1.1 ENVIRONMENT AND ENVIRONMENTAL POLLUTION

Environment means the surrounding, and it encompasses all living as well as non-living things. The environment comprises the interaction of all living species, climate, weather, and natural resources that affect human survival and economic activity and it can be divided into four major environmental spheres i.e. atmosphere, hydrosphere, geosphere, and biosphere. Each of these environmental constituents interacts with each other in some respect and some locations on the earth. Unfortunately, the environment gets polluted by anthropogenic as well as by natural causes. The environmental pollution can be defined as the contamination of the biological as well as physical components of the earth system to the extent at which it alters greatly normal environmental processes [Franklin (1991)]. The introduction of different types of undesirable and harmful contaminants substance unintentionally released into the atmosphere which deliberate adverse effect on the living organism known as pollution. Pollution is the cause of damage to the environmental functioning which may be in the form of heat, light, noise or any chemical changes. The pollutants may be of natural in origin and behave as contaminants when it is present in very high concentration. The major consequences of environmental pollution resulted in depletion of ozone layer, global warming, and desertification.

Among other components of the environment, water is one of the essential component for the sustenance of living organism on the earth. The water circulates throughout the Earth's environment through the solar powered hydrological cycle. The water covered the 3/4 of the surface of the earth. Out of this, about 97 % of the water in the hydrosphere is located in the sea as salty water. From the remaining 3%, 2% is located at the polar ice caps leaving only 1% water as the freshwater of the rivers,

lakes, ground water etc. **[**Dey (2008)**]** . Thus only 1% of Earth's water is commonly designated as freshwater which is treated as potentially accessible for human consumption [Sivashankar *et al.* (2014)]. The different types of pollution can be classified into five categories:

1.2 TYPES OF POLLUTION

Pollution may be characterized in the following types:

• Air pollution

• Noise pollution

• Soil pollution

• Radioactive pollution

• Water pollution

1.2.1 Air pollution

Air pollution includes both natural as well as anthropogenic causes. The main five types of air pollutant which contribute more than 90% air pollution globally are nitrogen oxide (NO_x), carbon monoxide (CO), hydrocarbons (HC), sulfur oxides (SO_2) and particulates **[**Dey (2008)**]**.

1.2.2 Noise pollution

Noise, defined as unwanted sound, is a pollutant and has an ability to cause deleterious health effects in living beings such as annoyance, sleep disturbance, cardiovascular disease, and impairment of cognitive performance in children [(Basner *et al.* (2014)].

1.2.3 Soil pollution

The chief source of soil contamination is the use of chemical fertilizers, sludge applications, dumping of solid waste, vehicular exhaust and industrial activities [(Khan *et al*. (2008)].

1.2.4 Radioactive pollution

Radioactive pollution includes deposition of radioactive substances on the surfaces or within the solid, liquid and gases where their presence is undesirable. These radioactive substances emit hazardous radiation such as gamma rays which is considered as potential carcinogenic.

1.2.5 Water pollution

Water is the most vital natural resources for sustainment of all life form on the earth and valuable natural resource for human civilization also. The suitability of the water for drinking, agricultural as well as industrial purposes depend upon its chemical composition [Jagtap *et al*. (2011)]. Unfortunately, the quality of water is being degraded due to vast population expansion, rapid industrialization, agricultural activities, and other geogenic and environmental causes. Water get polluted by different sources which is shown in Figure 1.1 [Sivashankar *et al*. (2014)].

Therefore, in the present scenario the water pollution has become a global concern which has affected the large population of the living organism by exerting various deleterious effects. Around the world, many countries are suffered by both surface as well as groundwater contamination with various types of pollutants which make water unfit for drinking purpose. It is estimated that by 2020 the world's population is expected to reach up to 7.9 billion and due to large population expansion the whole world will experience large scarcity of potable water [Gupta *et al*. (2012)].
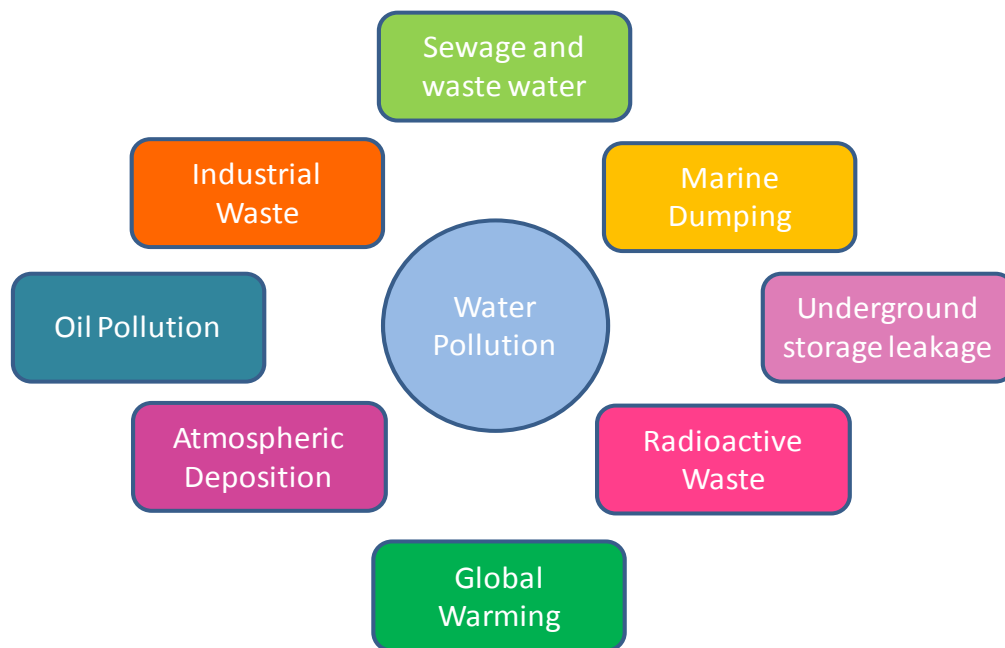
Figure 1.1 Sources of water pollution

It is reported that about 780 million people are still lacking clean drinking water sources around the world (Qu *et al.* (2013)]. Consequently, these pollutants must be removed from the water to make it suitable for drinking, agricultural as well as industrial needs. The persistent contaminant of the water may be broadly classified into inorganic, organic compounds and biological pollutants which is shown by Figure 1.2 [Ali (2012)]. Heavy metals are the most common type of the pollutants comes under the category of inorganic pollutant are highly lethal and carcinogenic in nature [Ansari and Malik (2007)]. Many inorganic anionic pollutants such as fluorides, nitrates, phosphates, sulfates, oxalates, and chlorides have also showed the various toxic effect in the living organism.
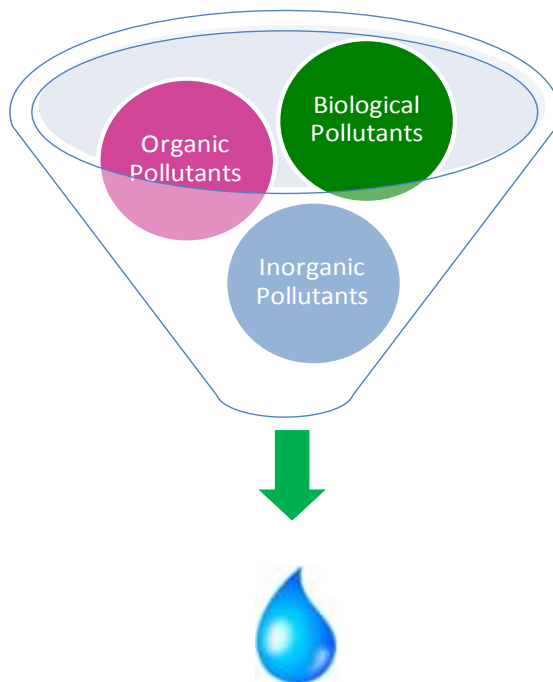
Figure 1.2 Schematic Diagram of various types of contaminants present in water

1.3 Types of Water Pollution

The water pollutants may be broadly classified into five main categories [(De (2008),

Ali (2012)]:

(1) Inorganic Pollutants

(2) Organic Pollutants

(3) Biological Pollutants

(4) Radioactive pollutants

(5) Thermal pollutants.

1.3.1 Inorganic Pollutants:

The most common inorganic water pollutants include heavy metals, which are highly toxic and carcinogenic in nature. Additionally, nitrates, sulfates, phosphates, fluorides, chlorides, and oxalates also have some serious hazardous effects.

1.3.2 Organic Pollutant

The toxic organic pollutants are emerges from pesticides which include herbicides, insecticides, polynuclear hydrocarbons (PAHs), fungicides; phenols, polychlorinated biphenyls, halogenated aromatic hydrocarbons, formaldehyde, greases, polybrominated biphenyls, biphenyls, oils, detergents, etc. In addition to these, normal hydrocarbons, alcohols, aldehydes, ketones, proteins, lignin, pharmaceuticals, etc. are also found in wastewater.

1.3.3 Biological Pollutant

Different types of microbes present in wastewater may be responsible for the various type of diseases which include bacteria, fungi, algae, plankton, amoeba, viruses, and worms. These water pollutants remain either in solvated, colloidal or in suspended form.

1.3.4 Radioactive Pollutant

Water gets contaminated with the discharge of radioactive waste into the sewer system. The nuclear power plant produces the low-level radioactive liquid waste, liquid waste from fuel elements, fission products, and heat which ultimately disposed into the water.

1.3.5 Thermal Pollution

Rivers and lakes which are located near the coal-fired power plants are associated with the thermal pollution. The temperature of the nearby lakes and river

increased during the cooling of condenser coil (cooling by ~10°C). This rise in temperature adversely affects the aquatic flora and fauna.

1.4 WATER POLLUTION BY FLUORIDE AND ITS TOXICITY

Fluoride (F⁻) is one of the hazardous anionic pollutants which is present in groundwater worldwide and creates a major problem in safe drinking water supply. Fluorine is the most electronegative and reactive among all the elements in the periodic table. Because of its great reactivity, fluorine cannot be found in nature in its elemental state. It exists either as inorganic fluoride (including the free anion F⁻) or as organic fluoride compounds, and always exhibit an oxidation number of -1. In the environment, inorganic fluoride are much more abundant than organic fluoride compounds [Jagtap *et al.* (2012)]. The toxicity of fluoride is depended upon its concentration. It is necessary ingredients of drinking water and show beneficial effects when present in the suitable amount i.e. in the range of 0.5–1.0 mg/L [(Teng *et al.* (2009)] is required for calcification of dental enamel, maintenance of healthy bones and prevention of dental cavities [Tripathy *et al*. (2006)].

