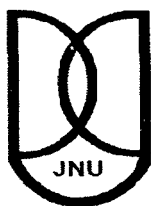


**EFFECTS OF NANOMATERIALS ON PHYSICO-  
CHEMICAL CHARACTERISTICS OF SALT-AFFECTED  
SOIL**

*Dissertation submitted to*  
**JAWAHARLAL NEHRU UNIVERSITY**  
*in partial fulfillment of the requirement*  
*for the award of the degree of*  
**MASTER OF PHILOSOPHY**

**SEEMA**



**SCHOOL OF ENVIRONMENTAL SCIENCES  
JAWAHARLAL NEHRU UNIVERSITY  
NEW DELHI – 110 067**

2010



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*CERTIFICATE*

This is to certify that the research work embodied in this dissertation entitled  
“Effects of nanomaterials on physico-chemical characteristics of salt-  
affected soil” has been carried out in the School of Environmental Sciences,  
Jawaharlal Nehru University, New Delhi. This work is original and has not been  
submitted in part or full for any other degree or diploma to any university or  
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*Dedicated*  
*to*  
*my family and friends.*

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# *Chapter-1*

## *Introduction*

## **CHAPTER-1**

### **INTRODUCTION**

Soil is one of the crucial national resources and, therefore, no country can afford to neglect or waste it. Salinity/sodicity of soil is a serious degradation problem, which is growing steadily in many parts of the world. It is multidimensional problem in many countries and has macro and micro-economic implications. It occurs mainly, but not exclusively, in arid and semi-arid regions, low-lying areas and river valleys. There are extensive saline areas on all the continents, but their extent and distribution has not been studied in detail. Estimates are in general close to 1 billion hectares, which represent about 7% of the earth's continental extent. In addition to these naturally salt affected areas, about 77 mha have become saline as a consequence of human activities, with 58% of these concentrated in irrigated areas.

During the past three decades, low-income countries in the dry regions of the world have greatly expanded the area under irrigation in order to produce the food needed by their rapidly growing human populations. Consequently, the proportion of arable land that is irrigated has increased dramatically, reaching about 45% in China, 25% in India, 72% in Pakistan, and 28% in Indonesia. Initially irrigation stimulated phenomenal increases in food-crop production. Unfortunately, many irrigation projects failed to provide for adequate drainage. As a result, the process of salinization has accelerated, and salts have accumulated to levels that are already adversely affecting crop production. In some areas, sodic soils have been created.

#### **1.1 FORMATION OF SOIL SALINITY**

In most cases the soluble salts in soils originate from the weathering of primary minerals in rocks and parent materials. In extremely dry regions (<25 cm annual precipitation), calcium sulphate accumulations (gypsic horizons) may form near the soil surface where this relatively soluble mineral may create a saline condition. However, salts are usually transported to a developing salt-affected soil as ions dissolved in water. The salt-containing water moves through a landscape from areas of higher to lower elevations, and form soil zones that are wetter to those that are drier. The water is

eventually lost by evaporation. However, the dissolved salts cannot evaporate and therefore they are left behind to accumulate in soil. Many salt-affected soils develop because changes in local water balance usually brought about by human activities; increase the input of salt-bearing water more than they increase the output of drainage water. Increased evaporation, waterlogging, and rising water tables usually results.

In non-irrigated soils, the salts are primarily chlorides and sulphates of calcium, magnesium, sodium and potassium. These salts accumulate naturally in some surface soils because there is insufficient rainfall to flush them from upper soil layers. In coastal areas, sea spray and inundation with seawater can be locally important sources of salts in soils.

In irrigated soils, irrigation not only alters the water balance by bringing in more water but it also brings in more salts. Water whether taken from a river or pumped from the groundwater, even the best quality freshwater contains some dissolved salts. The amount of the salt brought in with the water may seem negligible, but the amount of the water applied over the course of the time is huge. Again, pure water is lost by evaporation, but the salt stays and accumulates. The effect is accentuated in arid regions for two reasons: 1) the water available from the rivers or from underground is relatively high in salt because it has flowed through dry-region soils which typically contain large amounts of easily weatherable minerals, and 2) the dry climate creates a relatively high evaporative demand, so large amount of water is needed for irrigation.

## **1.2 PROCESSES OF SALINIZATION AND ALKALINIZATION**

The accumulation of soluble salts at the surface or near-surface of soil horizon is called salinization (Szabolcs, 1974). As a consequence, dominant salts in soil change to chlorides and sulphates of sodium, calcium and magnesium and soil properties such as electrical conductivity (EC) will be affected depending on the amount of accumulated salts. Besides the occurrence of salt crystals, salt crusts and salic horizons, saline soils often have some typical characteristics such as the presence of loose and quite porous granular structure. in the topsoil. With large amount of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) in

soil, the topsoil is puffy and the presence of  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  or nitrates gives the soil a moist appearance.

Alkalinization is a process leading to the formation of soils with high percentage of exchangeable sodium. The presence of carbonates and bicarbonates leads to formation of soils with high pH values, between 8.5 and 10 (FAO, 1988; Sparks 1995). The main cause of alkaline reaction of soils, as described by FAO (1988), is the hydrolysis of either exchangeable cations or of salts such as  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , and  $\text{Na}_2\text{CO}_3$ .

### 1.3 OVERVIEW OF SALT-AFFECTED SOIL CHARACTERISTICS AND CLASSIFICATION

Salt affected soils contain various proportions of cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ ) and anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ) that lead to different degrees of salinity. The main source of salt constituents are the primary minerals found in soils and exposed rocks, which appear in the form of a (1) salt crust as the result of evaporation, (2) deposit as the result of precipitation, or (3) solution as the result of dissolving in water in a soil profile (Richards, 1954; FAO, 1988). The minerals mainly responsible for soil salinity are found within four chemical groups namely carbonates, halides, sulfates, and borates. The mineral groups and their characteristics are extensively discussed by Klein and Hurlbut (1999).

Salinity in soil is expressed by different terms and units namely total dissolved solids (TDS) in milligrams per litre, total concentration of soluble cations (TSC) and total concentration of soluble anions (TSA) in equivalents per litre/kilogram (Tanji, 1990). The most frequently used indicator of salinity is electric conductivity of saturated soil extract (ECe). Electrical conductance (the reciprocal of resistance) is a quick and sufficiently accurate method for measuring soil salinity which is independent of the size of the sample (Richards, 1954). ECe increases with the concentration of soluble salts. Table 1 shows standard salinity classes proposed by the US salinity laboratory (Richards, 1954). The standard unit of electric conductivity is expressed in deci Siemens per meter (dS/m) at 25 °C.

Table 1.1. Classification of salt affected soils (USDA system)

Type of soil	ECe (dS/m)	ESP	pHs
Saline	> 4.0	< 15	< 8.5
Sodic	< 4.0	> 15	> 8.5
Saline-sodic	> 4.0	> 15	< 8.5

Table 1.2. Classification of salt affected soils (Indian system)

Soil characteristics	Saline soil	Alkali soil
pHs	< 8.2	> 8.2
ESP	< 15	> 15
ECe (dS/m)	> 4	Variable, mostly < 4
Nature of salts	Neutral, mostly $\text{Cl}^-$ and $\text{SO}_4^{2-}$ of Na, Ca and Mg. $\text{HCO}_3^-$ may be present but $\text{CO}_3^{2-}$ is absent.	Capable of alkaline hydrolysis, prevalence of $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ of Na.

Sodicity is characterized primarily by exchangeable sodium percentage (ESP), and the sodium adsorption ratio (SAR). The ESP identifies the degree to which the exchange complex is saturated with sodium.

$$\text{ESP} = \frac{\text{Exchangeable sodium, cmol}_c/\text{Kg}}{\text{Cations exchange capacity, cmol}_c/\text{Kg}} \times 100$$

The SAR is becoming even more widely used than ESP. The SAR gives information on the comparative concentrations of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  in soil solutions. It is calculated as

$$\text{SAR} = \frac{[\text{Na}^+]}{(0.5[\text{Ca}^{2+}] + 0.5[\text{Mg}^{2+}])^{1/2}}$$

Where  $[\text{Na}^+]$ ,  $[\text{Ca}^{2+}]$ , and  $[\text{Mg}^{2+}]$  are the concentrations (in mmol of charge per litre) of the sodium, calcium and magnesium ions in soil solution. A SAR value of 13 for the solution extracted from a saturated soil paste is approximately equivalent to an ESP value of 15. Using EC, ESP (or SAR), and soil pH, salt-affected soils are classified as saline, saline-sodic, and sodic.

#### 1.3.1. Saline soils

A saline soil has a pH value less than 8.5 (reduced to 8.2 in the Indian system) in the saturated paste of the soil, an ESP value less than 15 (or SAR less than 13) and EC of the soil saturation extract more than 4 dS/m along with preponderance of neutral salts i.e. chlorides and sulphates of sodium, calcium, magnesium and potassium excluding gypsum which are sufficient to interfere with the growth of most plants. In many cases the evaporation of water creates a white salt crust on the soil surface which accounts for the name **white alkali**.

#### 1.3.2. Saline- sodic soils

Soils that have both detrimental levels of neutral soluble salts ( $\text{EC}_e$  greater than 4 dS/m) and a high proportion of sodium ions (ESP greater than 13) are classified as saline-sodic soils. Plant growth on these soils can be adversely affected by both excess salts and excess sodium levels. **Saline-sodic soils exhibit physical conditions** intermediate between those of saline and sodic soils.

#### 1.3.3 Sodic soils

Sodic soils are the most troublesome of the salt-affected soils. While their levels of neutral soluble salts are low ( $\text{EC}_e$  less than 4.0 dS/m), they have relatively high levels of sodium on the exchange complex (ESP and SAR values are above 15 and 13 respectively). The pH values of sodic soils exceed 8.5, rising to 10 or higher in some cases. Few plants can tolerate these conditions because plant growth is constrained by



specific toxicities of  $\text{Na}^+$ ,  $\text{OH}^-$ , and  $\text{HCO}_3^-$  ions, as well as by the very poor soil physical conditions and slow permeability to water.

#### 1.4 EXTENT OF SALT AFFECTED SOIL IN WORLD

Salt affected soils are widely distributed throughout the world, the largest areas being found in Australia, Africa, Latin America, and the near Middle East. They are typically found in areas with precipitation to evaporation ratios of 0.75 or less, and in low, flat areas with high water tables that may be subjected to seepage from higher elevation.

Table 1.3. Area of salt-affected soils in different regions.

REGIONS	AREA, MILLION HA
Africa	69.3
Near and Middle East	53.1
Asia and Far East	19.5
Latin America	59.4
Australia	84.7
North America	16.0
Europe	20.7
<b>World Total</b>	<b>322.9</b>

*From Beek, et al. (1980)*

#### 1.5 SALT AFFECTED SOIL IN INDIA

In India, salt affected soils are known to have occurred even in the Vedic period, as deciphered from the terms like (Urvara (fertile), Anurvara (infertile), Kshariya (alkali) and lavaniya (saline) in the Vedas. In India the problem originated in the mid 70s during the green revolution but its visible impacts began to appear in mid 80s. Gupta and Abrol (1990) reported that in spite of the availability of many sources of information, accurate data concerning salt affected lands of the world are rather scarce. It is estimated that saline land extends over 8.6 mha in the country. Bhargava (2005) has attempted to compile the extent of salt affected soils occurring in different states by procuring the Soil Resource Maps published by the NBSS & LUP, Nagpur and extracting the data from the maps and executive summaries accompanying them. It emerges that without

including the area of the Rann of Kutchchh, the area occupied by salt affected soils comes to 13.1027 million ha, but with addition of the area of the Rann, a final figure of 15.2354 million ha is arrived at for the whole country. Out of this, 9.8897 million ha is saline and 5.3637 million ha is alkali.

