullet} + H_2O \rightarrow H_2O_2$ ......Eq. (5)

$H_2O_2 \rightarrow 2\ \bullet OH$ ......Eq. (6)

$\bullet\, OH + dye \rightarrow dye_{ox}$ ......Eq. (7)

$Dye + e^{-}_{cb} \rightarrow Dye_{red}$ ......Eq. (8)

But, TiO_2 has a band gap of 3.2 eV, therefore only light in the ultra-violet range (i.e., <390nm) can be utilized to excite the electrons in the valence band to the conduction band. [248].Thus new photocatalysts are still necessary to improve the energy and environmental technologies related with solar energy. In order to take advantage of the solar energy and in lieu of artificial light source for photocatalysis, the development of efficient visible-light-responsive photocatalysts is another alternative. Many investigations have been undertaken to exploit novel semiconductor materials that are responsive to visible light at a narrower band gap of less than 3.0eV [249, 250]. Composite oxides containing bismuth such asbismuthtitanate [251] bismuthmolybdate [252] and bismuthtungstate [253,254] are a large group of photocatalysts. That shows certain absorption ability in the visible light range. This visible-light sensitive property is related closely to the electronic structure of the semiconductor.

1.4.4.2.2 Ag Nanoparticles

Apart from metal oxides, AgNPs show efficient plasmon resonance and enhanced photocatalytic activity in the visible light region. AgNPs are well known to improve remarkable photocatalytic activity by the reduction of electro/hole recombination reaction due to shape-dependent optical properties, its localized surface plasmon resonance and the collective oscillations of their conduction band electrons [255]. Nanoparticles serve as better catalysts in the facile reduction process of pollutants like 4-nitrophenols due to the greater accessibility to surface atoms and low coordination number. It is well documented that metallic nanoparticles can catalyze the reduction of 4-nitrophenol by $NaBH_4$ to generate 4-aminophenol, which has become a model reaction for testing the catalytic activity of a catalyst [256-258]. 4-aminophenol is an important industrial raw material which has been widely used in many fields. For example, it is an important intermediate in the manufacture of many analgesic and antipyretic drugs is well known that 4-aminophenol can be synthesized by the hydrogenation reduction of 4-nitrophenol. A stabilizing agent (also known as capping agent) is used in the synthesis process to prevent nanoparticles from aggregation and to control the size of final product, with agglomeration mainly caused by excess surface energy and high thermodynamic instability of the nanoparticle surface [259]. A stabilizing agent relies on electrostatic repulsion force caused by surface charge, steric stabilization, or both [260-280].

Consequently, there is a wide selection of stabilizing agents to choose from which include surfactants such as sodium dodecyl sulfate (SDS) or ligands and polymers that contain functional groups such as thiol (–SH), cyano (–CN), carboxyl (–COOH) and amino (–NH_2) acting as stabilizers [267, 271]. The selection of stabilizing agent depends on the application. For example, poly (n-isopropylacrylamide) (PNIPAM) is commonly used as a temperature-sensitive polymer possessing a lower critical solution temperature (LCST). Below the LCST, it is hydrophilic and soluble in aqueous solution; however, the polymer becomes hydrophobic, insoluble and aggregates in solution when the temperature is raised above the LCST. Thus, silver nanoparticles capped by PNIPAM allow for combined surface plasmon and thermal switching applications [268]. In addition to the above, the stability, reactivity, solubility, particle shape and size are determined by the concentration of a given type of a stabilizing agent [272]. For instance, smaller particles are obtained by increasing the carboxylate stabilizer concentration [273]. The catalytic properties of silver nanomaterials can also depend on the type of stabilizers used (e.g., cetyltrimethylammonium bromide (CTAB, SDS), hence, decreasing the adsorption of reactants to the silver surface [274]. The commonly used synthesis methods usually produce negatively charged silver nanoparticles. However, the use of branched polyethyleneimine (BPEI) resulted in positively charged silver nanoparticles and has been used for the detection of thiocyanate and perchlorate ions. However, such reducing agents and stabilizing agents may be associated with environmental toxicity or biological hazards. It has been, therefore, of increasing interest to develop “green” synthesis techniques for AgNPs. Lately, a wide variety of biologically derived materials (including reducing sugars, chitosan, cellulose, worm silk, and plant extracts) and organisms (including bacteria and fungus), have been successfully used in the preparation of AgNPs [281-287].

