Chapter 1

Introduction

1.1 Water and its pollution

Earth is the only life-supporting planet known to us so far. Water is one of the key factors responsible for the existence of life on earth. Clean and plentiful water provides the foundation for prosperous communities. Unfortunately precipitation patterns, and hence distribution of freshwater resources, around the globe is far from even. Where precipitation does fall heavily, there are often difficulties with storage because of space constraints. Furthermore, the available freshwater has to be shared between natural biota and human demands. Growing population and its demands has resulted in scarcity of fresh water in several parts of the world.

With the growth of mankind, society, science, technology, our world is reaching new high horizons but the cost which we are paying or will pay in near future is surely going to be too high. The consequence of this rapid growth is environmental disorder with a big problem called pollution. Besides other needs, the demand for water has increased tremendously with agricultural, industrial and domestic sectors consuming large percentage of available fresh water. This has resulted in generation of large amount of wastewater containing a number of pollutants [1]. The pollution of water sources has doubled the problem of fresh water scarcity. During the past few decades rapid industrialization has led to water pollution all over the world. The water pollutants may be broadly categorized into organic and inorganic pollutants which are released from
various industries into fresh water streams. The organic pollutants include dyes, surfactants, herbicides, insecticides, solvents, polycyclic aromatic hydrocarbons (PAHs), and other industrial organics, while the inorganic pollutants include metals, metalloids, anions etc.

Contaminated drinking water is a major reason for health hazards in developing countries. This is particularly true for the poor and the vulnerable. The World Health Organization (WHO) estimates that about 1.7 million deaths worldwide per year are due to unsafe water, hygiene, and sanitation. Almost all of these deaths are in developing countries and nine out of ten are child deaths [2].

Water pollution is a serious problem in India as almost 70% of its surface water resources and a growing percentage of its groundwater reserves are contaminated by biological, toxic, organic, and inorganic pollutants. In many cases, these sources have been rendered unsafe for human consumption as well as for other activities, such as irrigation and industrial needs. This shows that degraded water quality can contribute to water scarcity as it limits its availability for both human use and for the ecosystem. In 1995, the Central Pollution Control Board (CPCB) identified severely polluted stretches on 18 major rivers in India. Not surprisingly, a majority of these stretches were found in and around large urban areas. The high incidence of severe contamination near urban areas indicates that the industrial and domestic sectors’ contribution to water pollution is much higher than their relative importance implied in the Indian economy [3].

Among all sources, organic pollutants are the major contributors towards water pollution. The production of synthetic organic chemicals has grown several folds over the past few decades. A small percentage of these chemicals enter water bodies as
wastewater. Their presence in water imparts objectionable and offensive tastes, odours, and colours affecting fish and aquatic plants, even when they are present in low concentrations. Above permissible limits these pollutants cause adverse effects on water-dependent life forms. For example, different classes of pesticides like chlorinated hydrocarbons, organophosphates, carbamates and chlorophenoxyacids were used on large scale for several decades. However appreciable quantities of these pesticide residues were found in the biota leading to biomagnification [4].

1.2 Dyes and their classification

Colour plays an important role in human life. Colour influences our mood, emotions and it provides the way in which we enjoy our life. The colour what we have are derived from two sources that is natural and synthetic. Natural colours are all around the earth in sky, sea, animals, birds, trees etc. Synthetic colours are products of chemical manufacturing industries. Colour is introduced into these materials using substances known as dyes.

Dyes constitute an important class of commercial compounds which are widely used in textile, leather, pulp and paper, printing, photographs, cosmetics, and pharmaceutical industries. Dyes are mainly used in textile industries for colouring fabrics and the art of textile dyeing dates back to ancient times. Because most of the dyes used in ancient times were discovered by accident, they often consisted of natural plants that were common in society. As dyes were developed and experimented with, people became more adventurous and would attempt different media as dyes. Hence, the dyeing industry developed [5]. Today, pre-packaged dyes are readily obtainable in almost every colour, and are available to anyone who can purchase the end product. The development of different dyes and techniques has made this transition possible.
Dyes are coloured ionizing and aromatic compounds which show affinity towards substrates to which it is being applied. The colour of the dye is because of the presence of substance called ‘Chromophore’. Basically the dyes are aromatic compounds in their structure having aryl rings which has delocalized electron system. These structures are responsible for the absorption of electromagnetic radiation having various wavelengths depends on the energy of the electron clouds. In fact chromophores do not make dyes coloured but it helps dyes to absorb radiation. They make energy change in electron cloud of the dye as a result of which the compound absorbs radiation within the visible radiation. So, human eyes detect this absorption and response to the colour. A chromophore is defined as any isolated covalently bonded group that shows characteristic absorption in the UV or the visible region. These are responsible for imparting colour to the compound. Some common chromophores are Ethylenes, Acetylenes, Carbonyls, Nitriles, Azo compounds etc. An auxochrome is any group which does not itself acts as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum. Groups like -OH, -OR, -NH₂, -NHR behave as auxochromes.

In order to classify dyes, a five digit colour index (C.I.) number is assigned to a dye when its chemical structure has been disclosed by the manufacturer. It is also worth to note here that though a dye has a C.I. number, the purity and precise chemical constitution may vary depending upon the name.

Dyes exhibit considerable structural diversity and hence they are classified in several ways. Based on solubility dyes may be classified into soluble and insoluble dyes. Soluble dyes include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes include azoic, sulphur, vat and disperse dyes. The dyes can also be
classified both by their chemical structure and their application to the fiber type. The classification of dyes based on their usage and properties is discussed below [1, 6].

**Acid Dyes:** These are sodium salt of sulphonic acids and nitro phenols. These dyes are used for nylon, wool, silk, modified acrylics, and also to some extent for paper, leather, ink-jet printing, food and cosmetics. They are generally water soluble. Application is generally made under acidic conditions that cause protonation of the basic groups. The principal chemical classes of these dyes are azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso.

**Cationic (Basic) Dyes:** These dyes are used for paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate and to some extent in medicine too. Originally they were used for silk, wool, and tannin-mordanted cotton. These water soluble dyes yield coloured cations in solution and hence they are called as cationic dyes. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine.

