

NANOTECHNOLOGY

Abstract

Nanotechnology, the manipulation of matter at the nanoscale, has emerged as a revolutionary field with profound implications across various disciplines. This abstract explores the fundamental principles of nanotechnology, its applications, and the transformative impact it holds for science, industry, and society. The ability to engineer materials at the molecular and atomic levels unlocks unprecedented possibilities, ranging from advanced medical diagnostics and treatments to innovative energy solutions and enhanced electronic devices. This abstract delves into key nanotechnological concepts, recent advancements, and the potential ethical considerations that accompany such transformative power. As nanotechnology continues to evolve, its multidisciplinary nature promises to reshape our understanding of the physical world and redefine the boundaries of technological innovation.

Keywords: Nanotechnology, Nanomaterials, Water pollution, Nano metal oxides

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I. INTRODUCTION

General Introduction: This chapter describes the significance of water and its pollution. The various types of pollutants present in water are described briefly. The environmental effects caused due to the presence of dyes in water and the various methods employed for their removal are discussed. The basic concepts related to nanotechnology, in particular nano metal oxides with special emphasis on nanocrystalline ZnO, α -Fe₂O₃ and nanocomposites are described. The need for the study and objectives of the present work are discussed at the end of the chapter.

II. WATER POLLUTION

Water is one of the important constituents and fundamental requirements for the survival of living beings. It is one of the precious gifts of nature. Water used for various purposes must be free from various types of pollutants and pathogens. The presence of these pollutants in water leads to various health hazards. Clean water is not only essential to human beings and other living beings, but is also a critical feedstock in various industries including electronics, pharmaceuticals and food. In addition to this, agricultural production mainly relies on the availability of clean water. The addition of any undesirable chemical substance to water results in its contamination and makes it unfit not only for human consumption but also for other living beings. Water usually contains some amount of physical, chemical and biological impurities. The quality of water is defined by the level of physical, chemical and biological impurities present in it. The water quality affects the health of living organisms since a number of diseases are caused due to the toxic chemicals and pathogens transmitted by water. The physical properties of water include color, turbidity, taste, temperature, pH and electrical conductivity. The chemical constituents include dissolved salts, dissolved gases, organic matter etc. It has been reported that all activities carried out on the land surface have the potential to pollute water. These activities may be associated with urban, industrial or agricultural land uses.

Industries consume large quantities of water for various industrial processes. However, only a small quantity of this water is incorporated in their products and is lost due to evaporation. The rest of the water reaches the water bodies as wastewater. These industrial wastes either join the streams or other natural water bodies either directly/or are emptied into the municipal sewers. These industrial wastes in some way or the other affect the normal life of a stream or the normal functioning of a sewerage and sewage treatment plant. The main cause for the contamination of surface and ground water is the discharge from industries. The characteristics of industrial wastes not only depend on the type of industry but also vary from plant to plant resulting in the production of same type of end products.

The pollutants from industries can be classified as follows:

- Organic compounds that result in the depletion of dissolved oxygen content of the receiving streams.
- Inorganic compounds such as carbonates, chlorides, nitrogen etc. the presence of which makes the water unfit for use.
- Acids or alkalis that make the receiving stream unsuitable for the growth of fish as

well as other aquatic organisms.

- Toxic substances such as cyanides, sulphides, acetylene, alcohols, petrol etc. that lead to damage of the flora and fauna of the receiving streams and also sometimes endanger the health and safety of the workmen.
- Colour producing substances such as dyes which impart colour and sometimes release carcinogenic substances into the water.
- Oil and floating substances which interfere in the self-purification process of the streams.

The pollutants can be broadly classified as biodegradable and non-biodegradable. The biodegradable substances can be broken down to harmless products. On the contrary, the removal of non-biodegradable organic chemicals is one of the challenging tasks for the environmental scientists.¹⁻³

III. NANOTECHNOLOGY AND NANOMATERIALS

In 1959, renowned physicist and Nobel Prize winner Richard P. Feynman said in his famous speech: "There is Plenty of Room at the Bottom." However, not much progress was made in the field of nanoscience and nanotechnology until 1980's when the scanning tunneling microscope (STM) was invented. This was due to the fact that not many suitable analytical tools were available for the investigation of materials at the nanometer scale. After the invention of STM, a number of highly advanced analytical tools were developed rapidly, which enabled the characterization and manipulation of small objects in the nanometer scale thus enabling the human being to view the real atomic world. An important result of the rapid developments in nanoscience is that nanotechnology had its breakthrough before the start of the new century. Presently, a number of important techniques including the self-assembly technique, nanoscale crystal growth technique and nanoimprint lithography are already available which enable large scale production of nanoscale products indicating the great potential of nanotechnology in real applications.

The term nanotechnology encompasses all the chemistry and physics of nanostructured materials. Nanotechnology has remarkably changed all the perspectives of the way of our thinking in science and technology and will definitely bring more and more astonishing facts into our daily life as well as in the world in future. The term "Nano" refers to one billionth (10^{-9}) of a meter and is expressed as 1 nm. 1 nanometer is so small that things which are smaller than it can only be molecules, clusters of atoms or particles in the quantum world. Hence, nanometer can be considered as a special point in the overall length scale since the nanometer scale is the junction between the smallest manufacturable objects and the largest molecules in nature.

When matter is arranged by exercising control over lengths of 1 to 100 nm and the resulting structures exhibit characteristics that are specific to their size and dimensions, the resulting materials are termed as nanomaterials. These nanomaterials have at least one dimension in the nanometer scale and are possibly the smallest solid materials that are being produced till date. Additionally, in the nanometer scale, the properties of materials such as colour, melting point, electronic, catalytic or magnetic properties will change dramatically or be replaced by completely novel properties due to size effect. Hence it can be considered that at the nanometer scale, everything, regardless of what it is, exhibits new properties.

