Chapter- 1

INTRODUCTION

Life on our planet is possible due to the presence of water. The importance of this resource is such that no living organism can survive without it. Therefore, there is a need of clean, unpolluted water for the survival of life on this planet. In order of sustainable development, it must be ensured the unpolluted rivers, streams, lakes and oceans. Due to increasing population, human activities creating threaten to the water sources. This resource meets the most fundamental and basic necessities of our day to day life. About 70% body weight of all the living organism is constituted by the water. Generally water found in gas, liquid and in solid states. Almost all the biochemical and chemical reactions occur in water media. It also serves as external, internal medium for several organisms.

Groundwater plays an important role as an indispensable and vital component of the environment and our life support system. Almost whole amount of the water on this planet is saline (97.2%), 2.8% constitute the fresh water and from this only 20% is present as ground water, which is of great importance. The presence of certain properties which is not possessed by the surface water, make it of highly importance (Goel, 2000). There are continental disparities in fresh water distribution. According to the United Nation World Development Report, the Asian subcontinent has only 36% of the world’s fresh water resources although it supports more than 50% of the world’s population (UNEP, 2003).

Sub-surface water contains natural and chemical constituents in solution, the geo-chemical environment, movement and source of ground water determines the kind and amounts of constituents in it. It has been considered qualitatively very safe and secure within the subsurface geological domain till recently. However, because of major changes in land uses pattern and a vast increase in the quantities and types of industrial, agricultural, domestic effluents and landfill leachates entering the hydrological cycle, the pressure on groundwater quality have grown many folds. Prevalence of high fluoride contamination, arsenic pollution, nitrate pollution, high salinity, enriched heavy metals load and organic pollution in many groundwater basins at global, regional and national level is a matter of great concern (Ngah et al., 2012; Nowak et al., 2012).
As a renewable natural resource, groundwater plays an important role in water management all over the world. In the developing country like India the groundwater resources are being utilized for drinking, irrigation and industrial purposes at large scale (Singh et al., 2006). Ground water generally founds in thousands of small aquifers which are present almost everywhere under the earth surface (Vasanthavigar et al., 2012). From contamination view point, groundwater is more reliable and cannot be polluted easily due to its protection naturally, no more effect of drought and less attention required for its treatment. (Kumar et al., 2010). In India the ground water quality is being accepted as the major problem.

1.1 Origin of Groundwater

Surface water bodies, canals and irrigated fields acts as supplier for rainwater, which is responsible for ground water recharge. Snow or rain is responsible for the precipitation, which is the main cause of origin of ground water as meteoric water. In the absence of stream runoff or evaporation water gets in to the ground from these sources. In the belt of soil mixture water from precipitation first get held very tightly as a film on the surface and some amount in the micro-pore of the dry soil particles. At this level the film covers the solid particles but some amount of air is still remain in the soil voids. This zone of the soil texture is known as aeration zone or unsaturated zone and the water as the Vados- water . Below this depth if water is present in sufficient amount all voids of soil become saturate and this zone is known as the saturated zone. Upper level of saturated zone is called as the water table, and water as Ground water. (Hiscock, 2005).

The type of aquifer, underground water circulation, depends on the porosity and structure of the ground. Aquifers are mainly of two types, confined and unconfined (Figure 1.1). Confined aquifer is covered by impermeable layer which prevents it from recharge (or contamination) by surface water or by rain fall (Bartrum and Balance, 1996). Recharging of the confined aquifer occurs due to the presence of outcrops of permeable rocks near or at the surface. While unconfined aquifer is covered by the permeable, unsaturated layer which permits the surface water to percolate in to the water table. Therefore unconfined aquifers are more prone to pollution in comparison to the confined aquifers from outside recharge.
1.2 Groundwater Quality

In respect of human health Groundwater Quality is of great interest, moreover 80% of all diseases directly/indirectly related to the unsanitary conditions and poor drinking water quality in the developing world (USEPA, 1990). Groundwater quality plays an important role for the determination of movement, storage, recharge of ground water and geological origin of rocks (Prasanna et al., 2011).

Groundwater is generally a renewable source. However, the natural supply of groundwater in hard rock is limited in time and space. Furthermore the quality of available fresh water resources is under severe threat. Management of ground water is the most important issues as it is extending minimum negative effect to the environment while exploiting it for the maximum economic benefits. Ground water equilibrium is decreasing gradually worldwide. Mainly three problems dominate over ground water uses, as reduction due to over drafting, water-logging due to insufficient drainage system and contamination due to industrial, agricultural and other anthropogenic activities. Practically, water quality depends upon the physical environment and the origin of water movement. As the water moves through the hydrological cycle, various chemical, biological and physical processes changes its original quality or through the reaction with soil, rocks and organic matter. Natural processes and human activities cause changes in groundwater quality directly or indirectly (USEPA, 1990).