Making use of the geomorphic settings in which the salt affected soils occur in different states, 9.8897 million ha saline soils have been grouped under five different classes, viz., inland saline (6.0987 million ha); coastal saline (0.800 million ha); deltaic saline (0.5384 million ha); acid sulphate saline (0.210 million ha) and marine saline soils (2.2426 million ha). A total of 5.3637 million ha alkali/sodic soils occur in the country, out of which 4.0992 million ha occur in the Indo-Gangetic alluvial plain and 1.2645 million ha in the deep black soil or vertisol region.

Table 1.4. Extent of saline/sodic soils in India (, 000 ha)

State	Saline	Sodic	Total
Punjab	10.2	190.9	201.1
Haryana	175.2	255.7	430.9
Rajasthan	490.4	9.5	499.9
Delhi	21.2	Nil	21.2
Uttar Pradesh	128.9	3394.1	3523.0
Bihar	-	229.0	229.0
West Bengal	377.7	-	377.7
Maharashtra	317.3	114.6	431.9
Andhra Pradesh	312.7	217.2	529.9
Madhya Pradesh	1743.4	26.6	1770.0
Karnataka	100.0	10.0	110.0
Orissa	74.5	-	74.5
Tamil Nadu	50.0	46.2	96.2
Goa	1.0	-	1.0
A & N Islands	91.9	-	91.9
Karaikal	1.7	1.8	3.5
Pondicherry	1.5	1.9	3.4
Kerala	203.0	-	203.0
Jammu & Kashmir	40.0	20.0	60.0
Gujarat	3598.4	846.2	4444.6
Rann of Kutchchh	2150.7	-	2150.7
<b>Total</b>	<b>9889.7</b>	<b>5363.7</b>	<b>15253.4</b>

## **1.6 DANGERS OF SOIL SALINITY**

The detrimental effect of adsorbed sodium on the physical properties of soils results in low water infiltration rate, low permeability to water and gases, increase of osmotic pressure of the soil, and poor soil structure. The increase of salts in soil also results in chemical dispersion, which increases susceptibility of soil to sealing and crust formation (FAO, 1988). Increasing exchangeable sodium promotes structural changes resulting in unstable and compacted soil (Mainguet, 1991). This is due to dispersion of soil particles and swelling of soil clay contents. Mainly in sodic soils, the content of organic matter tends to drop or does not decompose satisfactorily. Changes in soil properties (higher EC or ESP) as a result of salts accumulations in soil reduce soil productivity. The damaging effects of salt on plants are also caused by osmotic forces, as well as by toxic levels of sodium and chloride. This effect is mainly indirect by pulling moisture out of roots and reducing the uptake of water and nutrients (FAO, 2006). Plants respond to the various types of salt-affected soils in different ways. In addition to the nutrient deficiency problems associated with high pH, high levels of soluble salts affect plants by osmotic effect and specific ion effect. Most plants suffer salt injury at concentration equivalent of electrical conductivity of the soil saturation extract (ECe) of 4 dS m<sup>-1</sup> or higher.

## **1.7 TRADITIONAL METHODS OF RECLAIMING SALT-AFFECTED SOILS**

Management of salt-affected soil requires a combination of agronomic practices and socioeconomic considerations. For instance, reclamation of saline soils may begin with the provision of effective drainage and good quality irrigation water to lower the levels of soluble salts. If the natural soil drainage is inadequate to accommodate the leaching water, an artificial drainage network must be installed. The reclamation of saline-sodic and sodic soils requires an additional process before leaching of excess salinity can be achieved. In order to make these soils permeable enough for leaching to take place, the excess exchangeable sodium ions must first be removed from the exchange complex. This is accomplished by replacing the Na ions with either Ca<sup>2+</sup> or H<sup>+</sup> ions. The Ca<sup>2+</sup> and

$H^+$  ions then stimulate flocculation and increased permeability to the point that the replaced sodium and other salts can be leached downward and out of the profile. Gypsum,  $S^0$ ,  $H_2SO_4$  and  $CaCl_2$  improves the physical as well as the chemical properties of saline- alkali soil. Gypsum ( $CaSO_4$ ) and elemental sulphur ( $S^0$ ) are the two amendments that can supply the  $Ca^{2+}$  and  $H^+$  ions needed. Monitoring the chemical content of both the irrigation water and the soil is essential to achieve this goal of removing the  $Na^+$  ions from the exchange complex and, ultimately the soil.

### 1.8 NANOTECHNOLOGY-A BETTER TOOL

Nanotechnology is defined as the understanding and control of matter at dimensions of roughly 1-100 nm, where unique physical properties make novel applications possible (EPA, 2007). NPs are therefore considered substances that are less than 100 nm in size in more than one dimension. They can be spherical, tubular, or irregularly shaped and can exist in fused, aggregated or agglomerated forms. Properties of materials of nanometric dimensions are significantly different from those of atoms as well as those of bulk materials. It will offer better built, longer lasting, cleaner, safer, and smarter products for the home, for communications, for medicine, for transportation, for agriculture, and for industry in general. A key understanding of nanotechnology is that it offers not just better products, but a vastly improved manufacturing process. It covers fields from biology to material science, physics to chemistry and can include development in a variety of specialties.

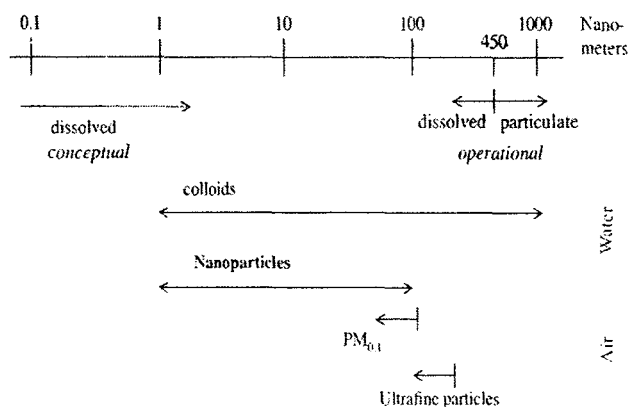


Figure-1.1. Definitions of different size classes relevant for nanoparticles.

Nanoparticles are highly active species. When the particle size is decreased to the nanoscale range, fundamental physical and chemical properties appear to change, often resulting in completely new and different than before physical/chemical properties. One of the most important attributes of all NPs is their high surface area per unit mass. As a result of this feature, the surface of NPs possesses a considerable surface energy (Feldheim and Colby, 2002). As the particle size is reduced, the proportion of atoms found at the surface related to the atoms in the interior of the particle increases and as a consequence, the nanoscale particles are more reactive. NPs differ from larger materials in that the number of atoms at the surface and their physical properties are different from those of bulk materials (Poole and Owens, 2003). Properties associated with the bulk materials are averaged properties, such as density, resistivity and magnetisation and the dielectric constant. Critically, however, many properties of these materials change over at the NP scale (Daniel and Astruc, 2004; Niemeyer, 2001). These differences arise from the small size and large number of surface atoms of the particles and related effects. The high surface area to mass ratio of nanoparticles can greatly enhance the adsorption capacities of the sorbent materials. Fundamental electronics, magnetic, optical, chemical, and biological processes are also different at this level.

NP can be divided into natural and anthropogenic particles. The particles can be further separated based on their chemical composition into carbon-containing and inorganic NP. Examples of natural NP are fullerenes and CNT of geogenic or pyrogenic origin, biogenic magnetite or atmospheric aerosols (both organic such as organic acids and inorganic such as sea salt). Anthropogenic NP can be either inadvertently formed as a by-product, mostly during combustion, or produced intentionally due to their particular characteristics. In the latter case, they are often referred to as engineered or manufactured NP. Examples of engineered NP are fullerenes and CNT, both pristine and functionalized and metals and metal oxides such as TiO<sub>2</sub> and Ag. Engineered NPs are the main focus of the current research on NP in the environment, but some of them

occur also naturally, e.g. as inorganic oxides or fullerenes. In the sections below the different types of natural and engineered NP are presented.

### 1.8.1 Basic approaches to synthesize nanoparticles

For the production of manufactured NPs, the main objective is not simply to obtain nanoscale materials. For most real world applications, experimental conditions need to be tightly controlled in order to obtain NPs with at least the following characteristics:

- 1) Identical particles in terms of size (a uniform size distribution)
- 2) Identical shape or morphology
- 3) Identical chemical composition and crystal structure (ideally, core and surface composition must be the same, unless specifically designed for other purposes)
- 4) Monodispersity (no aggregation)

Table-1.5-Classification of nanoparticles

		Formation		Examples	
Natural	C-containing	Biogenic	Organic colloids	Humic, fulvic acids	
			Organisms	Viruses	
		Geogenic	Soot	Fullerenes	
		Atmospheric	Aerosols	Organic acids	
		Pyrogenic	Soot	CNT Fullerenes	
		Inorganic	Biogenic	Oxides	Nanoglobules, onion-shaped nanospheres Magnetite
			Metals	Ag, Au	
		Geogenic	Oxides	Fe-oxides	
			Clays	Allophane	
		Atmospheric	Aerosols	Sea salt	
Anthropogenic (manufactured, engineered)	C-containing	By-product	Combustion by-products	CNT Nanoglobules, onion-shaped nanospheres	
		Engineered	Soot	Carbon Black Fullerenes	
				Polymeric NP	Functionalized CNT, fullerenes
	Inorganic	By-product	Combustion by-products		Polyethylene glycol (PEG) NP
		Engineered	Oxides		Platinum group metals TiO <sub>2</sub> , SiO <sub>2</sub>
			Metals		Ag, iron
		Salts		Metal-phosphates	
		Aluminosilicates		Zeolites, clays, ceramics	

They can be produced by a huge range of procedures which can be grouped into top-down and bottom up strategies (Fig. 1.2). Top-down approaches are defined as those by which NPs or well-organized assemblies are directly generated from bulk materials via

the generation of isolated atoms by using various distribution techniques (Niemeyer, 2001). The majority of the top-down strategies involve physical methods such as milling or attrition, repeated quenching and photolithography (Gao, 2004).

Bottom-up strategies involve molecular components as starting materials linked with chemical reactions, nucleation and growth process to promote the formation of more complex clusters (Gao, 2004; Rotello, 2003).

