"Water is the driving force of all nature"… Leonardo da Vinci

1.1 Introduction

In this era, the robust scientific and technological developments aimed at the elevation of living standards have succeeded to a great extent. Innovative avenues of human comforts have been commercialized continuously and even undeveloped countries are now capable of providing luxuries and comforts to the people. In recent years, the world's rapid economic improvement has gained momentum and has lead to climbing wages, as well as to a fast urbanization and an uncontrolled population growth. Therefore, the earth has experienced an assortment of pressing environmental challenges such as climate change, global warming, waste generation, and water pollution. This has led to serious environmental degradation and has contributed a major share to the overall imbalance of the ecosystem. The natural resources are depleted and are being contaminated continuously. The entire ecosystem comprising of air, water and soil is getting polluted with different hazardous materials causing detrimental effects as a whole.

From the beginning of civilization, human society has been significantly dependent on the natural and environmental resources including air, water, soil, vegetation etc. for its dwelling which in due course of time underpins all economic activities. However, rates of exploitation of these natural resources are far surpassing any of the past with a negative connotation of accompanying environmental degradation. The human society can embark

on a shift from an approach that has over exploited and misspent the environment to a strategy that derives full and sustainable benefits from environment.

Amid diverse natural resources, water is one of the most important and essential component sustaining life and making the earth as a green planet. It is not only a liquid but is an "elixir of life". The *Chhandogya Upanishad* quoted, "*It is the waters which pervade everything, big or small, the earth, the atmosphere, the heaven, the mountains, Gods, men, animals, birds, grass, plants, dogs, worms, insects, and ants. All these worldly manifestations are waters indeed*", which clearly depicted the essentiality of water in every sphere of life. The Gandhian quote "*Earth provides enough to satisfy every man's needs, but not every man's greed*" is quite true for the availability of water resources on the Earth.

1.2 Global water distribution

Water, a precious and finite resource sustaining life on this green planet, covers approximately 71% of the Earth. Out of total available water (Figure 1.1), 97% of water on the Earth is contained in the oceans and seas as saline water, leaving only 3% as fresh water of which slightly over two-thirds i.e. (79%) is frozen in glaciers and ice caps at the North and South Poles. The remaining unfrozen, ~20% is found as groundwater, with small fraction of only 1% as accessible freshwater. Out of that, small portion of accessible surface freshwater, 53% is in rivers and streams, and 8% there in the atmosphere as moisture. So, in freshwater lakes there is about 52% of the 1% accessible water, of the 3% of the total which is freshwater on the Earth.
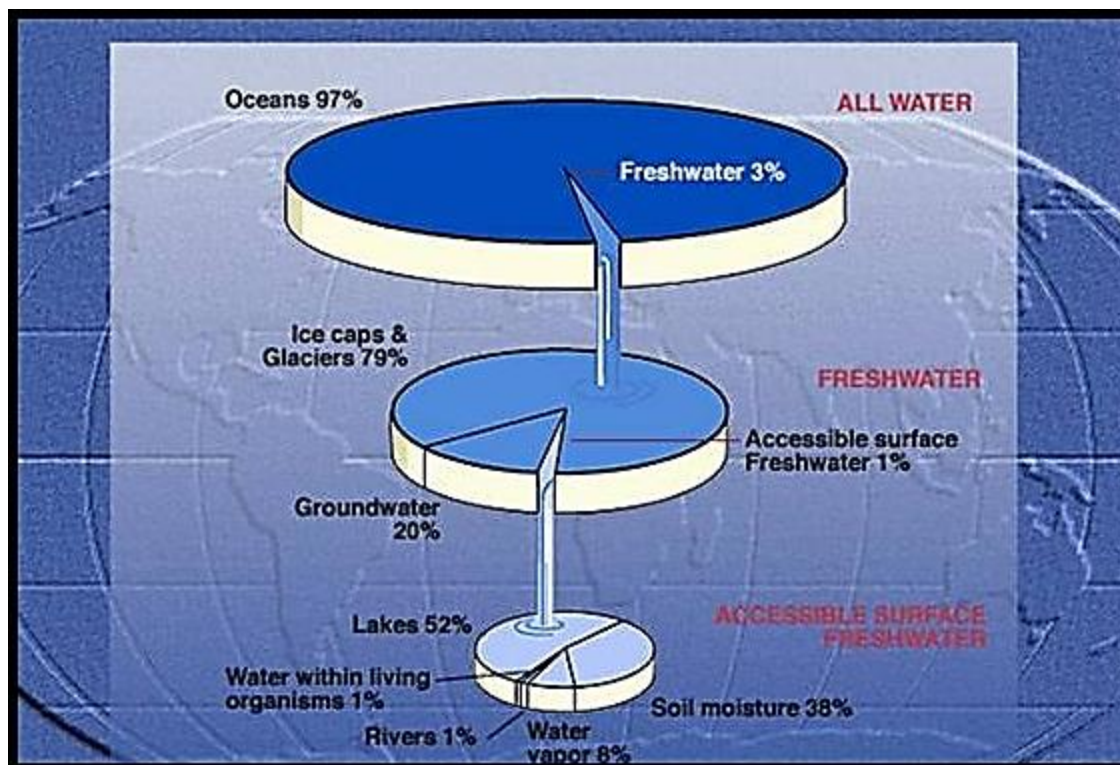
Figure 1.1 Distribution of World's Water

