CHAPTER-1
INTRODUCTION
Nanotechnology is a key technology for the 21st century. The growth of Nanoscience and nanotechnology in the last decade has been possible because of the success in the synthesis of nanomaterials in conjunction with the advent of tools for characterization and manipulation. The synthesis of nanomaterials spans inorganic, organic, and biological systems on manipulation. The subsequent assembling of the individual nanostructures into ordered arrays is often imperative. The physical and chemical properties of nanostructures are distinctly different from those of a single atom (molecule) and bulk matter with the same chemical composition. These differences between nanomaterials and the molecular and condensed-phase materials pertain to the spatial structures and shapes, phase changes, energetics, electronic structure, chemical reactivity, and catalytic properties of large, finite systems, and their assemblies. Some of the important issues in Nanoscience relate to size effects, shape phenomena, quantum confinement, and response to external electrical and optical excitations of individual and coupled finite systems. Nanotechnology has the power not only to improve existing technologies, but to dramatically enhance the effectiveness of new applications. Metal oxide nanopowders have broad commercial applications.

A revolution is occurring in science and technology, based on the recently developed ability to measure, manipulate and organize matter on the nanoscale 1 to 100 billionths of a meter. At the nanoscale, chemistry, physics, biology, material science, and engineering converge toward the same principles and tools. As a result, progress in nanotechnology and nanoscience are very farreaching impact. The nanoscale is not just another step toward miniaturization, but a qualitatively new scale. The new behavior is dominated by quantum mechanics, material confinement in small structures, large interfacial volume fraction, large surface area and other unique properties, phenomenon and processes. The nanoscale dimension which is taking the world into new functionalities and improved product's qualities as well as its providing better way of living. Many current theories of matter at the microscale have critical lengths of nanometer dimensions. These theories are inadequate to describe the new phenomenon at the nanoscale. Therefore nanotechnology and nanoscience are the latest technology and an area of special interest in research and study and as a result it is developing rapidly. Nanotechnology has great possibility for producing improvement and innovations in
many areas of life such as new and improved health treatments, reduce use of some harmful or scarce resources, cleaner, faster and safer manufacturing, quicker and smaller devices, increased life cycle of products, many other to existing products.

Synthesis of iron oxides in the nano range for various applications has been an active and challenging area of research during the last two decades. The processes include careful choice of pH, concentration of the reactants, temperature, method of mixing, and rate of oxidation [1]. The morphology of the iron oxide particles depends on the competition between several processes like nucleation, growth, aggregation and adsorption of impurities [2]. However, in many cases it is not possible to precipitate specific iron oxide particles directly in the desired size and shape. Instead, the synthesis must be done by the transformation of another iron oxide precursor particle [3].

The sensitivity of the preparative method complicates both the reproducibility and scale up of the process. Recently, several colloidal chemical synthetic procedures have been developed to produce mono-disperse nanoparticles of various materials. This includes the classical LaMer mechanism where in a short burst of nucleation from a supersaturated solution is followed by the slow growth of particles without any significant additional nucleation, thereby achieving a complete separation of nucleation and growth [4]. Synthesis procedure that combines slow, continuous nucleation and fast, autocatalytic surface growth have also been reported [5]. Further, in several preparative methodologies, agglomeration of the nano-oxide generated takes place on exposure to air. This is prevented by employing surfactants or by capping with organic acids. In general, for the solution-based synthesis of iron oxide colloids and nanoparticles several techniques such as chemical precipitation, sol-gel processes, forced hydrolysis, hydrothermal synthesis, electrochemical preparation methods [6-14]. Magnetic nanoparticles have attracted technological interest owing to their magnetic and catalytic properties, and many researchers have attempted to prepare magnetic nanoparticles with high functionality [15]. On the other hand, the surface modification of nanoparticles by organic molecules is also important for their functionalization not only for nanocomposite fabrication [16] but also for biological applications [17, 18]. They offer a high potential for numerous biomedical applications, such as cell separation, automated DNA extraction, gene targeting, drug delivery, magnetic resonance imaging, and
hyperthermia [19]. When coated with, for example, an antibody, they can be applied for highly sensitive immunoassays or small substance recoveries. Furthermore, single-stranded DNA or oligonucleotide immobilized on magnetic particles were successfully used for DNA hybridization analyses with the aim of identifying organisms and single-nucleotide polymorphism analyses for human blood. Magnetic nanoparticles displays the phenomenon of supermagnetism not keeping magnetized after the action of the magnetic field, offering advantages of reducing risk of particles aggregations. Iron oxide nanoparticle present higher performance in terms of chemical stability and biocompability as compared to other metallic nanoparticles.