**Disperse Dyes:** These are non ionic dyes having low molecular weight and are generally applied in the form of dispersion in soap solution in the presence of a stabilizing agent. These dyes are used mainly on polyester and to some extent on nylon, cellulose, cellulose acetate and acrylic fibers. These are substantially water-insoluble, nonionic dyes used for hydrophobic fibers from aqueous dispersion. They generally contain azo, anthraquinone, styryl, nitro and benzodifuranone groups.

**Direct Dyes:** These are also known as substantive dyes and can be applied to the fibre directly from an aqueous solution. Generally they have sulphonic acid groups. These are large, flat, linear molecules that can enter the water-swollen pores of cellulose and orient
themselves along the crystalline regions. They are economical and easy to apply. These are used in the dyeing of cotton and rayon, paper, leather, and to some extent to nylon. They are water-soluble anionic dyes, and, when dyed from aqueous solution in the presence of electrolytes, have high affinity for cellulosic fibers. Generally the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines and oxazines.

**Reactive Dyes:** These dyes form covalent bonds with fibres possessing hydroxyl groups. An important type of reactive dye has chlorine atoms which react with hydroxyl groups in cellulose when applied in the presence of alkali. It has been proved that an ether linkage is established between the dye and the fibre. Another important type of reactive dye involves an activated vinyl group that can react with a cellulose hydroxyl group in the presence of a base. They provide excellent fastness to washing as the dye become part of the molecule and the means by which it gets attached to the reactive part.

These are generally used for cotton and other cellulosics, but are also used to a small extent on wool and nylon. These dyes form a covalent bond with the fiber and contain chromophoric groups such as azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc. Their chemical structures are simpler, absorption spectra show narrower absorption bands and the dyeings are brighter making them advantageous over direct dyes.

**Solvent Dyes:** These dyes contain no sulpho or other water solubilizing groups. These are soluble in organic solvent, the nature of which changes according to application. These dyes are used for plastics, gasoline, lubricants, oils and waxes. These dyes are solvent soluble (water insoluble) and generally nonpolar or little polar, i.e., lacking polar solubilizing groups such as sulfonic acid, carboxylic acid or quaternary ammonium. The
principal chemical classes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane are also used.

**Sulphur Dyes:** These are insoluble dyes. When reduced with sodium sulphide, they become soluble and show affinity for cellulose. They are very resistant to removal by washing. They contain sulphur both as an integral part of the chromophore and in attached polysulphide chains. These dyes are used for cotton and rayon and have limited use with polyamide fibers, silk, leather, paper and wood. They have intermediate structures and though they form a relatively small group of dyes, the low cost and good wash fastness properties make this class important from an economic point of view.

**Vat Dyes:** These cannot be applied directly since they are insoluble in water. They are therefore, rendered soluble by reduction with sodium hydrosulphite to a colourless compounds known as ‘leuco compounds’. These dyes are applied in their reduced forms. The form is obtained by treating the compound with some reducing agents like alkaline sodium hyposulphite in a large wooden vat, giving rise to the name ‘vat dye’.

The vat dyes are used for cotton mainly to cellulosic fibers as soluble leuco salts and for rayon and wool too. These water-insoluble dyes are with principal chemical class containing anthraquinone (including polycyclic quinones) and indigoids.

Besides these, there are some other classes too like azoic having azo groups used for cotton and other cellulosic materials; fluorescent brighteners having stilbene, pyrazoles, coumarin and naphthalimides used for soaps and detergents, fibers, oils, paints and plastics, and mordant having azo and anthraquinone used for wool, leather, natural fibers after pretreating with metals and anodized aluminium.
1.3 Dyes as water pollutants

Dyes are released into wastewater from various industrial units, mainly from the dye manufacturing, textile and other fabric finishing industries. Colour containing wastewater is produced as an unavoidable byproduct during dyeing process in these industries. It is estimated that about 1–20% of dyes are wasted into the environment upon completion of their use in the dyeing unit and approximately 125-150 L of water is used for 1 kg of textile product, thus producing huge quantities of wastewater [7-11].

About half of global production of synthetic textile dyes are classified into azo compounds that have the chromophore of -N=N- unit in their molecular structure. The dyes are generally mutagenic and carcinogenic, and can cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, brain and central nervous system.

Reactive dyes are the largest single group of dyes used in textiles industry. These dyes are the most problematic compounds among other dyes in textile wastewater. They are highly water soluble and hence impart strong colour to the wastewater. It is estimated that about 10-20% of reactive dyes remain in the wastewater during the production process of these dyes and nearly 50% of reactive dyes may be lost to the effluent during dyeing processes of cellulose fibres. Reactive dye wastewater has limited biodegradability in an aerobic environment and many azo dyes under anaerobic conditions decompose into potentially carcinogenic aromatic amines [12].

The presence of dyes in aquatic ecosystems is not only aesthetically unpleasant but also leads to the reduction in sunlight penetration. This in turn decreases photosynthetic activity and dissolved oxygen concentration and had acute toxic effects on
aquatic flora and fauna [13-16]. Many of the azo dyes and/or their breakdown products have been shown to be toxic, potentially carcinogenic and can lead to the formation of bladder cancer in humans; tumours, allergies, nuclear anomalies in experimental animals and chromosomal aberrations in mammalian cells [17, 18]. Several researchers have performed toxicity tests on invertebrates, plants, algae, microorganisms, fishes and few mammals to assess risks caused by these dyes on human health and aquatic life. Inhibition of nematodes reproduction was observed in *Caenorhabditis elegans* [18]. A significant increase in chromosomal aberration, cytotoxic and genotoxic effects were observed in effluent treated root cells of *Allium cepa* [19]. The dye Disperse Orange 1 was found to induce DNA damage by frame shift mutations and cause cell death by apoptosis and DNA breakage in the human cell HepG2 [20]. Cytotoxicity and decline in cell viability was reported in rainbow trout cell lines treated with acid blue 80 [21].

1.4 **Remediation of dye containing effluent**

Nowadays finding new technologies to decontaminate wastewater has become a top priority among global environmental concerns [22]. Apart from its day-to-day use for drinking, irrigation and marine life, water is used for many applications. Today most of the countries are facing drinking water problems and conditions are very severe especially in developing countries. The world is facing formidable challenges in meeting the rising demands of clean water as the available supplies of freshwater are depleting.