Therefore, nanomaterials create a bridge between molecular and bulk materials.^{4,5}

There are two types of nanomaterials namely; inorganic and organic. Inorganic nanomaterials refer to nanostructures formulated purely by inorganic materials. Examples of inorganic nanomaterials include carbon nanotubes and nanowires, metal oxides etc. Organic nanomaterials are nanostructures of carbon compounds. When the particle size is reduced to a few nm, the constituting atoms will have highly defective coordination environments. Since the valencies of most of these atoms are unsatisfied, they are present on the surface. Depending on the synthetic route employed for the synthesis of nanomaterials, the changes in the morphology such as reduction in the grain size, presence of large number of interfaces and grain boundary junctions, pores and various lattice defects impart unique physical and chemical properties to them.

Nanomaterials encompass a wide range of materials in the domain of nanometers. However, nanoparticles are always being regarded as one of a few core materials both in nanoscience and nanotechnology. This is because in addition to their small size, nanoparticles exhibit the most popular morphology of the nanoscale world and are ideal manipulable building blocks for the construction of larger devices, structures and systems by what is referred to as the “bottom-up” approach in nanotechnology. A number of developments related to the synthesis of nanoparticles such as the synthesis of carbon nanotubes and quantum dots or the shape controlled synthesis of CeSe nanocrystals are being regarded as milestones in the history of nanoscience which further reflects the importance of the role played by nanoparticles in nanoscience.⁶⁻⁹

Nanomaterials can be produced either by the “top-down” approach or the “bottom-up” approach. The top-down approach involves the production of very small structures starting with a large part of the material by the process of mass removal. The bottom-up approach involves the production of nanomaterials by building up atom by atom, molecule by molecule. The bottom-up approach involves self-assembling in which the atoms or molecules are able to create structures according to their natural properties.

The major challenge facing the top-down approach is the creation of small structures with sufficient precision. On the contrary, the main challenge of the bottom-up approach is the creation of large structures with a good quality and resistance that can be used as nanomaterials.¹⁰

Applications of Nanomaterials: Nanomaterials find a number of applications in various fields. Some of these applications include the following:

- Nanomaterials are used as thin films of coverage, for example in electronics and as active surfaces such as windows self-cleaning. In many cases, the nanomaterials are bound or placed on some supports, but some types of nanoparticles are used free, like in sunscreens to absorb the UV radiations from the sunlight, thus protecting the skin from diseases carried by a typical long exposure to sunlight.
- Nanomaterials find applications in information technology, automobile and aerospace industry.
- They increase the performance of a variety of products such as silicon electronics, microsensors, display systems, catalysts and paints.
- Carbon nanotubes possess great resistance, good flexibility and high electrical

conductivity. These can revolutionize the field of electronics and communication.

- Nanomaterials can be used in metrology to find the morphology and electrical characterization of a number of materials.
- Nanomaterials are used in magnetic storage devices.
- Quantum dots are semiconductor nanoparticles which can be adjusted to emit or absorb light of a particular wavelength. These quantum dots can be used in solar cells or in fluorescence labeling for biological experiments.
- In medicine, nanomaterials are used in diagnosis of diseases, drug delivery in specific areas of the body and molecular imaging.
- In medical field, nanoparticles find applications in fluorescence biomarker, controlled drug release and gene therapy, photogenic bio-sensors, genetic structure probe, tissue engineering, hyperthermia, separation and purification of biomolecules or cells, MRI contrast agents, phagokinetic tracks etc.
- Nanoparticles can be functionalized (with a recognition system and a determine molecule) in order to concentrate the drug or the nanoparticles into a specific cell or part of the body. The release of the drug or the manipulation of the nanoparticles is usually controlled by various techniques such as pH, ultrasounds, magnetic fields etc.
- Graphene and carbon nanotubes are composed of carbon monolayers in two configurations: as monolayer (graphene) or tube (carbon nanotube). The physico-chemical properties of these materials make them highly useful materials in various fields, particularly in material science where new and more efficient materials are being developed.
- Nanoparticles are highly useful in heterogeneous catalysis since they exhibit large surface area to volume ratios. Additionally, the electronic atomic configuration of these materials makes them specific toward particular processes.
- Magnetic nanostructured systems are important in the development of faster writing-reading systems with high density of information storage mainly due to the reduction in bit size.^{11,12}

IV. NANO METAL OXIDES

Nano metal oxides represent an important class of inorganic nanomaterials. These nano metal oxides exhibit catalytic, optical, electrical, magnetic and mechanical properties which make them technologically useful materials particularly in the field of material science. The physical and chemical properties of these nano metal oxides are greatly affected by their structure and this relation has a great significance. For example, MgO, CaO and ZnO nano metal oxides are being used as adsorbents in defluoridation, reduction in chemical oxygen demand (COD) and removal of colour from drinking water as well as various industrial effluents.

The large surface area to volume ratio makes these nano metal oxides efficient catalysts in various chemical reactions. They possess excellent sintering characteristics and hence find applications in the manufacture of ceramics and composite materials. The dispersion of various fluids results in the formation of thin films and corrosion resistant coatings. Recently, these nano metal oxides have drawn the attention of many researchers across the world. It has been well established that a decrease in size of particles leads to remarkable variations in the properties of materials.

Some of these properties are as follows:

- Enhancement in catalytic activity.
- Enhancement in mechanical reinforcement.
- Enhancement in electrical conductivity in ceramics.
- Reduction in conductivity of metals.
- Enhancement in photocatalytic activity.
- Enhancement in luminescence of semiconductors.
- Super paramagnetic behaviour of magnetic oxides.^{13,14}

1. ZnO Nanoparticles: ZnO is one of the important inorganic compounds and is available in the form of a white powder. In the earth's crust, ZnO is present as the mineral zincite. However, most of the commercially used ZnO is being produced by synthetic methods. Crystalline ZnO exhibits thermochromic property and a change of colour from white to yellow on heating and reverts back to the white colour when cooled in air. This change in colour is attributed to the fact that at high temperature ZnO loses very small amount of oxygen to form $Zn_{1-x}O$ (where $x = 0.00007$ at $800^{\circ}C$).

The three different crystalline forms of ZnO include the hexagonal wurtzite, the cubic zinc blende and the cubic rock salt structure. Under ambient conditions, the hexagonal wurtzite structure (Figure 1.1) is the most common form of ZnO. Additionally, the zinc blende structure can be stabilized by the growth of ZnO on substrates having the cubic lattice structure. The ZnO centres are tetrahedral in both the wurtzite and the zinc blende structures. The rock salt structure is observed only at relatively high pressures of the order of 10 GPa.