Co-precipitation method of synthesis is a method with an advantage that it can be easily operated and produces large quantities of nanostructured material in a comparatively less time and no sophisticated instrumentation were required. The main thrust of research in this area is exploring synthesis routes involving minimum temperature, to minimize the grain growth associated with high temperature treatment. In nanotechnology especially Nanomaterials or nano adsorbent particles are receiving particular interest due to their novel physical and chemical properties, which are important for a wide range of applications, including environmental pollution remediation. New and innovative methods are of great importance for the development of new technologies that can help deal with environmental problems. This discussion represents an overview of the current advances on the most relevant nanomaterials and nanotechnologies employed for environmental pollution control. Nanotechnology has been considered as one of the most important advancements in science and technology. Its essence is the ability to fabricate and engineer the materials and systems with the desired structures and functionalities using the nano-sized building blocks [20]. Nanoparticles are one of the important building blocks in fabrication of nanomaterials. Their basic properties, extremely small size and high surface-area-to-volume ratio, provide better kinetics for the adsorption of metal ions from aqueous solutions. However, for such an application, it is necessary to use a method of purification that does not generate secondary waste and involves materials that can be recycled and easily used on an industrial scale [21].
The discharge of industrial effluents containing toxic heavy metals and organics into aquatic systems has been a matter of worldwide concern over the last few decades. These pollutants are introduced into aquatic systems significantly as a result of various industrial operations. Over a few decades, community is devoting concentrated efforts for the treatment and removal of heavy metals in order to combat this problem. The commonly used procedures for removing metal ions from dilute aqueous streams include chemical precipitation, reverse osmosis and solvent extraction [22]. However, these techniques have certain disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal. Heavy metals such as lead, zinc and chromium have a number of applications in basic steel works, paper and pulp, leather tanning, organochemicals, petrochemicals, fertilizers, etc. Major lead pollution is through automobiles and battery manufacturers. For zinc and chromium, their major application is in fertilizer and leather tanning, respectively [23].

The environment and all the life on earth face a very serious threat as a result of heavy metal pollution due to rapid industrialization and the increase in the world population. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not easily get converted into harmless end products. The metals that cause serious concern include Cr, Hg, Cu, Ni, Zn and Cd, which are commonly associated with pollution and toxicity problems [24]. Many processes have been developed to curtail heavy metal pollution, including chemical precipitation, electrode deposition, solvent extraction, ion-exchange, activated carbon adsorption and biological methods [25-26]. Among these methods, adsorption has increasingly received more attention in recent years because it is simple, relatively low-cost, and effective in removing heavy metal ions from wastewaters.