The most common methods of dye removal from dye containing industrial effluents may be categorized into physical, chemical and biological methods [23]. The advantages and drawbacks of some of the important methods have been discussed below.
1.4.1 Chemical methods

Chemical treatments are most commonly used methods for decolourisation due to its simplicity of application.

a) Ozonation: Ozone is a very good oxidizing agent compared to other oxidizing agents like chlorine and H₂O₂. Ozone is capable of degrading chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons [24]. Ozonation leaves the effluent with no colour and low COD suitable for discharge into environmental waterways. One major advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge. The disadvantages of using ozone include its short half-life (20 min), its instability due to the interferences like dyes, salts, pH and temperature. The other major drawback of ozonation is high cost associated with the process [25].

b) Fenton’s reagent: The combination of H₂O₂ and Fe(II) salt is called Fenton’s reagent and is employed for treating wastewater which are resistant to biological treatment [26]. This method involves the generation of hydroxyl radicals which further oxidize the organic pollutants. This method has been shown to be effective for decolourising both soluble and insoluble dyes [27]. One major disadvantage of this method is sludge generation through the flocculation of the reagent and the dye molecules. The resulting floc does not settle well and thus poses separation problems.

c) UV-H₂O₂ process: The irradiation of H₂O₂ by UV results in the production of high concentrations of hydroxyl radicals, which further catalyze the oxidation of organic material. This method degrades the dye molecules to carbon dioxide and water. However,
depending on the initial material and the extent of treatment, by-products such as halides, inorganic acids, organic aldehydes and acids may be formed [28].

**d) Sodium hypochloride (NaOCl):** This reagent attacks the amino group of the dye and it particularly initiates and accelerates azo bond cleavage. Coloured wastewaters can thus be chemically oxidized by chlorine compounds (NaOCl) although, for environmental reasons (release of toxic organochlorinated compounds), its use is becoming less frequent. This method is not efficient for the decolourisation of disperse dyes and longer times are required to decolourise reactive and metal-complex dyes.

**e) Electrochemical method:** Electrochemical degradation proceeds through either direct or indirect oxidation of pollutant. Direct electrochemical degradation involves adsorption and oxidation of dye directly on the anode. In indirect method, the dye is oxidized by an electrochemically generated oxidant such as chlorine or hydrogen peroxide [29]. This method is economical and shows high efficiency for colour removal and degradation of recalcitrant pollutants.

**1.4.2 Physical methods**

**a) Adsorption:** As synthetic dyes in wastewater cannot be efficiently decolourized by traditional methods, the adsorption of synthetic dyes on inexpensive and efficient solid supports was considered as a simple and economical method for their removal from wastewater. The most common adsorbents include activated carbon, peat, fly ash, coal, silica gel etc. The major disadvantage associated with adsorption is that the process is costly and also the regeneration of adsorbent is a serious problem in most of the cases [30].
b) **Membrane filtration:** This method has the ability to clarify, concentrate and to separate dyes continuously from effluent [31]. This method has advantages over other conventional methods such as resistance to temperature, chemical and microbial attack. However, high capital cost, possibility of clogging and membrane replacement are the major disadvantages. Also it is not possible to separate the dissolved solid content which makes the water reuse, a difficult task in industries.

c) **Ion exchange process:** In this method, wastewater is passed over the ion exchange resin until the available exchange sites are saturated. Both cation and anion dyes can be removed from dye containing effluent. The advantage is that there is no loss of adsorbent on regeneration and it is also possible to remove soluble dyes. A major disadvantage is the cost and also the ion exchangers cannot accommodate a wide range of dyes.

d) **Coagulation:** This method involves the addition of ferrous sulphate and ferric chloride to the dye containing effluent which results in coagulation of the dye. Although the process is economical, high cost of ferrous sulphate and ferric chloride in addition to poor results observed in case of acid dyes have limited its wide spread application. The formation of large amounts of sludge results in high disposal costs.

### 1.4.3 Biological methods

The application of microorganisms for the biodegradation of synthetic dyes is an attractive method. The biological method involves the use of effective strategies like activated sludge process, use of pure and mixed cultures of bacteria and fungi, and anaerobic decomposition of synthetic dyes. The use of microorganisms for the removal of synthetic dyes from industrial effluents offers considerable advantages. The process is relatively inexpensive and the running costs are low. However, the biological
mechanisms can be complex. A large number of species has been tested for the decolouration and mineralization of various dyes. Unfortunately, majority of these dyes are chemically stable and hence resistant to microbial attack.

Most of the dyes used in textile industries are aromatic organic compounds. The complex structure of these dyes is resistant to light, biological activity, ozone and other degradative environmental conditions. Thus conventional methods of wastewater treatment remain ineffective [32]. Hence there is a need to re-think on the existing methods and develop novel strategies for the treatment of wastewater containing textile dyes.

In recent years there has been an extensive interest in developing nanoparticles with high activities for environmental applications such as air purification, water disinfection, hazardous waste remediation and water purification. The nanomaterials have gained diverse environmental applications because of their ability to adsorb, sense and degrade some of the potential contaminants in air and water. These contaminants may be a poisonous gas, heavy metal or an organic molecule which are toxic to the ecosystem. Huge surface available on nanomaterials led to enhanced reactivity towards these hazardous materials. Research has shown that nanoparticles represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems [33]. Nanoparticles are expected to play a crucial role in water purification. Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly diminished by using nanoadsorbents, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, etc.
1.5 Nanoscience and Nanotechnology

Nanotechnology deals with small structures or small-sized materials. The typical dimension spans from sub-nanometer to several hundred nanometers. Nanotechnology literally means any technology performed on a nanoscale that has applications in the real world. Nanotechnology encompasses the production and application of physical, chemical and biological systems at scale ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems.