The wurtzite and zinc blende polymorphs do not possess any inversion symmetry. The absence of inversion symmetry and other properties results in piezoelectric properties of these structures. In case of the wurtzite structure ($a = 3.249\text{\AA}$ and $c = 5.206\text{\AA}$), the ratio $c/a \sim 1.60$ is much closer to the ideal value of $c/a = 1.633$ for the hexagonal cell. The Zn-O bond is largely ionic in nature which makes ZnO a strong piezoelectric material. The polarity of the Zn-O bond renders positive and negative charges respectively to the Zn and O planes. In most of the relative materials, electrical neutrality is maintained by the reconstruction of these planes at the atomic level. However, in case of ZnO there is no reconstruction of the planes and the surfaces are atomically flat and stable. This anomalous property of ZnO is however, not yet fully explained.

In view of its excellent optical, electrical and chemical properties ZnO is widely used in optical devices, sensors, piezoelectric devices, transparent electrodes, surface acoustic wave devices, solar cells and so on. It also exhibits good antibacterial activity. ZnO is widely used as an additive to several materials such as glass, cement, ceramics, paints, pigments, rubber, plastics, adhesives, ointments, sealants, batteries, ferrites, fire retardants, first aid tapes etc. It is also used as a source of zinc in various food products. Thin films of ZnO nanoparticles find applications as substrates in functional coatings, optical communications, printing inks, e-print and portable energy devices etc.

Nanoparticles of ZnO are used as pigments and UV light absorbing materials in paints, coatings and personal care products. As the particle size of the ZnO nanoparticles decreases, both their UV absorption efficiency and transparency to visible light increase. ZnO exhibits wide band gap energy (E_g) which makes it an important photocatalyst. In view of this, the ZnO nanoparticles are widely used in wastewater treatment for the photocatalytic degradation of a number of organic pollutants and dyes either in the presence of UV light or sunlight.¹⁵⁻¹⁷

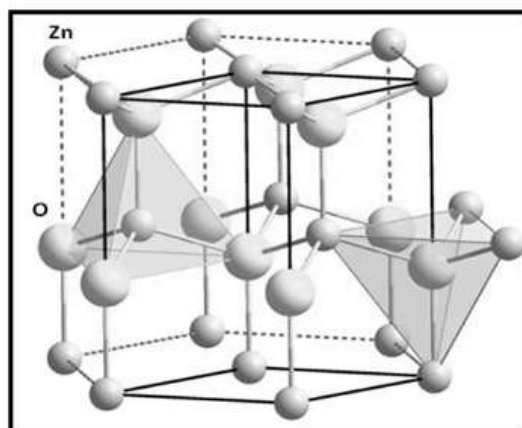


Figure 1: Wurtzite structure of ZnO

Zinc oxide has been widely investigated due to its properties of conductivity, optical absorption and emission, piezoelectricity and catalytic activity¹⁸. The synthesis of a variety of ZnO nano/microstructures such as nanorods, nanotubes, nanowires, lotus like, flower like and brush pen-like nanoparticles by different methods such as hydrothermal, thermal evaporation process and wet chemical methods has been reported.^{19,20}

The quantum efficiency of ZnO is greater than that of TiO₂. So far as the band gap energy (E_g) is concerned ZnO can be a better alternative to TiO₂. Additionally, ZnO can absorb over a larger fraction of the solar spectrum than TiO₂. It is due to this reason that ZnO can be used as a suitable photocatalyst for the degradation of various pollutants in wastewater in the presence of sunlight.²¹

The potential of ZnO in the removal of organic pollutants from wastewater has been extensively studied.²¹⁻²⁴ Recently, the emitting properties of ZnO are being used in setting up original catalytic system which has the ability to “sense and shoot” environmental pollutants thus paving the way for further exploration of its properties.

However, the susceptibility of ZnO to dissolve in water under highly alkaline conditions and its photocorrosion with subsequent release of Zn⁺² ions into the environment is a major obstacle in making it a competitively useful photocatalytic material.²⁵

In the present work, ZnO nanopowder was prepared by solution combustion

synthesis using zinc nitrate as oxidizer and oxalyldihydrazide (ODH) as fuel.

- 2. α -Fe₂O₃ Nanoparticles:** α -Fe₂O₃ is the highly stable form of iron oxide and possesses n-type semiconducting properties with a band gap of around 2.1eV under ambient conditions. The conduction band of α -Fe₂O₃ has empty d-orbitals of Fe⁺³ whereas valence band has the occupied 3d crystal field orbitals of Fe⁺³ along with some admixture from the 2p non-bonding orbitals of O.²⁶⁻²⁹ The potential applications of α -Fe₂O₃ include photocatalysis, gas sensors, lithium ion battery and production of magnetic materials. The magnetic properties of α -Fe₂O₃ have also been studied extensively both in bulk and nanoparticle form.³⁰⁻³³

α -Fe₂O₃ nanoparticles have attracted the attention of researchers working in the fields of nanoscience and nanotechnology due to their unique properties including superparamagnetism, high saturation fields and extra anisotropy contributions. These properties are the result of the effects of finite size and large surface area and make them highly useful materials in many areas including catalysis, magnetism, photocatalysis, electrochemistry, biotechnology and Li⁺ ion batteries etc. Nanocrystalline α -Fe₂O₃ is one of the frequently used catalysts in the chemical industry and is also used in gas sensors for the detection of combustible gases such as methane, propane and butane.³⁴⁻³⁷ It is also used in photoanodes used in solar hydrogen generation due to its high stability, band gap, ease of fabrication, close match between the energetics of its band edge positions and redox potentials of water dissociation.²⁸

Microwave assisted synthesized α -Fe₂O₃ nanoparticles have been used in humidity sensors. α -Fe₂O₃ synthesized by solution combustion method has been used for the adsorption of the azo dye Indacid Millingred from its aqueous solution.³⁸ The photocatalytic activity of α -Fe₂O₃ in the degradation of dyes has been reported in literature.³⁹