Water is continually cycled through its various reservoirs and this cycling occurs through the processes of evaporation, condensation, precipitation, deposition, runoff, infiltration, sublimation, transpiration, melting, and groundwater flow (Figure 1.2; (Source:United States Geological Survey). The oceans supply most of the evaporated water found in the atmosphere. 91% of this evaporated water is returned to the ocean basins by precipitation. The remaining 9% is transported to areas over landmasses where climatology factors induce the formation of precipitation. The resulting imbalance between rates of evaporation and precipitation over land and ocean is corrected by runoff and groundwater flow to the oceans.
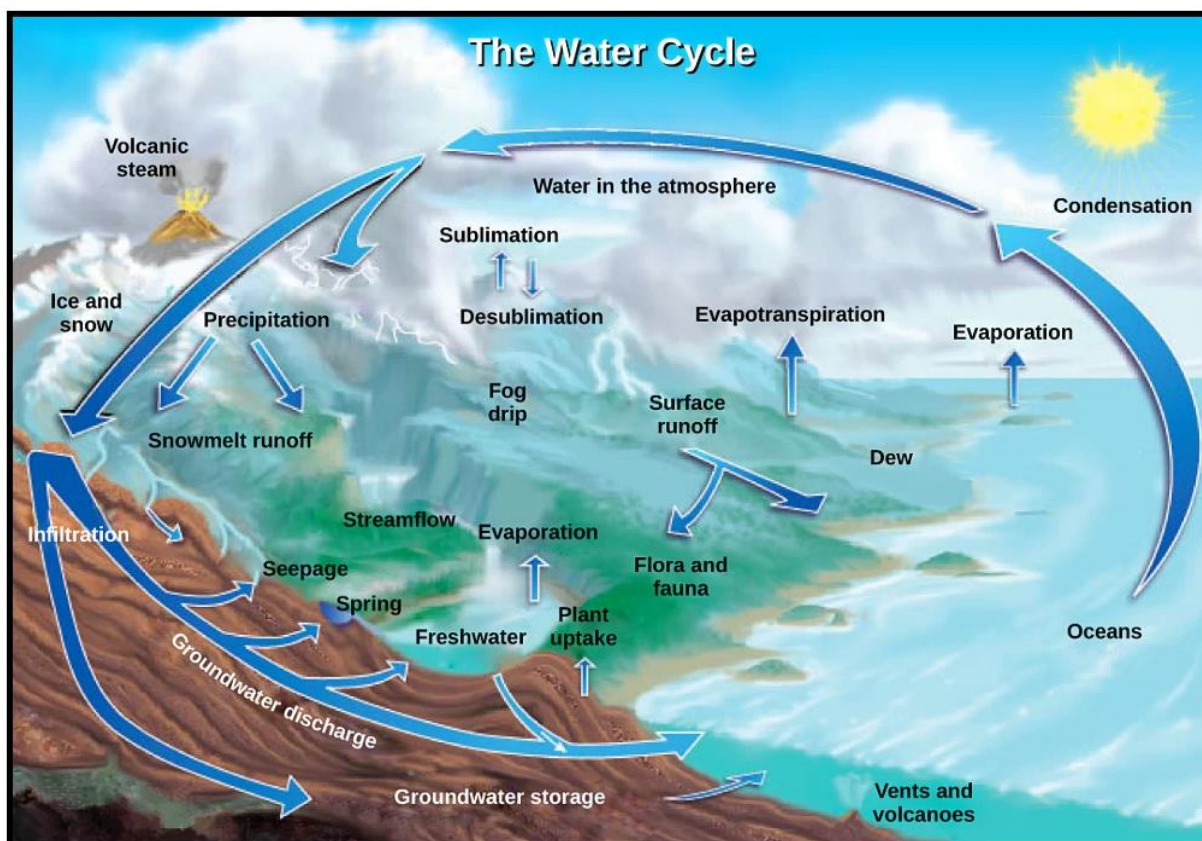
Figure 1.2 The Water Cycle

(http://science.nasa.gov/earth science/oceanography/physical-ocean/salinity/)

Water is present in almost purest form in its evaporated state and gets gradually contaminated in later stages of hydrologic cycle by means of materials present in the atmosphere as well as and on or underneath the surface of the earth. In due course of time, the contaminated water completes the entire hydrologic cycle and is returned back to the atmosphere again in moderately untainted state. In any case, it is the water quality in transitional stage which is of prominent concern since it is the quality at this stage which will influence the utilization of the water.

Freshwater is a renewable resource, yet the world's supply of clean, fresh water is steadily decreasing (Table 1.1). Water demand already exceeded supply in many parts of the world and as the world population continues to rise, so too does the water demand. Awareness of the global importance of preserving water for ecosystem services has only recently emerged because during the 20th century, more than half the world's wetlands have been lost along with their valuable environmental services. Biodiversity rich freshwater ecosystems are currently declining faster than marine or land ecosystems [Gleick, 1996].

It is well-known that fresh and clean water is vital for healthy living. Satisfactory supply of pure and clean drinking water is an essential need for all people on the earth, yet it has been perceived that millions of individuals worldwide are denied of this. Water resources onto every part of the planet are undermined by over abuse and poor administration as well as by environmental pollution. The major sources of water contamination might be ascribed to release of untreated waste, dumping of industrial effluents and run-off from agricultural fields. Moreover, indifferent behaviour of man towards nature and his activity at surface, unintentionally by farming, local effluents, surprisingly by sub-surface or surface disposal of sewage, industrial wastes, and geometrical growth of population have led to adverse effects on water quality.

Table 1.1 Estimate of global fresh-water distribution

Water source	Water volume, in cubic kilometres (km^3)	% of fresh water	% of total water
Oceans, Seas, Bays	1,338,000,000	--	96.5
Ice caps, Glaciers; Permanent Snow	24,064,000	68.7	1.74
Groundwater	23,400,000	--	1.7
Fresh	10,530,000	30.1	0.76
Saline	12,870,000	--	0.94
Soil Moisture	16,500	0.05	0.001
Ground Ice; Permafrost	300,000	0.86	0.022
Lakes	176,400	--	0.013
Fresh	91,000	0.26<	0.007
Saline	85,400	--	0.006
Atmosphere	12,900	0.04	0.001
Swamp Water	11,470	0.03	0.0008
Rivers	2,120	0.006	0.0002
Biological Water	1,120	0.003	0.0001
>Total	1,386,000,000	--	100

Unfortunately, due to rapid increase in industrialization, uncontrolled population growth, civilization, rural, and domestic practices, and various other land and ecological progressions, water quality of our water resources is getting deteriorated continuously. Therefore, in present situation, water pollution affecting all living creatures, household, recreation, transportation, and other commercial activities has become a serious issue of global concern for academicians, scientists and environmentalists all over the world.

1.3 Environmental pollution

Environmental pollution is man-made inauspicious alteration of material or energy into resources leading to a change in physical, chemical, radiological or biological quality of resource (water, air, soil) that causes or may cause discriminating or unremitting detriment to the Earth's ecological or that brings harm to humans or other living organisms. The term pollution is derived from a Latin word "*pollere*" which means "to defile." Pollutants are the natural as well artificial substances that when introduced in the environment above certain permissible limit render the air, soil, water, or other natural resources detrimental for explicit applications.

Environmental pollution is the gird and concentration of hazardous levels of certain chemicals in the resources (air, water and land) causing grave and irreparable damage which gradually diminishes their capacity to support life. The pollutants may be solids in the form of landfills and scrapyard; liquids such as discharges from industries and sewage system; and gaseous such as injurious gases emitted from various sources.