Small features permit more functionality in a given space, but nanotechnology is not only a simple continuation of miniaturization from micrometer scale down to nanometer scale. Materials in the micrometer scale mostly exhibit physical properties the same as that of bulk form; however, materials in the nanometer scale may exhibit physical properties distinctively different from that of bulk. Materials in this size range exhibit some remarkable specific properties; a transition from atoms or molecules to bulk form takes place in this size range. For example, crystals in the nanometer scale have a low melting point (the difference can be as large as 1000 °C) and reduced lattice constants, since the number of surface atoms or ions becomes a significant fraction of the total number of atoms or ions and the surface energy plays a significant role in the thermal stability. Ferroelectric and ferromagnetic materials may lose their ferroelectricity and ferromagnetism when the materials are shrunk to the nanometer scale. Bulk semiconductors become insulators when the characteristic dimension is sufficiently small (in a couple of nanometers). Although bulk gold does not exhibit catalytic properties, gold nanocrystals demonstrate to be excellent low temperature catalysts [34].
Nanotechnology is likely to have a profound impact on our economy and society in the early twenty-first century, comparable to that of semiconductor technology, information technology or cellular and molecular biology. Science and technology research on nanomaterials promises breakthroughs in such areas as materials and manufacturing, nanoelectronics, medicine and healthcare, energy, biotechnology, information technology and national security. It is widely felt that nanotechnology will be the next industrial revolution [35].

1.5.1 Synthesis of nanomaterials

There are two approaches to the synthesis of nanomaterials and the fabrication of nanostructures: top-down and bottom-up. Attrition or milling is a typical top-down method in making nanoparticles, whereas the colloidal dispersion is a good example of bottom-up approach in the synthesis of nanoparticles. The biggest problem with top-down approach is that the synthesized material is often associated with one or more types of defects.

Bottom-up approach refers to the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule, or cluster-by-cluster. In organic chemistry and/or polymer science, it is known that the polymers are synthesized by connecting individual monomers together. In crystal growth, growth species, such as atoms, ions and molecules, after impinging onto the growth surface, assemble into crystal structure one after another. Bottom-up approach also promises a better chance to obtain nanostructures with less defects, more homogeneous chemical composition, and better short and long range ordering. This is because the bottom-up approach is driven mainly by the reduction of Gibbs free energy, so that nanostructures and nanomaterials such produced are in a
state closer to a thermodynamic equilibrium state. On the contrary, top-down approach most likely introduces internal stress, in addition to surface defects and contaminations.

The general methods used for the preparation of nanomaterials may be broadly categorized into physical and chemical methods. The physical methods include inert gas condensation, ion beam technique, laser ablation, lithography, mechanical attrition, plasma pyrolysis and sputtering. The chemical methods include sol-gel method, co-precipitation, hydrothermal synthesis, microwave technique, combustion synthesis, electrochemical technique, micelles formation, etc.

In the present work various metal oxide nanoparticles have been synthesized by precipitation, sol-gel and electrochemical techniques. Therefore, considering the scope of the thesis only these three methods have been discussed in the following section.

a) Sol-gel method:
Sol-gel processing is convenient for its simple procedure requiring a little more than standard solution chemistry. The initial aim in the sol-gel technique is to produce a sol which is a suspension of solid colloidal particles in liquid. The colloidal particles may or may not have the chemical composition of the desired end product. The particles through van der Waal’s attraction eventually connect to form a gel, a three dimensional solid network having high porosity and high specific surface area. The gel can simply be dried and ground if a nano scale powder is the target material. The wet sol may be deposited onto a substrate and then allowed to gel if thin film is desired. The gel may be heated to induce chemical changes or to densify a thin film or ceramic structure. Sol-gel chemistry is mainly used to produce metal oxides. They can be synthesized directly in the initial
chemical reaction or a metal hydroxide which can be heated to yield the oxides [36-38]. The production of carbides, nitrides and sulfides is also possible through this route.

b) Co-precipitation method

This involves dissolving a salt precursor (chloride, nitrate, etc.) in water (or other solvent) to precipitate the oxo-hydroxide form with the help of a base. Very often, control of size and chemical homogeneity in the case of mixed-metal oxides are difficult to achieve. Many of the earliest synthesis of nanoparticles were achieved by the co-precipitation of sparingly soluble products from aqueous solutions followed by thermal decomposition of those products to oxides. Co-precipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening and/or agglomeration processes. However, the use of surfactants, sonochemical methods and high-gravity reactive precipitation appear as novel and viable alternatives to optimize the resulting solid morphological characteristics [39, 40].

c) Electrochemical method

The electrochemical technique was developed by Switzer and co-workers [41, 42] for the first time as a synthetic route to ceramic films as well as polycrystalline CeO$_2$ powders. The nano-sized metal oxide powder and films prepared by an electrochemical method is an active research area because of its simplicity, low temperature operation process and viability of commercial production. A number of metal oxides thin films, including ZnO, zirconium oxide, tungsten oxide, bismuth oxide, Cu$_2$O and CuO have been synthesized via electrochemical method. Reetz and co-workers [43-46] proposed a sacrificial anode electrochemical route to synthesize nanometal clusters. Mahamuni and co-workers further developed Reetz and co-workers’ route to prepare ZnO and CuO nanocrystals
(powders), using Zn/Cu as a sacrificial anode in the electrochemical bath comprising of tetraoctylammonium bromide and MeCN–THF mix-solvent (ratio 4:1) [47, 48].

The advantage of electrochemical pathway is that it reduces the contamination with by-products resulting from chemical reducing agents and the products are easily isolated from the precipitate. Further, the electrochemical preparation allows for size-selective particle formation. The particle size obtained by the electrochemical route depends on many factors, the distance between the electrodes, reaction time, temperature, and polarity of the solvent contribute to the particle size. Experiments have also showed that the applied current density, pH and concentration of electrolyte has a major influence on the particle size and architecture.

1.5.2 Properties of nanomaterials

a) Surface to volume (S/V) ratio

Basically, two key factors controlling the properties of nanomaterials are the size and surface characteristics of nanoparticles [49, 50]. These two factors are interrelated because the S/V ratio increases as the size decreases. As the size of the materials decreases, the S/V ratio increases and the surface effects become more apparent and thereby easier to explore. In addition, the surface states near the gap can mix with the intrinsic states to a substantial extent and these effects may also influence the spacing of the energy levels of nanoparticles. In a system containing only a few hundred atoms, a large fraction of these atoms will be located on the surface. The energy associated with such a surface will be large since the surface atoms are coordinatively unsaturated.
b) Melting point