α -Fe₂O₃ nanocrystals with various morphologies such as urchinlike, quasicubic, tubes, belts, rods, hollow spheres, nanorings and nanorhombhedra have been fabricated and their various functions have been tested.²⁶ Hu et al., obtained snowflake hierarchical structures of α -Fe₂O₃ on a large scale by microwave-assisted hydrothermal method.⁴⁰ The application of superparamagnetic (SPM) nanoparticles of α -Fe₂O₃ in biosensors, as drug carriers for magnetically guided drug delivery and contrast agents in magnetic resonance imaging (MRI) has been reported.²⁶

α -Fe₂O₃ crystallizes in the hexagonal rhombohedral crystal system (Space Group: *R*-3*c*; *a* = 5.0356 Å and *c* = 13.7489 Å) in which the iron atom is surrounded by six oxygen atoms not at the corners of a regular octahedron as shown in Figure 2.⁴¹ The Fe³⁺ ions occupy 2/3 of the octahedral sites between the nearly ideal hexagonal closed packed oxygen lattice; each FeO₆ octahedron shares a face with another in the layer above or below. The iron atoms lie on planes spaced approximately 1/3 and 2/3 of the distance between the oxygen layers.⁴²

The dense hexagonal close packing of oxygen atoms and the occupation of interstitial positions by the positioned iron atoms imparts high density to the structure (5.26 g cm⁻³) and hence α -Fe₂O₃ exhibits high values of polarizability and refractive index. The layered structure exhibits a complex behaviour when it interacts with photons

and electrons. This is of much interest to researchers in order to exploit α -Fe₂O₃ nanocrystals in numerous applications such as gas sensors, catalysts/photocatalysts, electrode materials in lithium ion batteries, magnetic recording media, photo-assisted electrolysis of water and optical and electromagnetic devices as well as in wastewater treatment.⁴³⁻⁴⁷

The morphology and size of α -Fe₂O₃ have a significant effect on its intrinsic physico-chemical characteristics and thus determine its applications.⁴⁸ Hence, a great deal of effort has been made by many researchers in the design of α -Fe₂O₃ materials with a desired structure and morphology.^{26,32}

In the present work, α -Fe₂O₃ nanopowder was prepared by solution combustion synthesis using ferric nitrate as oxidizer and ODH as fuel.

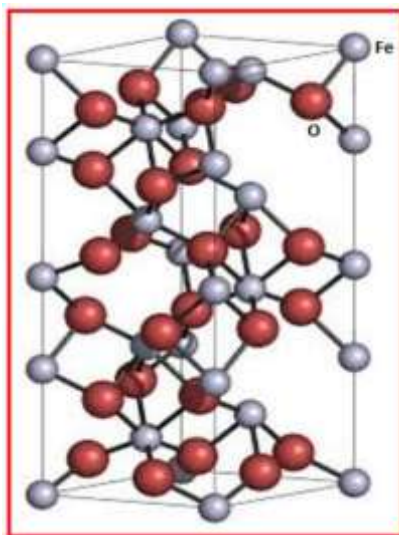


Figure 2: Rhombohedral structure of α -Fe₂O₃

- 3. Nanocomposites:** Nanocomposite materials have recently attracted the attention and interest of several researchers across the globe due to their improved properties compared to the single metal nanoparticles. These nanocomposites are regarded as materials of the 21st century since they have the potential to offer a number of technological and business breakthroughs in many sectors of human life. A nanocomposite is regarded as a combination or matrix, in which different materials combine to develop new properties apart from ensuring that at least one of the materials has size in range of 1 to 100nm.^{49,50} Hence, the nanocomposite can have a combination of or markedly different mechanical, thermal, electrical, electrochemical, catalytic and optical properties compared to those of the component materials.⁵¹⁻⁵⁴ The nanocomposites exhibit different phases which include zero-dimensional (core shell), 1D (nanowires and nanotubes), 2D (lamellar) and 3D (metal matrix) composites.⁵⁵

Core-shell nanocrystals are regarded as multicomponent nanostructures in which a spherical core made of one semiconductor is overlaid with one or more additional layers (shells) of secondary materials.⁵⁶⁻⁶⁰ These multicomponent systems introduce new possibilities for engineering photo-initiated flow of electrons from one material to

another based on the differences in energies of the valence bands (for holes) and conduction bands (for electrons).^{56,60} These core-shell nanocrystals can be of type I or type II. In the type I core-shell nanocrystals, both the electrons and holes can be isolated within the core or shell whereas in the type II core-shell nanocrystals, they can be separated in such a way that one carrier resides in the core and the other resides in the shell.^{56,59,61}

The rapid developments in the fields of nanoscience and nanotechnology for more than two decades have led to the development of nano-sized pure and composite photocatalysts which exhibit high activity. The synthesis of nanocomposite photocatalysts by coupling of two or more photocatalysts with mutually compatible characteristics, both chemically and energetically has created tremendous interest among the researchers working in the field of photocatalysis. These nanocomposite photocatalysts exhibit better light harvesting capacity and photocatalytic activity than their individual components by suppressing the electron-hole recombination to a greater extent which is a major drawback of the single phase photocatalysts.⁶²

The synthesis of several metal oxide nanocomposites such as $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{Al}_2\text{O}_3/\text{TiO}_2$, ZnO/CuO , $\text{MgO}/\text{Al}_2\text{O}_3$, ZnO/SnO_2 , MgO/CuO , $\text{ZnO}/\text{Fe}_3\text{O}_4$, $\text{NiO}/\text{CeO}_2/\text{ZnO}$, $\text{TiO}_2/\text{Fe}_2\text{O}_3$, WO_3/TiO_2 , $\text{Al}_2\text{O}_3/\text{TiO}_2$ by various methods such as sol-gel, co-precipitation and hydrothermal has been reported in the literature. The wet chemical methods provide an easy and economical route for the fabrication of nanocomposites. As a consequence of their simplicity in synthesis and wide range of tailorable properties, these nanocomposites find applications in various fields.