Natural resources are the important wealth of our country, water is one of them. Water is a wander of the nature. “No life without water” is a common saying depending upon the fact that water is the one of the naturally occurring essential requirement of all life supporting activities[27] Since it is a dynamic system, containing living as well as nonliving, organic, inorganic, soluble as well as insoluble substances. So its quality is likely to change day by day and from source to source. Any change in the natural quality
may disturb the equilibrium system and would become unfit for designated uses. The availability of water through surface and groundwater resources has become a critical day today. Only 1% part is available on land for drinking, agriculture, domestic power generation, industrial consummation, transportation and waste disposal [28]. The groundwater is believed to be comparatively much clean and free from pollution than surface water. But prolonged discharge of industrial effluents, domestic sewage and solid waste dump causes the groundwater to become polluted and created health problems [29]. The rapid growth of urban areas has further affected groundwater quality due to overexploitation of resources and improper waste disposal practices. Hence, there is always a need for and concern over the protection and management of surface water and groundwater quality. [30] Heavy metals are priority toxic pollutants that severely limit the beneficial use of water for domestic and industrial application [31]. The lakes have a complex and fragile ecosystem, as they do not have the self cleaning ability and therefore readily accumulate pollutants [32]. During the last decade, this is observed, that the surface water gets polluted drastically because of increased human activities [33-35].

Heavy metal contamination is one of the most noteworthy environmental problems of this century, chromium is the seventh most abundant element on earth. In the last few decades, the amount of chromium in aquatic and terrestrial ecosystems has increased as a consequence of different human activities. Chromium is the newest entry, after lead, cadmium and mercury in the major toxic metal series. The toxicity of chromium (VI) is the central theme of the Hollywood blockbuster movie “Erin Brockovitch”. The world production of chromite ore is several millions of tons per year. Ferrochromite is obtained by direct reduction of the ore while chromium metal is produced either by chemical reduction or by electrolysis of either CrO$_3$ or chrome alum solutions. Chromium and its compounds are extensively used in industry with the most common and important sources coming from the electroplating, tanning, water cooling, pulp production, dyes and pigments, film and photography, wood preservation and alloy manufacture industries. Petroleum refining processes have resulted in introduction in soil, air and water. Tanning is a process of converting raw hides or skins into leather. The conversion of animal hides and skins into useful artifacts may be man’s oldest technology Cr(VI) is produced in leather during photoaging [36]. Chrome plating, the result of which
is often referred to simply as chrome, is a technique of electroplating a thin layer of chromium onto a metal [37].

Chemical contamination of water from a wide range of toxic derivatives, in particular heavy metals, is a serious environmental problem owing to their potential toxicity for humans. Increasing quantities of chromium compounds have been used in anthropogenic activities and introduced into the environment as a consequence of its wide use in modern industries, mainly in electroplating and tanning factories. The effluents from these industries contain chromium on its most common oxidation states on aqueous phase, Cr (VI) and Cr (III). These two Cr forms exhibit very different toxicity; Cr (III) is an essential nutrient required for sugar and fat metabolism, it has a very large safety concentration range, though large amounts of it can cause allergic skin reactions and cancer [38]. On the other hand, Cr (VI) is highly active and very dangerous due to its carcinogenic and mutagenic properties. Consequently, the removal of Cr (VI) from industrial wastewater has attracted much interest. Chemical treatment of chromium waste water is usually conducted in two steps [39]. In the first step Cr (VI) is reduced to Cr (III) by use of a chemical reducing agent. Sulphur dioxide, sodium bisulphate and sodium metabisulphite are commonly used as reducing agents. Following reduction of Cr (VI), sodium hydroxide or lime is added to the wastewater to precipitate Cr (III). This procedure produces large quantities of solid sludge containing toxic chromium compounds with high cost of disposal and even a possibility of ground water contamination [40]. Chromium exists in trivalent [Cr (III)] and hexavalent [Cr (VI)] state. The hexavalent form has been considered more hazardous to public health due to its mutagenic and carcinogenic properties [41]. Various methods for chromium removal include filtration, chemical precipitation, adsorption, electrodeposition and membrane systems or even ion exchange process. Among these methods, adsorption is one of the most economically favorable and a technically easy method [42]. Textile industry effluents exhibit large amounts of dye chemicals which create severe water pollution.