Excess concentration of fluoride (>1.5 mg/L) causes various diseases such as osteoporosis, arthritis, brittle bones, infertility, thyroid problem, Alzheimer syndrome, brain damage and cancer. Dental and skeletal fluorosis are the most common diseases caused by the elevated concentration of fluoride and which is irreversible and cannot be treated. The only remedy is prevention by keeping fluoride intake within the safe limits [Li *et al*. (2011)]. In many cases, the excess concentration of fluoride may lead to embrittlement of bones and neurological damage on prolonged exposure [Meenakshi and Maheshwari (2006)]. Literature reports different sites of fluoride toxicity in the living organism such as it may disturb the DNA synthesis process, interfere the

metabolism of lipids, carbohydrates, proteins, vitamins and mineral thereby it causes many diseases. Generally, the gastrointestinal tract is the first organ which gets affected by fluoride toxicity and causes irritation in gastrointestinal tract because it moves to the intestinal mucosa after ingestion where it may form hydrofluoric acid in the stomach. It is also reported that it may interfere the mechanistic pathway of the various enzymes which are involved in oxidative phosphorylation, glycolysis, coagulation, and neurotransmission [Bhatnagar *et al*. (2011)].

1.4.1 Sources of fluoride contamination

Dissolution of natural fluoride minerals and industrial discharge into the water are the common sources of fluoride contamination. Now a day in various industries, the fluorochemicals are extensively used as essential ingredients, and their waste discharge usually contain the high concentration of fluoride which makes water polluted with fluoride [Tripathy *et al*. (2006)]. Various sources of fluoride contamination are schematically shown in the Figure 1.3.
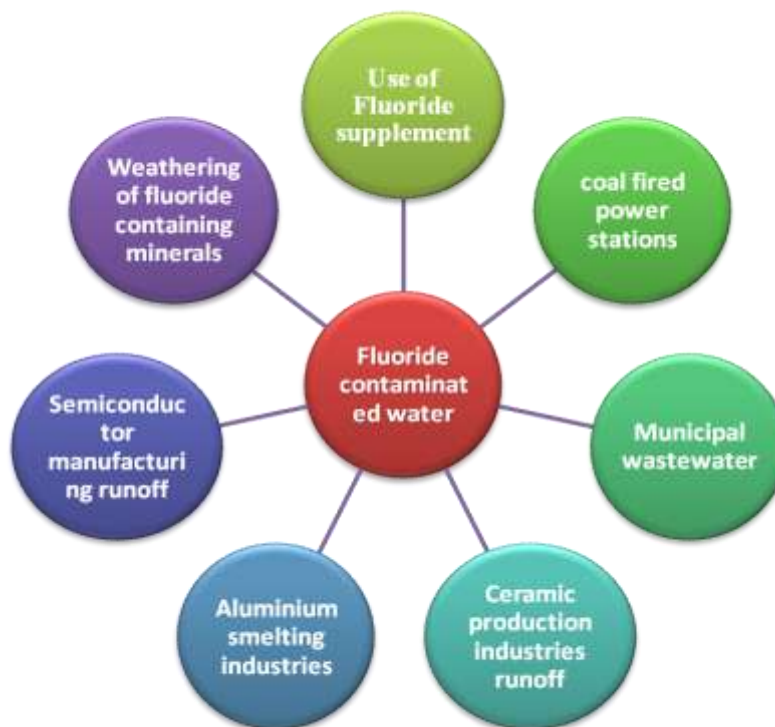
Figure 1.3 Sources of fluoride Contamination

1.5 WATER POLLUTION BY LEAD AND ITS TOXICITY

Lead [Pb(II)] is found ubiquitously in soil, air, and water [Luo *et al*. (2014)]. Lead is considered as one of the very toxic heavy metal along with the mercury and cadmium as they classified as a group "Big Three metals" which are known for their highly toxic nature [Volesky (2007)]. The permissible limit of lead recommended by World Health Organization is set to be 0.01 mg/L [Ahmaruzzaman and Gupta (2011)]. Lead exposure mainly arises from the contact with lead-based paints in the home,

fertilizers, cosmetics, automobiles, disposable batteries, etc., especially in developing countries [Nevin (2007)].

Several studies have been carried out previously which shows its toxic effect of lead in the human being. The high concentration of lead induces various chronic disorders which includes neurological, cardiac, behavioral, hepatic, renal, hematological, and immunological dysfunctions [Dewanjee *et al.* (2013), [Abbas *et al.* (2016), Li *et al.* (2002), Mohan *et al.* (2002)]. The mechanism of lead toxicity is not yet clear however, some researchers have reported that lead in the living tissue leads to the formation of reactive oxygen species which retard the antioxidant enzymes activity in the tissues [Pulido and Parrish (2003), Jurczuk et al. (2007), Franco *et al.* (2009)]. Some shreds of evidence has also showed that the process of lipid peroxidation also increased due to the presence of lead (Upasani *et al.* (2001)). As reported by Silbergeld *et al.* (2000) and Patrick (2006) the various pathological disorders induced by lead exposure is caused by mainly two factors, increased of lipid peroxidation and inhibition of the antioxidant activity of enzymes. The non-biodegradability nature of lead leads to its accumulation in the tissues of the living beings for many years which causes several disorders in the living organism [Saeidi *et al.* (2015)].

1.5.1 Sources of lead contamination

Lead is used in various industries as their essential ingredient [Dewanjee *et al.* (2013), Saeidi *et al.* (2015)] which is schematically shown in the Figure 1.4 The runoff from these industries pollute the water [Marques *et al.* (2000), Ledesma *et al.* (2013)].
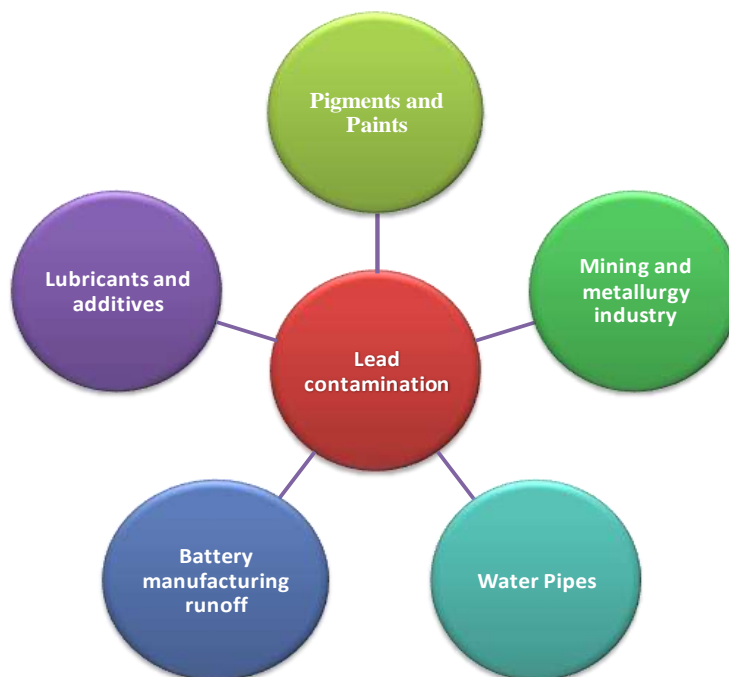
Figure 1.4 Sources of lead contamination

1.6 METHODS USED FOR REMOVAL OF IONIC IMPURITIES FROM WATER

Due to hazardous and deleterious effects of these pollutant species their efficient removal is necessary from the water. In the present time, several methods have been anticipated for the efficient heavy metal removal from the water which include chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation and electrochemical treatment [Fu and Wang (2011)]. Among these techniques, adsorption is l/lo y;widely used method for the abatement of ionic impurity from the water.

1.6.1 Chemical precipitation

Chemical precipitation is very effective and most commonly used process in industry because it is relatively simple and inexpensive to operate. The precipitation processes, involve the reaction of chemicals with the heavy metal which forms insoluble precipitates. Then the precipitates are separated from the water by sedimentation or by filtration and the purified water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation. The major drawback of this technique is that it is usually employed for the treatment of high concentrations of metal ions and is found to be ineffective for low concentration of metal ions. Besides, this process is also associated with the large amount of sludge production and higher operation costs.

1.6.2 Ion-exchange

Ion-exchange process is also a widely used technique for the removal of heavy metals from the water due to its many benefits i.e. high treatment capacity, high extraction efficiency, and fast kinetics. The important property of Ion-exchange resins (synthetic or natural) is the specific binding ability for cations as well as for anions which are specifically removed from the water. The exhausted ion exchange resin can be regenerated with the specific chemicals for reuse. However, this process can lead to secondary pollution. Ion exchange process is expensive when it is used for the treatment of a large amount of water with a low concentration of metal ions.

1.6.3 Membrane filtration

Membrane filtration technologies with various types of membranes show great promise for heavy metal removal for their simple operation, high efficiency, simple

operation and space saving. The membrane processes used to remove metals from the wastewater are ultra- filtration, reverse osmosis, nanofiltration, and electrodialysis. This technology showed high efficiency toward the removal of heavy metals, but several other factors which are assumed to be the limitation of this process includes complexity of the process, high operation and maintenance cost, fouling of the membrane.

1.6.4 Coagulation-flocculation

Coagulation and flocculation followed by sedimentation and filtration are also employed to remove heavy metal from the wastewaters. This technique of heavy metal wastewater treatment involved the dewatering and good sludge settling characteristics. The limitation of this method includes utilization of plenty of chemicals and the large volume of sludge generation which make this approach less accessible.

1.6.5 Flotation

Flotation involves the separation of metal ions from waste water by hydrophobic interaction using surfactants and the hydrophobic species then separated as air bubbles. This approach has several advantages over other conventional method which include high metal selectivity, high efficiencies for metal removal, high overflows rates, inexpensive to operate and generation of concentrated sludge [Rubio *et al*. (2002)]. This process also associated with many limitations i.e. high initial capital cost, high maintenance and operation costs.