1.4 Water pollution

Water is addressed as a necessary resource and life preservative. Any departure in its quality from the pure condition is a state of contamination and when it starts affecting the biotic life adversely, it is termed as pollution. The deterioration in water quality is brought about mostly by industrialization and anthropogenic activities which disturb the normal uses of water, e.g. potable water supply, agriculture, industry, aquatic life, recreation and aesthetics.
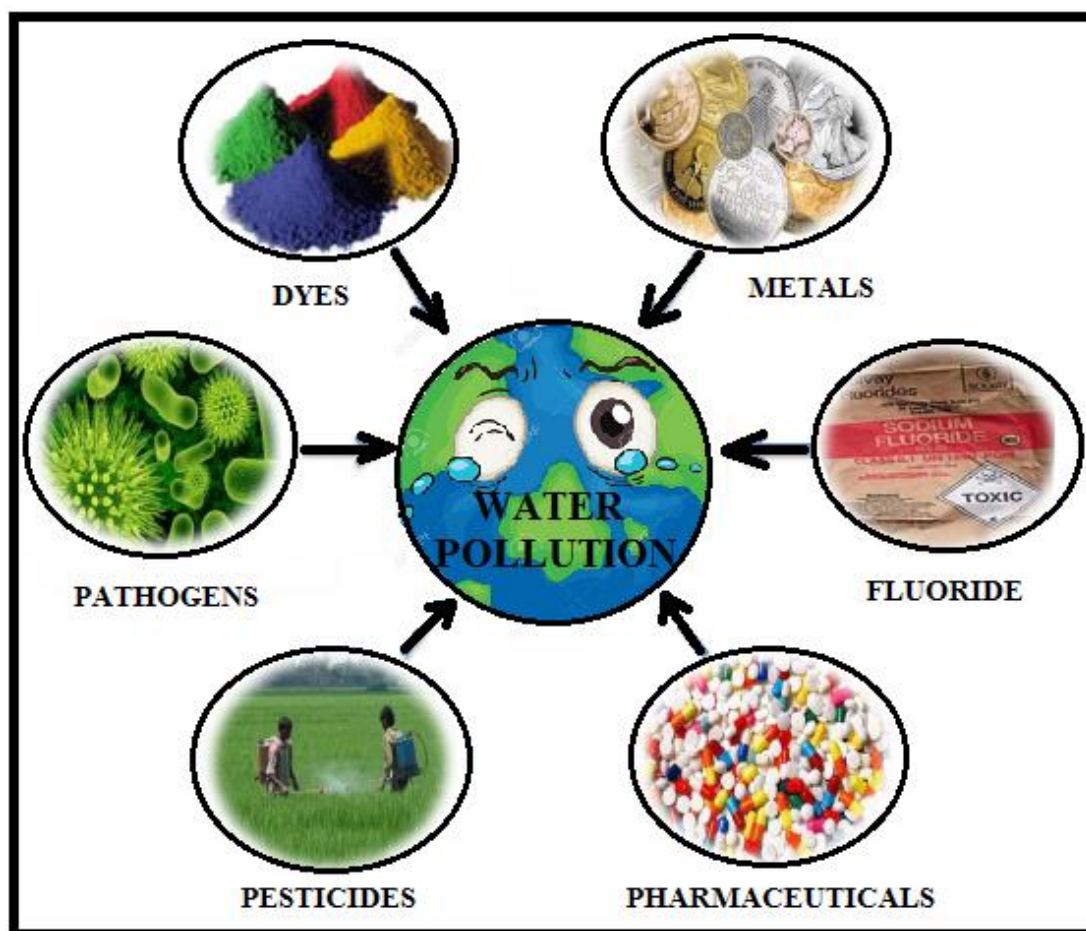
Figure 1.3 Major sources of water pollution

Although, the nature of pollutants may vary, quite significant quantities of pollutants are introduced into natural water through municipal sewage; the agricultural run-off containing residues of organo-metallic pesticides; corrosion in the pipes; pharmaceuticals; industrial effluents; etc. Furthermore, water borne pathogenic microorganisms as a consequence of untreated sewage, septic tanks, runoff from farms, are ubiquitous throughout the world. Major sources of pollution all over the world are shown in Figure 1.3.

1.5 Water pollutants

Pollutants known to contaminate water and deteriorate water quality are broadly classified into following types:

(i) Organic pollutants

(ii) Inorganic pollutants

(iii) Sediments

(iv) Radioactive materials

(v) Thermal pollutants.

1.5.1 Organic pollutants

This group comprises of pathogens, plant nutrients, oxygen demanding wastes, sewage, synthetic organic compounds, pesticides (insecticides, fungicides, herbicides), detergents, dyes and oil, etc.

1.5.2 Inorganic pollutants

Inorganic salts, trace elements, organometallic compounds, complexes of metals with organics in natural water, finely divided metal or metal compounds, mineral acids and acid mine drainage, phosphates, nitrates, sulphates, bicarbonates, hydrogen sulphides, chlorine, etc. may be listed under this category.

1.5.3 Sediments

The natural process of soil erosion gives rise to sediments in water. It represents the most extensive pollutants of surface water. Bottom sediments are important sources of

inorganic and organic matter in streams, fresh water, estuaries and oceans. The bottom sediments are subjected to anaerobic reduction and undergo continuous leaching. The level of suspended solid loadings reaching natural water is about 700 times as large as the solid loadings from sewage discharge. Sediments and suspended particles are important repositories for trace metals such as Cr, Mn, Cu, Mo, Ni and Co.

1.5.4 Radioactive materials

This category consists of various components of radioactive fuels, low grade radioactive liquid wastes, liquid and gaseous wastes from fuel elements, fission products and radionuclides, etc.

1.5.5 Thermal pollutants

Water is generally employed as coolant in many industrial processes and its temperature, sometimes rises by 10^0C or more during such operations. This rise in temperature decreases dissolved oxygen (D.O.) of water and adversely affects the fish and other aquatic life forms.

1.6 Heavy metal contamination in aquatic system

Being explicit to inorganic pollutants, heavy metals under this category are significant water contaminants with high degree of danger and carcinogenicity posing a concern of increasing significance for ecological, evolutionary, nutritional and environmental reasons. "Heavy metals" refer to any metallic element whose density exceeds 5 g cm^{-3} and is toxic or poisonous even at low concentrations. These metallic

species exert detrimental effects due to their non-biodegradable nature leading to their persistent nature as well as their solubility in water leads to their build-up in food chain [Maksin et al., 2012]. These metals cause serious health effects, including reduced growth and development, lower energy levels, damage to vital organs including lungs, kidneys and liver and blood composition, and damaged mental and central nervous functions. Long term exposure to metals may lead to slow progression of physical, muscular, and neurological degeneration process that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis, various types of cancers and in extreme cases, death also. In living species, heavy metals interrupt the overall cell metabolism by attacking the sulphur bonds, carboxylic acid, protein, and amino groups present inside the cell. The extreme presence of these metals in living species results in carcinogenic, mutagenic, and teratogenic effects on them. Upon accumulation in living tissues, they gradually disturb the microbial processes and have been reported to be fatal [Cimino and Caristi, 1990; Madoni et al., 1996; Goyer and Mehlman, 1977; Carson et al., 1986; Oelme, 1979]. Even slender excess of such metals in water is lethal to aquatic life forms such as, fish and can also damage algal growth.

The heavy metals find their way in aqueous systems both through natural and anthropogenic sources. There are different sources of heavy metals in the environment such as, natural sources (geologic parent material or rock outcroppings), agricultural sources (inorganic and organic fertilizers), atmospheric deposition (vehicle exhaust, tires, asphalt wear, gasoline/oil leakage, etc.) and industrial sources (electroplating and metallurgical activities, recycling of metals, mining, etc.). Table. 1.2 depicts some of the

heavy metals contained into effluent discharge of various industries that are supposed to be hazardous for living beings [Nagajyoti et al., 2010].

Other significant sources for the heavy metal include printed circuit board (PCB) manufacturing where tin, lead, and nickel solder plates are the most widely used resistant over-plates; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic-containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium. Subsequently, all these generators produce a large quantity of wastewaters, residues, and sludges that can be categorized as hazardous wastes demanding extensive waste treatment. Due to their high toxicity, industrial wastewaters containing heavy metals are strictly regulated and must be treated before being discharged into the water resources. Stricter wastewater regulations are established and being enforced particularly in industrialized countries to minimize human and environmental exposure to such hazardous chemicals.