Various physical, chemical and biological processes and many different factors influence this contaminants potential migration from the land surface to the water table of shallow aquifers.

1.2.1 Processes controlling Groundwater Quality

The different geochemical process which influences the groundwater greatly is discussed below (Todd, 1980; Drever, 1982, Subramani et al., 2010).

1.2.1.1 Reduction

The important constituents of the groundwater to be affected by this process are sulfate and nitrates. The importance of sulfate is generally due to microbial activity and is accompanied by the subsequent oxidation of the available organic matter (by released
oxygen) resulting in production of CO$_2$, which in turn produces large quantities of HCO$_3^-$, H$^+$ and CO$_3^{2-}$ ions.

1.2.1.2 Ion Exchange

The replacement of structural and adsorbed ions present in the solution has been termed as ion exchange (Mohammed et al., 2010). The degree to which the ion exchange (both cation and anion exchange) occurs, depend on:

- Exchangeable-ion concentration present in the solution.
- Type of the solid material or sediments in contact with solution.
- The state of ion in the solid structural adsorbed and
- Degree of saturation of those ions in the solid.

The exchangeability of an adsorbed ion is far greater than that of structural ion. The common exchange is, therefore, between the ions adsorbed by the solid, which is commonly seen in clay minerals, zeolites and organic substances. Besides the charge present on the adsorbed ion, ionic radius and degree of hydration also affect the adsorption capacity of minerals. Schoeller (1962) has given two types of bases exchange:

(i) Positive when alkaline (Na$^+$, K$^+$) in water get exchanged for alkaline earth(Ca$^{2+}$,Mg$^{2+}$) in the aquifer material.

(ii) Negative, when alkaline earth in the water get exchanged with alkalis in the rock. Former is generally the case, when saline water enters in the fresh water aquifers and later takes place in the areas of inland saline water or in transition zone between the fresh water and saline water.

1.2.1.3 Sediment water interaction

In controlling the dissolved trace element concentration in water the suspended solid surfaces (Colloids or Particles) play an important role. Maximum number of these elements eliminated either by complex formation with the surface sites or by the sedimentation in to or on to the particles. A large amount of the inorganic particles and colloids are as carbonates (Dolomite, Calcite); Non-clay silicates such as Quartz, Feldspar, Potash, Plagioclase, Silica; Clays (Smectite, Illite); Fe-Mn-oxide as Geothite, Magnetite; Phosphate ( apatite) and Sulphides. Colloids and particles present in the water can also be classified on the basis of their origin.
(i) Pedogenic compounds: Generally originates from soil. They are Fe, Mn oxy-hydroxides, clays and other silicates. Rain water leaching is the main source.

(ii) Aquagenic compounds: These are endogenic in nature and produced in water column. Further can be classified in to the organic and in-organic compounds. In these the organic compounds “backbone of micro-organism” released in water after their death (CaCO3, SiO2) and inorganic originate from chemical precipitation. These are the hydroxides of Fe and Mn, Carbonates of Ca and Mg and Sulphides of Fe present in anoxic water.

The accumulation of an element in an aquatic system through the organism depends upon the sediment retention capacity. In sediment-water system this capacity is destabilized by the anthropogenic activities. Dissolved concentration of these elements decided by the solid component of sediment through various reactions such as precipitation/dissolution, desorption/sorption followed by the acidification and complex reactions.

1.3 The Groundwater Pollution

In the environmental studies the pollution or contamination can be used to explain the entry of a matter/ substance in such a concentration that would be unsafe for human, animal and for plant life (UNEP, 2003). Pollution in the case of water affects its quality leads threatening to the human health, social prosperity and even to economic development. In India more than 80% of rural domestic water supply depends on ground water. Most parts of country facing the problem of groundwater quality (CGWB, 2002). About 10 million people due to arsenic contamination, 66 million due to fluoride contamination are at risk level as a result of dependency on ground water in the country (Ghosh et al., 2007).

In coastal areas excessive salinity, high concentrations of iron and nitrates in groundwater led to deteriorate groundwater quality. High arsenic concentration in groundwater has been reported from Nadia, Murshidabad, Malda, Bardhman and North and South Pararganas district of West Bengal (Chakraborty, 2004). In different parts of Bihar, Eastern UP and Jharkhand the higher level of arsenic has also been reported
Presence of Iron, Salinity and Hardness give rise to indigestible taste of water making it unsuitable for drinking purpose. Excessive amount of Chloride, Fluoride, Nitrate and Conductivity were found in a number of coastal districts of India (CGWB, 2002) (Figure 1.2-1.5).