Some of the applications of these metal oxide nanocomposites are given below:

- They are used as adsorbents, photocatalysts and sensors in problems related to environmental remediation. High reactivity and large surface make these nanocomposites highly effective materials in water purification as well as early sensing of pollutants.^{63,64}
- They can be used in combination with silica, graphene, other oxides, carbon nanotubes and polymers for the treatment of wastewater containing dyes, heavy metal ions etc.
- They are widely employed in packing of various types of foodstuff. The nanocomposites provide strength to the packing as filler material and also act as antimicrobial agents and oxygen scavengers.
- In the field of agriculture, they are used as nanosensors for the detection of pesticides and pathogens in plants. They are also used as sources for the delivery of genetic material in order to improve the crops.
- Nano metal oxides such as ZnO , CuO and CeO along with their nanocomposite with fertilizers and zeolites are used in slow and controlled release of fertilizers to provide nutrients to plants for a long time. They also play a role in prevention of soil degradation thus resulting in improvement of sustainable agriculture.
- In medical field, metal oxide nanocomposites are employed in delivery of drugs and imaging, diagnosis and screening of various types of diseases, DNA sequencing, gene therapy, tissue culture, surgical tools and treatment of cancer.

- They also find applications in solar cells and fuel cells

In the present work, two metal oxide nanocomposites: ZnFe₂O₄-ZnO and MgFe₂O₄-MgO were prepared by solution combustion synthesis. In the preparation of the ZnFe₂O₄-ZnO nanocomposite, the oxidizers were zinc nitrate and ferric nitrate and the fuel was ODH. In the case of MgFe₂O₄-MgO nanocomposite the oxidizers were magnesium nitrate and ferric nitrate and the fuel was Glycine. The ZnFe₂O₄-ZnO nanocomposite exhibited the spinel and wurtzite phases of ZnFe₂O₄ and ZnO respectively. On the other hand, the MgFe₂O₄-MgO nanocomposite exhibited the spinel phase of MgFe₂O₄ and the cubic phase of MgO.

Figure 1.3 depicts the crystal structure of the spinel ferrite AB₂O₄ (A = divalent metal ion and B = trivalent metal ion). Spinel ferrites crystallize into the spinel structure.

The lattice of the O²⁻ ions determines the crystal structure of the spinel. The radii of the oxygen ions are several times greater than those of the metal ions A and B. As a consequence of this, it can be considered that the crystal structure consists of the closest possible packing of layers of O²⁻ ions, with the metal ions occupying the interstitial positions **A** and **B**. The metal ion located at the site **A** is surrounded by four nearest O²⁻ ions resulting in a tetrahedral coordination while the metal ion located at the site **B** is surrounded by six nearest O²⁻ ions as neighbours leading to an octahedral coordination.

Based on the point of view of valency, it can be considered that the A²⁺ ions occupy the **A**-sites and while the B³⁺ ions occupy the **B**-sites since the number of O²⁻ ions surrounding the sites **A** and **B** are in the ratio 2:3. The unit cell size has 96 interstitial sites: 64 tetrahedral and 32 octahedral out of which 8 and 16 sites are respectively occupied by the cations. Normal spinel structures generally form oxides with the cubic closed-packed structure having one octahedral and two tetrahedral sites per oxide. The octahedral sites are larger than the tetrahedral sites. The octahedral sites are occupied by the B³⁺ ions due to the charge factor. However, only half of the octahedral sites are occupied by the B³⁺ ions. The A²⁺ ions occupy 1/8 of the tetrahedral sites. This maximizes the lattice energy provided the ions have a similar size.⁶⁵

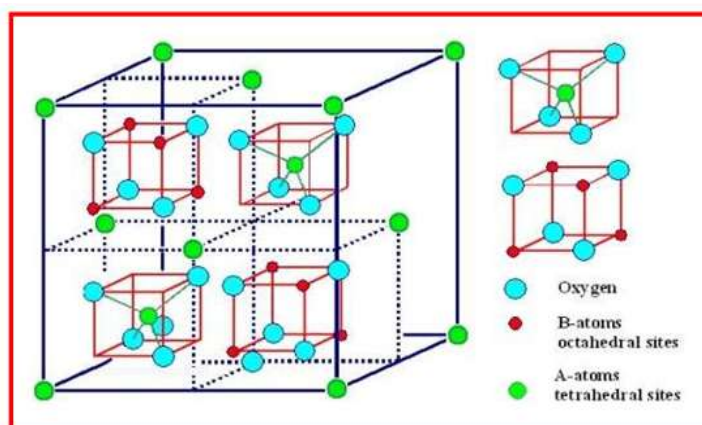


Figure 3 : Crystal structure of the spinel ferrite AB₂O₄

MgO crystallizes in the cubic rock-salt structure (Figure 4) which is the most common structure for compounds of the type MX. The crystal structure is a face centred cubic lattice of Mg^{+2} ions where all the octahedral sites are occupied by the O^{-2} ions or vice versa ($a = 4.212\text{\AA}$). MgO is one of the important oxides in minerals, defective systems and adsorption phenomena. Hence, despite its simplicity MgO has been the subject of several research studies.⁶⁶

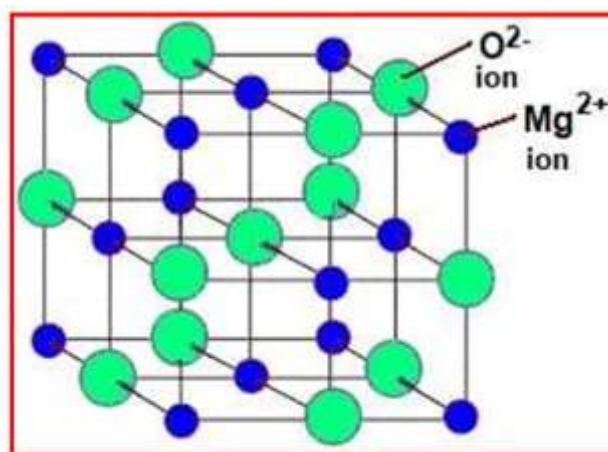


Figure 4: FCC crystal structure of MgO

V. SYNTHETIC DYES

A dye is a coloured substance that has an affinity to the substrate on which it is being applied. Generally, most of the dyes are applied in aqueous solutions and require a mordant to improve their fastness on the fibre. Since antiquity, fabrics were being dyed with extracts from minerals, plants and animals. Earlier, dyeing was considered as a form of art and the most beautiful and exotic pigments were reserved only for those who had the status to wear them. However, things began to change around 1856 when several different methods were discovered by scientists to prepare synthetic dyes. These synthetic dyes are less expensive, brighter, more colour-fast and can be easily applied on the fabric. As a consequence of these benefits, scientists started to formulate gorgeous new colours; and within a short period, dyed fabrics were easily available to all and the natural dyes became obsolete in majority of cases.^{67,68}