Table 1.2 Occurrence of metals in industrial effluents of various industries

Industry /source	Metals									
	Al	As	Cd	Cr	Cu	Fe	Hg	Pb	Ni	Zn
Acid mine drainage	X				X	X				X
Automobile			X	X		X		X	X	X
Chemical industries	X	X	X	X	X	X	X	X		X
Coal and gasoline						X		X		
Dyes and pigments	X	X	X		X	X		X		
Fertilizers	X	X	X	X	X	X	X	X	X	X
Glass		X	X					X		
Leather tanning and finishing	X		X	X	X					X
Metallurgy and electroplating			X	X	X					X
Mining	X	X	X				X	X		
Nuclear technology			X							X
Petroleum refining		X		X	X	X		X	X	X
Pharmaceuticals	X				X	X	X			
Pulp and paper	X			X	X		X	X	X	X
Steel power plant				X			X			X
Textiles	X	X	X	X		X	X		X	

* X indicates presence of the metal and blank indicates absence of the metal

These regulations include limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The Maximum Contaminant Level (MCL) standards, for those heavy metals, established by United States Environmental Protection Agency (USEPA) [Babel and Kurniawan, 2003] are summarized in Table 1.3.

Table 1.3 Metals with their toxicities and MCL standards

Heavy metals	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhoea, nausea, vomiting, carcinogen	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Lead	Damage the foetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80

1.6.1 Technologies for heavy metal removal from water and waste water

For a couple of decades, distinctive techniques have been developed and utilized for treatment of metal bearing water. These techniques also focus on decreasing the production of heavy metal contaminated water in addition to the improvement in the quality of treated hazardous wastes. The most common methods used for treatment of metal bearing effluents are chemical precipitation, electro-dialysis, ion-exchange, adsorption, etc. Although, numerous methods have been devised and employed for the

treatment of water contaminated with metals, each one possesses its own inherent

advantages and limitations, some of which have been summarized in Table 1.4.

Table 1.4 Limitations of various physico-chemical methods used for treatment of
metal rich effluents

Treatment methods	Limitations
Activated carbon adsorption	Expensive, higher quality higher cost, carbon dependent performance, requirement of complexing agents for improved removal performance, non-selective, high reactivation cost, reactivation results in loss of carbon.
Chemical precipitation	Excessive chemical requirement, sludge generation, extra operational cost for sludge disposal, ineffective for low concentration of metal
Reverse osmosis	Low recovery, brine disposal, high operational cost, effective only for very low concentration, membrane fouling, decrease in productivity with time, pre-treatment
Electro-dialysis	High operational cost due to membrane fouling and energy consumption, pre-treatment.
Ion-exchange	Fouling, replacement in every cycle and high cost, presence of ions impede removal capacity of metals.

Adsorption is acknowledged as one of the most suitable water treatment strategies

because of its simplicity of operation, the accessibility of an extensive variety of high

adsorption limit and large scale sections [Crini, 2005]. Moreover, adsorption can also be

utilized for source diminishment and recovery for consumable, mechanical, and other purposes. Despite, adsorption has specific limits, for example, it couldn't attain a decent status at business levels because of the absence of suitable adsorbents of high adsorption limit and business scale sections. Furthermore, a single adsorbent can't be utilized for various types of pollutants. It was observed that, regardless of a few impediments, it will be an exceptional water treatment innovation in the near future.

1.7 Adsorption

The term adsorption was proposed by du Bois-Reymond but was introduced into literature by Kayser [Kayser, 1881]. It was first observed by C.W. Scheele in 1773 for gases and followed by Lowitz in 1785 for solutions [Kraemer, 1930]. The phenomenon of adsorption involves accumulation of a substance at a surface or interface between any two phases such as liquid-solid, liquid-liquid, gas-liquid or gas-solid. The substance being accumulated is called adsorbate and the adsorbing phase is called adsorbent.

1.7.1. Types of adsorption

Adsorption can be classified on the basis of the forces which are operative between the adsorbate species and the adsorbents during the entire process.

(i) Physical adsorption

In physical adsorption, the adsorbate species interact with the adsorbents due to physical forces (van der Waals' forces, hydrogen bonds, etc.), hence called physical

adsorption [Scott et al., 1995]. This is most common in cases where the adsorbed molecules do not stick to the specific sites at the surface but are rather free to make translational movement within the interface. At a low temperature, there is a greater concentration of the adsorbate and the adsorption is marked out by low heat of adsorption of the order of 42 kJ mol^{-1} ($\approx$ 5-10 kcal mol^{-1}) [Edwards, 1994]. Under suitable conditions of temperature and pressure, adsorbed layers having thickness of several diameters of the adsorbate molecules are formed. The adsorbed substance can be easily removed from the surface when physical adsorption is involved and such an adsorption is usually rapid and reversible in nature.

(ii) Chemical adsorption

In chemisorption, the adsorbate molecules are adsorbed at the active sites of the adsorbent due to the formation of chemical bonds. In such type of adsorption, adsorbate-adsorbate forces are usually small compared to the adsorbate-adsorbent binding forces, so that the adsorbate locations or sites are determined by the optimum adsorbate-adsorbent bonding. The chemical reaction occurring on the surface may be either exothermic or endothermic and an increase or decrease in temperature, affect the amount of the product formed. Generally, it is favoured by higher temperature because chemical reactions proceed more rapidly at elevated temperatures. The heat of adsorption is generally greater than 83 kJ mol^{-1} (15-30 kcal mol^{-1}). Such an adsorption is generally irreversible and is associated with monolayer coverage. All adsorption processes, whether physical or chemical in character, are accompanied by a decrease in free energy [Somorjai, 1994].

1.7.2 Adsorption from solutions

In contact with a solution, any solid surface has the tendency to build up a surface layer of solute molecules due to imbalance of surface forces. At the interface, most of the accumulated molecules are adsorbed on to the large surface area within the pores of adsorbents and comparatively few are adsorbed on the surface of the particles [Alauddin, 2000]. The affinity of adsorbed molecules for adsorbent varies with force field at liquid-solid interface.

The tendency of a particular solute to get adhered on the surface is ascertained by the difference in the potential of adsorption between the solute to be adsorbed and the solvent. Whenever, the solute-solvent affinity is appreciable, the ability of the adsorbent to adsorb solute is usually limited. In general, the lower the affinity of the adsorbent for the solute the higher will be the adsorption capacity. Adsorbents like activated carbons and polymeric adsorbents have high adsorption capacities in water because of which a low adsorption potential energy is needed on the part of an adsorbate to displace water from the surface of these adsorbents.

The affinity of the solute for the surface must also be larger than the affinity of the solute for the solvent for adsorption to be highly favoured. The solubility of the solute is a direct measure of its affinity towards solvent and a reciprocal relationship between the adsorbate solubility and adsorption capacity has been noticed. Generally, less soluble solutes have a tendency to get adsorbed promptly and on contrary, more soluble ones get adsorbed less readily [Vilyssider, 1998].

Adsorption from solutions is generally circumscribed to monolayer coverage on the adsorbent surface. The adsorptive forces are weak ahead of the first monolayer. During the transfer of adsorbate from solution to adsorbent's sites, the high energy sites are occupied instantaneously and succeeding adsorption process, as the surface coverage increases, takes place at low energy level sites i.e. at less favourable sites. Under this situation, the heat of adsorption and effective diffusion rate turn down swiftly with an increasing surface coverage. This preferential trend continues until the solute phase concentration remaining in the solution attains equilibrium with the adsorbed phase concentration [Ramaswamy, 2000].