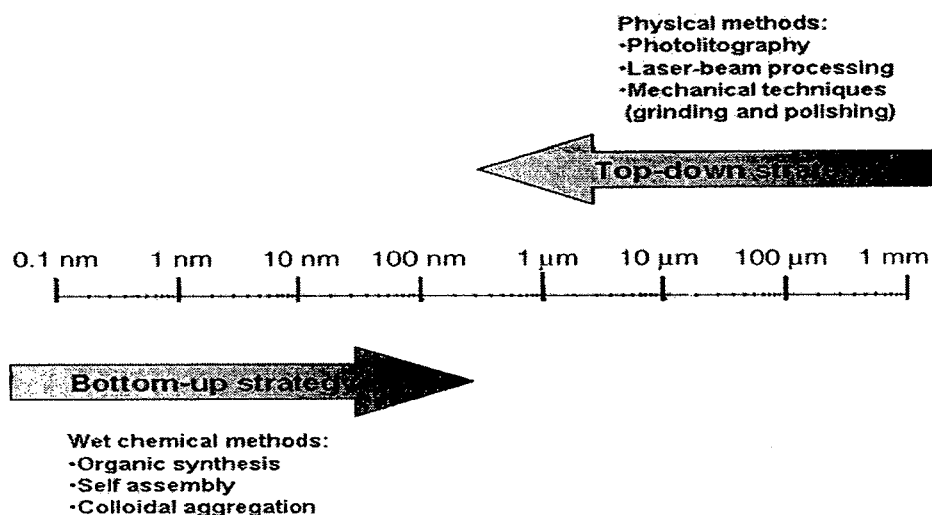


Fig. 1.2 –Top-down and bottom-up strategy

### 1.8.2 Characterization methods for nanoparticles

Characterization of nanomaterial and nanostructure has been largely based on the surface analysis technique and conventional characterization method developed for bulk material. XRD (X- ray diffraction) has been widely used for the determination of crystallinity, crystal structure and lattice constant of nanoparticle, nanowire and thin film. SEM (Scanning electron microscope) and TEM (Transmission electron microscope) together with electron diffraction have been commonly used in characterization of nanoparticles; optical spectroscopy is used to determine the size of semiconductor quantum dot. The most common characterization technique for manufactured NPs is high-resolution transmission electron microscopy (HRTEM) (Giersig and Mulvaney, 1993; Hasan et al., 2002), from which an electron micrograph of the NPs can be obtained. However, their dimensions can be determined by a number

of Other methods including scanning tunneling microscopy (STM) (Grabar et al., 1997), atomic force microscopy (AFM) (Junno et al., 1998; Li et al., 2003), small-angle X-ray scattering (SAXS) (Nakamura et al., 2003), and X-ray diffraction (Leff et al., 1995). By counting a suitable number of particles (either manually or automatically) size distributions of these NPs gives relevant information on the dispersity of the NPs (Giersig and Mulvaney, 1993).

### 1.8.3 Applications of nanoparticles

Nanoscience and nanotechnology study have received much attention in the last decade because of our increasing ability to synthesize and manipulate such materials. Today, manufactured NPs are currently used in different areas such as electronics, biomedicine, pharmaceuticals, energy, cosmetics, environmental analysis and remediation, catalysis and material sciences, due to the relative ease with which they can be prepared and manipulated, their generally high reactivity and surface area and the tuneable nature of their optical and other properties (Niemeyer, 2001; Poole and Owen, 2003; Schmid, 2004). Because of the potential of this technology there has been a worldwide increase in investment in nanotechnology research and development (Guzman et al., 2006). Data on the current use and production of NP are sparse and often conflicting. One estimate for the production of engineered nanomaterials was 2000 tons in 2004, expected to increase to 58,000 tons in 2011-2020 (Maynard, 2006).

### 1.8.4 Environmental risks of nanoparticles

The forecasted huge increase in the manufacture and use of NP makes it likely that increasing human and environmental exposure to NP will occur. As a result NP are beginning to come under scrutiny and the discussion about the potential adverse effects of NP has increased steadily in recent years; in fact it has become a top priority in governments, the private sector and the public all over the world (Roco, 2005; Helland et al., 2006; Siegrist et al., 2007). Most attention has thus far been devoted to the toxicology and health implications of NP (e.g. Oberdörster et al., 2005; Kreyling et al., 2006; Lam et al., 2006; Nel et al., 2006; Helland et al., in press), while the behavior of NP in the environment (Biswas and Wu, 2005; Wiesner et al., 2006; Helland et al., in



press) and their ecotoxicology (Colvin, 2003; Moore, 2006; Oberdörster et al., 2006a) have been less often reviewed.

Biological and chemical properties of nanoparticles may also differ from the macro form of these substances. This has given rise to some safety concerns for production workers and consumers. Previous reviews (Biswas and Wu, 2005; Handy et al., 2008a, b; Nowack and Bucheli, 2007) have focused on ecotoxicological effects and environmental transport generally. A consistent body of evidence shows that nano-sized particles are taken up by a wide variety of mammalian cell types is able to cross the cell membrane and become internalized (Lynch et al., 2006; Rothen-Rutishauser et al., 2006; Smart et al., 2006). The uptake on NP is size-dependent (Limbach et al., 2005; Chithrani et al., 2006). Aggregation and size-dependent sedimentation onto the cells or diffusion towards the cell were the main parameters determining uptake (Limbach et al., 2005). The uptake occurs via endocytosis or by phagocytosis in specialized cells. Within the cells NP are stored in certain locations (e.g. inside vesicles, mitochondria) and are able to exert a toxic response. The small particle size, a large surface area and the ability to generate reactive oxygen species play a major role in toxicity of NP (Nel et al., 2006). Several respiratory and cardiovascular diseases in humans are caused by BC (Avakian et al., 2002; Morawska and Zhang, 2002; Armstrong et al., 2004).

### **1.9 HAP FOR SALT-AFFECTED SOIL**

Hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  is one of the most popular phosphate mineral in last decade due to its importance in the environment and biological system, and numerous application in various fields of science and technology. HAP is the naturally occurring mineral, present in phosphate rocks and sediments, together with the other members of the “apatite family” (fluoro, chloro and carbonated apatites), and non-apatite minerals like calcite ( $\text{CaCO}_3$ ) and gypsum ( $\text{CaSO}_4$ ). The structure of HAP belongs to the hexagonal system with a  $\text{P6}_3/\text{m}$  space group. The unit cell, the smallest building unit and a complete representation of the HAP crystal, consists of  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{2-}$  and  $\text{OH}^-$  groups closely packed together in a hexagonal arrangement. A significant detail of crystal structure is that  $\text{Ca}^{2+}$  occupies two different crystallographic sites. According to

the position in the unit cell, ten calcium (Ca) atoms can be classified into two types: Ca<sub>1</sub> and Ca<sub>2</sub>. Four calcium atoms occupy the Ca<sub>1</sub> positions, which locate in an octahedral site of a hexagonal array, and six calcium atoms live in Ca<sub>2</sub> position (Narasaraju et al., 1996), which locates at the corners of the hexagonal column and surrounds the OH<sup>-</sup> ions. However, six Ca<sub>2</sub> atoms are not in the same plane, each three arrange in triangle positions at z = 0.25 and at z = 0.75.

The ability of HAP for various cationic and anionic substitutions leads to the formation of solid solutions or isomorphous compounds (Narasaraju et al., 1996). Substitution may involve ions of such as Sr<sup>2+</sup>, Ba<sup>2+</sup>, Mg<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Na<sup>+</sup> or K<sup>+</sup> for Ca<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> for PO<sub>4</sub><sup>3-</sup> and F<sup>-</sup>, Cl<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> for OH<sup>-</sup> in the apatite crystal lattice. All these properties make HAP a powerful material for reduction of the concentration of many organic and inorganic substances. It is especially useful in immobilization of heavy metals such as Cd<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, U (VI) etc., through coprecipitation and sorption processes (Reichert et al., 1996; Xu et al., 1994; Jeanjean et al., 1995; Kaluderovic et al., 2001; Raicevic et al., 2000).

### **1.10 OBJECTIVES OF THE STUDY**

Nano-materials represent a promising application in a variety of areas due to their high surface area and reactivity and their ability to become dispersed in aqueous solution. Nano-material usually displays higher reactivity and sorption ability than the same material of normal size. Upto now, there is limited information about the effect of hydroxyapatite on salt-affected soils. However, a few studies have been conducted to study the remediation of heavy metals in soil using nano-HAP. So the objectives of the study were:

- 1) To study the mineralogical and physico-chemical characteristics (texture, pH, EC, TDS, major ions, SAR, CEC, ESP and heavy metals) of salt affected soil.
- 2) To study the effect of HAP nanoparticles on major ions, ESP, CEC and SAR of salt affected soil.
- 3) To study the effect of HAP nanoparticles on heavy metal (Pb, Cr, Cu and Ni) concentration of salt affected soil.

## *Chapter-2*

*Review of literature*

## **CHAPTER 2**

### **REVIEW OF LITERATURE**

The problem of soil salinization/sodification is age old but its magnitude and intensity has been increasing fast because of large scale efforts to bring additional lands under irrigation with marginal quality waters in recent decades. The problem has been worsened by the development of the irrigation system without adequate provision of drainage and is being aggravated by unscientific water management practices and inappropriate reclamation procedures along with obstruction of natural drainage through construction of roads, buildings etc. Different attempts have been made to counter the adverse effects through crops, amendments and tillage on a number of physical and chemical properties of saline/sodic soils. The following section pertains to brief review on different aspects of salt-affected soils and efforts made for their production and economic utilization.

#### **2.1 SALT AFFECTED SOIL**

Soils having soluble salts in the solution and or  $\text{Na}^+$  ions on the exchange sites exceeding the specified limits those can adversely affect soil and plant health are called salt-affected soils. Soils were historically classified as saline, sodic and saline-sodic based on the total concentration of salt and the ratio of  $\text{Na}^+$  to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the saturated extract of the soil (Dudley., 1994). Salt-affected soils are generally divided into saline, sodic, saline-sodic (Richards, 1954) and recently recognized categories acid sulphate, high boron and high magnesium soils (Szabolcs, 1994). Terms like black alkali (sodic), white alkali (saline), slick-spots (sodic), solonchak (saline) and solonetz (sodic) also exist for these categories in some parts of the world.

In general, the two major salt-affected soil groups are saline and alkali (sodic). The two classes can be distinguished considering the nature of salts present in them, their physico-chemical characteristics and their ameliorative requirements (Bhargava et al., 1976). Although the above two categories account for a very large fraction of salt-affected soils the world over, there are transitional or borderline formations which are

likely to have intermediate properties (FAO, 1988). According to United States Department of Agriculture (Richards, 1954), a soil having  $EC \geq 4$  dS/m and  $SAR < 13$  is called a saline soil. Soils with  $EC < 4$  dS/m and  $SAR \geq 13$  are designated as sodic soils. If a soil has  $EC$  and  $SAR \geq 4$  dS/m and 13, respectively, it is called saline-sodic soil.

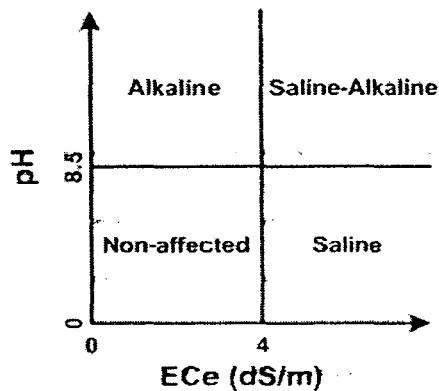


Figure-2.1 Traditional classification of soils into saline, alkaline and saline-alkaline soils (Richards., 1954)

The distribution of salt-affected lands is closely related to environmental factors, in particular arid and semi-arid climates. The extent to which salinity is increasing in arid and semi-arid lands has recently become a problem of great concern in agriculture. Recent estimates shows total area of salt affected soils at some 9.5 million km<sup>2</sup> on a world scale (Szabolcs., 1989) much of it due to inadequate irrigation practices in arid and semiarid regions, and the consequent loss of agricultural production is enormous. It is believed that about 7% of the total surface area of the world is salt affected and approximately 10% of the world's  $7 \times 10^9$  ha arable land surface consist of saline or sodic soils (Francois and Maas., 1994). The percentage of cultivated lands affected by salinity is even greater of the  $1.5 \times 10^9$  ha cultivated lands, 23% are considered as being saline and another 37% are sodic. It has been estimated that one-half of all irrigated lands (about  $2.5 \times 10^8$  ha) are seriously affected by salinity or water logging (Rhoades and Loveday., 1990). Salinity is one of the major abiotic stresses to crops and affecting about  $950 \times 10^6$  ha of land worldwide (Flowers and Yeo., 1995).