1.6.6 Electrochemical treatment

Electrochemical methods include the plating of metal ions on a cathode surface, from where the metal can be recovered in the elemental state. Electrochemical

wastewater technologies involve relatively large capital investment and the expensive electricity supply, so they haven't been widely applied.

1.7 Adsorption

The adsorption process is widely used techniques for the removal of several kinds of the pollutant from water such as soluble and insoluble organic, inorganic, and biological contaminants. The molecules of gases or liquids or the solutes in solutions attach on the surface of the solids. Adsorption process involves two important terminologies i.e. adsorbent and adsorbate. The adsorbent can be defined as the solid or liquid phase on which adsorption takes places whereas the substance whose molecule gets adhere or adsorb on the adsorbent known as the adsorbate. Adsorption process can be divided into two categories depending upon the nature of the interaction between adsorbate and adsorbent:

1.7.1 Physical Adsorption

Physical adsorption is characterized by the presence of weak attractive forces between the adsorbate and adsorbent molecules which include Van der Waals and hydrogen bonding. During the interaction, no exchange of electron occurred between both the species. This process does not the required the involvement of activation energy hence, the equilibrium established in the very short period of time.

1.7.2 Chemical Adsorption

In this type of adsorption process, the interaction between adsorbate and adsorbent occurs by chemical bonding which can be ionic or covalent bonding. Adsorbate attached on the adsorbent surface by the formation of the new chemical bond.

1.8 Mechanism of Adsorption

The adsorption process involves the transfer of pollutant species from solution phase to the adsorbent surface. There are four steps involved in the transfer of adsorbate from the liquid phase to a solid adsorbent surface [Mohan *et al*. (2016)]

(a) The transportation of adsorbate species from solution to boundary film.

(b) External diffusion: adsorption of pollutant species on the adsorbent surface by diffusion of adsorbate from boundary film to the adsorbent surface.

(c) Intraparticle diffusion: transfer of adsorbate to the internal pore and spaces present in between the active sites of the adsorbent.

(d) Adsorption and desorption of the adsorbate at the active site of the adsorbent surface.

1.9 Factors affecting the rate of adsorption

In this thesis work, the whole work is concentrated on the removal of toxic pollutant from the water through adsorption process. Therefore this section focuses on the factors affecting the adsorption of toxic heavy metal ions from aqueous solution onto the solid adsorbent. The rate of adsorption of pollutant ions from aqueous solution to the surface of solid depends on the following factors:

1.9.1 Nature of adsorbent

The extent of adsorption increases with increase in surface area of the adsorbent. Greater the specific surface area of the adsorbent, greater is the amount of substance adsorb from the bulk phase. As the size of the adsorbent particles decreases, their specific surface area increases. Concurrently, the surface also shows an increase in the number of residual valences i.e. edge, corners, and cracks. Hence, the magnitude of

adsorption increases with the availability of surface active sites, as long as other factors remain constant.

1.9.2 Nature of adsorbate

Adsorbate-adsorbent interactions depend on the polarity of the adsorbent and on the nature of the medium in which the adsorbate is dispersed. Adsorption increases with the decrease in solubility of adsorbate (solute) in the solvent. Lesser the solubility of adsorbate, weaker the adsorbate-solvent interaction and hence more is the adsorption. Adsorbate solubility is a controlling factor for the adsorption equilibrium. Landelius rule state that, there is an inverse relationship exist between the extent of adsorption and solubility of adsorbate in the solvent in which adsorption has to occur. In an aqueous solution of a ion or molecule (adsorptive) the degree of ionization, ionic radii, molecular weight, electrical charge as well as the hydration energy of the adsorption comes into play and affect the adsorption process.

1.9.3 Effect of pH

The degree of ionization of a species is also affected by the pH (e.g., a weak acid or a weak base). An adsorbent-adsorbate interaction is the interplay of the polarity of the adsorbent surface and the acidity or the basicity of the adsorptive solutions. Therefore, pH has also been referred to as the master variable. Consequently, the overall uptake process for the adsorption of ionic species by the functionalized metal oxide or hydroxide nanoparticles are governed by the electrical double layer viz. surface charge density, zeta potential and number of the charge density on the adsorbent surface.

1.9.4 Effect of concentration

Adsorbate concentrations significantly affect the adsorption process. High adsorption capacity is observed at low adsorbate concentrations, and low adsorption capacity is found at high adsorbate concentrations. The adsorbate concentration dependence of the adsorption process is expressed in terms of adsorption isotherms. The adsorption isotherm is defined as the amount of adsorbate (x) on the surface of adsorbent (m) as a function of adsorptive concentration in the bulk phase at the constant a temperature. In other words, it is the mathematical expression or graphical expression, which represents the variation of the extent of adsorption at equilibrium with concentration at the constant temperature. Adsorption increases with the increase of adsorbate concentration and reach to a maxima at a particular adsorbate concentration.

1.9.5 Effect of temperature

Most of the adsorption processes are exothermic with some exceptions where the adsorption is an endothermic process [Cui *et al*. (2015), Li *et al*. (2015), Jin *et al.* (2014), Fu *et al*. (2015)]. The process of adsorption of an adsorbate onto the surface of the adsorbent balance the residual forces on the adsorbent surface and thereby decrease its surface energy. This decline in surface energy appears in the form of heat. The heat of adsorption is defined as the amount of heat evolved or absorbed when one mole of the adsorbate adsorbs onto the surface of the adsorbent. The heat of adsorption depends on nature of adsorbent and adsorbate. The physisorption process is characterized by low heats of adsorption (i.e. about 10-40 kJmol-1), while in the case of chemisorption the heat of adsorption i.e. about 40-400 kJmol^{-1}. Accordingly, lower temperatures should favor physisorption process whereas, higher temperatures favor chemisorption. According to Le-Chatelier's principle, the magnitude of the adsorption of ionic species

from its aqueous solution by solid surfaces increases with the decreases of temperature in the case of the exothermic process while in the case of an endothermic process the extent of adsorption of ionic species increases with rise in temperature.

1.10 Advantages of the Adsorption Process

Adsorption process involves the passage of polluted water through adsorbent bed where pollutant species is removed either by chemical reaction at the surface or by ion exchange with the adsorbents molecules. Adsorption has several advantages so that it can be easily used at large scale in the treatment plants at high flow rates and removes pollutant ions very effectively without producing sludge. Adsorption method offers high flexibility in design and operation, produces superior quality of treated water. Also, this process is sometimes reversible so that it and be reused for many cycles of adsorption and desorption after regeneration by a suitable adsorbent. The advantages of adsorption can be summarized as below:

(a) Low running cost

(b) Easy to operate

(c) High adsorption capacity

(d) Number of useful cycles

(e) Possibility of regeneration

1.11 Conventional adsorbents for the Fluoride and Lead Removal

Many adsorbents have been reported in the literature for the removal of lead such as clay minerals, metal oxides, and activated carbon however these adsorbents showed many shortcomings due to their high costs and low adsorption capacities [Luo *et al.* (2014)]. Similarly fluoride being removed by various adsorbent such as activated

alumina [Ku and Chiou (2002), Ghorai and Pant (2004)], layered double hydroxides [Lv *et al*. (2007)], bone char [Medellin-Castillo *et al*. (2007)], zeolites [Onyango *et al*. (2004)], calcite [Turner *et al*. (2005)] etc. However, these adsorbent are experiencing the drawback of low uptake capacity. The following table (Table 1.1 and 1.2) presents a summary of various conventional adsorbent used for the remediation of fluoride and leads from water.

Table 1.1

Summary of various conventional adsorbents for the removal of fluoride from water

S.No.	Adsorbent	Conditions	Model used to calculate adsorption capacity	Uptake capacity Mg/g	References
1	Activated carbon (rice straw)	Co= 5–20, pH=2–10, T=25–55	Langmuir	18.9	Daifullah *et al*. (2007)
2	Activated carbon (Morringa Indica)	Co=2–10, pH= 2–12, T=30–50°C	Langmuir	0.2314	Karthikeyan and Ilango (2007)
3	Activated carbon (Acacia	Co=1.5–15, pH= 5–8, T=	Freundlich	2.622	Hanumantharao *et al*.

	farnesiana)	Ambient			(2011)
4	Activated carbon (Pithacelobium dulce)	Co=1–8, pH= 6–9, T= Ambient	Freundlich	1.9333	Emmanuel *et al.* (2008)
5	Basic oxygen furnace slag	Co=1-50, pH= 7, T= 25–45 °C	Langmuir	4.58–8.07	Islam and Patel (2011)
6	Activated alumina (γ-Al$_2$O$_3$)	Co=15-100 mg/L, pH= 5-6, T= 30°C	Langmuir and Freundlich	0.86 mmol/g	Ku and Chiou (2002)
7	Manganese oxide-coated alumina	Co=2.5-30 mg/L, pH=7±0.2, T= 30±2°C	Langmuir	2.851	Maliyekkal *et al.* (2006)
8	Hydrous manganese oxide-coated alumina	Co=10-70 mg/L, pH=5.2±0.05, T= ca. 25°C	Langmuir	7.09	Teng *et al.* (2009)

9	Copper oxide coated alumina (COCA)	Co=10 mg/L, pH=5.2±0.05, T= 30 ± 1	Langmuir	7.770	Bansiwal *et al.* (2010)
10	Magnesia amended activated alumina	Co=5-150 mg/L, pH=6.5-7.0, T= 30 ± 1	Sips	10.12	Maliyekkal *et al.* (2008)
11	Quick lime	Co=10-50 mg/L, T= 25 ± 2°C	Langmuir	16.67	Islam and Patel (2007)
12	Lime stone (LS) Aluminium hydroxide and impregnated lime stone	Co=0-100 mg/L, pH=8.0, T= 298K	Freundlich	43.10	Jain and Jayaram (2009)
13	Granular ferric hydroxide	Co=1-100 mg/L, pH=6-7,	Langmuir	7.0	Kumar *et al.* (2009)