Persistent research carried out in the twentieth century and thereafter has resulted in the development of dyes with every imaginable form of colour. Apart from being pretty, these synthetic dyes have become indispensable tools for various types of industries. These synthetic dyes are used as colourants in plastic, textile dyeing and the highly sophisticated biotechnology industry. Dyes are also employed by industries for inks and tinting. Additionally, dyes are also used by other industries such as paper and pulp, adhesives, ceramics, art supplies, beverages, food, soaps, cosmetics, construction, glass, paints, polymers, waxes, biomedicines etc. Presently, a large number of dyes are being manufactured to cater to the needs of various types of industries.

Dyes are available in different forms such as dry powders, granules, pellets, pastes,

liquids and chips.

Dyes that cater to the needs of different industries often possess certain specialized properties that include the following:

- Resistance to heat and weather conditions.
- Resistance to UV light.
- Some of the products are water soluble.
- Electrical conductivity.
- Contain reinforcing fibers.
- Free from heavy metals.

Dyes can be classified as cationic, anionic and non-ionic dyes. Basic dyes are cationic dyes while direct and reactive dyes are anionic dyes. The non-ionic dyes include the disperse dyes.

The chromophores in the anionic dyes are probably the azo groups or the anthraquinone groups. The presence of azo groups results in the formation of toxic amines. Sulphonated azo dyes are readily soluble in water and hence are difficult to remove. Anthroquinone-based dyes exhibit high resistance to degradation due to the presence of fused aromatic structure in them. Hence, the effluents containing such dyes retain their colour for a longer period of time. Basic dyes possess a high brilliance and intensity which makes them visible even at very low concentrations. The metal- complexed dyes contain the metal chromium which is carcinogenic in nature. Among the several types of dyes, the azo dyes account for more than 60% of the total dyes manufactured.⁶⁹⁻⁷¹

1. Harmful Effects of Synthetic Dyes: More than 1,00,000 commercially available dyes exist while their annual production exceeds 7×10^5 tonnes. However, this brightly coloured, changed new world is not without a downside. The chemicals used in the preparation of these dyes possess toxic and carcinogenic effects. Some of these chemicals are even explosive. For example, the chemical aniline is the basis for the preparation of azo dyes which are considered to be highly poisonous and release carcinogenic amines in water. Aniline is dangerous to work with due to its toxic and highly inflammable properties.^{72,73} In addition to aniline, some of the other toxic chemicals used in the dyeing process include the following:

- Dioxin - a carcinogen as well as a possible hormone disrupter.
- Heavy metals such as Cr, Cu and Zn - toxic and possess carcinogenic effects and other health hazards; and
- Formaldehyde - a suspected carcinogen.

It is obvious that the workers involved in the manufacture of dyes and dyeing of garments are at a greater risk of tumours, cancers, cerebrovascular diseases and lung diseases. Almost all industrial dyeing processes involve immersion or washing the fabrics with an aqueous solution of a dye. After dyeing a batch of fabrics, it is less expensive to release the dye effluent (used water) into nearby sources of water rather than to clean and reuse it. It is due to this fact that most of the dyeing industries throughout the world are releasing millions of tonnes of these dye effluents into the rivers. Since most of the dyes are readily soluble in water and are also quite stable, they ultimately find their way into

the aquatic ecosystem and have adverse and sometimes irreversible effects on both animals and plants. Some of the dye effluents are known to release potentially harmful and carcinogenic substances into the water which pose a serious threat to the aquatic organisms. Apart from being carcinogenic, these dyes are known to have adverse effects on mankind including malfunctioning of kidneys, lungs, intestine, liver etc.

Dyes inhibit the penetration of light into the water which leads to the death of the phytoplankton. The treatment of wastewater containing these dyes is very difficult since these dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to heat, light and oxidizing agents.^{74,75}

Emerging research has examined both short and long term effects of the potential absorption of dyes and finishing chemicals by the skin through clothing. It has been reported that young babies and children actually possess increased levels of chemicals in their skin and bloodstream. This is due to the fact that the long period of contact between the skin and the clothing facilitates the absorption of toxic chemicals by the skin, particularly when the body is warm and the skin pores have opened up to allow perspiration. Some individuals suffer from “chemical sensitivity,” including when the skin is exposed to various types of garments. In adults, the symptoms of chemical sensitivity include headache, fatigue, dizziness, nausea, diarrhea, skin rashes, muscle and joint pain, irregular heart beat difficulty in concentrating, and difficulty in breathing, etc. On the other hand, the symptoms in children include hyperactivity, redness of the cheeks and ears, dark circles under the eyes as well as behavioural and learning problems.

Dyes are problematic since the chemical compounds used in their preparation are also toxic to human beings. Every new dye is a brand new chemical compound and since it is new, its effects on the living beings and the environment are not known. The textile industry poses a big pollution problem. As per the estimates of The World Bank, 17 to 20% of the industrial water pollution is the result of textile dyeing and treatment processes. It has also listed 72 toxic chemical substances in the effluent water solely from textile dyeing, 30 of which cannot be removed. This presents an appalling environmental problem both for the fabric designers as well as other textile manufacturers.^{76,77}

VI. METHODS OF DYE REMOVAL

In view of these adverse effects, the industrial effluents containing dyes have to be treated so that they are free from these dyes. The different methods used for removal of dyes from various industrial effluents are given in Table 1.1.⁷⁸ Each method has its own merits and demerits. The conventional biological methods used for the treatment of industrial wastewater are ineffective and result in the release of an intensely coloured discharge from the treatment facilities.⁷⁹ Recently, nanocatalysis (photocatalysis using nanomaterials) and adsorption using nano metal oxides have proven to be good techniques for dye removal. In the following sections, a brief discussion of photocatalysis, nanocatalysis and adsorption is presented.