The mechanisms for the formation of AgNPs by biologically derived materials is known to involve the oxidation of hydroxyl groups in the sugars, phenolic groups in the amino acid, and terpenoids in the plant extract [281-285]. Thus various categories of compounds in plants that have potential biological activities and phytochemicals are emerging as an important natural resource for the synthesis of metallic nanoparticles. They play important roles in both reduction and stabilization of nanoparticles bydecreasing the use of toxic chemicals and eliminating biological risks in biomedical applications**. Plantmediated synthesis** of metal nanoparticles is gaining more importance owing to its simplicity, rapid rate of synthesis of nanoparticles and inbeing environment friendly.

1.4.4.2.3 Immobilisation of catalysts

The immobilization of the catalyst on support materials with large specific surface areas presents numerous advantages in comparison to homogeneous catalysts such as easy separation by filtration, robustness, high stability, potential recyclability and provides more catalytic active centers. There are various porous support materials available on which metal complexes have been immobilized. Among them, silica gel is very advantageous since it possesses high surface area, good thermal and mechanical stability, easy availability, economic viability, and relatively simple and robust covalent modification with organic or organometallic moieties [286-294].

Catalyst immobilization has attracted wide attention due to the advantage of facile recovery and recycling of the catalysts. In the past decades, some researchers have studied TiO_2 immobilization over various inactive supports such as glass, zeolite, silica, and ceramic; Titania pillared zirconium phosphate and titanium phosphate towards the photodegradation of cationic dye, methylene blue (MB) under solar radiation [295-306, 306a].

However, a substantial decrease in photocatalytic activity and selectivity can be caused because of the immobilized catalysts due to reduced active surface area-to-volume ratios and inefficient light harvesting introduced by high content of inactive supports. Therefore, it is of great challenge to design a multi-functional photocatalytic system that is both highly photoactive and costeffectively recyclable. The drawbacks of homogeneous fenton process mentioned above can be overcome by using heterogeneous fenton-type catalysts. Some attempts have been made to develop heterogeneous catalysts by incorporating Fe ions or Fe oxides into porous supports [301-306]. Recently, colloidal magnetic nanospheres have long been of great interest as composite materials, because of their perfect combination of flexible surface functionalization and sensitive magnetic response [307-309]. In particular, functionalization of Titania by incorporating magnetic iron oxide colloids allows a convenient recovery of magnetic photocatalyst under an appropriate magnetic field [247]. One significant advantage of magnetic iron oxide contributes to this desirable photocatalytic system: the super paramagnetic iron oxide cores sensitively respond to a magnetic field but retain negligible remanent magnetism as the external magnetic field is removed. In this regard, this low magnetic remanence largely avoids forming magnetized clumps in the reaction media, although high magnetization moments allow the use of low-field magnets to efficiently concentrate magnetic particles. A combination of useful properties such as optical/catalytic/ conductive is achieved when silver nanoparticles are integrated into polymer matrices to form nanocomposites or when they are combined with other metal nanoparticles acting as a shell or a core to form bimetallic nanoparticles [307, 308]. For example, the antibacterial activity of silver nanoparticles was enhanced when it was incorporated into an Ag/TiO_2 nanocomposite.

The successful catalytic reduction of specific dyes may be achieved via use of silver nanoparticles supported on silica spheres [274]. Furthermore, silver is often used as a substrate for magnifying the Surface Enhanced Raman scattering (SERS) providing stronger spectrum than data obtained from using each individual nanoparticle [275]. More details about SERS are given in Chapter 2.

AgNPs thus can be prepared through a wide range of pathways by the reduction of silver salt solution and using various reducing reagents in the presence of a stabilizer. The reducing agents include sodium borohydride, hydrazine, hydrogen peroxide, sodium citrate, ascorbic acid, and formaldehyde [261-265].

1.4.4.2.4 Iron Oxide nanoparticles

Magnetic nanoparticles offer advantages over non-magnetic nanoparticles because they can be easily separated from water under a magnetic field. Separation using magnetic gradients, the so-called high magnetic gradient separation (HGMS), is a process widely used in medicine and ore processing. This technique allows one to design processes where the particles not only remove compounds from water but also can be easily removed, recycled or regenerated. Approaches have been proposed with magnetite (Fe_3O_4), maghemite (Fe_2O_3) and jacobsite ($MnFe_2O_4$) nanoparticles loading on or in the polymer matrix such as alginate beads. A series of magnetic alginate polymers were prepared and batch experiments were conducted to investigate their ability to remove heavy metal ions (Co(II), Cr(VI), Ni (II), Pb (II), Cu (II), Mn (II), La (III)) and organic dyes (methylene blue and methyl orange) from aqueous solutions. Magnetic particles in the nanocomposites allowed easy isolation of the beads from the aqueous solutions after the sorption process.