## **2.2 CAUSES OF SOIL SALINITY**

### **2.2.1 Primary cause of soil salinity**

Most of the saline-sodic soils develop due to natural geological, hydrological and pedological processes. Some of the parent materials of these soils include intermediate igneous rocks such as phenolytes, basic igneous rocks such as basalts, undifferentiated volcanic rocks, sandstone, alluvium and lagoonal deposits (Wanjogu et al. 2001). Climatic factors and water management may accelerate salinization. In arid and semi-arid lands (ASAL) evapotranspiration plays a very major role in pedogenesis of saline and sodic soils. Wanjogu et al. (2001) reported that most of the ASAL receive less than 500 mm of rainfall annually and this coupled with an annual potential evapotranspiration of about 2000 mm leads to salinization. Another type of salinity occurs in coastal areas subject to tides and main cause is intrusion of saline water into rivers (Cyrus et al., 1997) or aquifers (Howard and Mulling, 1996). Coastal rice crops in Asia, for instance, are frequently affected by exposure to seawater brought in by cyclone around the Indian Ocean (Suktana et al., 2001).

### **2.2.2. Secondary salinization**

Secondary salt-affected soils are those that have been salinized by human-caused factors, mainly as a cause of improper irrigation methods. Poor quality water is often used for irrigation, so that salts eventually build up in the soil unless management of the irrigation system is such that salts are leached from the soil profile. Szabolcs (1992) estimated that 50% of all irrigated soils are salt-affected. Too few attempts have been made to assess the degree of human-induced secondary salinization and according to Flowers and Yeo (1995) this makes it difficult to evaluate the importance of salinity to future agricultural productivity. Anthropogenic salinization occurs in arid and semi-arid areas due to waterlogging brought about by improper irrigation (Ponnampereuma, 1984). Secondary salt-affected soils can be caused by human activities other than irrigation and include, but not limited to, the following:

- a) Deforestation is recognized as a major cause of salinization and alkalization of soils as a result of effects of migration of salts in both upper and lower layers.

In South-east Asia, vast areas of former forestlands became increasingly saline and alkaline a few years after the felling of the woods (Szabolcs, 1994).

b) Accumulation of air-borne or water-borne salts in soils:

Szabolcs (1994) has reported that chemical accumulation from industrial emissions may accumulate in soil, and if the concentration is high enough can result in salt accumulation in upper layer of soil. Similarly, water with considerable salt concentration such as waste water from municipalities and sludge may contaminate the upper layer of the soil causing salinization/alkalinization (Bond., 1998; Bouwer., 2002).

c) Salinization caused by contamination with chemicals:

This kind of salinization more often occurs in intensive agricultural systems, particularly greenhouses and intensive farming systems. In closed or semi-closed systems (greenhouses) salts tend to accumulate if chemicals are not removed regularly, resulting in salinity or alkalinity. In countries with intensive agriculture like Japan and Netherlands, this type of salinization appears more frequently (Pessarakli, 1991).

d) Overgrazing:

Szabolcs (1994) has reported that this process occurs mainly in arid and semi-arid regions, where the natural soil cover is poor and scarcely satisfies the fodder requirement of extensive animal husbandry. Because of the overgrazing, the natural vegetation becomes sparse and progressive salinization develops, and sometimes the process ends in desertification as the poor pasture diminishes.

### **2.3 RECLAMATION OF SALT-AFFECTED SOILS**

Several methods have been adopted for reclamation of salt-affected soils. The suitability of each method depends upon a number of considerations. These are physical, chemical and mineralogical characteristics of soils, internal soil drainage, presence of pan(s) in the subsoil, climatic conditions, content and type of salts present, quality and quantity of water available for leaching, quality and depth of ground water, desired rate of replacement of excessive exchangeable  $\text{Na}^+$ , presence of lime or

gypsum in soil, availability and cost of amendments, topographic features of land, and time available for reclamation ( Richards., 1954; Frenkel and Meiri., 1985; Ghafoor et al., 1990). Good internal soil drainage, land leveling and deep ground water table are considered essential pre-requisites for successful reclamation (Muhammed, 1983; Hoffman, 1986; Muhammed et al., 1998).

### 2.3.1 Inorganic materials and physical and cultural practices

Equilibrium reactions occur between the cations in the soil solution and those adsorbed on the exchange complex of the soil. The use of amendments for changing the exchangeable-cation status of soil depends upon these equilibrium reactions. Adsorption of excessive amounts of sodium is detrimental to the physical status of the soil and may be toxic to plants. When the exchangeable- sodium content of soil is excessive or tends to become so, special amendment, leaching, and management practices are required to improve and maintain favorable soil conditions for plant growth ( USDA Handbook 60).

~~Reclamation of saline soils uses many~~ different methods as physical amelioration (deep ploughing, subsoiling, sanding, profile inversion), chemical amelioration (amending of soil with various reagents: gypsum, calcium chloride, limestone, sulphuric acid; sulphur, iron sulphate) and electro-reclamation (treatment with electric current). Chemical amendments are materials that supply divalent cations usually  $\text{Ca}^{2+}$  for replacement of adsorbed  $\text{Na}^+$ . Organic and biological amendments act like acids to solubilize native lime sources.

Saline soils are generally reclaimed by leaching with excess water that carries salts into the deeper layers. The quantity of water that must leach through the soil profile to remove soluble salts depends primarily on the initial soil salinity level, the technique of applying water and soil type. The most effective hydrotechnical amelioration methods are based on the removal of exchange and soluble sodium and changing the ionic composition of soils by added chemicals with parallel leaching of sodium salts out of the soil profile (Chhabra., 1994). The result of such procedures is the decrease of pH and osmotic pressure of soil solution thus promoting good conditions for the



decrease of the dispersion of soil colloidal fraction. Water suitable for irrigation is normally considered suitable for soil reclamation (Hoffman., 1986) although, low quality water may prove even better during initial reclamation (Ghafoor et al. 1987).

According to Szabolcs (1989), for reclaiming saline soils, excess salinity has to be removed, or at least diminished. For this purpose leaching and drainage are two basic methods. The only practical way to remove excess soluble salts from the soils is by washing them out. Efficient irrigation practices can be developed more readily in the planning of irrigation systems than by applying corrective measures on the farm. Limited quantities of water should be supplied, based upon consumptive use and leaching requirements for the area in question. The leaching of soluble salts from the root zone is essential in irrigated soils. Evidently provisions must be made for disposing of the water in order to prevent re-salinization. Drainage draws the water off, thereby improving saline soils. A proper drainage system for saline soils must be designed to desalinate not only the top soil layer but also the upper subsoil and water-bearing horizons. It will regulate both the water and salt balances of the soil and subsoil. Various types of drainage used are vertical, deep horizontal, shallow horizontal; etc.

Irrigation, leaching, and tillage practices can all be directed toward salinity control. In general, irrigation methods and practices that provide uniformity of application and downward movement of water through soils favor salinity control. From the standpoint of efficiency in replacing exchangeable sodium, it is advantageous to leach most of the soluble salts out of the soil before applying chemical amendments. As a result of the removal of soluble salts, a higher proportion of the calcium supplied by the addition of amendments is adsorbed by the soil exchange complex. Improvement of the physical condition of alkali soils involves the rearrangement and aggregation of soil particles as well as the replacement of exchangeable sodium. This has been demonstrated and emphasized by Gardner (1945). The rearrangement of soil particles so as to improve physical condition is facilitated by alternate wetting and drying, by alternate freezing and thawing and by the action of plant roots.

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There has been a long history of sodic soil amelioration research and practice. Research on sodic soil amelioration, documented since the early 1900s, provides evidence of such work in many areas of the world (deSigmund., 1924; Kelley and Brown., 1934; Wursten and Powers., 1934; Puri and Anand., 1936). Several methods have been used to ameliorate a variety of sodic soils, which include: leaching without amendment application to ameliorate gypsiferous soils, leaching with high electrolyte water containing divalent cations, using chemical amendments, modifying soil profile through tillage, surface flushing of low-permeability soils where vertical leaching is not efficient, passing electric current through soils and growing salt resistant crops to ameliorate calcareous sodic soils through phytoremediation. These methods or these combinations have been used under specific condition. Among these methods, chemical amendments have an extensive usage (Hoffman., 1986; Gupta and Abrol., 1990; Keren and Miyamoto., 1990; Rhoades and Loveday., 1990; Oster et al., 1999). Some amendments supply  $\text{Ca}^{2+}$  directly to the soil while other helps in dissolving native soil calcite ( $\text{CaCO}_3$ ) to provide  $\text{Ca}^{2+}$ . Consequent to high cost incurred on sodic soil amelioration, efforts have been made to search for ways to minimize the cost of amelioration, particularly the cost of using chemical amendments.

For sodic/saline-sodic soils, reclamation generally proceeds by increasing  $\text{Ca}^{2+}$  on exchange complex at the expense of  $\text{Na}^+$  and the desorbed  $\text{Na}^+$  being removed along with the excess soluble salts, if present, to lower depths (Qadir et al., 2001). It is achieved by leaching after adding chemical amendments to soil or irrigation water (Keren and Miyamoto., 1990) and organic and biological amendments (Ilyas et al., 1990) with certain flow of water through the soil. According to Szabolcs (1989), the application of gypsum or other chemicals (sulphur, calcium chloride, calcium nitrate etc.) is inevitable in the reclamation of alkali soils. Chemical amendments as gypsum, sulfur and limestone are normally applied broadcast and then incorporated with the soil by means of a disk or plow. Thorough incorporation is especially important when sulfur is used to insure rapid oxidation to the sulfate form. Except where sulfur is used, saline-alkali soils should be leached immediately following the application of amendments. Leaching dissolves and carries the amendment downward, and it also

removes the soluble sodium salts that form as a result of cation exchange. Soils receiving sulfur ordinarily should not be leached until sufficient time has been allowed for most of the sulfur to oxidize and form gypsum, but the soils should be kept moist, as moisture is essential to the process of microbial oxidation (USDA handbook 60).

In addition to the removal of excess salts and exchangeable sodium, other practices are usually required for complete reclamation. Plant nutrients that are leached from the soil must be replaced and fertilizer practices following leaching should compensate for plant nutrient losses. Nitrogen is the principal nutrient subject to leaching loss. Soil structure that may have deteriorated during the salinization or alkalization process must be restored. Unfavorable soil structure after leaching is sometimes a special problem and may be improved by adding manure or other forms of organic matter, by growing crops that are beneficial to structure, or by alternate wetting and drying, as indicated by the field tests of Reitemeier and associates (1948) and Bower and coworkers (1951).

Several products have been used as soil amendments application on salt leaching in a tropical alkaline soil in or to reclaim alkaline soils. Examples of these products are  $\text{CaCl}_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{CaSO}_4$  (Ryan et al., 1989), also organic amendments such as agricultural and industrial waste, including sewage sludge (Anjos et al., 1998) and rice stubble. The application of manure by farmers often improves hydraulic conductivity and the use of products commercially available (e.g polyalcohols and substances derived from humic acids) have shown promise, but their cost is high (Herrero., et al., 1997). For many years, sulphur and sulphuric acid have been used for reclamation and improvement of alkaline soils (Hilal et al., 1987).

Gypsum has low solubility of  $28 \text{ mmol}_c \text{ L}^{-1}$  at  $25^\circ\text{C}$  and in soils seldom exceeds  $15 \text{ mmol}_c \text{ L}^{-1}$  (Rhoades., 1982). However, it has low dissolution but effectively sustain the electrolyte concentration for longer periods, which in turn, is very useful for water conducting characteristics of soils (Muhammed & Khaliq., 1975; Frankel *et al.*, 1978; Ghafoor *et al.*, 1989; Baumharat *et al.*, 1992; Raza *et al.*, 2000).