	(GFH)	T= 25 ± 2°C			
15	Synthetic siderite	Co=3-20 mg/L, pH=4.0-9.0, T= 25°C	Freundlich and Redlich-Peterson	1.775	Liu *et al.* (2010)
16	Iron(III)-tin(IV)	Co=10-50 mg/L, pH=6.4 ± 0.2, T= 303 ± 1.6 K	Langmuir	10.47	Biswas *et al.* (2009)
17	Hydrated iron(III)–	Co= 10–80 mg/dm^3 pH=5.6	Langmuir	31.89	Biswas *et al.* (2010)

	aluminium(III) chromium(III) ternary mixed oxide	$\pm$ 0.2, T= 30°C			
18	Al–Ce hybrid adsorbent	Co= 2-15 mg/L pH=6.0, T= 25°C	Langmuir	27.5	Liu *et al*. (2010)
20	Chemically modified bentonite clay (10% La-bentonite)	pH=7.0, T= 30$\pm$2°C	Langmuir and Freundlich	4.24	**Kamble** *et al.* (2009)

21	Magnesium Incorporated clay bentonite	Co= 5.0 mg/L pH=3-10.0, T=25± 2°C	Langmuir	2.26	Thakre *et al.* (2010)
22	Neodymium modified chitosan	Co= 10-100 mg/L pH=7.0 T=303 K	Langmuir	22.38	Yao *et al.* (2009)
23	La(III) incorporated Carboxylated chitosan bead	Co= 11-19 mg/L pH=7.0 T=303 K	Freundlich	4711 mg/kg	**Viswanathan and Meenakshi (2008a)**
24	Fe(III) loaded Carboxylated chitosan beads	Co= 11-19 mg/L pH=7.0 T=303 K	Freundlich	4230 mg/kg	**Viswanathan and Meenakshi (2008b)**

25	Magnesia /chitosan composite	Co= 10-23 mg/L pH=10.1-10.4 T=RT	Freundlich	2175 mg/kg	**Sundaram** *et al.* **(2009)**
27	Zirconium(IV) tungstophos- phate/chitosan composite	Co= 10 mg/L pH=7.0, 3.0 T=303 K	Freundlich	2025–2142 mg/kg	**Viswanathan and Meenakshi (2010)**
28	Lanthanum Incorporated chitosan beads	Co= 5.34 mg/L pH=5.0 T=30±1°C	Langmuir	4.7 mg/g	Bansiwal *et al.* (2009)

29	Aluminium impregnated chitosan	Co= 10.0 mg/L pH=6.5 T=25±2°C	Freundlich	1.73 mg/g	Swain *et al.* (2009)
30	Spirogyra IO2	Co= 5.0 mg/L pH=7.0 T=30°C	Langmuir	1.272 mg/g	Mohan *et al.* (2007)
31	Eichhornia Crassipes biomass And its carbonized form	Co= 2-25 mg/L pH=5.5 T=25°C	Freundlich	0.523–1.54 mg/g	Sinha *et al.* (2003)
32	Zirconium(IV) impregnated Collagen fiber	Co= 1-5mmol/L mg/L pH=5-8 T=303 K	Langmuir	41.42	Liao and Shi (2005)

33	Zirconium Impregnated coconut Shell carbon	pH=4.0 T=RT	Langmuir	6.41 mg/g	Sathish *et al*. (2007)
34	Zirconium ion Impregnated coconut fiber carbon	pH=4.0 T=RT	Langmuir	40.016 mg/g	**Sathish *et al*. (2008)**
35	Waste carbon slurry	Co= 1-11 mg/L pH=7.58 T=298K	Langmuir	4.306 mg/g	**Gupta *et al*. (2007)**

36	Activated Titanium rich bauxite	Co= 2-50 mg/L pH=ca. 6 T=27±0.5°C	Langmuir	3.70–4.13	Das *et al.* (2005)
38	Zn/Al hydrotalcite- Calcined like compound	Co= 10 mg/L pH= 6 T=30±1°C	Langmuir	13.43	Das *et al.* (2003)
46	Granular ceramic	Co= 5-50 mg/L pH= 6.9±0.1 T=20°C	Freundlich	12.12	Chen *et al.* (2010)

47	Magnesialoaded ash Cenosphere fly (MLC)	Co= 100 mg/L pH= 3.0 T=318K	Langmuir	6.0	Xu *et al.* (2011)
		Co= 10 mg/L			
48	Al and Fe dispersed in porous granular ceramics	pH= 6.0 T=25±1°C	Langmuir- Freundlich	1.79	Chen *et al.* (2011)
50	Glass derived Hydroxyapatite (G-HAP)	Co= 100 mg/L pH= 6.72 T=35°C	Freundlich	17.34	Liang *et al.* (2011)
51	Chitosan based Mesoporous alumina	Co= 5.0 mg/L T=30±2°C	Langmuir	8.264	Jagtap *et al.* (2011)

52	KMnO$_4$ modified carbon	Co= 20 mg/L pH= 2.0 T=25°C	Langmuir- Freundlich	15.9	Daifullah *et al.* (2007)
53	Zirconium-iron oxide	Co= 10 mg/L pH= 7.0 T=25±1°C	Freundlich	9.80	Dou *et a*l. (2011)
54	Pyrophyllite	Co= 10 mg/L pH= 4.9 T=24°C	Langmuir	2.2 mg/L	Goswami, and Purkait (2011)

55	Calcium Chloride modified natural Zeolite	Co= 25-100 mg/L pH= 6.0 T=25±1°C	Langmuir, Freundlich	1.76	Zhang *et al*. (2011)
56	Alginate entrapped Fe(III)-Zr(IV) binary mixed oxide	Co= 10 mg/L pH= 2-12 T=10-50°C	Langmuir	0.981	Swain *et al.* (2013)
57	Apatitic tricalcium phosphate	Co= 30-60 mg/L pH= 4-11 T=20-40°C	Langmuir	15.15	Mourabet *et al*. (2012)
61	Hydrous bismuth oxides	Co= 10–35 mg/L pH= 4–12 T=20–40	Langmuir	1.93	Srivastav *et al.* (2013)

62	Hydrogen peroxide modified pumice	Co= 5–20 mg/L pH= 2–10 T=10–50	Freundlich	11.765	Sepehr *et al.* (20130
63	HFO doped alginate beads	Co= 5–10 mg/L pH= 3.5–9 T=20–40	Langmuir	8.90	Sujana *et al*. (2013)
64	Pumice	Co= 2-7 mg/L pH= 4-9 T= Ambient	Langmuir	0.31	Malakootian et al. (2011)
65	Siderite (modified)	Co= 2-25 mg/L pH= 2-12 T= 15-45°C	Langmuir	5.460	Shan and Guo (2013)

66	Sm(III)-loaded orange waste	Co= 10–240 mg/L pH= 1–8 T= 30°C	Langmuir	1.22	Paudyal *et al*. (2012)
67	TiO$_2$	Co= 2-20 mg/L pH= 2-11 T= Ambient	Langmuir	0.2703	Babaeivelni and Khodadoust (2013)
68	Zirconium(IV) ethylenediamine hybrid material	Co= 2-50 mg/L pH= 2-12 T= 10-50°C	Dubinin-Radushkevich	37.03	Swain *et al*. (2012)
69	Zirconium-iron oxide	Co= 10-150 mg/L	Freundlich	9.80	Dou *et al.* (2011)

pH= 3-11 T= 25°C

Table 1.2

Summary of various conventional adsorbents for the removal of Lead from water

| 1 | Zeolite | Co= 0-35 mg/L pH=4-7 | Langmuir | 14.22 | Pandey *et al.* (2015) |
| | | T=35-45 K | | | |

2	Activated carbon by cocconut shell	Co= 10-50 mg/L pH=4.5 T=35-45 K	Langmuir	26.5	Sekar *et al*. (2004)
3	Bagasse fly ash	Co= 0-80 mg/L pH=6.0 T=30°C	Langmuir	11	Gupta *et al*. (2004)
4	Banana Peel	Co= 30-80 µg/mL pH=5.0 T=25°C	Langmuir	2.18	Anwar *et al*. (2010)
5	TiO$_2$	pH=5.6	-	53.6	Lee and Yang (2007)

6	PASBAC	Co= 50-300 mg/L pH=2-8 T=25°C	Langmuir	51.81	Mohammadi *et al*. (2010)
7	ZCSBAC	Co= 50-300 mg/L pH=2-8 T=25°C	Langmuir	25.91	Mohammadi *et al*. (2010)
8	Humic acid	Co= 0-40 mg/L pH=6.0 T=25°C	Langmuir	22.7	Wo *et al*. (2003)
9	Goethite	Co= 0-40 mg/L pH=6.0 T=25°	Langmuir	11.04	Wo *et al*. (2003)

10	Al$_2$O$_3$-supported iron oxide	Co= 0.1-0.8 mmol pH=5.0 T=318K	Langmuir	28.98	. Huang *et al*. (2007)
11	Iron-coated sand	pH=6.0 T=25°C	Langmuir	1.21	Lai and Chen (2001)
12	Manganese oxide-coated sand	Co= 0. 0.097 to 1.54 mmol/ 1 pH=4.0 T=318K	Langmuir	1.9	**Han** *et al.* (2006)
13	Diatomite	Co= 0-300 mg/L pH=4 T= 23±1°C	Langmuir	24	Al-Degs (2001)

14	Manganese oxide– carbon nanotube	$Co=$ 10-60 mg/L pH=7 T= 323K	-	78.7	Wang *et al.* (2007)
15	Sawdust	$Co=$ 5-500 mg/L pH=5 T= RT	-	3.19	Yu e*t al.* (2001)
16	Activated carbon (Merck)	$Co=$ 5-200mg/dm^3 pH=5.5 T= 298K	-	21.5	Rivera-Utrilla et al. (2001)
17	Pine wood char	$Co=$ 0-1200 mg/l pH=5.0 T= 40°C	Langmuir	11.3	Mohan *et al.* (2007)

18	Dairy manure biochar	-	Langmuir	109.40	Cao *et al.* (2009)
19	Pine wood biochar (P300)	- Co= 5-40 mg/l pH=5.0 T= 318K	Langmuir	4.25	Liu and Zhang (2009)
20	Digested sugarcane begasse biochar	Co= 5-200 mg/l pH=5.0 T= 22±0.5°C	Langmuir	135.40	Inyang *el al*. (2011)
21	Digested dairy waste biochar	Co= 5-600 mg/l pH=5.0 T= 22±0.5°C	-	51.38	Inyang *et al.* (2012)