Table 1: Various methods used for the removal of dyes from industrial effluents

Method of Dye Removal	Merits	Demerits
Fentons reagent	Effective removal of both water soluble and water insoluble dyes	Sludge generation
Ozonation	No change in the volume of the effluent	Short half-life of about 2 minutes
Photochemical	No sludge production	Formation of byproducts
Sodium hypochlorite	Initiates and accelerates cleavage of the azo linkage	Release of aromatic amines into the water
Cucurbuturil	Efficient adsorption of various dyes	Expensive
Electrochemical destruction	Break-down compounds are harmless	High electricity consumption
Activated carbon	Better removal of several types of dyes	Highly expensive
Peat	Better adsorption due to cellular structure	Lower specific surface area for adsorption in comparison to that of activated carbon
Wood chips	Better adsorption of acid dyes	Long retention time
Silica gel	Effective removal of basic dyes	Commercially not applicable due to side reactions
Membrane filtration	Effective removal of almost all types of dyes	Concentrated sludge production
Ion exchange	Adsorbent can be regenerated	Not effective for all dyes
Irradiation	Effective oxidation of dyes at the laboratory scale	Requires high concentration of dissolved oxygen
Electrochemical coagulation	Economical	High sludge production

- 1. Photocatalysis:** A photocatalyst is a substance which exhibits catalytic activity in the presence of light and the phenomenon is referred to as photocatalysis. Heterogeneous photocatalysis using semiconductor nano metal oxides is being considered as a promising technology for the reduction of environmental pollutants on a global scale. The treatment of coloured wastewater not only involves its decolouration, but also its detoxification. The main goal of heterogeneous photocatalysis is complete mineralization of pollutants into harmless compounds. In some cases, complete mineralization of organic matter to carbon dioxide and mineral acids has been achieved. It is one of the advanced techniques coupling ultraviolet light or sunlight with nanomaterials as photocatalysts.⁸⁰⁻⁸³

Some of the important conditions for a substance to exhibit efficient photocatalytic activity are given below:

- The chemical elements making up the semiconducting material should be capable of reversibly changing its valence state in order to accommodate a hole without decomposing the semiconductor.
- It should not have only one stable valence state in the semiconductor material.
- The semiconductor must possess suitable band gap energy (E_g), stable towards photocorrosion, non-toxic in nature and less expensive.
- It should also possess the physical and chemical properties that enable it to act as a catalyst. Several nano metal oxides including ZnO, CaO, MgO, TiO₂, CeO₂, ZrO₂, Fe₂O₃, WO₃ etc. have been extensively used for the photocatalytic degradation of several dyes as well as organic and inorganic pollutants from wastewater.^{28,84-88}

The pulp and paper industries manufacture paper and similar products. It is also one of the industries contributing towards water pollution. The waste from the pulp and paper industry characteristically contains very high values of COD and colour. The presence of lignin in the waste which is derived from the raw cellulosic materials makes the COD/BOD ratio of the waste very high. Apart from this the textile mills also utilize pulp for making rayon fabrics. In order to get different shades of colours to the papers and textiles, different types of dyes are being used. The presence of these dyes also increases the COD of the effluent and causes a number of aesthetic problems. This limits the possible use of water and reduces the efficiency of microbial wastewater treatment since some of the dyes are harmful to the microorganisms themselves.

Azo dyes which contain one or more azo groups ($-N=N-$) are of much greater concern. The products of degradation of these azo dyes can be mutagenic and carcinogenic causing long term health effects. These azo dyes do not undergo biodegradation by aerobic treatment processes. Under anaerobic conditions, they are reduced to potentially carcinogenic aromatic amines.^{26,89-91} Hence, the removal of dyes and reduction in chemical oxygen demand (COD) levels of the effluent water from industries has become a matter of great concern. A number of physical, chemical and biological methods are being employed for the treatment of dye effluents from various industries. Most of these methods are found to be ineffective and expensive.^{27,92}

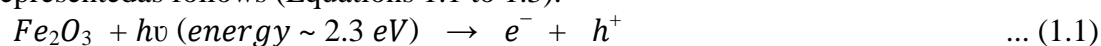
In nanocatalysis, nanoparticles are used to catalyze the reactions. The catalysis can be homogeneous or heterogeneous. At the nano level, the particles have larger surface area to volume ratio compared to that in the bulk materials. The reduction in size leads to the involvement of a large number of atoms in the catalysis process. These properties make the nanoparticles attractive catalysts. The surface atoms occupy the corners and edges of the nanoparticles and are thus chemically unsaturated apart from being more active. The smaller size increases the activity of the surface atoms and leads to surface reconstruction.

Nanocatalysis is found to be shape dependent. In homogeneous catalysis, a colloidal solution of transition metal nanoparticles is used. The colloidal nanoparticles can be dispersed in an organic solvent or an aqueous solution or in a solvent mixture

depending on their nature. In heterogeneous catalysis, the catalyst consists of transition metal nanoparticles supported on various substrates. The catalysis is affected by the nature of the support.¹⁰¹

The possible mechanism of photocatalysis by these nano metal oxides can be explained as follows (Figure 5). When UV or visible radiation is used in the photocatalytic reaction; the electrons in the photocatalyst are excited from the valence band to its conduction band by the absorption of energy of the photons while positive holes are left behind in the valence band. These excited electrons in the conduction band react with the oxygen molecules adsorbed on the surface of the photocatalyst forming the O_2^\bullet species, while the holes in the valence band react with the adsorbed hydroxyl ions to generate the hydroxyl radicals.^{89,102,103}

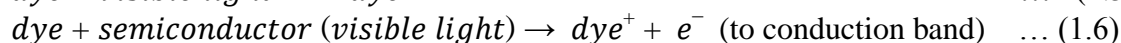
In the case of Fe_2O_3 nanocatalyst, for example, these processes can be represented as follows (Equations 1.1 to 1.3).^{104,105}



The hydroxyl radicals are highly reactive and combine with the dye molecules, thus degrading them (Equation 1.4).