1.4 Heavy metal distribution in India

In water system Heavy metals behave as a special group of toxicants/pollutants. Their accumulative nature makes them of highly ecological importance. Moreover they are not eliminated due to self-purification, and gathered in water system; lastly enter in to the food chain of an ecological system. Heavy metals level increases in the water system due to the increase their concentration in the bottom sediment. Generally anthropogenic activities are responsible for their presence in the water system. Sometimes natural processes also play an important role for their occurrence. In an aquatic system they enter through human activities such as processing, mining, by the use of substances having heavy metal pollutants, and due to the volcanic eruption, weathering of rocks and soil (Ibrahim et al., 2010; Camacho et al., 2011) Fig. 1.6-1.7.

1.5 Traditional decontamination methods for toxicants (Heavy metals)

Nowadays Heavy metals become an important group of toxicants and concern with the several public health problems. From time to time a number of decontamination methods/techniques have been developed such as: Polymer-based filtration method, Membrane separation method (Kozlowski and Walkowiak, 2002); Adsorption (Mohan and Singh, 2002; Merceille et al., 2012); Ion-Exchange method (Melo et al., 2012; Rengaraj et al., 2003); Reduction method, Precipitation (chemical) method (Mouflih et al., 2005; Zhou et al., 1993); Electro-chemical Precipitation method (Polprasert and Kongsricharoern, 1996); Solvent-Extraction method(Canter and Pagilla, 1999); Cementation (Lin et al., 1992); and Electro-kinetic remediation method (Sawada et al., 2004). The disadvantages of the above methods, especially at lower concentrations, are the high cost and low efficiency and necessary disposal of sludge containing heavy metals. Among these methods, Electro-dialysis, Electrolysis, ion exchange, reverse osmosis, adsorption media etc. are supposed as the better-developed technologies.
1.5.1 Electro dialysis

In Electro-dialysis SPM (Semi-Permeable Membrane) acts as intermediate membrane and allowed the water soluble ions to pass through itself under the electric current effect (Gottberg et al., 1998). The SPM is selective in nature and made up of the ion-exchange material. Ion-Exchange material is cation exchanger and anion exchanger. Cations and anions pass through the cation and anions exchanger respectively. In this technique the demineralization is carried out by arranging the membrane either in series combination or in parallel combination. Electromotive force is applied in batch mode or in continuous mode. Removal processes is affected by a number of factors such as the solution pH, Electric current intensity, membrane selectivity, temperature of the medium, flow rate of the solution, contaminant nature and the stages of configuration. Brackish water can be converted to the drinking water through this technique. The pollutant can be reduced up to 90% such in case of total dissolved solid. Reverse osmosis can cause fouling of the membrane. This technique is not cost effective and still is in under-developing condition.

1.5.2 Electrolysis

In Electrolysis water soluble inorganic/organics generally decomposed or deposited on the respective electrode through the electro-chemical redox reaction. In this technique the organic pollutant decomposed in to some less toxic or non-toxic product such as water and carbon dioxide where as the metals get deposited on the surface of the respective electrode. This technique is used for the removal of color and turbidity from the polluted water. Total dissolved solid (< 200 mg/l) can be removed by this technique so waste-water required pre-treatment processes. Process is carried out in a tank or a number of tanks in series combination having the desired metal electrodes also in series fashion. Factors affecting the process are temperature, pH, contact time and the electric current. This technique is mostly used for metal bearing industrial waste-water treatment. This is also not a cost effective method and still is in under developing condition.
1.5.3 Reverse-osmosis (RO)

This is the replacement of the ion-exchange and distillation method. It is the reciprocal of the Osmosis process in which a solvent moves from its higher concentration to its lower concentration (concentration gradient) through SPM. This process continues till the osmotic pressure of the both side become equal. On applying the pressure more than osmotic pressure on concentrated side (contaminated water side) solvent (pure water) moves in backward direction through SPM by forming the purified water this is the reverse osmosis. The residuals (contaminants) are left behind and discharged into the drains. In starting phase cellulosic membranes were used, which has been replaced by the modern Polyamide thin film membrane having a higher water purifying efficiency. About 95 to 98 % inorganic contaminants along with organic molecule of molecular weight higher than 100 and larger non ionic toxicants can be removed by this film. This is cost effective and can prevent pathogen or bacterial growth also. The main drawback of this method is its low rate of water purification and ineffectiveness towards the gaseous contaminants. To improve water quality it is combined with the ion-exchange process (http://www.elgalabwater.com).