The literature shows that first time, acid ( $H_2SO_4$ ) was used in crop husbandry in 1916 (Lipman et al., 1916). During the following years, extensive experimentation was conducted in various parts of the world on the use of acids and acid formers (Thorne., 1944; Olson., 1950; Kelly., 1950; Meller., 1956; Sengupta & Cornfield., 1966; Gupta & Veinot., 1974; Manukyan., 1976; Wallace et al., 1976; Ryan et al., 1975a & b; Miyamoto et al., 1975, 1977; Stroehlein et al., 1978; Ryan & Stroehlein., 1973, 1979; Rashid & Hamid., 1979; Ghafoor & Muhammed., 1981; Ghafoor et al., 1986, 1997; Brauen et al.1997). Acids could affect soil reclamation at rates faster than that with gypsum, sulphur, pyrite or calcium poly-sulphide. The important discouraging aspect has been its high cost and handling hazards. Ghafoor et al. (1981, 1986) reported that sulphuric acid application was 5-8 times expensive than gypsum while corresponding value for HCl was higher by 10 times. Oxidation of  $S^0$  to  $H_2SO_4$  by soil microorganisms is particularly beneficial in alkaline soils to reduce pH, supply  $SO_4$  to plants, improve soil structure and increase the availability of certain plant nutrients such as phosphorus, iron, manganese and zinc etc (Burns, 1967).

Previous work has shown that sulfuric acid proved to be more effective in reducing Exchangeable Sodium Percentage (ESP) of the soil than gypsum (Vadyanina & Roi., 1974). Water penetration into sodic soil was also improved with sulfuric acid treatment.

A major amount of gypsum added to the soil is utilized in neutralizing or precipitating the soluble carbonates and bicarbonates. Since carbonates and bicarbonates in the soil are in the solution phase, they freely react with added gypsum (Abrol et al., 1978). It was economically feasible to reclaim most alkali soils provided that effective drainage and adequate irrigation water is available. Simple leaching can reclaim saline soils whereas black alkali soils need proper amount of gypsum, sulfur, iron sulfate and aluminium sulfate along with leaching. Sulfuric acid dissolved  $CaCO_3$ , which in turn enhanced water penetration. Gupta and Bajpai (1977) observed that addition of gypsum,  $H_2SO_4$  or  $CaCl_2$  improved the physical as well as chemical properties of saline-alkali soil under regular flushing.

According to Rachev et al (2000), the soil can be amended with black or brown coal powder, possibly as waste materials from coal mines. The powder can be applied in the air dry state or as water suspensions. Doses of about 20 t ha<sup>-1</sup> or higher can be recommended, depending on soil properties. The presence of humus-like substances in coal materials enriches the soil in stable organic matter of high cation exchange capacity and aggregation properties. The iron II sulphate can be applied simultaneously as water solution in doses equivalent to the dose of gypsum. Its hydrolysis and oxidation can lead to further reductions of soil pH and the production of amorphous iron hydroxides, which serve as cementing agents. Iron industrial wastes can also be applied. The interaction of the added materials with soil minerals and solutes results in diminishing toxic concentrations of salt and stabilize aggregation state of the soil.

Soil properties as influenced by flyash addition in soil have been studied by many researchers (Sharma et al., 2002; Aitken et al., 1985; Sikka et al., 1994; Kalra et al., 1997; Deshmukh et al., 2000; Grewal et al., 2001; Garg et al., 2003). The concentration of all elements (except N) is higher in flyash than in soil. Therefore, flyash as an amendment for agricultural soils can improve the physical and chemical properties of deficient soil, thereby improving soil fertility and crop yield. According to Sharma et al. (2006), the pH of soil is significantly influenced with ash application and there is marked reduction in pH with increase in percentage of flyash and the values being minimum under 30 percent flyash application and maximum under the control.

### 2.3.2 Biological reclamation methods

The biological amelioration methods involve living or dead organic matter eg: crops, stems, straw, green manure, barnyard manure, compost and sewage sludge (Matsumoto et al, 1994; Wang et al, 1990). They have two principal beneficial effects on reclamation of saline and alkaline soils: improvement of soil structure and permeability thus enhancing salt leaching, reducing surface evaporation and inhibition of salt accumulation in surface soils, and release of carbon dioxide during respiration

and decomposition. In the latter methods large amounts of organic matter should be applied in a long term treatment.

Several lysimeter and field experiments conducted during the last two decades have shown that the most sodic soils can be ameliorated by a low initial capital investment, i.e. phytoremediation (Robbins., 1986; Ahmad et al., 1990; Ilyas et al., 1993; Batra et al., 1997; Qadir et al., 2001). This amelioration strategy works through plant root action that helps dissolve native soil  $\text{CaCO}_3$  to supply adequate levels of  $\text{Ca}^{2+}$  without the application of an amendment.

Afforestation has been recommended as one way to reclaim sodic lands (Yadav., 1980). Trees tend to improve the site by changing the chemical properties, physical structure, microclimate, infiltration capacity and moisture regime of the soil (Prinsely and Swift., 1986). With time, process such as litter fall, nitrogen fixation, root extension, crown expansion and nutrient cycling contribute to nutrient and organic matter build-up in the top soil leading to physical, chemical and biological improvement in the critical rooting zone (Gill et al., 1987; Gill and Abrol, 1991; Evans, 1992; Garg and Jain, 1992). According to USDA handbook 60 (1954), salt-tolerant crops eg: alfalfa, barley, sugar beets, and cotton can often be grown where salinity is a problem.

Plants not only improve water flow in soils, they also cause changes in the chemical properties of soils. In previous studies it has been shown that plants decrease soil pH (Liu et al., 1989; Youssef and Chino., 1989), add organic matter and nutrients in soil (Yamoah et al., 1986) and increase dissolution of lime in the presence of  $\text{CO}_2$  evolved from decomposition of organic matter and plant root respiration (Gupta and Karan, 1985; Gupta et al., 1988). These changes occur because of the release of organic carbon and exudates (Dormaar., 1988; Treeby et al., 1989).

Salinity is not inimical to all plants. A wide range of plant species grows naturally on the coastal and inland saline areas such as salt marshes and salt deserts (halophytes), which survive salt concentration equal to or greater than that of seawater. The

compartmentation of ions in the vacuoles and accumulation of compatible solutes in the cytoplasm and presence of genes for salt tolerance confer salt resistance to halophytes (Gorham., 1995). Carty et al. (1997) stated that saline soil reclamation can be carried out using halophytic vegetation, chemical remediation by using organic or mineral amendments and mechanical remediation by utilizing excavation and removal of the salt-affected soil. However, the cost of leaching by chemical and mechanical or by drainage system is higher in India. Revegetation of a salt-affected land with halophytes is an example of proactive phytoremediation (Yensen et al., 1999).

Gorham et al. (1987) observed that vascular halophytes accumulated high levels of sodium and other salts in their above ground tissues while others did not. Boyko (1966) was the first to suggest that halophytic plants could be used to desalinate soil and water. Bio-reclamation studies of saline-sodic soil were made by Helalia et al. (1990) in northern Egypt and they reported that Amshot grass (*Echinochloa stagninum*) when compared to ponding and gypsum treatment reduced the exchangeable sodium percent (ESP) of the soil. Ravindran et al (2007), showed that *S. maritima* and *S. portulacastrum* exhibit greater accumulation of salts in their tissues and higher reduction of salts in the saline land. *S. maritima* and *S. portulacastrum* could therefore be used successfully to accumulate NaCl in highly salinized areas for crop production after a few repeated cultivation and harvest.

The process of leaching through the soil profile can be enhanced by growing crops with deep rooting systems and the ability to tolerate both high concentrations of soluble salts and water-logged conditions. Deep-rooted perennials, such as alfalfa, sweet clovers (*Melilotus spp.*), kudzu (*Pueraria lobata sp.*) and bahiagrass (*Paspalum notatum* Fluegge) have been recommended for improving internal water flow in soils with poor physical condition (Charles and Sickle., 1984; Meek et al., 1989, 1990; Ilyas et al., 1993). *Suaeda salsa* is a halophyte which can absorb salts from saline soils and accumulate them within the plant. *S. salsa* grows normally in highly saline soils and the accumulation of salt in the plant tissue may significantly decrease the salt content of these soils (Liu., 1974; Sharma and Gupta., 1986; Staples and Toenniessen., 1984; Zhao., 1984). If *S. salsa* were harvested at the end of the growing season, a significant

reduction in soil salinity might be achieved. It is possible that many other halophytes, including species of the genera *Atriplex*, *Salicornia* and *Aster* could also be used in soil improvement (Flowers., 1986; Staples and Toenniesson., 1984).

Mishra et al (2003) observed that 3, 6 and 9 years of *Eucalyptus tereticornis* plantation clearly brought out the qualitative changes in some important physico-chemical properties of sodic wastelands. It was observed that the porosity, water holding capacity and field capacity of the soil increased with the age of plantation whereas, the bulk density decreased. The pHs reduced with the increasing age of plantation and the reduction was more pronounced at the soil surface in comparison to lower layers. The  $\text{Na}^+$  decreased with the age of plantation and the significant reduction in  $\text{Na}^+$  content was marked upto 60 cm depth in all the age groups. It was noted that the  $\text{Na}^+$  decreased in the upper layers and increased in the lower depths probably due to leaching of salt and accumulation in the lower layers.

#### **2.4 NANOPARTICLES IN SOIL TREATMENT**

Despite their minuscule status, nanoscale particles may hold the potential to cost-effectively address some of the challenges of site remediation (Masciangioli and Zhang., 2003; EPA, 2003d, e). Two factors contribute to the nanoparticles' capabilities as an extremely versatile remediation tool. The first is their small particle sizes (1–100 nm). Equally important, they provide enormous flexibility for both in situ and ex situ applications. For example, nanoparticles are easily deployed in slurry reactors for the treatment of contaminated soils, sediments and solid wastes.

Several types of polymeric NP have also been developed and proposed for soil and groundwater remediation. Micelle like amphiphilic polyurethane particles have a hydrophilic outer side and a hydrophobic inner core and are therefore very well suited for the removal of hydrophobic pollutants (e.g. phenanthrene) from soils (Kim et al., 2000, 2003a, b, 2004a, b; Tungittiplakorn et al., 2004, 2005). The NP are able to extract the PAH in a similar manner to surfactant micelles but unlike the micelles they do not sorb to soil particles.



Metallic iron is very effective in degrading a wide variety of common contaminants such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes, other polychlorinated hydrocarbons, pesticides and dyes (Zhang., 2003).

Oxidized and hydroxylated CNT are also good adsorbers for metals. This has been found for various metals such as Cu (Liang et al., 2005a), Ni (Chen and Wang, 2006; Lu and Liu, 2006), Cd (Li et al., 2003; Liang et al., 2004), Pb (Li et al., 2002, 2006b), Ag (Ding et al., 2006), Am (III) (Wang et al., 2005) and rare earth metals (Liang et al., 2005b). In most cases adsorption is highly pH-dependent with increasing sorption with increasing pH as expected for adsorption of metals onto hydroxyl groups.

Liu and Zhao (2007) studied the immobilization of Cu (II) in soil using iron phosphate nano-particles and found nano-particles had higher performance than normal particles. The environmental risk of nano scale hydroxyapatite itself can be neglected because it has displayed good cytocompatibility (Lin et al., 2005).

Several recent studies provided valuable insights into key nZVI properties associated with the potential to transform metal ions such as Cd, Ni, Zn, As, Cr, Ag and Pb as well as notorious inorganic anions like perchlorate and nitrate (Cao et al., 2005; Sohn et al., 2006; Ponder et al., 2000; Cao et al., 2006; Li et al., 2006). ZVI nanoparticles can rapidly remove and/or reduce these inorganic ions.