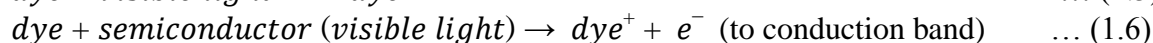
In cases involving solar radiation, photosensitization occurs. The sensitizer (the dye) molecules absorb visible light radiation of the sunlight and go to an excited state forming the dye^\bullet radicals. These dye^\square radicals then inject electrons into the conduction band of the semiconductor and form the dye^+ radicals. This process of electron transfer is usually very fast (Equations 1.5 and 1.6).



The dye^+ species react with the dye molecules in the same way as the hydroxyl radicals react with them. This can be represented by Equation 1.7.¹⁰⁶



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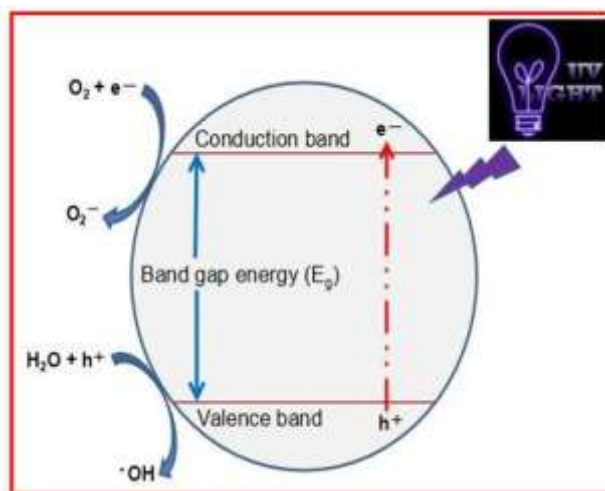


Figure 5: Schematic representation of semiconductor photocatalysis

- 2. Adsorption:** Adsorption refers to the process of accumulation of a particular substance resulting in a higher concentration of molecular species on the surface of another substance compared to that in the bulk. If a solid surface is exposed to a gas or a liquid, there is concentration of molecules from the gas or the solution on its surface. This accumulation of molecules of a gas or liquid on the surface of a solid is referred to as adsorption. Adsorption is one of the powerful techniques in the treatment of industrial effluents. Adsorption is necessarily a surface phenomenon and is different from absorption which involves uniform distribution of the substance throughout the bulk. A process in which both adsorption and absorption occur simultaneously is referred to as sorption. Desorption is the reverse process of adsorption.

Adsorption involves two components: the adsorbent and the adsorbate. Adsorbate is the substance which concentrates at the surface while the substance on the surface of which adsorption occurs is referred to as the adsorbent. Adsorbents are available in several forms such as spherical pellets, rods, mouldings or monoliths having hydrodynamic diameters in the range of 0.5-10 nm. A good adsorbent must possess high abrasion resistance, high thermal stability and small pore diameter. The small pore diameter results in higher exposed surface area which leads to a higher surface capacity for adsorption. The pore structure must be distinct in order to facilitate fast transport of the gaseous vapours.¹⁰⁷

Generally, industrial adsorbents are classified into 3 categories:

- Oxygen containing adsorbents such as zeolites and silica gel which are generally hydrophilic and polar in nature.
- Carbon-based adsorbents such as graphite and activated carbon which are typically

hydrophobic and non-polar in nature.

- Polymer-based adsorbents which contain polar and non-polar functional groups in a porous polymer matrix.

Adsorption is a spontaneous process (ΔG is negative). In adsorption, the adsorbate gets adsorbed on the surface of the adsorbent. Forces of attraction exist between the adsorbate molecules and the surface of the adsorbent. These forces of attraction are responsible for the release of heat energy, thus making adsorption an exothermic process.¹⁰⁸

In adsorption, the reactant molecules get adsorbed on the active sites of the adsorbent material. Based on the type of attractive forces between the adsorbate and the surface of the adsorbent, adsorption can be classified into two types: physical adsorption or physisorption and chemical adsorption or chemisorption (Figure 6). In case of physisorption, the forces of attraction are the weak Vander Waals forces of attraction whereas chemisorption involves chemical forces of attraction or chemical bonds between the adsorbate and the adsorbent surface. In physisorption a multilayer of adsorbate is formed on the adsorbent surface and the enthalpy of adsorption is low (ΔH_{ads} lies between 20 and 40 kJmol^{-1}). It occurs at low temperatures (usually below the boilingpoint of the adsorbate) and decreases with increase in temperature. Chemisorption involves the formation of a single layer of adsorbate on the surface of the adsorbent. It has a high enthalpy of adsorption (ΔH_{ads} lies between 200 and 400 kJmol^{-1}) and occurs at all temperatures. With increase in temperature, it first increases and then decreases.¹⁰⁹

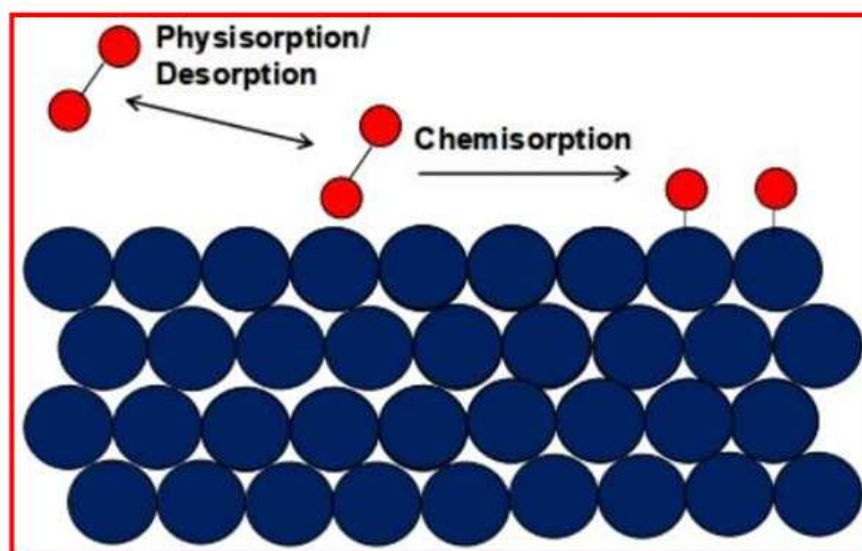


Figure 6: Physisorption and Chemisorption