Before adsorption starts, the adsorbate molecules are dispersed in the bulk liquid. The rate of adsorption is determined by the rate of transfer of the adsorbate from bulk solution to the adsorption sites within the particles. For getting adsorbed at a particular site, the adsorbate must diffuse across a stationary solvent film surrounding each adsorbent particle through the macro pores and then through the micro pores. The time for adsorption to take place is the sum of the time taken for each step. The slowest one will determine the rate for the whole process and is called the rate determining step.

1.7.3 Film diffusion

The random movement of adsorbate molecules resulting out of the collisions with the solvent molecules leads to their diffusion. In a solution with uniform concentration, the random diffusion of adsorbate in all direction leads to equal transfer rates in to and out of any specific region. When a concentration gradient exists, more molecules are

available in the high concentration region to diffuse towards the region of low concentration and a net transfer of adsorbate occurs. It is the concentration difference between the solution phase which causes more adsorbate molecules to diffuse towards the adsorbent site and fewer to diffuse away, leading to a mass transfer in to and on to adsorbent.

1.7.4 Pore diffusion

Adsorbate molecules must diffuse through the static liquid in the pores of an adsorbent particle to reach the adsorption sites. The rate of diffusion through the solution in macropores is usually assumed to be the same as the rate of diffusion through the static bulk solution since the adsorbate molecules collide with the pore walls infrequently relative to the rate of collision with solvent molecules. The rate of mass transfer through the pores varies inversely with the adsorbate concentration and inversely with the square of the particle radius. Mass transport becomes slower due to molecular size pore dimensions.

During adsorption, the exterior surface of the particle becomes saturated with the adsorbent. A sharp boundary exists between saturated adsorbent and bare adsorbent. The adsorption zone becomes thicker as the time passes with the boundary moving towards the centre of the particles. Adsorption and mass transfer get terminated when the particles become fully saturated.

1.8 Factors influencing adsorption

During the adsorption of solutes on adsorbents, various factors such as initial adsorbate concentration, temperature, pH, agitation speed, nature of adsorbent, particle size and presence of foreign ions affects the rate and extent of adsorption.

1.8.1 Concentration

The extent of adsorption of ionic species is highly affected by the concentration of adsorbate in the system. Sometimes the process becomes complicated due to formation and overlapping of mono and multilayer adsorption as well as capillary condensation. Various types of isotherms have been classified by Giles et al., (1960). The adsorption of some ions obeys the Langmuir isotherm, whereas for a limited concentration range at constant temperature, the variation of adsorption with concentration can also be depicted by Freundlich isotherm.

1.8.2 Temperature

Adsorption reactions are normally exothermic [Weber, 1972]. Thus, the extent of adsorption generally increases with decreasing temperatures. However, in certain cases, as in the case of activated adsorption [Myers and Zolandy, 1980], the rise in temperature favours the extent of adsorption. The temperature dependence of equilibrium capacity for adsorption is defined by activation energy, E_a. Thus, the adsorption phenomenon can be anticipated by the extent of activation energy. Physi-sorption, for example, possesses the heat of adsorption of ~5 kcal mol^{-1} which indicates the presence of van der Waals' force between the adsorbate and adsorbent. For chemisorptions, it is generally more than 20

kcal mol^{-1} [Edwards, 1994] which indicates formation of certain new chemical bonds between adsorbate and adsorbent.

1.8.3 pH of the solution

The pH of the solution governs the overall process of adsorption by influencing the surface charge of the adsorbent as well as the adsorbate, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the adsorbent. In some cases, adsorption is favoured by low solution pH, and in others, a higher pH favours the removal of adsorbates [Johnson, 1990]. Generally, the adsorption of cations increases and that of anions decreases with the rise in pH of solution, possibly because of competition between H^+/OH^- ions and the adsorbate species present in the solution. Since H^+ and OH^- ions are adsorbed readily, the adsorption of other ions is affected by pH of the solution [Farrell, 2001].

According to Helfferich (1962), the film diffusion will control hydrogen ion uptake only under extreme conditions in rapidly stirred adsorption reactions. The surface adsorbs anions favourably at low pH range due to presence of H^+ ions, whereas, the cations are preferably adsorbed at higher pH values due to deposition of OH^- ions.

1.8.4 Nature of adsorbate and adsorbent

The nature, weight, size, degree of ionization and electrical charge of the adsorbate species significantly affects the extent of adsorption. Likewise, physico-chemical nature of adsorbents also affects the uptake of ions in a marked way. The adsorbent's efficiency

is the product of two factors i.e specific surface area and adsorption affinity. Thus, the overall adsorption may be affected by chemical characteristics of surface, porosity and physical states of sorbent and solute-solvent interactions. When the solute-solvent interactions are predominantly strong enough to overcome the forces extended by the solvent or solution, then the mono-layer and multi-layered adsorption will result [Raghavan et al., 1998].

1.8.5 Particle size

Adsorption is a surface phenomenon as such and the extent of adsorption is proportional to specific surface area. Specific surface area can be defined as that portion of the total surface area that is available for adsorption. The adsorption capacity is directly proportional to the total exposed surface and inversely proportional to the particle diameter for non-porous adsorbents while for highly porous adsorbents, it should be independent of the particle sizes. It is, therefore, logical to infer that bigger solute particles get adsorbed less than the smaller solute particles for a fixed amount of adsorbent [Weber and Morris, 1963]. Thus, amount of adsorption accomplished per unit weight of a solid adsorbent is greater for a more finely divided and the more porous solid. Because the extent of a surface reaction will vary with available surface area, adsorption rate should exhibit a monotonic increase with some function of the inverse of the diameter of the adsorbent particles. The adsorption capacity of nonporous adsorbents should also vary as the inverse of the particles diameter [Krishna and Swamy, 2012].

1.8.6 Agitation speed

Rate of adsorption is controlled either by pore diffusion or film diffusion depending upon the degree of agitation of solid-solution system. The adsorption of solid-solution interface generally proceeds via following three steps: (i) transfer of adsorbate species from bulk to the solid surface through the aqueous film that surrounds the adsorbent, (ii) diffusion through the pores if adsorbent is porous and (iii) the uptake of the adsorbate species by the active surfaces including formation of bonds between the adsorbate and adsorbent. Film diffusion is often the rate limiting step for low agitation speeds (continuous flow system) while for high speeds (rapidly stirred batch reactors), pore diffusion is important [Nomanbhay and Palanisamy, 2005].

1.8.7 Presence of foreign ions

At low concentrations, the extent of adsorption is affected in the presence of foreign ions in solution due to changes in the chemical properties of the adsorption surface and also because of competitive adsorption of the ions [Hu et al., 2010].

1.9 Contacting systems and modes of operation

Various experimental techniques have been employed by many scientific workers to ensure the intimate contact between adsorbate and adsorbent for the effective removal of pollutants from water and waste-waters. The contacting systems are broadly classified into two categories.

1.9.1 Batch System

In batch-type contact operations, a definite quantity of adsorbent is agitated with a specific volume of contaminated water or solution of an adsorbate until the contaminant or the adsorbate in the aqueous phase has either decreased to a desired level or completely removed. The quantity of adsorbent and time of contact are adjusted according to the needs. The adsorbent is then separated from solution and either discarded or regenerated for reuse. The batch process is the most common mode of operation and employed for the removal of several pollutants [Hameed et al., 2008].