Therefore, it is important to reduce the dye concentration in the wastewater before discharging it into the environment. Discharging large amounts of dyes into water resources, accompanied by organics, bleaches, and salts, can affect the physical and chemical properties of fresh water. Dyes in wastewater can obstruct light penetration and
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removal of dyes is stringent due to their complex structure and synthetic origins. The
effluents of wastewater in some industries such as dyestuff, textiles, leather, paper,
plastics, etc., contain various kinds of synthetic dyestuffs. Among textile effluents,
reactive dyes are hardly eliminated under aerobic conditions and are probably
decomposed into carcinogenic aromatic amines under anaerobic conditions. Furthermore, it is difficult to remove reactive dyes using chemical coagulation due to the
dyes’ high solubility in water. A very small amount of dye in water is highly visible and
can be toxic to creatures in the water [43]. Hence, the removal of color from a process or
waste effluents becomes environmentally important. Among some existing technologies,
adsorption has been shown to be an effective technique with its high efficiency, capacity
and applicability on a large scale to remove dyes as well as having the potential for
regeneration, recovery and recycling of adsorbents. Many studies have been undertaken
to find suitable adsorbents to lower dye concentrations of aqueous solutions [44-46].
Removal of dyes from aqueous solutions using activated carbons by adsorption process is
currently of great interest [47-49].

As a pure substance, phenol is used as a disinfectant, for the preparation of some
cream and shaving soap for its germicidal and local anesthetic properties, in veterinary
medicine as an internal antiseptic and gastric anesthetic, as a peptizing agent in glue, as
an extracting solvent in refinery and lubricant production, as a blocking agent for blocked
isocyanate monomers, as a reagent in chemical analysis and as a primary petrochemical
intermediate. Its largest use (35%) is to produce phenolic resins like phenol–
formaldehyde resins (Bakelite) which are low-cost thermosetting resins applied as
plywood adhesive, construction, automotive and appliance industries. By reaction with
acetone it may also be converted into bisphenol A, a monomer for epoxy-resins (28%). It
is also used to produce cyclohexanone and cyclohexanone–cyclohexanol mixtures by
selective catalytic hydrogenation. Cyclohexanone is later converted into its oxime and
further to ε-caprolactame, the monomer for nylon 6 (16% of phenol applications). The
mixture cyclohexanone–cyclohexanol is oxidized by nitric acid to adipic acid, one of the monomers for the production of nylon-6,6. Phenol is also used to produce polyphenoxy and polysulphone polymers, corrosion-resistant polyester and polyester polyols. Phenol may be converted into xylenols, alkylphenols, chlorophenols, aniline, and other secondary intermediates in the production of surfactants, fertilizers, explosives, paints and paint removers, textiles, rubber and plastic plasticizers and antioxidants, and curing agents and so on.

Phenol is also a building block for the synthesis of pharmaceuticals, such as, e.g., aspirin. The sterilizing activity of phenol was discovered by the English surgeon Joseph Lister in 1865. The germicidal activity of phenol appears associated to its protein denaturing ability. It has lipophile properties, so it binds itself to the battery protein by hydrogen bonds. On the other hand, phenol has relevant health effects for humans [50]. The manufacture and transportation of phenol as well as its many uses may lead to worker exposures to this substance, through inhalation, ingestion, eye or skin contact, and absorption through the skin. Phenol is rapidly absorbed through the skin and can cause skin and eye burns upon contact. Comas, convulsions, cyanosis and death can result from overexposure to it. Internally, phenol affects the liver, kidneys, lungs, and vascular system. The ingestion of 1 g of phenol is deadly for man. Industrial processes generate a variety of molecules that may pollute air and waters due to negative impacts for ecosystems and humans (toxic, carcinogenic and mutagenic properties). Phenol is one of the most common organic water pollutants, because it is toxic even at low concentrations, and also its presence in natural waters can lead further to the formation of substituted compounds during disinfection and oxidation processes. Phenol is also relevant in the field of environmental research, because it has been frequently chosen as a model pollutant and many data are available on its removal and destruction in particular with respect to wastewater treatments. During this investigation some recent advances in the methods for phenol removal from fluid streams will be shortly reviewed. The idea is to summarize all possible techniques to remove phenols from fluid streams, considering the most recent literature data. This research work is expected to be useful to support the choice of the best technique to treat phenol emissions in practical cases. According to the polarity of phenol and their partial reciprocal solubility, water can be chosen to remove
phenol from gaseous streams. However, according to the weak acidity of phenol and the large solubility of sodium phenate in water, 3–20% sodium hydroxide is mostly used as the scrubbing agent [51].