1.5.4 Ion-Exchange Process

In Laboratory the supply of experimental water is completed through this method. The water production unit contains cartridge in mixed bed pattern made up of ion-exchange resins. Exhausted cartridge (due to long time uses) either regenerated or discarded. The mechanism is based on the replacement of the cations and anions with the H⁺ and OH⁻ ions, which in-turn form the water molecules. In the feed water the cationic pollutants are replaced or exchanged with the H⁺ ions and anionic with OH⁻ ions. In ion-exchange resin the feed water passes through beds of small round shaped beads having active sites of OH⁻ and H⁺ ions. So it is required to replace or regenerate the cartridge after long time use (http://www.elgalabwater.com).
1.5.5 Adsorption

Heavy metal ions are generally removed by the Adsorption process method. Adsorption is surface phenomenon, which may be defined in terms of a unit operation in the chemical engineering sense, and that operation which deals primarily with the utilization of surface forces; the concentration of materials on the surface of solid bodies referred to as adsorption. It is assumed to be the most effective method for waste water treatment due to its inexpensiveness, wide application field and easy operative nature. It shows its applicability toward the biological, in-organic and organic (soluble and insoluble) contaminants. It shows approximately 90-99% removal efficiency due to which it is of industrial as well as of domestic importance.

1.5.5.1 Adsorbents

Adsorption capacity of an adsorbent depends on the surface area and the size of micro-pores present in them. Adsorbents may be amorphous or crystalline in nature. Presence of micro-pores makes the molecular sieves as adsorbent (Motsi et al., 2011). The mass transfer rate, adsorption capacity, long term stability and the selectivity are the basic properties of an adsorbent. Micro-porous solids behave as adsorbent due to the presence of micro pore of nanometer size. The principal non-polar-type adsorbent is activated carbon.

Now a day’s disposal of the industrial waste having heavy metals contaminants becoming the most important issue in the view of environmental protection. Heavy metal contamination exists in natural tanneries, water, drinking water and in the disposal waste of different industries as tanning, galvanization, dyeing, inorganic pigment manufacturing, printed circuit board (PCB) manufacturing, petroleum refining, wood processing industries etc. For eliminate this problem even then there is a need to find out an economically feasible, environmentally viable method to convert it into a non toxic form. In views of this the conversion of fly-ash in to zeolite is a better option, due to its application as adsorbent/ion-exchanger or a catalyst on industrial applications.

1.5.5.2 Fly ash
Globally, millions of tonnes of miscellaneous solid, liquid and gaseous waste materials, such as household, commercial, industrial, agricultural, radioactive and clinical wastes, are generated annually. The disposal of waste materials poses major challenges and can cause serious hazards to human health and the environment, if they are handled incorrectly. Moreover in future the discharging of the waste (industrial/domestic) will increase in considerable manner (Nibou et al., 2011).

As a part of the sustainable development, waste management should be attempted to minimize the effect of disposed waste to environment, finally to the human health and conversion of them into useful products by recycling. This can be beneficial in many ways, such as reducing the amount of raw materials used and/or operating costs, reducing the volume of waste materials and reducing their environmental impact. Mining industry is of importance around the world. However, it presents several environmental problems, such as soil erosion, impacts on local biodiversity and water pollution. The quality of life in many countries around the world is strongly affected by the products and processes of mining industries.

Fly ash (FAs) is a fine particulate mineral residue left behind after all the combustibles in the coal or any pulverized fuels are burnout at temperature in the range of 1000-1450 °C. At present India is producing about 125 million ton ash annually and expected to increase in future. The generated FAs have been used for reclamation and in road construction. A large amount of fly ash using in landfill sites causes different water contamination problems through leaching the toxicants present in it. So in the view of environment protection there is a need to develop new strategies for fly ash disposal. Conversion of fly ash into zeolite may be an economically and environmentally feasible method in this series.

1.5.5.3 Zeolite

These are the special class of allumino-silicates minerals having three-dimensional network, made up of the tetrahedral units of $\text{AlO}_4^{5-}$ and $\text{SiO}_4^{4-}$ connected to
each other through oxygen atom. The active sites present in the internal cavities responsible for their catalytic and adsorptive property (Shavandi et al., 2012).