AOPs are considered cleaner because dyes totally decompose to CO_2, H_2O, low-molecular-weight compounds (e.g., small aldehydes, carboxylic acids or small inorganic compounds) and no significant or solid secondary pollution is generated. The drawback is that they can be energy-intensive and costly. However, considerable effort is being made toimprove them with the following possibilities: constructing reactors that can use sunlight as asource of irradiation [310]. Incorporating new materials or catalysts (e.g., composites of TiO_2/ZnO) [216] photocatalysis using a heterogeneous Fenton catalyst with a Fe zeolite,which has a better microporous structure and ion-exchange capacity (among other advantages) [311] or, immobilizing the photocatalyst on inert surfaces, which favors recovery of the catalyst [312] Other tendencies in dye-degradation treatments are combinations of: oxidants (e.g., O_3/H_2O_2, O_3/Fe^{3+}, $O_3/H_2O_2/Fe^{3+}$, UV light /O_3/Fe^{3+}, UV light /$O_2/H_2O_2/Fe^{3+}$) [205]; or degradation processes. Some examples of this last approach are: (a) the combination of wet-air oxidation and electrochemical oxidation to make wet-electrochemical oxidation [221]; (b) the use of photocatalysis or an anaerobic biotreatment in a first stage and subsequent degradation of by-products by electrochemical oxidation [221]; (c) the combination of ozonation, photocatalysis or biodegradation with sonolysis

[215-218]; (d) coagulation-flocculation coupled with membrane processes or adsorption [313] and (e) activated organic carbon in combination with high-voltage pulse discharge [219]. The rate of organic pollutant degradation could be increased by irradiation with UV light (UV/Fenton process). UV light leads not only to the formation of additional hydroxyl radicals but also to recycling of ferrous catalyst by reduction of Fe^{3+} (Eqs. (9) and (10)):

$H_2O_2 + h\nu \rightarrow \bullet OH + \bullet OH$ ……Eq. (9)

$Fe^{3+} + H_2O + h\nu \rightarrow \bullet OH + Fe^{2+} + H^+$ ……Eq. (10)

In this way, the concentration of Fe (II) is increased and the overall reaction is accelerated. The oxidation using UV/Fenton process has been found to be a promising treatment method for the effective degradation of different pollutants including organic synthetic dyes [314-321].

1.4.4.2.5 Sonication

When sonication is added to the photocatalytic system, the transformation of organic products occurs through reactions with hydroxyl radicals generated from the collapsing bubbles. The synergistic effects between photocatalysis and sonocatalysis may be attributed to several factors, such as the increased amounts of the reactive radical species inducing the oxidation of the substrate and the degradation of intermediates [227], the acceleration of the mass transport of chemical species between the solution phase and the photocatalyst surface and vice versa [227] and the reduction in the recombination of excited electrons and holes on the photocatalyst as a result of electron trapping by the residual H_2O_2 generated to produce additional$\bullet$OH radical [289].

Table 4: Comparision of various catalysts and method used for degradation

Catalyst	Dye degraded	Method of degradation	Reference
TiO_2/SiO_2Composite	Indigo carmin	Photocatalytic	[322]
CdS quantum dots	Methyl Orange	Photocatalytic	[323]
chitosan–niobium (V) oxide	Indigo carmine	Photocatalytic	[324]
chitosan-TiO_2	Methyl Orange	Photocatalytic	[325]
Composite of Iron Oxide and Silicate Nanoparticles	Azo-dye Orange II	Photoassisted Fenton Reaction	[326]
PANI-Modified TiO_2 Composite	Methyl Orange	Photocatalytic	[327]
Carbon-Modified Vanadium-Doped TiO_2	Acid Orange 7	Photocatalytic	[328]
Copper Phthalocyanine Hollow Spheres	Rhodamine B	Photocatalytic	[329]
ZnO-Carbon Nanofiber	Rhodamine B	Photocatalytic	[330]
Copper(I) Coordination Polymer Materials Cu(ptz) -1 and Cu(ptz) -2	Methylene blue rhodamine B methyl orange	Photocatalytic	[331]
Ag_3PO_4	Rhodamine B	Sunlight-Assisted photoactivity	[332]

The Removal processes during degradation of dyes can be monitored by determining:

(1) Analytical indices and

(2) Dye or sub-product concentrations.

Determination of analytical indices

The most common analytical indices used to monitor removal processes are total organic carbon (TOC), chemical oxygen demand (COD) and absorbance in UV-visible at the wavelength of maximum absorption. The value of these three indices is directly related to the dye concentration, so a decrease in any one of them in the process indicates a decrease in the dye concentration. Nevertheless, it should be pointed out that none of them is selective. TOC is usually determined by catalytic oxidation followed by quantification of the CO_2 formed through infrared spectrometry [333, 334].