1.9.2 Continuous-flow-system

In such type of operations, the adsorbent is always in contact with a fresh solution. The solution flows upward/downward through a column of fine particulate adsorbent at a velocity sufficient to suspend the solid particles. The adsorbent is added at the top of the column and the spent adsorbent is withdrawn from the bottom [Sivaprakash et al.,2010].

1.10 Nanotechnology and Wastewater Treatment: A General Vision

Nanotechnology is the application of nanoscience for the manipulation, control, and integration of atoms and molecules to form materials, structures, components, devices, and systems at the nanoscale that exhibit remarkable properties, functionality, and phenomena due to the influence of small dimensions and can be used across all the other fields.

At nanoscale, some novel size-dependent chemical, biological, physical, mechanical, electrical, and magnetic properties, such as surface area, intra-particle diffusion distance, compressibility, number of available adsorption sites, etc. of the materials change drastically. Accordingly, it is recommended that nanotechnology holds out the guarantee of enormous improvements in environmental remediation together with other areas of manufacturing, health, electronics, telecommunication, etc.

In the last two decades, nanotechnology has undergone a full-fledged advancement with its requisition in almost all branches of science and technology. In this arrangement, nanotechnology is also used for water remediation. Recent advances in nanotechnology offer significant chance to build up cutting edge water supply frameworks. The current water treatment, dispersion, and discharge practices, which vigorously rely on conveyance and brought together frameworks, are no more reasonable. The highly prolific, meticulous, and multifunctional processes empowered by nanotechnology are envisaged to give superior, reasonable water and wastewater treatment arrangements that depend less on substantial infrastructures. Nanotechnology-empowered water and wastewater treatment assures to overcome major challenges confronted by existing treatment advancements, additionally they provide new treatment capacities that could permit financial use of whimsical water sources to enlarge the water supply [Qu et al., 2013; Kumar et al., 2009; Whitesides, 2005].

Advances in nano-scale science and engineering are providing unprecedented opportunities to develop more cost effective and environmentally acceptable water purification processes. In recent years, a great deal of attention has been focused on the

synthesis and application of nano-structured materials as adsorbents to remove toxic and harmful compounds from water and wastewater [Ali, 2012; Qu et al., 2013; Khajeh et al., 2013]. Resurgence to synthesize and manipulate nano-particles finds use in improving water quality in the environment. In perspective of the vitality of water quality and increasing applications of nanotechnology, endeavours have been made to talk about different parts of water remediation by adsorption utilizing nano-adsorbents.

1.10.1 Nano-adsorbents

Nano-particles are the engineered materials having at least one of its atomic dimensions in nano (10^{-9}m) range. These atomic particles exhibit certain most striking and fascinating characteristics that enable them to be used in various branches of science and technology including medicines, optics, electronics, environment, etc. These engineered nano-particles have significant amount of surfaces and thus attract interest to be applied as adsorbents in comparison to macromolecules and hence given the name of "Nano-adsorbents". Nano-adsorbents offer the potential for treatment of contaminated water. The engineered nano-particles have proven to be excellent adsorbents due to their unique features. The most important characteristics of these particles which makes them ideal adsorbents are small size, catalytic potential, high reactivity, large surface area, ease of separation and large number of active sites for interaction with different contaminants [Hristovski et al., 2007; Khaleel et al., 1999; Li et al., 2006]. Due to the increasing electronic density at their edges, various functional groups may be attached to the nano-particles to enhance their reactivity, affinity, capacity, and selectivity towards target

pollutants in aqueous solutions [Mauter et al., 2008]. So they provide the ability to combine a number of reactive agents together and allow fine control over mass transport properties. These properties are responsible for high adsorption capacities by increasing the surface area, free active valences and surface energies of nano-particles. In light of their high porosity, minor measure, and dynamic surface, nano-adsorbents not just are fit for sequestering contaminants with shifting atomic size, hydrophobicity, and speciation behaviour; additionally, empower assembling methodology to devour crude materials productively without discharging its poisonous payload [Pacheco et al., 2006]. Nano-adsorbents work quickly, as well as have significant metal-binding capacities. Additionally, they can be regenerated in the wake of being exhausted. Various nanomaterials have been applied in removing radio-nuclides, adsorption of organic dyes, remediation of contaminated water, and magnetic sensing.

1.10.2 Metal oxide nanoparticles as nano-adsorbents for sorption of heavy metals

Metal oxides play a significant role in many fields of nano-technology including nano-catalysis, sensing, super-magnetic properties, and nano-energy storage. Nano-sized metal oxides adsorbents have been fabricated and utilized for the treatment of various pollutants present in aquifers. Metal oxides at nanoscale dimension exhibit unique physical and chemical properties due to their limited size, large surface areas, and high activity due to high density of surface reaction sites at corners, edges, vacancies caused by the size-quantization effect turning them particularly attractive as adsorbents. Particle size is anticipated to influence basic properties in any material, such as structural

characteristics, namely the lattice symmetry and cell parameters [Ayyub et al., 1995], electronic properties in terms of quantum confinement related to the energy shift of exciton levels and optical band-gap, and physical and chemical properties of materials leading to change in the magnitude of the band gap [Fernández-García et al., 1996; Rodriguez et al., 1998], with strong influence in the conductivity and chemical reactivity [Hoffmann, 1988; Albright et al., 1985]. The size and shape of the metal oxide nanomaterials are both key factors that conjointly affect their adsorption process, and consequently, effective synthetic methods have been devised for synthesizing shape-controlled, highly stable and highly dispersed nanomaterials [Hua et al., 2012]. The mechanism of adsorption is essentially controlled by complexation amongst dissolved metal ions and the oxygen atoms of metal oxides. It is a two-step process, in which the first one involves fast adsorption of metal ions on the external surface, followed by the rate-limiting intraparticle diffusion along the micropore walls of the nanoadsorbent. Metal oxides can be easily impregnated into porous supports such as, activated carbon, natural materials, synthetic polymeric hosts, etc. to improve their applicability in wastewater treatment [Hua et al., 2012]. Besides these, metal oxide nano-adsorbents can be easily regenerated by changing the solution pH and can be reused up-to several cycles without exhibiting any significant decline in the adsorption capacity. All these features of metal-based nano-adsorbents including relatively low cost of synthesis, high adsorption capacity, ability of removing pollutants even at very low concentration, ease of separation, regeneration and reuse make metal oxide nano-adsorbents technically and economically advantageous.

The commonly used nanoparticles for water treatment are made of akaganeite [Deliyanni and Matis, 2005], alumina [Sharma et al., 2010], anatase [Gao et al., 2004], cadmium sulphide [Hayes et al., 1987], cobalt ferrite [Biasi et al., 2007], copper oxide [Martinson and Reddy, 2009], maghemite [Park et al., 2004], iron [Wu et al., 2012], iron oxide [Takami et al., 2007], iron hydroxide [Fan et al., 2005], nickel oxide [Srivastava et al., 2014], silica [Wang et al.,2014], titanium oxide [Ku and Jung, 2001], zinc oxide [Srivastava et al., 2013], zinc sulfide, zirconia [Gusain et al., 2015], and some alloys [Ban et al., 2006].