22	wheat bran	Co= 50-400 mg/l pH=5.0 T= 60°C	Langmuir	86.96	Bulut and Baysal (2006)
23	*Bacillus* sp. ATS-2 immobilized in silica gel	Co= 25-150 mg/l pH=4.0 T= 20°C	Langmuir	2.36×10^{-5} mol/g	C¸abuk *et al.* (2006)
24	Sulphuric acid-treated wheat bran	Co= 25-150 mg/l pH=6.0±0.2 T= 25°C	Langmuir	55.56	¨Ozer (2007)
25	Modified kaolinite clay	Co= 50-800 mg/l pH=7 T= 30°C	Langmuir	32.2	Jiang *et al.* (2009)

26	Garcinia mangostana L. fruit shell	Co= 0-350 mg/l pH=5.5 T= 30°C	NA	3.56	Zein *et al.* (2010)
27	Tobacco stems	Co= 10-50 mg/l pH=5.0 T= 299 K	Langmuir	5.5	Li *et al.* (2008)
29	Modified silica	pH=5.5-6.0 T= 20°C	Langmuir	38.12	Chiron *et al.* (2003)
30	Sawdust	Co= 5-50 mg/l pH=4.0±0.2 T= 298K	Langmuir and Freundlich	21.05	Li *et al.* (2007)

31	Modified peanut husk	Co= 5-50 mg/l pH=4.0±0.2 T= 298K	Langmuir and Freundlich	29.14	Li *et al.* (2007)
32	N-Bentonite	Co= 5-50 mg/l pH=5.0 T= 25°C	Langmuir	82.05	Liu *et al.* (2006)
33	MB15C5-Bentonite	Co= 5-50 mg/l pH= 5.0 T= 25°C	Langmuir	101	Liu *et al.* (2006)
34	Activated carbon coconut shell	Co= 0-120 mg/l pH= 4.5 T= 45°C	Langmuir	26.5	Sekar *et al.* (2004)

35	Eupatorium adenophorum spreng	Co= 10-50 mg/l pH= 5.0 T= 299K	Freundlich	2.2	Guo *et al*. (2009)
36	Activated carbon originating from cow bone	Co= 25-400 mg/l pH= 4.0±0.3 T= 25°C	Langmuir	47.6	Cechinel *et al.* (2014)
37	Pine cone Activated carbon	Co= 50-200 mg/l pH= 5.0 T= 25°C	Langmuir	27.53	Momcilovic *et al.* (2011)
38	Polygonum orientale activated carbon	Co= 50-75 mg/l pH= 5.0 T= 25°C	Langmuir	98.39	Wang *et al*. (2010)

39	Activated carbon prepared from Van apple pulp	Co= 25-40 mg/l pH= 5.0 T= 298K	Langmuir	15.96	Depci *et al*. (2012)
40	Apricot stone A.C.	Co= 45 mg/l pH= 4.0 T= 25°C	Langmuir	22.85	Kobya *et al*. (2005)
41	Hazelnut husk A.C	Co= 5-200 mg/l pH= 5.7	Freundlich and Langmuir	13.05	Imamoglu and Tekir (2008)
42	Portulaca plant	Co= 100–600 mg/l pH= 6.0 T= 25°C	Langmuir and Freundlich	17.24	Dubey and Shivani (2012)

43	Maize tassel	Co= 10–50 mg/l pH= 5.4	Langmuir	37.31	Moyo *et al.* (2013)
		T= 25°C			
44	Tree fern	Co= 74.1–350 mg/l pH= 5.4	Langmuir	40.0	Ho *et al.* (2004)
		T= 20°C			
45	Hevea	Co= 0-80 mg/l pH= 5.0	Langmuir	46.73	Hanafiah *et al.* (2006)
		T= 20°C			

1.12 NANOMATERIALS OVERVIEW-UNIQUE PROPERTIES AND APPLICATION

Nanotechnology refers to a growing field of science and technology which includes the synthesis and application of various nanosized materials. In 1959, Nobel award winner Richard Feynman firstly anticipated the important idea of nanotechnology by suggesting the fabrication of molecular machines. Since that time the researchers of the scientific community has focussed on this topic and observed that the nanotechnology could play a major role in every field of science, technology, and society [Zhang and Webster (2009)]. In the last two decades, nanotechnology has been emerging as a new branch which proved as a boon for all branch of science and technology. The term 'nano' is a Greek prefix which means very tiny or dwarf and represent the one billionth (10^{-9}) of a unit. Nanomaterials, therefore, are the class of materials with at least one of the dimension present in the nanometre range. Nanomaterials can be metals, ceramics, polymers or composites.

1.12.1 CLASSIFICATION OF NANOSTRUCTURED MATERIALS

Siegel classified nanostructured materials into four categories (Figure 1.5) according to their dimensionality: 0D: nanoclusters, 1D: multilayers, 2D: nanograined layers and 3D: equiaxed bulk solids [Carrow and Gaharwar (2015)].
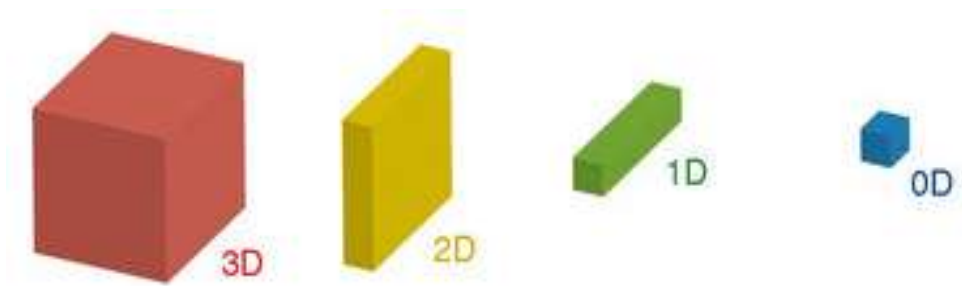
Figure 1.5 Schematic presentation of reduced-dimensional systems.

- **Zero-dimensional (0-D) systems** – In zero-dimensional systems, all three dimensions lies in the nanometer range. The most common type of zero-dimensional system includes nanoparticles. They can be amorphous or crystalline and exhibit various types of shapes. Fig. 1.7, showed the different types of the Zero dimensional nanostructure. Example – Quantum dot, nanospheres, etc [Tiwari *et al.* (2012)].

- **One-dimensional (1-D) systems** – In these systems of nanomaterials, one of the dimension is out of the nanoscale while other two dimensions are in nano range which gives rise the formation of needle shaped nanostructures. Figure 1.8, showed the different types of one-dimensional nanostructure. The one-dimensional material may be Metallic, ceramic, or polymeric. Example – Quantum wire, Nanowires [Tiwari *et al.* (2012)].
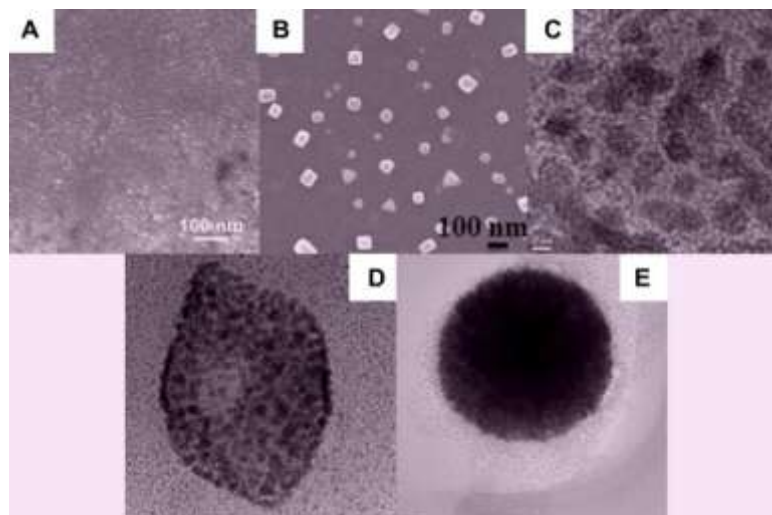
Figure 1.6 Typical scanning electron microscope (SEM) and transmission electron microscope (TEM) image of different types of 0D NSMs, which is synthesized by several research groups. (A) Quantum dots, (B) nanoparticles arrays, (C) core–shell nanoparticles, (D) hollow cubes, and (E) nanospheres
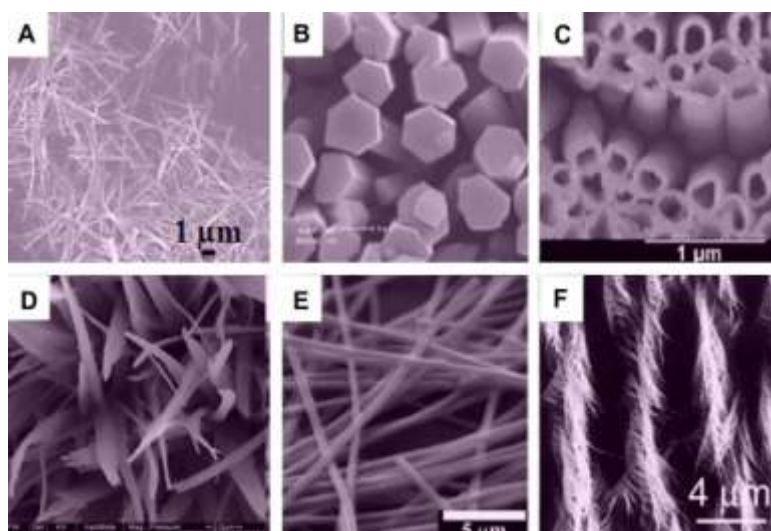

Figure 1.7 Typical SEM image of different types of 1D NSMs, which is reported by various researchers. (A) Nanowires, (B) nanorods, (C) nanotubes, (D) nanobelts, (E) nanoribbons, and (F)hierarchical nanostructures