The presence of heavy metals in the environment is one of the major concerns because of their toxicity and threat to human life. They accumulate in living tissues throughout the food chain which has humans at its top. These toxic metals can cause accumulative poisoning, cancer, and brain damage when found above the tolerance levels. Lead compounds are very toxic to humans. The presence of lead in drinking water above the permissible limit (5mg/ml) may cause adverse health effects such as anaemia, encephalopathy, hepatitis, and nephritic syndrome. Hence it is very important that lead should be removed from wastewater before being discharged into an aquatic environment. Several conventional methods exist for the removal of heavy metal pollutants from wastewater. These methods include precipitation, electroplating, chemical coagulation, ion-exchange, membrane separation, and electrokinetics. However, these methods often incur high operational costs [52–54]. A number of studies have demonstrated the feasibility of using plant biomass [55-57] and also using biomass of micro-organisms [59-60] to remove heavy metal ions from wastewater streams. During the past decade, an immense amount of work has been done on nanostructured materials because of their unusual physical and chemical properties owing to their extremely small size and large specific surface area. Recently, considerable effort has been made on the surface modification of nanoparticles and the preparation of organic–inorganic nanocomposites. The combination of inorganic and organic components in a single particle at the nano-sized level has made accessible an immense area of new functional materials.

The presence of toxic metal ions in wastewater remains a serious environmental concern. Therefore, it is necessary to develop various efficient technologies for their removal. A number of techniques have been used to remove the metal ions from wastewater effluents; including chemical precipitation, ion exchange process [61,62], electrolytic methods, adsorption onto activated carbon, organic-based ligand precipitation [63], membrane and reverse osmosis processes. These methods have been found to be limited, because of the high capital and operating costs and/or the ineffectiveness in
meeting stringent effluent standards. Therefore, several approaches have been studied for the development of inexpensive and abundant metal sorbents, such as sawdust [64], live biomass [65], clay [66] and agricultural byproducts [67–69]. These approaches, however, suffer from some challenges; including the huge amount of sludge waste generated from the spent adsorbents, the high regeneration cost and the low adsorption rate and capacity, especially at very low pollutant concentration [70,71]. An excellent adsorbent should generally possess high surface area and short adsorption equilibrium time, so that it can be used to remove high amount of pollutant in shorter time. Addition, it should generate a minimum amount of sludge.

Nanoadsorbents could be employed most effectively not only in a very low concentration range (≈1ppm) of pollutant, but also in a very high concentration range (≈1000ppm), where other techniques are ineffective, time-consuming, or costly. Nanoadsorbents have particularly high adsorption capacities because of their specific functionality and large specific surface areas i.e. surface area per unit mass. In addition, nanoadsorbents are highly mobile in porous media because they are much smaller than the relevant pore spaces, so they can be transported effectively by the flow in porous media [72]. Therefore, the nanoadsorbents can be employed in situ, within the contaminated zone where treatment is needed. In situ, involves treatment of contaminants in place, in comparison to ex situ where treatment occur after transferring the contaminated material to a more convenient location [73], adding more cost and environmental impact to the process (e.g. pumping, transportation, instrumentations and treatment of contaminants). Certain types of nanoadsorbents have been found to be effective in metal ion removal [72,74,75]. Although previous research has highlighted the ability of metal oxide nanoadsorbents for metal ion adsorption, few metal ions were actually tested [72, 75–77].