In a wide variety of materials ranging from metals to semiconductors to insulators, a decrease in solid to liquid transition temperature has been observed with decreasing nanocrystal size [51, 52]. Because surface atoms tend to be coordinatively unsaturated, there is a large energy associated with this surface. The key to understanding this melting point depression is the fact that the surface energy is always lower in the liquid phase compared to the solid phase. In the solid phase, rigid bonding geometries cause stepped surfaces with high energy edge and corner atoms. By melting, the total surface energy is thus reduced. This stabilizes the liquid phase over the solid phase. Smaller the nanocrystal, larger the contribution made by the surface energy to the overall energy of the system and thus, more dramatic will be the melting temperature depression [53].

c) Nanocatalysis

The field of nanocatalysis has undergone an exponential growth during the past decade. Two types of studies have been carried out, homogeneous catalysis in solution and heterogeneous catalysis in which the nanoparticles are supported on a substrate. Because nanoparticles have a large S/V ratio compared to bulk materials, they are attractive to use as catalysts [54]. Being small has the advantage that a larger fraction of the atoms is used in the catalysis process. Furthermore, surface atoms can occupy the corners and edges of the nanoparticles and thus become chemically unsaturated and also much more active. In homogeneous catalysis, transition metal nanoparticles in colloidal solution are used as catalysts [55]. In heterogeneous catalysis, transition metal nanoparticles are supported on various substrates and used as catalysts. The effect of the support used on the catalytic activity of monometallic and bimetallic nanoparticles has been studied [56].
1.5.3 Applications of nanomaterials

There are several applications of nanomaterials that would play important role in future: improving the quality of life through the nanomedicine, electronics and other nano fields. The established applications of nanomaterials include microelectronics, synthetic rubber, catalytic compounds, photographic supplies, ink and pigments, coatings and additives, ultrafine polishing compounds, UV absorber for sunscreens, synthetic bone, ferro fluids, optical fiber cladding and cosmetics. Applications currently entering in widespread uses includes: fibers and their treatments, filtration, dental materials, surface disinfectants, diesel and additives, hazardous chemical neutralizers, automotive components, electronics, scientific instruments, sports equipments, flat panel displays, drug delivery system and pharmaceuticals.

1.6 Metal oxide nanoparticles

Metal oxides constitute a class of inorganic materials that have an extraordinary range of properties and are therefore used in many technological applications. The metal oxides constitute a diverse and fascinating class of materials whose properties cover the entire range from metals to semiconductors. Their surfaces play crucial roles in an extremely wide range of phenomena. The study of transition metal oxides play a very important role in many areas of chemistry, physics and materials science and often exhibit enhanced physical, chemical, thermal, electrical, optical or magnetic properties, which lead to the extensive applications in electrochemistry, biomedical device and other fields of technological importance. The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator characteristics. Metal
oxides are also themselves catalysts for a variety of commercially important reactions. The current knowledge on oxide materials allows affirming that most of their physico-chemical properties display acute size dependence. Physico-chemical properties of special relevance in chemistry are mostly related to the industrial use of oxides as sensors, ceramics, absorbents and/or catalysts.

When the dimensions of metal oxide particles decrease to the nanoscale range, there are significant changes in its optical and electronic properties due to both quantum and size effects. This is mainly due to the increasing role of the surface in controlling the overall energy of the particles. The remarkable stability of nanoparticles in solution might be explained by the lack of defects on the surface, the strong surface passivation or the altered surface composition due to adsorption of surfactants or oxidation.

In the present work the adsorption and photocatalytic properties of metal oxide nanoparticles have been exploited for the removal of commercial dyes widely used in textile industries. The general theory and principles of adsorption and photocatalytic processes have been discussed below.

### 1.7 Adsorption – a surface phenomenon

Adsorption arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Thus, when a solid surface is brought into contact with a liquid or gas, there is an interaction between the field of forces of the solid surface and that of liquid or gas. The solid surface tends to satisfy these residual forces by attracting and retaining the molecules, atoms or ions of the gas or liquid on its surface [57]. Adsorption is a mass transfer operation where, constituent in the liquid phase is transferred to the solid phase. The adsorbate is the substance that is being removed from
the liquid phase at the interface and the adsorbent is the solid onto which the adsorbate accumulates. The interaction of ions in the hydrosphere with solid components is influenced by various factors. These factors are related with the properties of water (temperature, pH), the speciation of ions and their concentrations, the structural characteristics of the solid components like porosity, surface area, swelling, grain size, in addition to them, factors that include are period of contact, degree of mixing and solid/liquid ratio.

The adsorption process generally takes place in four definable steps: (1) bulk solution transport, (2) film diffusion transport, (3) pore transport and (4) adsorption. Bulk solution transport involves the movement of material to be adsorbed through bulk liquid to the boundary layer. Film diffusion transport, involves the transport of material by diffusion through stagnant liquid film to entrance of the pores of adsorbent. Pore transport involves transport of material through the pores by molecular diffusion along the surface of adsorbent. Adsorption can occur on outer surface of adsorbent and in macropores, mesopores, micropores and submicropores [58].

1.8 Adsorption characteristics

Depending upon the nature of forces involved, the adsorption is of two types: physisorption and chemisorption. Physisorption occurs whenever an adsorbable fluid (the adsorptive) is brought into contact with the surface of the adsorbent. The intermolecular forces involved are of the same kind as those responsible for the imperfection of real gases and the condensation of vapours. The molecules are adsorbed when their potential energy is at a minimum. In addition to attractive dispersion forces and short range repulsive forces, the so called van der Waals forces, dipole–dipole, induced dipole–
induced dipole and dipole–induced dipole interactions all occur as a result of particular geometric and electronic properties of the adsorbent and adsorbate.

Chemisorption, involves exchange or sharing of electrons between the adsorbate molecules and the surface of adsorbent resulting in a chemical reaction. The bond formed between adsorbate and the adsorbent is essentially a chemical bond and is thus much stronger than physisorption.

Adsorption proceeds through three steps: (a) mass transfer – adsorbate molecules transfer to the exterior of the adsorbent, (b) intragranular diffusion – molecules move into the pores of adsorbent and (c) physical / chemical adsorption. The adsorption process is dependent on several factors which govern the nature and extent of adsorption. The factors which affect adsorption include (i) physical and chemical characteristics of the adsorbent and adsorbate and (ii) concentration of the adsorbate, temperature, concentration, pH, etc [59].

A proper understanding of the adsorption process and design of adsorption equipment demands knowledge of equilibrium isotherms, adsorption kinetics and thermodynamics. The first determines the adsorption capacity and the second determines the adsorption velocity and the later determines the feasibility of the process.