- **Two-dimensional (2-D) systems** – In this types of systems, out of three only one dimension is in nanorange whereas other two dimensions are out of nanoscale. Figure 1.9, showed the different types of the two-dimensional nanostructure. These nanostructures can be amorphous or crystalline in nature and made up of the various chemical compositions. Example – nanoplates, graphene sheets etc. [Tiwari *et al.* (2012)].
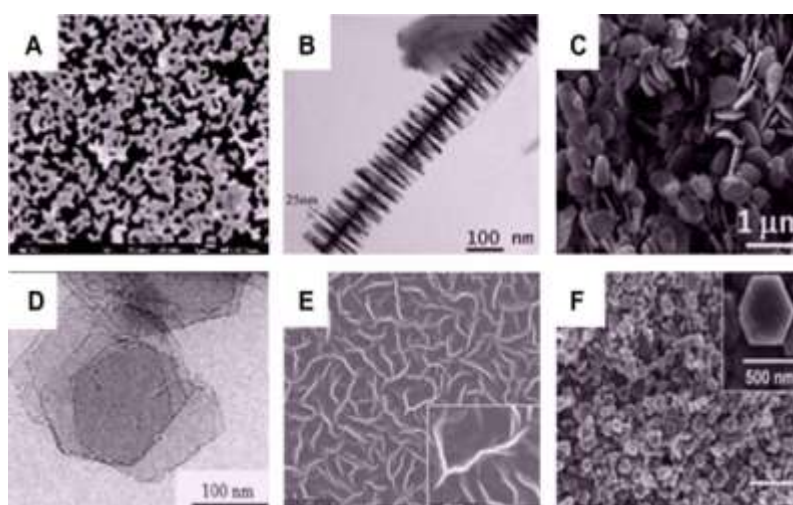

Figure 1.8 SEM and TEM image of different kinds of 2D NSMs (A) Junctions (continuous islands), (B) branched structures, (C) nanoplates, (D) nanosheets, (E) nanowalls, and (F) nanodisks.

- **Three-dimensional (3-D) systems** – This system comprises bulk materials in which all the dimensions are in macroscale. Thus, the 3D materials are characterized by having dimensions above nanoscale range. A bulk material concerning the nanocrystalline structure is made up of several nanosized crystals. Figure 1.10, showed the various types of three-dimensional nanostructure. Example – Bulk material, nanoflowers, nanocone etc [Tiwari *et al.* (2012)].
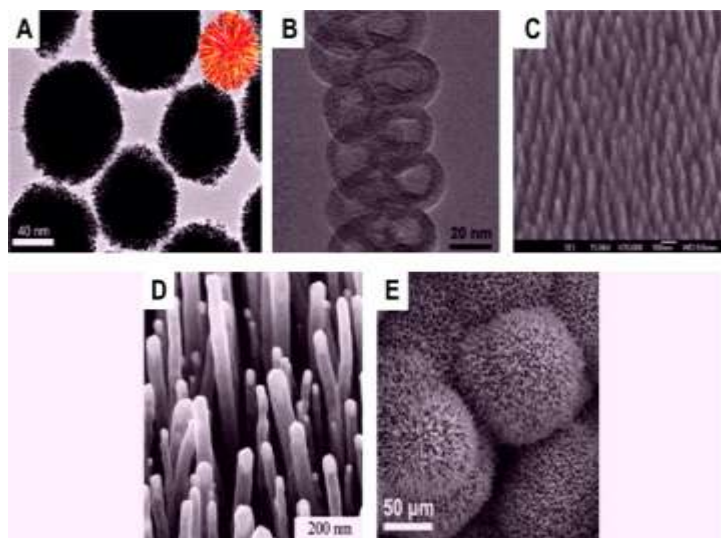
Figure 1.9 Typical SEM and TEM image of different kinds of 3D NSMs, which is synthesized by several research groups. (A) Nanoballs (dendritic structures), (B) nanocoils, (C) nanocones, (D) nanopillers, and (E) nanoflowers

1.12.2 UNIQUE PROPERTIES OF NANOSTRUCTURED MATERIALS

Nanomaterial showed special physiochemical properties due to the two most important factors which are discussed below:

(i) **Quantum confinement effects**: One of the most important characteristic of the nanomaterial is the quantum confinement effect which arises due to the direct influence of the reduction in the size to nanoscale on the energy band structure. The quantum confinement effect is observed when the size of the particle is too small to be comparable to the wavelength of the electron. Quantum confinement effect arises in the extremely small materials which restrict the movement of the electron in any particular direction and thus results in unusual properties [Eustis and El-Sayed (2006)].

(ii) **Large surface area to volume ratio:** Nanomaterials showed different characteristic than bulk materials because they have large surface area to volume ratio as they have a very large surface area as compared to the bulk materials made up of same volume or mass. Therefore, nanomaterials are characterized by presence of more surface atoms in comparison of the inner atoms which result in increased surface energy of the particles. As a consequence, the rate of chemical reaction also increased due to increase in surface area and thus material become more chemically active.

1.13 Classification of Nanomaterials as Nanoadsorbents

(i) **Metal based Nanoparticles (NPs):** Nanoparticles (NPs) include metallic nanoparticles (gold and silver NPs), magnetic NPs (iron di-and trioxide), metal oxide NPs (aluminum trioxide or titanium dioxide), and nanostructured mixed oxides (nanostructured binary iron- titanium mixed oxide particles) [Khajeh *et al*. (2013)].

(ii) **Carbon based nanomaterials (CNMs):** These are the most important group of nanoadsorbent which showed enhances adsorption capabilities. This group of adsorbents includes carbon nanotubes (CNTs), carbon nanoparticles, and graphene sheets (GNSs). Graphene and its different forms received attention as a excellent adsorbent for pollutant removal due to its exceptionally high surface area and presence of various functional groups.

(iii) **Silicon nanomaterials (SiNMs)**: silicon nanotubes (SiNTs), silicon nanoparticles (SiNPs), and silicon nanosheets.

(iv) **Nanocomposites:** The term composite can be defined as a combination of two materials, a filler and a matrix, to obtain a material with the superior properties is called

a composite. The term "nanocomposite" is more recent and indicates that the composite has at least one of its component dimensions below 100 nm.

1.14 NANOADSORBENT FOR FLUORIDE AND LEAD REMOVAL

The nanoadsorbent has been found to be superior to other conventional adsorbent and has excellent adsorption capacity for the various pollutant of water. The materials with the size ranging in between 1-100 nm and exhibit the unique properties due to nano range which is not shown by bulk sized materials [Stone *et al*. (2010), Wang *et al*. (2010)]. For the purpose of water treatment different adsorbent have been used i.e. carbon, silica gel [Parida *et al*. (2006)], activated alumina [Lin and Wu (2001)] and polymeric materials [Pan *et al.* (2009)], in which carbon based materials was found to be more promising adsorbents. In addition to conventional carbon adsorbents such as activated carbon, some new type of carbon nanomaterials [Mezohegyi *et al.* (2012)] are also being employed in water purification i.e. carbon nanotubes (CNTs) [Ren *et al*. (2011), Wang *et al*. (2012)], carbon nanofibers (CNFs), [Liang *et al*. (2011)] and graphene [Bradder *et al*. (2010), Yao *et al*. (2012), Li *et al*. (2011), Zhao *et al*. (2012)]. Although much progress has been made in recent years on adsorption application of CNTs, the high fabrication cost of these engineered carbon materials limits their practical applications [Tibbetts *et al*. (2007)]. Hence, the exploration of new potential carbon based adsorbents with improved adsorption capacity is still desirable. It is well documented that carbon has been considered as the most versatile ancient material used for removal of the contaminant from water and the Vedic literature also supported the use of charcoal in water purification. In ancient time, the carbon and porous materials used as earthen vessel for storage and filtration of the drinking water. Nowadays activated carbon has been used as a adsorbent for the water purification [Gupta *et al*.

(2012)]. The following table represents a summary of various nanoadsorbent used for removal of fluoride and lead from water.

Table 1.3

Summary of various nano adsorbents for the removal of fluoride from water

S.No.	Adsorbent	Conditions	Model used to calculate adsorption capacity	Uptake capacity/% Removal	References
1	Nanohydroxyapatite/chitin composite	Co= 10 mg/L pH=7.0 T=303 K	Freundlich	1.2	Sundaram *et al.* (2009)
2	Nano-geothite	Co=5-150 mg/L, pH=5.75, T= 303K	Freundlich	59	Mohapatra *et al.* (2010)

3	Nano hydroxyapatite	Co= 10 mg/L pH= 3	Langmuir	1.8	Sundaram *et al.* (2008)
4	Al$_2$O$_3$/CNTs	Co= 50 mg/L pH= 6 T=25°C	Freundlich	28.7	Li *et al.* (2001)
5	Aligned carbon Nanotubes (CNTs)	Co= 15 mg/L pH= 7.0 T=25°C	Freundlich	4.5	Li *et al.* (2003)
6	carbon nanotube supported alumina	Co= 6 mg/L pH= 6-9.0 T=25°C	Freundlich	9.6	Li *et al.* (2003)
7	nano-AlOOH	Co= 3-35 mg/L pH= 5.2±0.2 T=298 K	Langmuir	3.2	Wang *et al.* (2009)

8	Nano-alumina	Co= 1-100 mg/L pH= 6.15	Langmuir	14.0	Kumar *et al.* (2011)
		T=25±2°C			
9	PPy/Fe$_3$O$_4$ Nanocomposites	Co= 5-100 mg/L pH= 6.5 T=25°C	Langmuir-Freundlich	17.6-22.3	Bhaumik *et al.* (2011)
10	CeO$_2$-ZrO$_2$ nanocages	Co= 5-40 mg/L pH= 2-8 T=25-45°C	Langmuir	175	Wang *et al.* (2013)
11	Fe–Al–Ce nano-adsorbent	Co= 42 mg/L pH= 6.5–7.5 T=ambient	Langmuir	2.77	Chen *et al.* (2011)
12	Graphene	Co= 25mg/L pH= 7.0 T=298K	Langmuir	35.5	Li *et al.* (2011)