The concentration and type of the cations present in the elementary cell determine their chemical and physical properties. From the point of research this is the point which determine the new ways for zeolite synthesis. Raman and infrared spectroscopy applied to find out the active site reactivity. At present 150 synthetic and 40 natural zeolite has been discovered. Zeolite structure can be assumed by the substitution (isomorphous) of AlO$_2^-$ with SiO$_2$ unit in the neutral frame-work of SiO$_2$ and give rise a negative charge on aluminium frame-work. K$^+$, Na$^+$ and sometimes NH$_4^+$ ions balance this negative charge. These ions are responsible for the ion-exchange property of a zeolite. Amount of Silica in respect of Alumina, size of pore and structure of a zeolite are the basic properties. Zeolite can be represented by the formula as shown below

$$M_{a/b} [Al_{a}Si_{b}O_{2(a+b)}]qH_2O$$

Where M denote the Na, K Li or Ca, Ba ,Mg, Sr and n-cation charge, a/b=1 to 6; q/a=1 to 4. The oxidative formula of zeolite is represented as

$$M_{2/n}O.Al_2O_3.aSiO_2.bH_2O.$$ 

![Figure 1.8 Structure of Zeolite](image)

The joining of tetrahedral atoms in two-dimensional manner form the pore size, further arrangement in three dimensional manners form structure of zeolite. These
three dimensional array connected through pore opening form the larger inner cavities. In some cases there may be one or two or three dimensional channels in successive manner in place of inner cavities throughout the zeolite structure. These customize property of the zeolite make them a valuable molecular sieves and adsorbent which are selective in nature (Melo et al., 2012).

Properties of zeolite: Zeolites are specific and selective in nature. Their thermal stability may be from 500 to 1000 °C, ion exchange capacity may be up to 700 meq./100g, surface area ranges up to 900 m2/g, cavities size from 6.6 to 11.8 Å and channels from 2.2 to 8 Å.

Fly-ash cause adverse impact on water resources and loss of soil fertility in disposal areas, we have to find methods for its safe disposal and utilization. Moreover in past few years fly ash has been accepted as the economically feasible adsorbent for contaminants (heavy metals), in waste water treatment. Indian coal have on an average 45% ash content fly ash mission, as establish by the Indian government 1994, to development of technology for their safe disposal and utilization in economically and environmentally viable fashion.

The presence of silica, alumina, ferric oxide, calcium oxide, and reactive phases such as aluminosilicate glass which are suitable starting material for the synthesis of zeolite promote it as raw material for it. Moreover, the differences in the mineralogical and chemical composition of it according to their origin place encourage researcher to develop synthesis methods for each type of fly-ash (Querol et al., 2001). Synthesis of zeolite from the fly ash fulfill both the requirement in the present day, first the conversion of fly ash (industrial waste product) into an adsorbent and secondary disposal problem. Further the synthesized zeolite can show good adsorption capacity toward heavy metals in aqueous solution.

In this study the conversion of Industrial by-product thermal power plant fly ash into zeolite will be in economically and environmentally viable in the series of development of low cost adsorbents.
1.6 Purpose of study
In view of the increasing pollution load and consequent degradation of the Ground water, the present study will be undertaken so that the extent and rate of pollution may be known. Therefore, it is proposed to undertake extensive study on monitoring of the ground water resources for natural compositional elements, anthropogenic contaminants (metals, industrial-chemicals) in the Ghaziabad District of Uttar Pradesh. The data base would be help to assess the actual toxic potential of the ground water and would make it easier to take prompt and proper steps for ground water quality assessment, identification and source apportionment of contaminants, and ground water quality mapping in the region. Since conventional treatment technologies have not been adopted by various industries due to their infeasibility in respect of cost and technical methodology to achieve the required stringent standards, sets for the disposal of effluent on surface water that directly affect the ground water quality. This calls to develop some cost effective adsorbent/s for remediation of water/waste water.

1.7 Objective of the Study
Since the study area involved in industrial activities on a large scale, may be responsible to deteriorate the water quality with particular reference to heavy metal pollution. In this study agricultural/industrial waste material which currently have serious disposal problem will be taken up for developing low cost adsorbents. Hence it is proposed to investigate such possibilities in an economic fashion. Thus the taken as whole objectives of the proposed study comprise:

a) The preliminary investigation of ground water quality of Ghaziabad.

b) Find out the suitability of ground water for various purposes such as drinking, irrigation, industrial etc.

c) Assessment of the anthropogenic pollution in the identified study region with particular reference to physico-chemical parameter, metals etc.

d) Synthesis of cost effective adsorbent/s their characterization.

e) Treatment of water/waste water for metal removal using the developed adsorbent.