Nano ZVI has great potential in a wide range of environmental applications such as soil, sediments and groundwater remediation (Ponder et al., 2000; Kanel et al., 2005). Various methods for the synthesis and applications of nano ZVI in environmental clean up are continuously being developed (Wang and Zhang., 1997; Lien and Zhang., 2001; Zhang., 2003; Nurmi et al., 2005; Cheng et al., 2007b). Satapanajaru et al., (2008) showed that nano ZVI can be successfully used to remediate water and soil contaminated with atrazine. Reductive dechlorination was the major process in destruction of atrazine by nano ZVI.

Earlier work with zerovalent iron demonstrated the utility of metals to treat soils contaminated with dichlorodiphenyltrichloroethane (DDT) (Staiff et al., 1977), methyl parathion (Butler et al., 1981), and polychlorinated biphenyls (Cutshall et al., 1993). More recent research indicates the tremendous potential of Fe<sup>0</sup> to remediate soils contaminated with 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro- 1,3,5-triazine (RDX) (Hundal et al., 1997; Singh et al., 1998a, 1999), and atrazine (Singh et al., 1998b). In 2001, Comfort et al. used zerovalent iron for large-scale remediation of metachlor-spilled site.

Mercury (Hg) is one of the most pervasive and bio-accumulative contaminants. In water and sediments, Hg undergoes a number of complex chemical and biological speciation and transformation processes, of which Hg methylation has been the primary environmental concern (Stein et al., 1996). Traditionally, remediation of severely Hg-contaminated soils or sediments employs excavation and subsequent disposal in a landfill (Barnett et al., 1997). However, this method is not only costly and environmentally disruptive, but the landfilled Hg is prone to leaching back into the environment (Barnett et al., 2001). Xiong et al., (2009), investigated a method to immobilize mercury using stabilized iron sulphide (FeS) nanoparticles.

## **2.5 HAP FOR SOIL TREATMENT**

Hydroxyapatite (HAP) (Ca<sub>10</sub> (PO<sub>4</sub>)<sub>6</sub> (OH)<sub>2</sub>) is a unique inorganic compound because of its high removal capacity for divalent heavy metal ions and synthetic HAP has been used to remove Pb, Cu, Zn, Cd and other heavy metals from water and soil effectively ( Ma et al., 1993; Jeanjean et al., 1995; Mandjiny et al., 1995; Laperche et al., 1996; Cao et al., 2004; Reible et al., 2006; Chen et al., 2007; Corami et al., 2007). Currently, four possible immobilization routines, including ion-exchange process, surface complexation, dissolution and precipitation and coprecipitation are generally suggested for immobilization mechanism of hydroxyapatite. It was found to be effective in immobilizing heavy metals due to its moderate solubility (Hodson et al., 2000; Simiciklas et al., 2008). Hydroxyapatites has been investigated in environmental control. as catalyst for chlorinated organic pollutant decompositions from the

metallurgical industry and incineration of industrial wastes (Akazawa., 1996), and as effective catalysts for dehydration and dehydrogenation of primary alcohols for obtaining aldehydes and ketones at high temperature (Bett et al., 1967 and Opre ., 2005). Zhang et al. (2010) reported that nano-HAP is a potential material to remediate lead and cadmium in sediments. They showed higher immobilizing capacity of HAP nanoparticles for Cd than normal HAP material due to its high surface area. Nanomaterials display higher reactivity and sorption ability than the same material of normal size due to its high surface area. Therefore, they have promising applications in different areas such as electronics, biomedicine, pharmaceuticals, cosmetics, environmental analysis and remediation.

## *Chapter-3*

*Analytical techniques  
& methodology*

## **CHAPTER-3**

### **ANALYTICAL TECHNIQUES AND METHODOLOGY**

The methodology adopted for this research work was categorised in five parts:

- 1) Sample collection and preparation
- 2) Particle Size and mineralogical analysis and analytical methodology for soil
- 3) Characterization of nanoparticle
- 4) Application of nanoparticles on salt-affected soil
- 5) Effects of nanoparticles on salt-affected soil.

The field work involved salt-affected soil sample collection. Distribution of different size particles i.e. sand, silt, and clay in soil mass was determined by the sieve analysis. The mineralogical study involved mineralogical analysis using XRD. Analytical methods involved determination of some physical and chemical properties of soil (such as pH, EC, TDS, major cations and anions, exchangeable bases and heavy metals). Characterization of nanoparticles involves determining the shape, size and mineralogy using SEM-EDX, TEM and XRD. Part 4 and 5 of this research work involved application of nano-HAP to salt-affected soils and to study their effects on the physical-chemical properties of the affected soil.

#### **3.1 SAMPLE COLLECTION AND PREPARATION**

Surface soil samples affected with salinity were collected in polypropylene bags from the salt-affected area. The sampling site was chosen to get the broader picture of the impact of salinity on physicochemical properties of soil. Samples were collected from village Chhapra in Narnaul (Haryana). The sampling site lies in Mahendragarh district of Haryana. It is located at 28.04° N and 76.11° E and has an average elevation of 298 meters. The Mahendragarh district is the domain of dry-land topography throughout. Presence of inland streams, sandy plain, shifting sand dunes devoid of vegetation, fixed or fossil sand dunes, dissected upland tract, and often barren, denuded rocky hill ranges and their outcrops provide an ensemble of terrain features truly associated with semi-

arid to arid environment. The climate except during the monsoon is characterized by the dryness of air, a hot summer and a cold winter. The normal annual rainfall in this region is 454.6 mm and the mean daily maximum and minimum temperatures during hottest and coldest months are about 41<sup>0</sup>C and 5-6<sup>0</sup>C. This area in Haryana is rich in mineral resources like iron ore, copper ore, feldspar, beryl, tourmaline, Muscovite mica, Biotite mica, albite, calcite, and quartz.

The samples (1 kg each) were collected using stainless steel scoopers. The collected samples were kept in ice chest and transported to laboratory, where they were kept at 4°C until further analysis. The soil samples were air-dried, grinded in mortar-pestle and passed through a 2-mm sieve. The grinded samples was placed on a butter sheet and homogenized thoroughly by lifting alternate corners of the butter sheet for about 20 minutes and about half of the homogenized powder was collected by coning and quartering method and ground to ~ 200 mesh sizes in a mortar-pestle. This ~200 mesh size sample powder was stored in plastic vials and the same was used for XRD and XRF analysis. The 2-mm sized soil samples were analyzed for some physical and chemical properties.

### **3.2 PARTICLE SIZE ANALYSIS AND ANALYTICAL METHODOLOGY FOR SOIL**

#### **3.2.1 Particle Size Analysis**

The grain size distribution of the sediment/soil is a function of the size range of available material, its accessibility for weathering, erosion and transportation, and the energy input into the sediments (Pandey et. al., 2002). The soils can be classified on the basis of particle size, or the diameter of individual grain of sediments. This classification is based on  $\Phi$  logarithmic scale (which is krumbein's modification of the Wentworth scale)

$$\Phi = -\log_2 D/D_0$$

Where  $\Phi$  is the krumbein phi scale, D is the diameter of the particle and  $D_0$  is a reference diameter. Grain size analysis discloses the texture and composition of soils in a given sample.

Table-3.1. Sediment Classification based on particle size

Grain Size		Descriptive terminology			
Phi	mm/ $\mu$ m	Udden (1914) and Wentworth (1922)	Friedman and Sander (1978)	GRADISTAT program	
			very large boulders		
-11	2048 mm		large boulders	very large	} boulders
-10	1024		medium boulders	large	
-9	512	cobbles	small boulders	medium	
-8	256		large cobbles	small	
-7	128		small cobbles	very small	
-6	64		very coarse pebbles	very coarse	} gravel
-5	32		coarse pebbles	coarse	
-4	16	pebbles	medium pebbles	medium	
-3	8		fine pebbles	fine	
-2	4	granules	very fine pebbles	very fine	
-1	2		very coarse sand	very coarse	} sand
0	1	very coarse sand	coarse sand	coarse	
1	500 $\mu$ m	coarse sand	medium sand	medium	
2	250	medium sand	fine sand	fine	
3	125	fine sand	very fine sand	very fine	
4	63		very coarse silt	very coarse	} silt
5	31		coarse silt	coarse	
6	16	silt	medium silt	medium	
7	8		fine silt	fine	
8	4		very fine silt	very fine	
9	2	clay	clay	clay	

To determine the grain-size distribution, the samples were air-dried, gently pounded and homogenized using coning and quartering procedure (Ingram.,1971). The granulometric separation was carried out by dry sieving (Lindholm.,1987). The dry sieving method was used to fractionate a sediment/soil into its proportion of coarse sand, fine sand, very fine sand, silt and clay. For this analysis sieves of 0.5mm, 0.35mm, 0.25mm, 0.171mm, 0.125mm, 0.088mm, 0.063mm were used. A representative weighed (20 g) sample was poured into the top sieve which has the largest screen openings. Each lower sieve in the

column has smaller openings than the one above. At the base is a round pan, called the receiver. The column is typically placed in a mechanical shaker. The shaker shakes the column, usually for some fixed amount of time (usually 30 mins). After the shaking was complete, the material on each sieve was weighed. The weight of the sample of each sieve was then divided by the total weight to give a percentage retained on each sieve.

### 3.2.2 X-Ray analysis for mineralogy

Mineralogy of soil sample was studied using PANalytical X' pert PRO with an accelerating voltage of 50 kV, a tube current of 40 mA and a scanning speed of 2 degrees 2 $\theta$  per minute.

### 3.2.3 Analytical methodology for soil

#### 3.2.3.1 pH measurement

The pH value of an aqueous solution is the negative logarithm of the hydrogen-ion activity. Soil characteristics that are known to influence pH readings include: the composition of the exchangeable cations, the nature of the cation-exchange materials, the composition and concentration of soluble salts, and the presence or absence of gypsum and alkaline-earth carbonates.

Soil pH was measured in the 1:2 soil water suspensions using water and soil analysis kit model 161 E. The pH meter was calibrated with the help of standard buffer solutions having pH 7.0 and 9.2. The samples were stirred continuously in order to maintain homogeneity before noting down the pH.

#### 3.2.3.2 EC measurement

Electrical conductivity (K) is defined as the reciprocal of the electrical resistivity (specific resistance). The resistivity (S) is the resistance (R) in ohms of a conductor whose length (l) is 1 cm and cross sectional area (a) is 1 cm<sup>2</sup>. Hence, electrical conductivity is expressed in reciprocal of ohms per cm or mhos per cm.



Conductivity was measured in micro-Siemens/cm ( $\mu\text{S}/\text{cm}$ ) using water and soil analysis kit model 161 E. Soil EC was determined in the 1:2 soil water suspensions. The instrument was calibrated and set for 0.01M KCl solution ( $1.413 \mu\text{S}/\text{cm}$  at  $25^\circ \text{C}$ ).

### 3.2.3.3 Major soluble cations and anions:

Analyses of saline and alkali soils for soluble cations and anions are usually made to determine the composition of the salts present. Complete analyses for soluble ions provide an accurate determination of total salt content. Determinations of soluble cations are used to obtain the relations between total cation concentration and other properties of saline solutions, such as electrical conductivity and osmotic pressure. The relative concentrations of the various cations in soil-water extracts also give information on the composition of the exchangeable cations in the soil. The soluble cations and anions commonly determined in saline and alkali soils are calcium, magnesium, sodium, potassium, carbonate, bicarbonate, sulfate and chloride.