13	HAP nanoparticles	Co= 10–50 mg/L pH= 2-11 T=25-55	Langmuir- Freundlich	40.818	Jagtap *et al.* (2011)
14	Basic aluminum sulfate@graphene hydrogel	Co= 10 mg/L pH= 3.2–11.8 T= 298 K	Langmuir	33.4 mg g	Chen *et al.* (2013)
15	MOGO	Co= 10 mg/L pH= 5.5-6.7 T= 25	Langmuir	11.93	Li *et al.* (2013)
16	FAC was granulated by immobilizing FAC	Co= 19 mg/L pH= 6.5 T= 25	-	4.46 mg/g	Wu *et al.* (2011)
17	alginate bioencapsulated nano-hydroxyapatite	Co= 10 mg/L pH= neutral T= 25	Langmuir	3.87	Pandi and Viswanathan (2014)

| 18 | nano-scale aluminum oxide hydroxide | Co= 10 mg/L pH= 7 T= 25 | Langmuir | 3.2 | Wang *et al*. (2009) |

Table 1.4

Summary of various nano adsorbents for the removal of lead from water

1	SWNT	Co= 0-50 μg/mL pH=5.0 T=321K	Langmuir	35	Li *et al*. (2005)
2	MWNT	Co= 0-18 μg/mL pH=5.0 T=RT	Langmuir	97.08	Li *et al*. (2003)
3	TiO$_2$	pH=5.6	--	53.6	Lee and Yang (2007)

4	Graphene	Co= 0-80 µg/mL pH=4 T=30C	-	22–35	Huang *et al*. (2011)
5	GO	pH=5.6	-	36–659	Lee and Yang (2007)
6	magnetic carbon nanotubes/diatomite earth composite	Co= 10-140 µg/mL pH=6.0 T=295K	Langmuir	60.8	Alijani *et al.* (2014)
7	MNPs	Co = 10-60 µg/mL pH=6.0 T=295K	Langmuir	66.31	Zhou *et al.* (2014)
8	MNPs–CTS	Co= 10-60 µg/mL pH=6.0 T=295K	Langmuir	140	Zhou *et al.* (2014)

9	GO-TiO$_2$	pH=5.6	-	65.6	Lee and Yang (2007)
10	CS-GO	pH=5.0 T=295K	-	77	Fan *et al*. (2013)
13	Magnetic magnetite (Fe$_3$O$_4$)	Co= 2-100 mg/L pH=2-8 T=25-45°C	Langmuir	53.11	Rajput *et al.* (2016)
14	Fe$_3$O$_4$ nanoparticles	Co= 0-800 mg/L pH=5.5 T=298-328K	Langmuir	36.0	Nassar (2010)
15	Montmorillonite	Co= 10-250 mg/L pH=5.7 T=303 K	Langmuir	33	Bhattacharya and Gupta (2007)

16	Manganese oxide–carbon nanotube	Co= 10-60 mg/L pH=7 T= 323K	-	78.7	Wang *et al.* (2007)
17	Carbon nanotubes	Co= 5-200mg/dm^3 pH=5.5 T= 298K	Langmuir and Freundlich	17.44	Li *et al.* (2002)
18	Nanoscale Zero-valent iron (n ZVI)	Co= 1-200 mg/l T= 25°C±2°C	Langmuir	50.3±4.2	Arancibia-Miranda *et al.* (2016)
19	Fe$_3$O$_4$@SiO$_2$	Co= 10-1000 pH=6.2±0.2 T= 25°C	Langmuir	76.59	Wang *et al.* (2010)
20	Poly(amidoamine) modified graphene oxide	-	Langmuir	10.6	Yuan *et al.* (2013)

21	SiO$_2$/graphene	Co= 10-50 pH=6.0 T= 25°C	Langmuir	113.6	Hao *et al.* (2012)
22	Exfoliated Graphene Nanosheets	Co= 5-80 mg/L pH=4.0 T= 30°C	Langmuir		Huang *et al.* (2011)
	GNS			22.42	
	GNS500			35.21	
	GNS700			35.46	
23	graphene oxide/chitosan/FeOOH	Co= 5-80 mg/L pH=5.5 T= 40°C	Langmuir and Freundlich	111.1	Sheshmani *et al.* (2015)
24	Fe$_3$O$_4$@SiO$_2$-IIP	Co= 0-250 mg/L pH=7.0 T= 25°C	Langmuir	32.58	Guo *et al.* (2014)

25	Fe$_3$O$_4$@SiO$_2$-NIIP	Co= 0-250 mg/L pH=7.0 T= 25°C	Langmuir	16.50	Guo *et al.* (2014)
26	Oxidized multiwalled carbon nanotubes	pH=6.0±0.2 T= 25°C	Langmuir	2.05	Xu *et al.* (2008)
27	Oxidizes CNT	Co= 100-1200 mg/L pH=7.0 T= 25°C	Langmuir	117.6	Tofighy and Mohammadi (2011)
28	Fe$_3$O$_4$-GS	-	Freundlich	27.95	Guo *et al.* (2014)
29	Gum kondagogu modified magnetic iron	Co= 25-300 mg/L pH=5.0 T= 30°C	Langmuir	56.6	Saravanan *et al.* (2012)

oxide nanoparticles

30	carbon nanotubes	pH=5.0 T= 25°C	Langmuir	102.04	Kabbashi *et al.* (2009)
31	Amino-functionalized MNPs	Co= 1-50 mg/L pH=5.0 T= 25°C	Langmuir	40.10	Tan *et al.* (2012)
32	Maghemite nanotubes	Co= 20-400 mg/L pH=6.0±1 T= 25°C	Langmuir	71.42	Roy and Bhattacharya (2012)
33	Anatase nanoadsorbent	Co= 0.1-20 mg/L pH=6.0 T= 25°C	Langmuir	31.05	Kocabaş-Ataklı and Yürüm (2013)
34	graphitic carbon nitride	pH=5.0 T= 298K	Langmuir	65.6	Hu *et al.* (2015)

35	Nanoadsorbent	Co= 2-80 mg/L pH=5.2 T= 25°C	Langmuir	169.34	Shahat *et al.* (2015)
36	amino-functionalized Fe$_3$O$_4$/SiO magnetic nanoadsorbent	Co= 5-250 mg/L pH=4.0 T= 27°C	Langmuir	17.65	Mahdavi *et al.* (2013)
37	MWCNTs/Fe$_3$O$_4$	Co= 10-60 mg/L pH=5.3 T= 30°C	Langmuir and Temkin	41.77	Ji *et al.* (2012)
38	MWCNTs/Fe$_3$O$_4$-NH$_2$	Co= 10-60 mg/L pH=5.3 T= 30°C	Langmuir and Temkin	75.02	Ji *et al.* (2012)

1.15 CARBON-BASED NANOADSORBENTS

Carbon nanomaterials are the important class of inorganic materials due to their environmentally benign nature, mass scale availability, and simplicity. The carbon based nanomaterials has attracted the attention of the scientists of all the field for exploring their fascinating size dependent properties. The carbonaceous nanoadsorbent include all the allotropic forms of the carbon nanomaterials such as fullerene, carbon nanotubes (CNT), and graphene derivatives. Among other member of carbon nanomaterials, graphene seems to be most potential material for various application due to its extraordinary chemical, physical, and electronic properties.

1.15.1 GRAPHENE AND ITS DERIVATIVES AS ADSORBENT

Graphene-based materials have found to be more capable of removing the pollutant due to its planar structure and unusual chemical and physical properties [Upadhyay *et al.* (2014)]. Graphene is a two-dimensional carbon allotrope made up of an array of single carbon atoms (sp^2 hybridized) which is found to be hardest and thinnest material known till date (so far) [Lee *et al.* (2008), Zheng *et al*. (2011), Geim (2007)]. The graphene was discovered by Andre Geim and co-workers in 1968 at the University of Manchester by simple Scotch tape method [Loh *et al.* (2010)]. The carbon atoms in the graphene are arranged in the hexagonal array of the two-dimensional planar sheet which is suitable for other molecules and metal ions to interact strongly. Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms densely packed in a honeycomb crystal lattice. It is the mother element of some carbon allotropes, including graphite, carbon nanotubes, and fullerenes (Figure 1.10) [Kuila *et al.* 2012)]. Pure graphene is hydrophobic in nature and shows very low solubility in most of the solvent [Li *et al*. (2008)] which induces hindrance in the adsorption of metal ions or pollutants. To overcome this problem, the graphene sheets has been functionalized to make

its application in many fields as well as in the water treatment process [Georgakilas *et al*. (2012)].
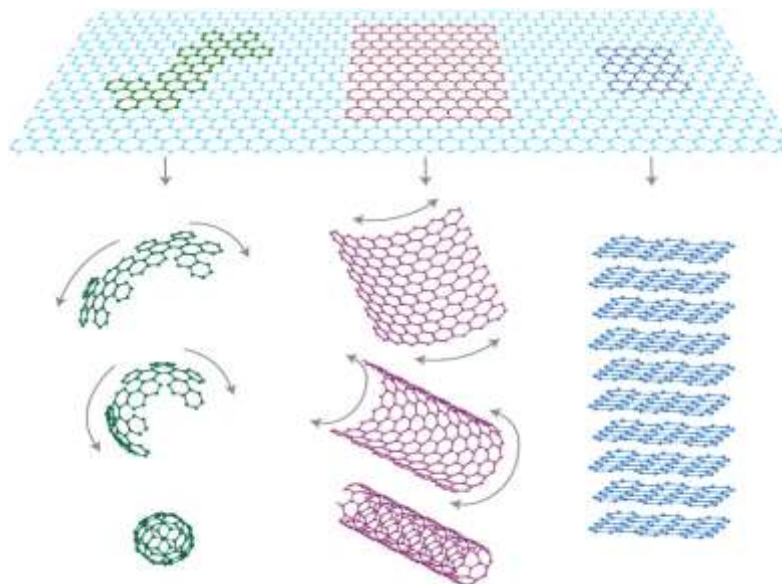

Figure 1.10 Different allotrope of carbon derived from the graphene sheets

The graphene oxide (GO) which is synthesized by oxidizing the graphite by using strong oxidizing agent e.g. $K_2Cr_2O_7$ or $KMnO_4$ i.e. by Hummers method [Chandra *et al*. (2010), Wang *et al*. (2009)]. The schematic diagram of preparation of GO is shown in Figure 1.11 [Garg *et al.* (2014)].