Heavy metals such as zinc (Zn), lead (Pb), cadmium (Cd), nickel (Ni) and copper (Cu) are prior toxic pollutants in industrial wastewater, which become common groundwater contaminants and they tend to accumulate in organisms, causing numerous diseases and disorders. The complexity of effluents makes the process of heavy metals removal more difficult due to presence of organic legends, phosphate, cyanide and humic
matter that can be added to complexity of removal, as well as strict limitations that have been imposed to wastewater discharge everywhere in aquatic recipients.

Removal of metal ions from dilute or concentrated solutions has received a great deal of attention for recovery of valuable metals or decontamination of effluents. Among all heavy metals, copper, chromium and zinc ingestion beyond permissible quantities causes various chronic disorders in human beings. The extensive use of chromium in leather tanning, metallurgy, electroplating and other industries has resulted in the release of chromium to the sub surface at numerous sites thereby releasing undesirable amounts of chromium (VI) according to the water standards. Chromium is found in various oxidation stages ranging from −2 to +6 and also +3 and +6 states are most prevalent in the environment. The toxic hexavalent chromium anions such as chromate (CrO$_4^{2−}$), bichromate (HCrO$_4^{−}$) and dichromate (Cr$_2$O$_7^{2−}$) are not strongly sorbed in many soils under alkaline to slightly acidic conditions. Thus, they can be very mobile in subsurface environment and exert toxic effects on biological systems. Potable waters containing more than 0.05 mg/L chromium are considered to be toxic for living beings [78]. Hence their effective removal from the waste waters before disposal is very important. Various methods such as ion-exchange, solvent extraction, liquid membrane and adsorption have been studied for the removal of hexavalent chromium and liquid–liquid extraction amongst those is the most effective conventional method which is extensively used in separation science. The optimization of water and wastewater purification processes requires the development of new operations based on low-cost raw materials with high pollutant-removal efficiency. Many toxic heavy metals are being discharged into the environment as industrial wastes, causing serious soil and water pollution.

The removal of heavy metals from contaminated water has become a major research topic due to the toxicological problems caused by the toxic metals to the environment and to human health in recent years. Among the various methods, adsorption has been proven to be an efficient technology while its large-scale application is limited by the high cost of the adsorbent. One of the powerful treatment processes for the removal of dyes from water at low cost is adsorption. Adsorption techniques have proven successful on lowering dye concentration from industrial effluents by using adsorbents such as activated carbon, peat, chitin, clay, and others. Adsorption is a process
by which atoms, molecules or ions are retained on the surfaces of solids by chemical or 
physical bonding. Activated carbon has been the most widely used adsorbent because of 
its high capacity for the adsorption of organic species and dye. However, due to the 
difficulty and expense involved in regeneration, magnetic nanoadsorbents are considered 
as alternative low cost, effective and Eco-friendly novel nanoadsorbent. Since some 
magnetic nanoadsorbents can be easily synthesized by co-precipitation method, they are 
proposed as an inexpensive removal technique.

This research was conducted to investigate the removal of heavy metals and dye 
from industrial effluent through adsorption process using magnetic nanoadsorbent. The 
main objective of this research is the synthesis of magnetic nanoadsorbent by simple 
techniques, their characterization and develop new treatment/removal methods for the 
removal toxic heavy metals and organics from industrial effluents. The employed 
magnetic nanoadsorbent on adsorption process for the removal of heavy metals and 
organics along with the influence of different parameters have been studied such as 
initial metal concentration, contact time, the effect of adsorbent dose, pH toward heavy 
metals and dye removal performance. The equilibrium and thermodynamic of metals 
adsorption have been investigated. The physicochemical status and the evaluation of 
statistics of obtained physicochemical data of industrial wastewater samples were 
studied. In order to minimize the processing costs for textile industry effluents, one of the 
best ways is to manufacture the local sources.

In the following chapters Review of Literature, Results and discussion, 
Experimental, Summary and Conclusion are being described and discussed.
References:


[61] Smara, A., Delimi, R., Chainet, E. and Sandeaux, J. Removal of heavy metals from