The decay of this parameter in all degradation processes involves ultimate mineralization of both parent dye and its intermediate [202]. COD evaluates the oxygen required for the oxidation of organic and inorganic matter in the sample and is determined by oxidizing the sample with potassium dichromate and then titrating its excess with a standard solution of ferrous ammonium sulfate. TOC and COD can provide complementary information. It is generally observed that COD removal is always greater than that of TOC, suggesting that conversion rather than combustion plays an important role in the degradation process [195]. Evaluation of λ_{max} is experimentally simple but does not consider possible changes in color or formation of intermediates. For this reason, some studies monitor not only maximum wavelength but also the total integrated area of the spectrum in order to take into account the conversion of dye molecules to other compounds absorbing at different wavelengths. Dye spectra can also be used to characterize the dye solution with regard to the two main absorption bands – one in the visible region and the other in the UV region. The disappearance of peaks and the appearance of new peaks in the UV and visible region indicate that dyes degrade into low-molecular-weight aromatic compounds [205, 206]. Other indices are less generalized than those mentioned above: turbidity, which can be important in coagulation processes [313] or conductivity, which may be related to ions such as proton, nitrate or bromine [314] although some parameters are measured, others can be calculated using TOC, COD and A_{max} measurements. One commonly calculated parameter is color removal, in which the initial and final λmax are compared [196]. Another very similar parameter, if degradation processes are used [383, 335] is removal efficiency or degradation efficiency, which compares the concentration of initial and final, remaining dye. This parameter can be the same as color removal, if the concentration is calculated using the wavelength of maximum absorbance. If TOC values are used instead of Amax or concentration values, the parameter is called percentage of mineralization [334]. COD-removal efficiency can be calculated in the same way using COD values. Parameters based on COD and TOC give some idea of the quality of the treated wastewater.

Determination of dye degradation products is monitored generally to study the mechanism of degradation

From the above brief discussion it is evident that

- Composites more specifically biocomposites/ bionanocomposites are more advantageous as adsorbents. AOPs have emerged as attractive clean technologies for degradation of dyes.
- Since advanced oxidation processes involving H_2O_2 are based on the generation of hydroxyl radicals by the dissociation of hydrogen peroxide, novel materials like nano capped silver, nano capped iron oxide or some materials which readily form peroxy complexes could be used as sources of hydroxyl radicals.
- Green synthesis of these materials would be an added advantage.
- Polymer supported materials would be more advantageous for the generation of hydroxyl radicals.
- The use of bleaching wastewater as a source of hydrogen peroxide can be a new option that can considerably reduce resource consumption and environmental pollution without incurring expensive investments of a technical and financial nature.
- It is well known that 4-aminophenol can be synthesized by the hydrogenation reduction of 4-nitrophenol an important intermediate in the manufacture of many analgesic and antipyretic drugs. Therefore, it is interesting and meaningful to develop a process for the conversion of 4-nitrophenol to 4-aminophenol in aqueous solution under mild conditions. Moreover, the process might be used to advantage for the treatment of wastewater containing the 4-nitrophenol pollutant instead of conventional adsorption process

1.5 The main objectives thus are

- Green Synthesis of nano silver using palm shell extract and guar gum.
- Synthesis of capped nano iron oxide using palm shell extract as fenton’s reagent.
- Synthesis of nano layered solid acid materials-zirconium phosphate and tungstate.
- Prepare bio nano composites using synthesized nano materials and chitosan.
- Characterisation of the synthesised novel materials using various spectroscopic techniques and study the SERS behaviour of palm shell extract capped Ag and its bionanocomposites.
- Study the potential of synthesised nanomaterials as catalysts for the degradation of anionic dyes like reactive blue 21 (phthalocyanineazo dye), reactive red 141 (azo dye) and cationic dye Rhodamine 6G (xanthene dye) as well as their binary mixtures as model dye pollutants. The degradation efficiency would be monitored by the decolorisation efficiency as well as TOC removal. Nitrophenol would be used as another model pollutant for catalytic studies.
- Prepare novel biocomposites and bionano composites as adsorbents using layered materials like clay (montomorillonite), activated clay, nano organically modified clay (Cloisite 30A) and nanohydrotalcite.
- Characterisation and investigation of the adsorption potential of the prepared biocomposites as well as bionano composites for the removal of dyes using anionic dyes like reactive blue (phthalocyanineazo dye), reactive red (azo dye) and cationic dye Rhodamine 6G (xanthene dye) as well as their binary mixtures as model dye pollutants.

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