1:2 soil-water suspensions was prepared, shaken for one hour on a shaker and filtered through Whatman filter paper ( $0.45\mu$ ). The supernatant obtained was used for determining the concentration of cations and anions (Jackson., 1962). Concentration of major soluble cations (e.g.:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) were determined by AAS (Thermo scientific). The concentration of sulfate ( $\text{SO}_4^{2-}$ ) and chloride ( $\text{Cl}^-$ ) were determined by spectrophotometer (HACH DR 2700). Carbonates and bicarbonates in soil were determined by titrating a known volume of extract (2ml) against standard  $\text{H}_2\text{SO}_4$  (0.01N) using phenolphthalein and methyl orange indicators respectively.

### 3.2.3.4 Exchangeable bases

Determinations of the amounts and proportions of the various exchangeable cations present in soils are useful, because exchangeable cations markedly influence the physical and chemical properties of soils. Exchangeable cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) were extracted from the soil with normal neutral ammonium acetate (Jackson., 1967). The amounts of exchangeable sodium, potassium, calcium and magnesium in the extract were determined by AAS. Sodium absorption ratio (SAR) was calculated from

water soluble Na, Ca and Mg and exchangeable sodium percentage (ESP) was calculated from exchangeable Na and CEC.

#### 3.2.3.5 Heavy metals

For analysis of heavy metals (Cu, Pb, Cr and Ni) in soil, samples were ground in a mortar-pestle with boric acid to reach graining below 63  $\mu\text{m}$  and next 2 g of sample with binder i.e; boric acid (0.2gm) was tableted under a pressure of 13 t/cm<sup>2</sup>. Then a direct XRF analysis of heavy metals was carried out using these pellets on PANalytical Epsilon5.

### 3.3 CHARACTERIZATION OF HAP NANOPARTICLES

Hydroxyapatite (HAP) nanoparticles (cat. no. 677418) purchased from Sigma-Aldrich Chemicals (St. Louis, MO, USA) was used in the present investigation. The purchased nanoparticle was characterized by XRD, SEM-EDX and TEM.

#### 3.3.1 Mineralogy

A mineralogical analysis by X-Ray diffraction was studied for nano-HAP. The samples were placed in a holder of lucida (zone of interaction with the electron beam), later they were placed on the goniometer of the diffractometer. The solid sample was characterized by X-Ray diffraction using PANalytical X'pert PRO with an accelerating voltage of 50 kV, a tube current of 40 mA and a scanning speed of 2 degrees 2  $\theta$  per minute.

#### 3.3.2 Morphological study and elemental analysis

Morphology and size of the nanoparticles were characterized by SEM using a Zeiss Evo 40 microscope equipped with an EDX probe. The soil samples were placed on a holder of aluminium, adhered with an adhesive conductive carbon tape. The samples were later coated with a 15 nm gold layer for high quality images. Elemental composition was also studied by Energy Dispersion Spectroscopy (EDS).

TEM images were observed with a JEOL-2100F, UHR, transmission electron microscope operating at 200 KV. The samples were prepared by placing a drop of homogeneous suspension on a copper grid and allowing it to dry in air.

### **3.4 APPLICATION OF HAP-NANO ON SALT-AFFECTED SOIL**

To study the effects of nano-HAP on sodic soil, the experiment was performed in duplicates (S1 and S2). Nano-HAP at six different concentrations (0%, 2%, 4%, 6%, 8% and 10% nano-HAP/dry soil respectively), were added to 5 grams of processed soil. Soil and nanoparticles were thoroughly mixed in order to obtain homogeneity. A 1: 2 soil-water suspensions of the above mentioned soil samples containing nanoparticles were prepared. Samples were then tumbled on a rotary shaker at a speed of 100 rpm for seven days. After seven days of interaction between the soil samples and the nano-HAP, samples were centrifuged at 3000 rpm. Following this, the supernatant was removed and the settled soil was air-dried.

### **3.5 EFFECT OF HAP-NANOPARTICLES ON SALT-AFFECTED SOIL**

The supernatants were filtered through 0.45 $\mu$  Whatman filter papers and analyzed for the concentration of the various soluble cations and anions using the above mentioned methods. An aliquot of the supernatant was also used to measure few physical properties (e.g. pH, EC and TDS) of the soil. The air-dried pellets of the soil applied with different concentrations of nano-HAP were analyzed to determine variations in heavy metal concentrations using XRF. Exchangeable bases were also determined using the above mentioned method.

## *Chapter-4*

*Results & discussion*

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 PARTICLE SIZE ANALYSIS AND MINERALOGICAL STUDY OF SOIL

##### 4.1.1 Particle Size Analysis

The textural analysis of the soil is shown in table-4.1. On the basis of grain size analysis, the soil sample was found to be silty sand. The sample was very poorly sorted in nature. Muddy sand nature of the soil is shown in fig-4.1.

Table-4.1. Texture of the salt- affected soil sample used in this study.

TEXTURE OF SEDIMENT SAMPLES				
SAMPLE	SIEVING ERROR	SAMPLE TYPE	TEXTURAL GROUP	SEDIMENT NAME
S	0.41%	Bimodal, Very Poorly Sorted	Muddy sand	Very Coarse Silty Very Fine Sand

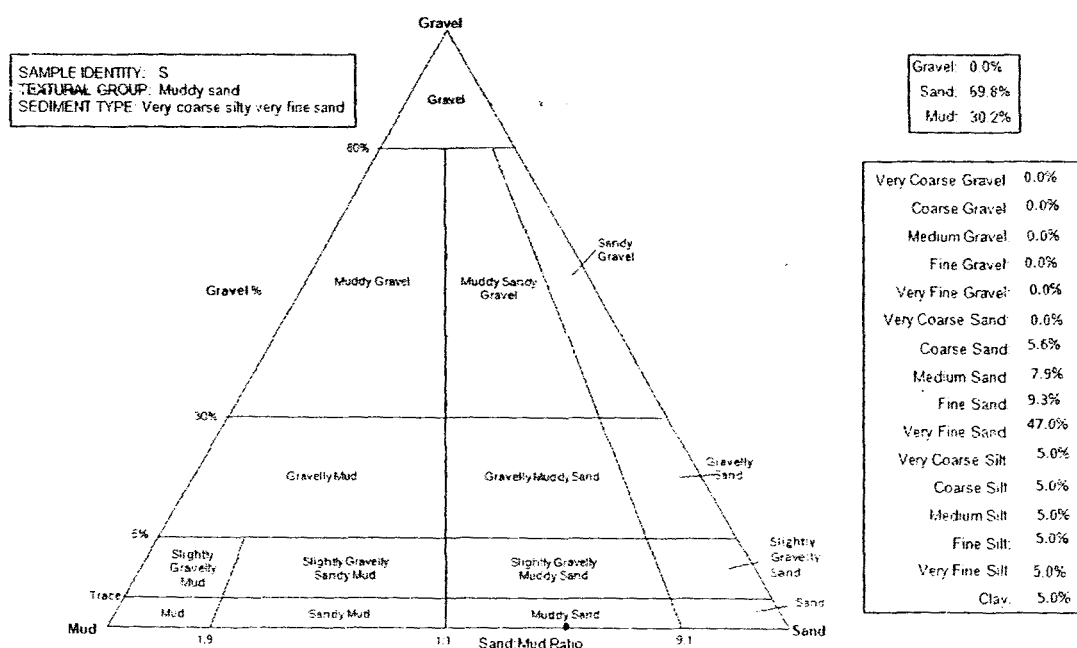


Figure-4.1. Sand: mud diagram of the soil used in this study.

#### 4.1.2 Mineralogy of soil

Figure-4.2 shows the XRD pattern of the soil used in this study. The mineralogical composition of soil estimated from XRD data showed that quartz was the dominant mineral which was followed by albite and hornblende.

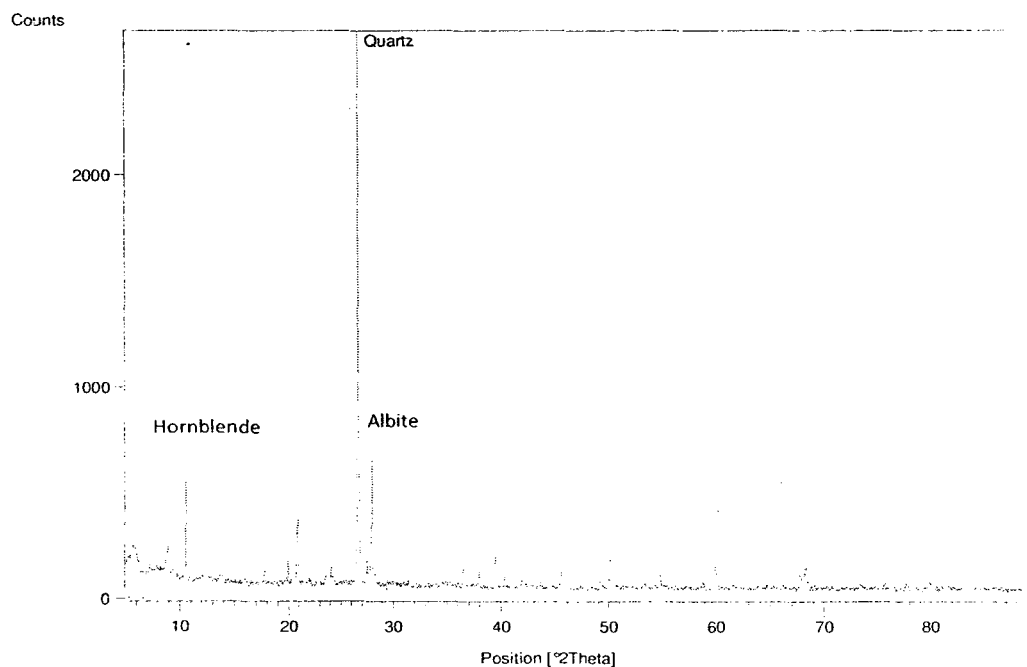


Figure-4.2. X-ray diffraction pattern of the soil used in this study.

## 4.2. ANALYTICAL METHODOLOGY FOR SOIL

### 4.2.1 Physical and chemical characteristics of sampled soils

Several physical and chemical properties of the soil studied in this research are presented here.

#### 4.2.1.1 pH, EC and TDS

pH, EC and TDS values of the salt affected soils are shown in table-2. pH was alkaline in nature and its average value was found to be 8.96. The extremely high pH levels were due to the dominance of sodium ions among the cations and bicarbonates or carbonates from the anions. Average EC and TDS values of the soil were determined to

be 0.83 dS/m and 401.50 ppm respectively. Both pH and EC values were found to be in the classification limits of sodic soils.

Table-4.2. pH, EC and TDS of the soil used in the experiment.

Samples	pH	EC(dS/m)	TDS(ppm)
S1	8.96	0.753	358
S2	8.95	0.897	445
Average	8.95	0.825	401.5

#### 4.2.1.2 Soluble cations and anions

Table-4.3 shows the average concentrations of the major soluble cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ ) and anions ( $\text{HCO}_3^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) in the soil samples taken from the salt-affected area. These figures represented data that were taken prior to any application of nanoparticles. Among the soluble cations in the pre-experiment soil, average  $\text{Na}^+$  concentration (162.47 ppm) was found to be higher in the soil than other cations,  $\text{Ca}^{2+}$ (43.37 ppm),  $\text{K}^+$ (16.90 ppm) and  $\text{Mg}^{2+}$ (7.06 ppm) . Among the anions, bicarbonate was dominant with a maximum average concentration of 6.11 meq/l and sulphate was least with an average concentration of 0.33 meq/l. Carbonates and chloride had an average concentration of 3.64 and 0.55 meq/l respectively. Prevalence of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in soil solution suggested the sodic nature of soil.