1.8.1 Adsorption Equilibrium

When a solid surface is exposed to a gas/liquid, the molecules strike the surface of the solid. Some of the striking molecules stick to the solid surface and become adsorbed while the others rebound. Initially the rate of adsorption is large as the whole surface is
bare but as more and more of the surface becomes covered by the molecules, the available surface decreases and so does the rate of adsorption.

As time passes, the rate of adsorption continues to decrease while the rate of desorption increases until an equilibrium is reached between the rate of adsorption and the rate of desorption. At this stage the solid is in adsorption equilibrium with the gas/liquid molecules and the rate of adsorption is equal to the rate of desorption. It is a dynamic equilibrium because the number of molecules sticking to the surface is equal to the number of molecules rebounding from the surface. For a given adsorbate-adsorbent system, the equilibrium amount adsorbed \((x/m)\) is a function of pressure and temperature and is given by [60]:

\[
\frac{x}{m} = f(P, T)
\]  

(1.1)

where, \(x/m\) is the amount of adsorbate adsorbed per unit mass of the adsorbent at equilibrium pressure \(P\) and temperature \(T\).

The adsorption equilibrium can be approached in three different ways: adsorption isotherm (at constant \(T\)), adsorption isobar (at constant \(P\) or \(C\)) and adsorption isostere (at constant \(x/m\)).

As the amount of adsorbate adsorbed at the equilibrium for a given adsorbate-adsorbent system depends upon the pressure \((P)\) of the gas or concentration \((C)\) of the solution and the temperature of adsorption, the adsorption equilibrium can be represented as an adsorption isotherm at constant temperature, the adsorption isobar at constant pressure and the adsorption isostere for a constant equilibrium adsorption. In actual practice the determination of adsorption at constant temperature is most convenient and
therefore, the adsorption isotherm is the most extensively employed method for representing the equilibrium state of an adsorption system.

**Adsorption Isotherm**

If the temperature is kept constant, then for a given adsorbent-adsorbate system \( x/m \) depends on the equilibrium pressure or concentration, such equilibrium is called an adsorption isotherm (Figure 1.1) and the equilibrium can be represented by the following equation at constant \( T \) [61].

\[
\frac{x}{m} = f(P \text{ or } C)
\]  

(1.2)

![Figure 1.1: A typical adsorption isotherm.](image)

Adsorption is usually described by an isotherm which shows the amount of adsorbate adsorbed by the adsorbent at a given temperature. An adsorption isotherm relates the concentration of solute on the surface of adsorbent to the concentration of
solute in the bulk with which the adsorbent is in contact. These values are usually
determined experimentally, but there are also models to predict them, both for single
component adsorption and multi component adsorption.

Although the Langmuir and the Freundlich adsorption isotherms are the two well
established types of adsorption isotherms for a given adsorbate, there are many other
equations available to model adsorption equilibrium. Adsorption isotherms are the
mathematical models that describe the distribution of adsorbate species among liquid and
solid phases, based on a set of assumptions that are related to the
heterogeneity/homogeneity of the solid surface, type of coverage and possibility of
interaction between the adsorbate species.

**Langmuir isotherm**

The Langmuir isotherm equation is the first theoretically developed adsorption isotherm.
Many other isotherm equations were proposed later and all of them are either based on
Langmuir equation or have been developed using the Langmuir concept. Thus, the
Langmuir equation still retains an important position in physisorption as well as
chemisorption theories. The equation has also been derived using thermodynamic and
statistical approaches. An American scientist I. Langmuir derived this equation based on
certain assumptions such as:

- The adsorbed entities (atoms or molecules or ions) are attached to the surface at
definite localized sites.
- Each site accommodates one and only one adsorbed entity.
The energy state of each adsorbed entity is the same at all sites on the surface independent of the presence or absence of other absorbed entities at neighboring sites.

Thus, the Langmuir model (also called localized model) assumes that the surface is perfectly smooth and homogenous and that the lateral interactions between the adsorbed entities are negligible [62]. The mathematical equation for Langmuir adsorption isotherm is given by the following equation [63].

\[
q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{1.3}
\]

where, \(C_e\) : Equilibrium concentration of adsorbate in the bulk phase after adsorption (mg L\(^{-1}\)),

\(q_e\) : Amount of dye adsorbed per unit weight of adsorbent at equilibrium (mg g\(^{-1}\)),

\(K_L\) : Empirical Langmuir constant related to affinity of binding sites (L g\(^{-1}\)) and

\(a_L\) : Empirical Langmuir isotherm constant (L g\(^{-1}\)).

Characteristic constants of Langmuir equation, \(K_L\) and \(a_L\) can be determined from the linearized form of equation given below (1.4).

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{1.4}
\]

The slope and intercept of the linear plot of \(C_e/q_e\) versus \(C_e\) gives the values of \(a_L/K_L\) and \(1/K_L\) respectively. The theoretical maximum adsorption capacity \(q_{\text{max}}\) corresponding to Langmuir constants is numerically equal to \(K_L/a_L\).
Freundlich isotherm

The Freundlich isotherm describes the physical adsorption from liquids. This empirical isotherm can be used for non-ideal sorption that involves heterogeneous adsorption from solution phase. Freundlich isotherm is represented by the following equation [64].

\[ q_e = K_f C_e^{1/n} \]  \hspace{1cm} (1.5)

where, 
- \( C_e \): Equilibrium concentration of adsorbate in the bulk phase after adsorption (mg L\(^{-1}\)),
- \( q_e \): Amount of dye adsorbed per unit weight of adsorbent at equilibrium (mg g\(^{-1}\)),
- \( K_f \): Empirical Freundlich constant or capacity factor (mg g\(^{-1}\)) and
- \( 1/n \): Freundlich exponent, it is an index of the feasibility of adsorption of a given system which varies between zero and one.

The Freundlich equation does not consider all sites on the adsorbent surface to be equal. Furthermore, it is assumed that, once the surface is covered the additional adsorbed species can still be accommodated. In other words, multilayer adsorption is predicted by this equation [65, 66]. The good fit of Freundlich isotherm to an adsorption system means there is almost no limit to the amount of adsorbate and there is a multilayer adsorption.