1.10.3 Synthesis and characterization of nanoadsorbents

The synthesis of nano-particles is the first and most important step in the process of water treatment through engineered nano-particles. In terms of synthesis of nano-particles, there are two general strategies involved viz., the bottom-up approach (that entails the arrangement of smaller molecules atom-by-atom or molecule-by-molecule into more complex assemblies with the help of certain physical or chemical forces via chemical synthesis, positional assembling, or self-assembling), and the top-down approach (that involves the generation of nano-particles from large size (i.e., granular or micro-scale) materials via mechanical and/or chemical steps including milling, etching etc.) as represented in Figure 1.4.

There are a number of methods devised for preparation of nano-particles based on the desired morphology, properties, applications etc. which incorporate sol-gel process [Srivastava et al., 2013], precipitation [Phiwdang et al., 2013], co-precipitation [Petcharoen et al., 2012], catalytic growth [Li et al., 2003], mechanical alloying/milling

[Arbain et al., 2011], mechano-chemical synthesis [Tsuzuki et al., 2004], impregnation [Kukovecz et al., 2002], electro-deposition [Park et al., 2008], laser ablation [Thareja et al., 2007], inert gas condensation [Nanda et al., 2002], spark discharge generation [Rexer et al., 2000], spray pyrolysis [Ghaffarian et al., 2011], thermal plasma synthesis [Jankeviciute et al., 2013], severe plastic deformation [Long et al., 2014], ion sputtering [Urban et al., 2002], flame synthesis [Kumfer et al., 2010], flame spray pyrolysis [Ma¨dler et al., 2002] and laser pyrolysis [Figgemeier et al., 2007].
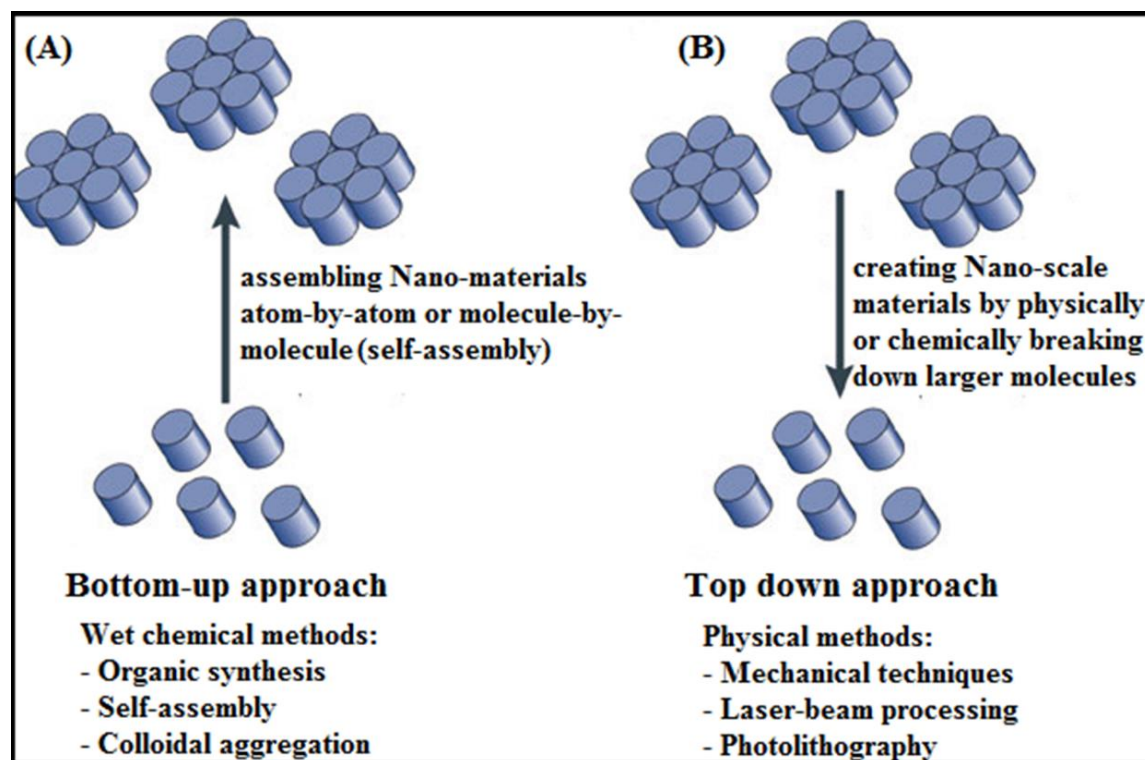

Figure 1.4 Top down and bottom up approaches for the synthesis of nanomaterials

The composition and molecular structure of the nano-particles can be altered through these methods. Among various methods of synthesis of nano-particles proposed so far, sol-gel method is widely used because it provides fine control over molecular structure, morphology, pore volume, surface area, density etc. of the materials fabricated for water treatment processes. The various nano-particles synthesized so far for water remediation and their corresponding method of synthesis is tabulated in Table 1.5.

Further, based on the size and shape of the synthesized nano-materials, these can be classified into nano-particles, nano-tubes, nano-wires, nano-belts, nano-capsules, nano-fibres, nano-polymers, nano-springs, quantum dots, etc. Each of these nano-materials possesses unique properties that are extensively explored for various applications.

Nanoparticles	Methods	Diameter(nm)	Starting materials	Reference
Table 1.5 Different methods of synthesis of nanoparticles used as an adsorbent for water treatment				
Akaganiete	Precipitation method	2.6	Iron(III) chloride, ammonium carbonate	Deliyanni and Matis, (2005)
Alumina	Sol−gel method	6−30	$AlCl3 \cdot 6H2O$	Zeng, (1998)
	Sol−gel method	50	Aluminum isopropoxide, Cyclohexane, NH4OH	Pacheco and Rodriguez, (2001)
	Hydrolysis	80	Aluminum isopropoxide, sodium bis-2- ethyl hexylsulfosuccinate	Park et al., (2005)
Alumina−silica	Sol−gel method	30	Tetra ethyl orthosilicate, ethanol, NH4OH, 2-propanol, aluminium tri-sec-butoxide	Pacheco et al., (2006)
Anatase	Solvo-thermal method	8−20	Titanium(IV) ethoxide, ethanol	Gao et al., (2004)
Ceria	Flame electrospray pyrolysis	2.4-6	Cerium(III) nitrate hexahydrate, ethanol, diethyl glycol butyl ether	Oh and Kim, (2007)
Chromium-doped zinc oxide	Chemical vapour synthesis	18	Zinc acetyl acetonate, chromium acetyl acetonate	Jin et al., (2007)
Cobalt ferrite	Combustion wave	2.7-17	Iron nitrate, cobalt nitrate, glycine	Biasi, (2007)
	Wet chemical route	15-48	Ferric chloride, cobalt chloride, NaOH	Hu et al., (2005)
CdS	Sol-gel method	1.66	$Si(OC_2H_5)_4,$ C_2H_5OH, HCl, cadmium acetate, Sodium sulphide	Hullavarad and Hullavarad, (2007)
CuO	Reverse micelles	5-25	Copper chloride, ammonia, Triton-X-100, n-hexanol, n-pentanol, cyclohexane	Han et al., (2008)
Gum arabic modified magnetic nano-adsorbent	Co-precipitation	3-67	$FeCl_3.6H_2O$, gum arabic, NH_4OH	Banerjee and Chen, (2007)