The Graphene oxide sheets is decorated by plenty of oxygen functionalized groups i.e. hydroxyl, carboxyl and epoxy [Dreyer *et al*. (2014)]. Due to oxidation process which increases the spacing between layers of graphite from 0.335 to 0.625 nm for GO [Hontoria-Lucas *et al*. (1995)]. Figure 1.12 shows the schematic representation of the graphene and graphene oxide [Malhotra *et al.* (2015)]. Due to these functional groups, the GO becomes hydrophilic than that of graphene. The oxygen group of the GO has lone pair of the electron, and by sharing it, they can interact with the pollutant ions.
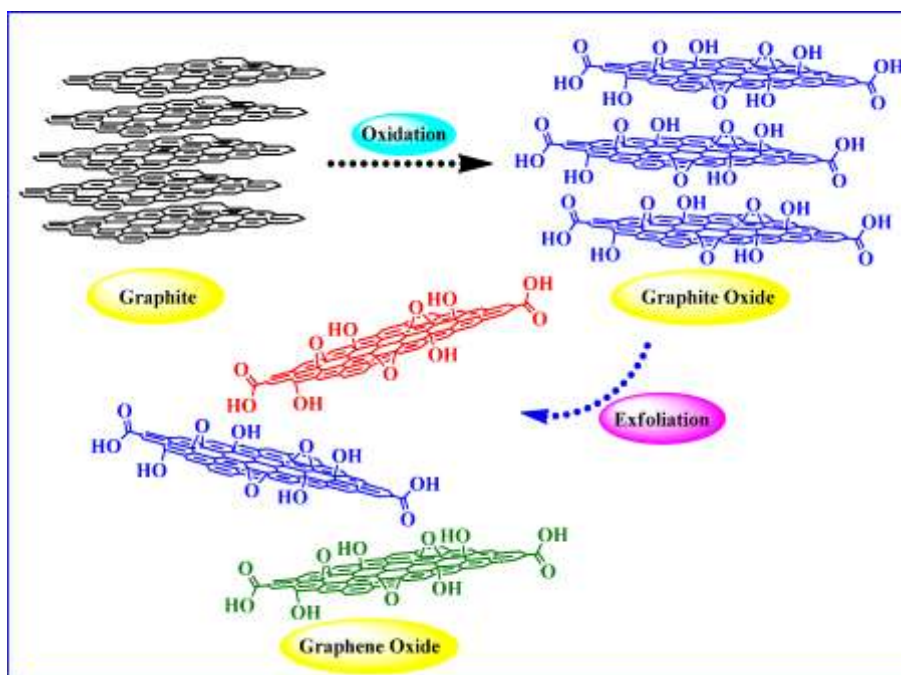
Figure 1.11 Schematic diagram of preparation of Graphene oxide.

The adsorbent composed of graphene oxide has large adsorption capacity due to large exposed surface area. It is reported in the literature that GO showed very high adsorption capacity in comparison to many recently reported adsorbent i.e. carbon nanotubes [Sitko *et al*. (2012), Chowdhury and Balasubramanian (2014)].
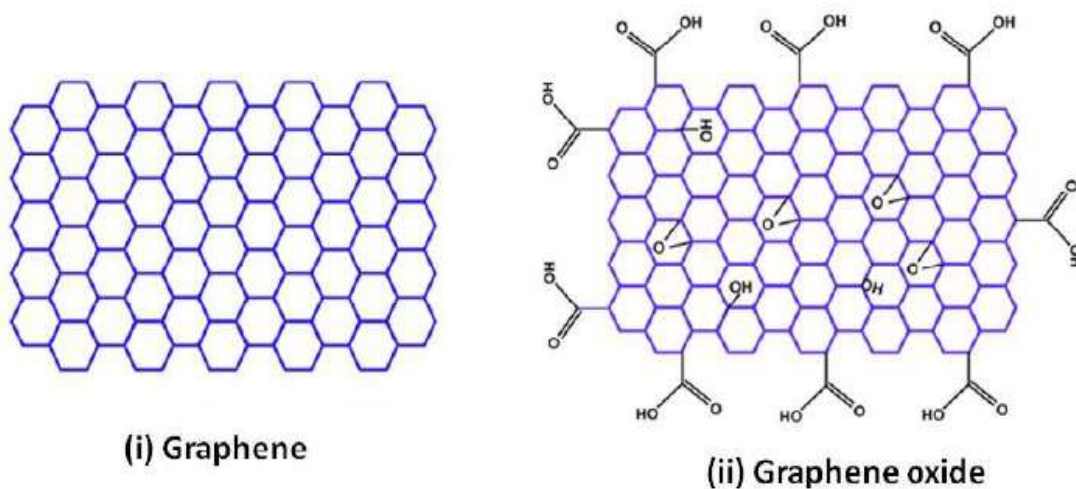

Figure 1.12 Schematic representation of the graphene and Graphene oxide

1.16 METAL OXIDE NANOPARTICLES

Among the available adsorbents, nanosized metal oxides (NMOs), including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides, and cerium oxides are classified as the promising ones for the heavy metals removal from aqueous system [Vanbenschoten *et al*. (1994), Coston *et al.* (1995), Agrawal and Sahu (2006)]. Similarly, many metal hydroxide and metal oxide are being used for fluoride removal such as fe-Al-Ce oxide [Wu *et al.* (2007)], aluminum oxide [Tchomgui-Kamga *et al*. (2010)], CaO nanoparticles [Patel *et al.* (2009)], Copper oxide incorporated mesoporous alumina [Bansiwal *et al*. (2010)], CeO_2–ZrO_2 nanocages [Wang *et al.* (2013)], hydrous zirconium oxide [Dou *et al.* (2012)] etc. which are proved to be excellent adsorbent for fluoride ions.

Metal oxide nanoparticles showed good adsorption properties due to their large surface area and size quantization effect [Hua *et al*. (2012)]. In addition, it is reported that nanosized metal oxide showed high selectivity for the heavy metals as well as high uptake capacity [Deliyanni *et al.* (2009)]. However, The stability of metal oxide decreases as its size reduces from micrometer to nanometer due to increase in surface energy and they agglomerate due to Van der Waals forces between the layers. The agglomeration causes the loss of surface area which in turn decrease in adsorption capacity occurred. In addition, the nanosized metal oxide also difficult to utilize in the continuous column system due to excessive pressure drop and very low mechanical strength. So, to make metal oxide nanoparticles applicable in field application they should be combined with other porous support which acts as host to anchor these nanoparticles on their surface.

1.17 NANOCOMPOSITE

The combination of two materials, a filler and a matrix, to obtain a material with the superior properties is called a composite. The term "nanocomposite" is more recent and indicates that the composite has at least one of its component dimensions below 100 nm. The different types of the host are being used such as activated carbon, natural materials, polymers, etc. Recently many researchers used to form a composite of specific metal oxide with graphene-based materials due to its planar structure for removal of different types of the pollutant from the water. There have been many previous reports on the modification of graphene with metal oxide NPs, such as TiO_2, SnO_2, and Fe_2O_3. The incorporation of such nanomaterials on the graphene surface is highly desirable for tuning surface morphology, electronic structure, and following intrinsic properties of graphene. Moreover, graphene sheets decorated with metal oxide NPs combined the outstanding properties of them and might result in some different properties because of the synergetic effect between them [Hao *et al.* (2012)]

The metal oxides self-assemble on the surface of graphene which hindered the restacking of the various layers of graphene and maintains its large surface area whereas, in situ growth of metal oxide nanoparticles on the graphene surface resist them to agglomerate and keep them in dispersed form. Graphene oxide sheets contains various functional groups as well as defects which act as building blocks and nucleation sites for the nanoparticles growth. Further, another advantage of the nanocomposite of metal oxide and graphene oxide increases the mechanical strength of the resulting adsorbent. The graphene sheets restrict the metal oxide to leaches into the treated water [Hao *et al.* (2012), Williams *et al.* (2008)]. The fabrication of graphene-based composites provides an important objective to enhance the performance of nanosized metal oxide in other fields such as storage devices, energy harvesting, conversion photocatalysis, and photovoltaic devices etc. because the hybrids have

versatile and tailor-made properties with performances superior to those of the individual components of the nanocomposites [Bell *et al*. (2011), Huang *et al*. (2011)].

Therefore, the graphene-based nanocomposites of metal oxide are supposed to show excellent adsorption capacity for various pollutants of the water.

1.18 Objective of the present work

Most of the pollutant of water involves cationic as well as anionic impurities and they have high potential to create environmental hazards. Thus because of deleterious consequences of the heavy metal pollution it is necessary to eliminate these ions from the water. So keeping these harmful effects of pollutant ions on the living being in mind the present work is focused on to the study other remediation of fluoride and lead ion by graphene oxide nanocomposites in batch as well as continuous mode both. The objective of the present study is summarized as follows:

- To synthesize of the graphene oxide and it's composite with the metal oxide (rGO/ZrO_2 and GO/MgO).

- To characterized the as prepared nanocomposites of graphene oxide through various spectroscopic techniques (FTIR, XRD, Raman, EDX, BET, SEM, XPS etc.).

- To utilize the rGO/ZrO_2 and GO/MgO nanocomposite for the removal of fluoride and lead respectively.

- To investigate the effect of the different parameters on the adsorption capacity i.e. pH, adsorbent dose, initial metal ion concentration and temperature in batch mode.

- To study the thermodynamics of adsorption and to evaluate its parameters i.e. $\Delta H°$, $\Delta S°$ and $\Delta G°$ to determine the adsorption feasibility and endothermic/exothermic nature of the adsorption process.

- To explore the kinetics of the adsorption using different models in order to evaluate the rate determining step of the adsorption and mechanism of adsorption.

- To study the adsorption isotherm by using different isotherm models to achieve the maximum uptake capacity of fluoride and lead in batch mode.

- To examine the pollutant retention potential of the prepared nanocomposites in fixed bed column configuration in order to fabricate the treatment plants in future.

- To investigate the effect of flow rate, bed height and initial concentration of metal ions on the removal of fluoride and lead in column system.

- To evaluate the regeneration efficiency of GO/ZrO$_2$ and GO/MgO nanocomposites in order to explore the reusability of the adsorbent.