The applicability of Freundlich equation to a particular case is tested by plotting \( \log q_e \) versus \( \log C_e \) from the logarithmic form of equation 1.6.

\[ \log q_e = \frac{1}{n} \log C_e + \log K_f \]  \hspace{1cm} (1.6)
Such a plot should yield a straight line with an intercept equal to $\log K_f$ and slope equal to $1/n$.

1.8.2 Adsorption Kinetics

The dye sorption kinetics are influenced by sorption reactions and the mass transfer steps that govern the transfer of dyes from bulk solution to the sorption sites on surface and inside the adsorbent particles, i.e. external and intra-particle diffusion. In turn, these mechanisms depend on the physical form and the intrinsic structure of the adsorbent, nature of the dye and the solution, as well as the process conditions (temperature and pH). Simplified models can be used to test experimental data and identify the rate-controlling mechanisms for the adsorption process. Of these models, the pseudo first-order model, the pseudo second-order model and the intra-particle diffusion model are the most widely used kinetic models to describe the sorption of dyes [67]. The kinetics of adsorption process can be studied by carrying out a separate set of adsorption experiments at constant temperature. The adsorption rate can be determined quantitatively and tested by the pseudo-first-order and pseudo-second-order models. This information is useful for further applications of system design in the treatment of groundwater and waste effluents.

Pseudo-First-Order Model

The pseudo-first-order kinetic model has been used to predict the dye adsorption kinetics. The pseudo-first-order model is given by the equation [68]:

$$\frac{d_q}{dt} = k_1(q_e - q)$$  \hspace{1cm} (1.7)
where, $q$: Amount of dye adsorbed at any time $t$ (mg $\text{g}^{-1}$),

$q_e$: Amount of dye adsorbed at equilibrium (mg $\text{g}^{-1}$) and

$k_1$: Pseudo-first-order rate constant (min$^{-1}$).

Integrating equation 1.7 with respect to boundary conditions $q=0$ at $t=0$ and $q=q_e$ at $t=t_e$, the above equation becomes:

$$\ln\left(\frac{q_e}{q_e - q}\right) = k_1 t$$  \hspace{1cm} (1.8)

On applying the logarithm on both the sides of equation 1.8, it follows:

$$\log(q_e - q) = \log q_e - \left(\frac{k_1}{2.303 t}\right)$$  \hspace{1cm} (1.9)

The values of $k_1$ and $q_e$ can be calculated from the slope and intercept of the linear plot of $\log(q_e - q)$ versus $t$.

**Pseudo-Second-Order Model**

The adsorption kinetic data can be further analyzed using pseudo-second-order kinetic model and it is represented by the following equation [69]:

$$\frac{dq}{dt} = k_2 (q_e - q)^2$$  \hspace{1cm} (1.10)

where, $q$: Amount of dye adsorbed at any time $t$ (mg $\text{g}^{-1}$),

$q_e$: Amount of dye adsorbed at equilibrium time (mg $\text{g}^{-1}$) and

$k_2$: Pseudo-second-order rate constant (g mg$^{-1}$ min$^{-1}$).

Separating the variable in equation 1.10 gives:
\[
\frac{d_q}{(q_e-q)^2} = k_2(d_t)
\]  

(1.11)

Integrating equation 1.11 at boundary conditions \( t=0 \) to \( t=t \) and \( q=0 \) to \( q=q \) gives

\[
\frac{t}{q} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]

(1.12)

The values of \( k_2 \) can be determined from the linear plot of \( t/q \) versus \( t \).

**Intra-Particle diffusion Model**

The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting the experimental data in an intra-particle diffusion plot. Previous studies by various researchers showed that the plot of \( q_t \) versus \( t^{0.5} \) may sometimes exhibit multi-linearity, which characterizes two or more steps involved in the adsorption process [70]. According to Weber and Morris an intra-particle diffusion coefficient \( K_i \) is defined by the equation:

\[
q_t = k_i t^{0.5} + C
\]

(1.13)

where, \( q_t \) : Amount of dye adsorbed at any time \( t \) (mg g\(^{-1}\)),

\( k_i \) : Intra-particle diffusion rate constant (mg g\(^{-1}\) min\(^{-1/2}\)) and

\( C \) : Boundary layer thickness.

Upon fitting the data to equation 1.13, two or three steps may sometimes occur in a plot. The first portion represents external surface adsorption or an instantaneous adsorption stage. The second portion is a gradual adsorption stage, where the intra-particle diffusion is the controlling factor. The third portion is a final equilibrium stage.
where the intra-particle diffusion starts to decelerate due to the extremely low solute concentrations in the solution [71, 72].

1.8.3 Adsorption Thermodynamics

For designing adsorption column or batch adsorption systems, the designer should be able to understand the following: what changes can be expected to occur and how fast will they take place. The fastness of the reaction can be calculated from the knowledge of kinetic studies. But the changes in reaction that can be expected during the process require a brief idea of thermodynamic parameters. The concept of thermodynamics assumes that in an isolated system where energy cannot be gained or lost, the entropy change is the driving force [73]. The thermodynamic parameters that must be considered to determine the process are enthalpy of adsorption ($\Delta H^\circ$), free energy change ($\Delta G^\circ$) and entropy change ($\Delta S^\circ$) that occur due to the transfer of unit mole of solute from solution to the solid–liquid interface.

The thermodynamic function $\Delta H^\circ$ is very useful whenever there is a differential change in the heat content of the system. Enthalpy is an additive property that is its value is preservative. The negative value of $\Delta H^\circ$ indicates the exothermic process and positive value indicates the endothermic process. The parameter $\Delta G^\circ$ is used to identify the spontaneity of adsorption process. The values of $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ are computed using the following equation [74].

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT}$$  \hspace{1cm} (1.14)

where, $R$ : Universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$),
\( T \) : Absolute temperature (K) and

\( K_C \) : Distribution coefficient.

The distribution coefficient \( K_C \) can be calculated by the following equation:

\[
K_C = \frac{q_e}{C_e}
\]  

(1.15)

where, \( q_e \) : Amount of dyes adsorbed per unit weight of solid (mg g\(^{-1}\)) and

\( C_e \) : Equilibrium concentration of solute in solution (mg L\(^{-1}\)).