Iron oxide	Hydrothermal synthesis	14-25	Iron sulphate, n-decenoic acid or n-decylamine	Takami et al., (2007)
FeOOH-coated Maghemite(γ-Fe$_2$O$_3$) Nanoparticles	Surface precipitation	15	γ-Fe$_2$O$_3$ (nanoscale), ferric salt, NaOH, H$_2$O$_2$	Hu et al., (2007)
MgAl$_2$O$_4$	Thermal Decomposition	10	Al(NO$_3$)$_3$.9H$_2$O, Mg(NO$_3$)$_3$.6H$_2$O	Zawrah and Kheshen, (2002)
Maghemite	Sol-gel method	10	FeCl$_3$, FeCl$_2$, NH$_4$OH	Hu et al., (2005)
NiO	Sol-gel synthesis	4-22	Nickel acetate tetrahydrate, oxalic acid, Ethanol	Thota and Kumar, (2007)
SiO$_2$	Sol-gel method	15-700	Si(OC$_2$H$_5$)O$_4$	Chrusciel and Slusarski, (2003)
SnO$_2$	Precipitation route	20-60	SnCl$_2$.2H$_2$O, NH$_4$OH	Ibarguen et al., (2007)
TiO$_2$	Combustion method Laser pyrolysis Solvothermal method Sol-gel method	100-1000 14 10-20 5	Titanium powder, sodium perchlorate TiCl$_4$ Ti(OR)$_4$, toluene n-butyl-methylimidazolium hexafluoro phosphates [BMIM] [PF$_6$]	Kitamura et al., (2007) Figgemeier et al., (2007) Kim et al., (2007) Zhai et al., (2007)
ZnO	Laser ablation Sonochemical synthesis Thermolysis	14-20 70-80 18-45	2-propanol, acetone, zinc metal ZnCl$_2$, KOH Zinc nitrate, polyvinyl alcohol	Thareja and Shukla, (2007) Kandjani et al., (2008) Patil and Joshi, (2007)
ZrO$_2$	Precipitation method	15	Zirconium oxychloride octahydrate, zirconyl chloride, ammonia solution	Guo and Chen, (2005)
ZnS	Sol-gel	2.3-4.5	Tetraethyl orthosilicate, 2-propanol, thiourea,Zn(NO$_3$)$_2$.6H$_2$O	Bhattacharjee et al., (2003)

The engineered nanoparticles are characterized with the help of certain analytical techniques such as X-ray diffraction (XRD), Fourier Transform IR (FTIR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA), differential thermo-gravimetric analysis (DTA), triple-point-N_2-Brunuaer-Emmett-Teller (BET) adsorption etc. and the information altered over through these techniques is summarized in Table 1.6. Basically, the reported methods are used for the preparation of different types of nano-particles with slight modifications for various applications such as biomedical, biotechnology, materials, electronics, mechanical, optical, environmental sciences, etc. The selection of the technique depends on the size, properties, starting materials, and the required applications of the nano-particles.

Table 1.6 Characterization techniques of nano-particles synthesized as an adsorbent for water treatment

Characteristics	Analytical Techniques
Morphology	Scanning Electron Microscope (SEM)
	Environmental Scanning Electron Microscope (ESEM)
	Field Emission Scanning Electron Microscope (FESEM)
	Transmission Electron Microscope (TEM)
Particle size	Laser diffraction particle size analyser
Crystal structure	X-ray diffraction (XRD)
Specific surface area	Triple-point N_2 Brunauer-Emmett-Teller (BET) adsorption
pH $_{zpc}$	Potentio-metric titration
	Zeta potential analyser
Heavy Metal-NPs interaction	Extended X-ray absorption fine structure (EXAFS) spectroscopy
	X-ray absorption near edge structure (XANES) spectroscopy
	X-ray photoelectron spectroscopy (XPS)
	UV-Vis diffuse reflectance spectrometer
	Diffuse reflectance infrared fourier transform (DRIFT) spectroscopy
	Fourier transform infrared (FTIR) spectroscopy
	Attenuated Total Reflectance infrared (ATR-IR) spectroscopy
	Raman spectroscopy
	C^{14} peak
Magnetic properties	External magnetic fields
	Vibrating sample magnetometer (VSM)
Thermal properties	Thermo-gravimetric analysis (TGA)
	Differential scanning calorimetry (DSC)
Metal concentration (aqueous phase)	Atomic absorption spectroscopy (AAS)
	Inductively coupled plasma (ICP)
	UV-Vis spectrophotometer

1.11 Scope of the work

Extensive growth in industrial sector has resulted in rapid development of various industries such as metal plating facilities, mining operations, tanneries, batteries, paper industries, fertilizer industries, pesticides, etc., and has generated a platform for the rise of myriad environmental problems, out of which water pollution accounts for the major concern of global scientists and environmentalists. The major cause of water pollution is indiscriminate discharge of industrial effluents containing different types of harmful and toxic metals directly or indirectly into the aquatic systems beyond their acceptable limits. Like many organic contaminants, metallic species, especially heavy metals are also non-biodegradable and tend to accumulate in living organisms. The presence of heavy metals in the aquatic systems can pose serious threat to the environment. Among various toxic heavy metals Cr(VI) and Ni(II) are of particular concern because of their adverse effects on fauna, flora and human beings.

Adsorption is considered to be the most effective technique in treating industrial discharges which hinges to its low initial cost, simplicity of design, ease of operation, large scale applicability, insensitivity to toxic substances, no harmful by products formation and complete removal of pollutants even at trace level from dilute solutions. Perusal of literature suggested that number of different adsorbent materials had been used for the removal of heavy metals from aqueous solutions and waste water. Conventional low cost adsorbents are being superseded by nano-adsorbents in terms of their large surface area which enables them to adsorb larger amounts of metal ions with enhanced adsorption capacity and rapid sorption rate. Furthermore, their ability of regeneration and

reuse; and requirement in low quantity make their application economical. In this context, nano-alumina (n-Al$_2$O$_3$) and nano-cupric oxide (n-CuO) nano-adsorbents were synthesized and applied for their adsorption potential in removal of Cr(VI) and Ni(II) from aqueous solutions.

1.12 Objective of the Present work

The objective of the present study was the synthesis, characterization and evaluation of adsorption capacity of two nano-adsorbents namely nano-alumina (n-Al$_2$O$_3$) and nano-cupric oxide (n-CuO) for the removal of chromium, Cr(VI) and nickel, Ni(II) ions from aqueous solutions by batch systems. In order to achieve this objective, the following investigations were carried out:

(i) Synthesis of the nano-adsorbents for their application in removal of Cr(VI) and Ni(II) from aqueous solution.

(ii) Physico-chemical characterization of the synthesized nano-adsorbents in order to assess their different physical and chemical properties.

(iii) Application of Box-Behnken experimental design (BBD) of response surface methodology (RSM) for modelling of the adsorption process and optimization of various experimental parameters for optimum removal of chromium and nickel.

(iv) Establishing kinetic, isotherm and thermodynamic parameters using model equations and evaluation of efficacy of linear and non-linear approaches in their determination.

(v) Regeneration of the nano-adsorbents for further use.