The values of \( \Delta H^0 \) and \( \Delta S^0 \) were obtained from the slope and intercept of van’t Hoff plot of \( \log K_C \) versus \( 1/T \). Another most important thermodynamic parameter involved in the adsorption process is the free energy change and can be calculated using the relation:

\[
\Delta G^0 = -RT \ln K_C
\]  

(1.16)

where, \( R \) : Universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)),

\( T \) : Absolute temperature in K,

\( K_C \) : Equilibrium constant and

\( \Delta G^0 \) : Gibbs free energy change.

As the particle shrinks to the nanometer range, an increasing fraction of atoms are exposed to the surface, giving rise to excess energy. Consequently, nanoparticles are thermodynamically metastable compared to macro crystalline materials. They tend to approach the minimum free energy state (equilibrium state) through several ways such as: phase transformation, crystal growth, surface structural changes, aggregation and surface adsorption. Therefore, nanoparticles with a higher total energy should be more prone to
adsorb molecules onto their surfaces in order to decrease the total free energy. Hence, adsorption should be favored on nanoparticles [75].

1.9 Adsorption of Dyes

Adsorption on activated carbon has attracted much attention in recent times. Activated carbon in its broadest sense includes a wide range of processed amorphous carbon-based materials. It is not truly an amorphous material but has a microcrystalline structure. Activated carbon has high porosity and an extended inter-particulate surface area [76]. Although, the adsorption on activated carbon is considered to be a particularly competitive and effective process for the removal of pollutants in trace quantities, the use of activated carbon is not suitable in developing countries due to high cost associated with the production and regeneration of spent carbon [77, 78]. Therefore, searching for low-cost and effective adsorbents should be of considerable significance for practical application of adsorption [79].

The growing importance of adsorption (e.g. in separation technology, industrial catalysis and pollution control) has resulted in the appearance of an ever increasing volume of scientific and technical literature on novel adsorbents and catalysts. Also, various new procedures have been introduced over the past few years for the interpretation of adsorption data. Researchers have shown the use of materials like walnut husk [80], composites [81], biochars from crop residues [82], natural clinoptilolite [83], sesame hull [84], biomass of Penicillium YW01 [85], natural zeolite [86], cross-linked succinyl chitosan [87], modified bentonite [88], modified attapulgite [89], clay material [90-92], activated carbon [93], dehydrated beet pulp carbon [94], polyurethane foam [95] etc., as adsorbents for the removal of dyes from wastewater.
1.10 Heterogeneous photocatalysis

Heterogeneous photocatalysis is another important application of semiconducting metal oxide nanoparticles. In the photocatalytic degradation of dye using UV irradiation, electron in the semiconductor is excited from the valence band to the conduction band. The electrons in the conduction band reacts with the adsorbed oxygen molecule to form \( \text{O}_2^- \) species, while the positive holes react with the adsorbed hydroxyl ions to produce hydroxyl radicals. The highly reactive hydroxyl radicals have the ability to oxidise the organic pollutants in the surrounding environment. Photocatalyst has shown great promise as an innovative and green technology due to its ability to generate electron and holes under UV illumination which can produce radical and initiate the redox reaction to degrade trace level environment pollutants [96].

A photocatalyst can transform light energy into chemical energy by creating strong oxidative and reductive species which greatly enhance the rate of the spontaneous reaction. During this transformation the photocatalyst itself remains unchanged. Photocatalysts are heterogenous catalysts usually in the form of a powder or a thin film. Studies related to photocatalysis have increased immensely over the past few years and currently well over 1000 research papers are published annually [97]. Photocatalytic materials have raised a lot of attention lately in the application areas such as air and water purification and sterilization. Also, photocatalytic self-cleaning windows, tiles and building materials are currently being used in many locations to tackle various fouling and pollution related problems.

Many semiconductors, due to their electronic structure (filled valence band and empty conduction band) can act as a catalyst for photoinduced processes (\( \text{TiO}_2 \), \( \text{ZnO} \), etc.).
Fe\(_2\)O\(_3\), WO\(_3\), CdS, SiO\(_2\) or ZrO\(_2\), etc.) [98]. Among those, zinc oxide (ZnO) and titanium dioxide (TiO\(_2\)) are two well-known semiconductors that have shown merits of high photosensitivity, non-toxic nature, low-cost and eco-friendly features for photocatalytic applications. However, the band gap energies are large (about 3.2 eV), which means that both the semiconductors can only be excited for photocatalytic uses under UV light illumination with the wavelength equal to or less than 385 nm. Gouvea et al. [99] have reported that the photocatalytic activity of nano-ZnO was higher than nano-TiO\(_2\). They also used three methods to prepare nano-ZnO and the results indicated that the smaller particle size could lead to higher photocatalytic activity.

ZnO has several drawbacks including the fast recombination rate of photogenerated electron-hole pair and a low quantum yield in the reactions, which seriously obstruct commercialization of the photocatalytic degradation process [100]. Consequently, there has been a lot of interest in improving the photocatalytic activity by suitable modification of semiconductors for the degradation. It has been found that the interfacial electron transfer efficiency and rate of the recombination of electron–hole pairs of semiconductor materials can be easily tuned by various surface modification methods such as surface chelation, surface derivatization, platinization, selective metal ion and nitrogen doping [101-103]. It has also been demonstrated that the presence of heavy metals such as Pt, Pd, Au and Ag on semiconducting metal oxides can enhance the degradation efficiency of photocatalytic reactions [104].

The most widely used and practically applicable catalysts were nano-sized TiO\(_2\) and TiO\(_2\)-based catalysts, due to their chemical stability, non-toxicity, chemical reactivity and low price. The photoinduced phenomena (photocatalysis, photovoltaics, and
superhydrophilicity) occurring on the catalyst surface according to the way of action of generated electron-hole pairs will determine the possible application of nano-sized TiO$_2$ and TiO$_2$-based catalysts.

1.11 Thesis outline

The present work is an attempt to explore the possibilities of using metal oxide nanoparticles in dye wastewater treatment. The nano-sized metal oxides such as MgO, Al$_2$O$_3$, ZnO and TiO$_2$ were synthesized via different techniques and employed for the removal/degradation of textile dyes. The textile dyes from reactive, vat and acid dye families were chosen as model organic pollutants in the present study. Properties like high surface area and wide band gap exhibited by metal oxides at the nanoscale level were exploited to achieve removal/degradation of dyes from their aqueous solutions.
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