Table-4.3. Major soluble cation and anion concentration in the soil used.

Samples	Soluble cations (ppm)				Soluble anions (meq/l)			
	Na	K	Ca	Mg	Carbonate	Bicarbonate	Sulphate	Chloride
S1	148	14.6	43.64	9.952	4.2857	5.714	0.422	0.41
S2	177	17.78	43.1	4.16	3	6.5	0.24	0.698
Average	162.5	16.19	43.37	7.056	3.643	6.107	0.33	0.55

#### 4.2.1.3 Exchangeable bases

Table-4.4 shows that the solid phase (surface exchange sites), which provides the ultimate control over the soluble salts in the soil solution was 18.816% occupied by  $\text{Na}^+$  in the soil. The pre-application of the HAP nanoparticles results indicated that the soil contained an average of 5.64 Cmol<sub>c</sub>/Kg of Na, 17.53 Cmol<sub>c</sub>/Kg of Ca, 0.64 Cmol<sub>c</sub>/Kg of K and 6.17 Cmol<sub>c</sub>/Kg of Mg. Sodium can cause problems when it replaces calcium and magnesium as an exchangeable cation on soil clays. High sodium concentrations in soil generally cause soil dispersion as a result of breakdown of soil aggregates, which, subsequently, settle into soil pores. Soil dispersion causes soil pore blockage resulting in the reduction of soil permeability. Three main problems caused by sodium-induced dispersion are reduced infiltration, reduced hydraulic conductivity and surface crusting (Frankel *et. al.*, 1978).

Table-4.4. Concentration of exchangeable bases in the soil used.

Samples	Exchangeable bases (Cmol <sub>c</sub> /Kg)			
	Na	K	Ca	Mg
S1	5.53	0.59	20.55	5.71
S2	5.75	0.68	14.5	6.63
Average	5.64	0.64	17.53	6.17

#### 4.2.1.4 ESP, SAR and CEC

The exchangeable sodium percentage (ESP), CEC and sodium adsorption ratio (SAR) of the studied soil is shown in table-4.5. Average ESP and SAR were found to be 18.82 % and 7.32 mmol/l respectively. Any soil that has more than 15% exchangeable Na (15% of the cation exchange capacity filled with Na) are sodic in nature and may have a permeability problem. While Ca and Mg cause soil clays to flocculate and encourage good soil aggregation, Na causes clays to disperse and breaks down aggregation, which can lead to surface sealing and slow water infiltration. The average CEC of the salt-affected soil was estimated to be 29.97 Cmol<sub>c</sub>/Kg. Cation exchange capacity is a means of estimating soil fertility. Soils with high CEC values are considered fertile and vice



versa. In general, CEC ranges from a minimum of 2 Cmol<sub>c</sub>/Kg soil in sands and up to a maximum of 60 Cmol<sub>c</sub>/Kg in clay soils (Brady., 1990).

Table-4.5. ESP, CEC and SAR of the soil used in this study.

Samples	ESP (%)	CEC (Cmol <sub>c</sub> /Kg)	SAR (mmol/l)
S 1	17.09	32.38	5.6
S 2	20.85	27.56	10.41
Average	18.82	29.97	7.32

#### 4.2.1.5. Classification of the affected soil

Table-4.6 shows the classification of the soil used in this study. From the pH (8.96), EC (0.81dS/m), ESP (18.82 %), HCO<sub>3</sub><sup>-</sup> (6.11 meq/l) and CO<sub>3</sub><sup>2-</sup> (3.64 meq/l) values, the soil can be classified as sodic in nature.

Table-4.6. Classification of the soil used in this study.

Soil characteristics	Average value	Sodic soil values	Soil class
pH	8.955	> 8.2	Sodic soil
EC (dS/m)	0.811	Variable, mostly < 4	
ESP (%)	18.8161	> 15	
HCO <sub>3</sub> <sup>-</sup> (meq/l)	6.107	prevalence of HCO <sub>3</sub> <sup>-</sup>	
CO <sub>3</sub> <sup>2-</sup> (meq/l)	3.643	and CO <sub>3</sub> <sup>2-</sup> of Na	

#### 4.2.1.6 Heavy metals

In soils, metals exert a marked impact on the quality of soils and food production. Many investigations have been conducted on the health and ecological effects produced by contamination of terrestrial ecosystems with metals (Li et al., 1995; Caussy et al., 2003). Waste water irrigation is known to contribute significantly to the heavy metal content of soils (Nyamangara and Mzezew., 1999; Nan et al., 2002; Singh et al., 2004; Mapanda et al., 2005). Other sources of heavy metal contamination associated with agricultural soil are sewage sludge, fertilizer, and pesticides (Alloway and Ayres., 1993; Ross., 1994). Table-4.7 shows the concentration of various heavy metals e.g. Copper, Nickel, Chromium and lead in the salt-affected soil. The XRF results indicated that Cr with an average concentration of 28.54 ppm was dominant in the soil and Ni least (7.62

ppm). The initial metallic concentration of Pb and Cu in the sampled soil was found to be 12.84 ppm and 10.01 ppm respectively. The concentrations of mentioned heavy metals were found to be below the permissible limits.

Table-4.7. Heavy metal concentration in the studied soil.

Sample	Metals (ppm)			
	Cr	Pb	Ni	Cu
S1	28.89	13.51	7.69	9.28
S2	28.19	12.18	7.56	10.74
Average	28.54	12.84	7.62	10.01

### 4.3. CHARACTERIZATIONS OF HAP NANOPARTICLES

#### 4.3.1 Mineralogical characterization by X-ray diffraction

In figure-4.3, XRD data of HAP- nanoparticle has been shown. The XRD pattern for HAP has many peaks in the range from about  $7^\circ$  to about  $60^\circ$   $2\theta$   $\text{CuK}\alpha$ . The most intense peaks are in the range 30 to  $35^\circ$ .

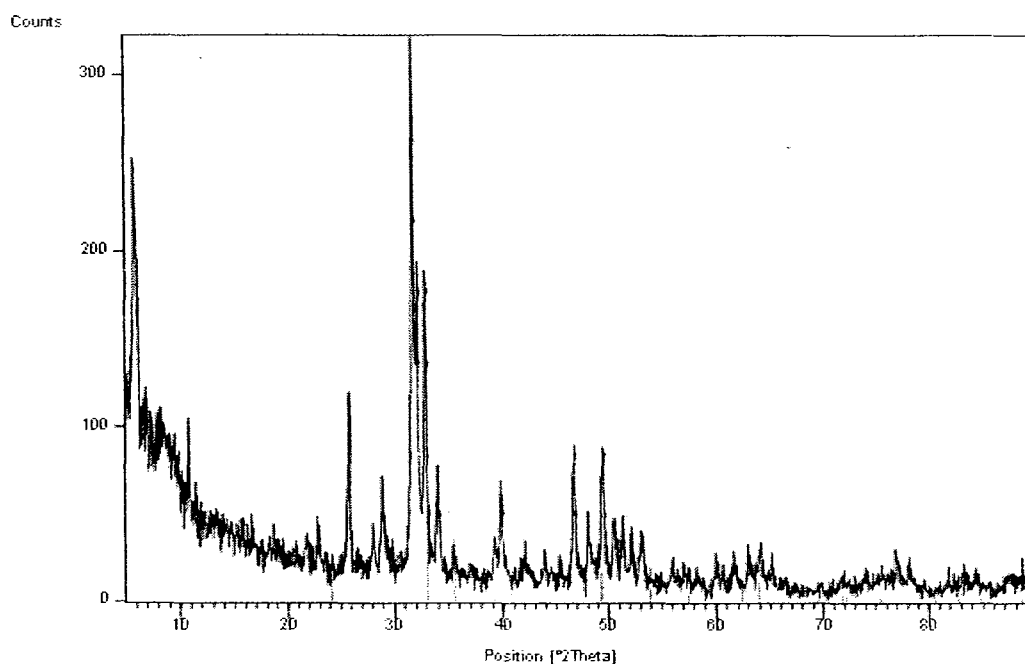


Figure-4.3. X-ray diffraction pattern of HAP nanoparticles.

#### 4.3.2 Morphological study and elemental analysis

The morphology and elementary chemical composition of HAP nanoparticle was determined by means of SEM. Figure-4.4 shows the morphological characteristics of the particles of HAP which indicated that the material was a homogeneous powder. The HAP particles consisted of crystalline hard agglomerates. The size of the particles of hydroxyapatite was similar, ranged from 50 nm or larger. Besides, this technique allowed realizing elementary chemical analyses of the material. SEM-EDX pattern of the HAP nanoparticles is shown in Figure-4.5 which indicated a composition of oxygen, phosphorus and calcium. Oxygen was dominant and occupied 88.74% of the total weight which was followed by calcium (6.46 wt. %) and phosphorus (1.65 wt. %). Figure-4.6 shows a representative TEM image of number of HAP nanoparticles at a magnification of 20,000. TEM observations showed clusters that contained spherical particles about 50 nm to 120 nm in diameter.

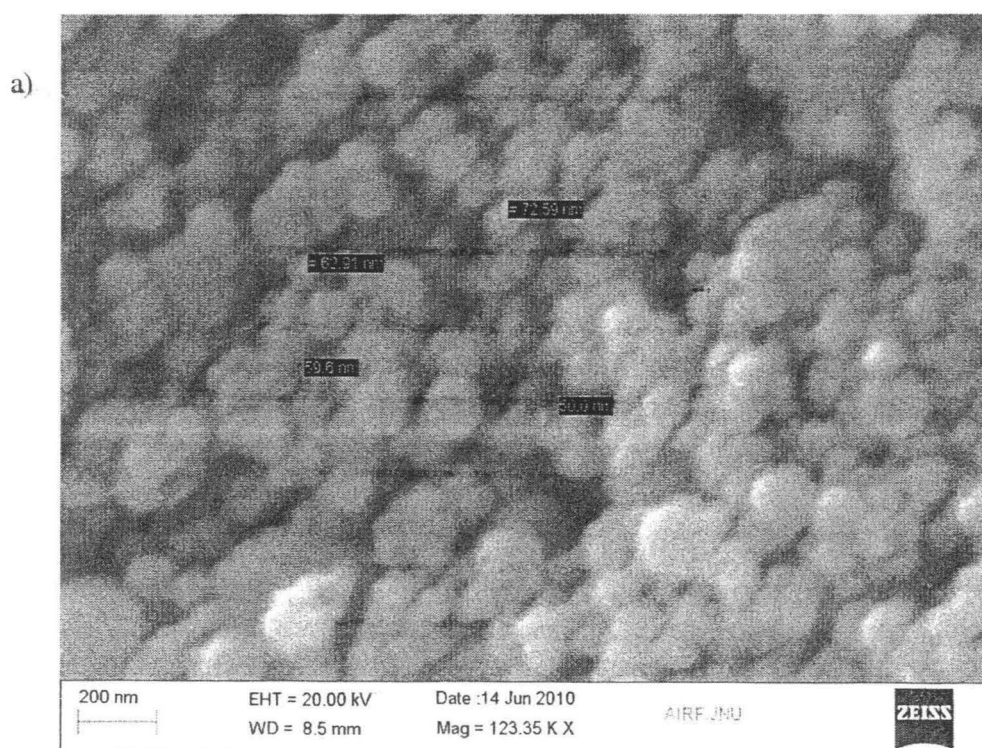


Figure-4.4 (a) SEM micrographs of HAP nanoparticles at mag= 123.35 KX

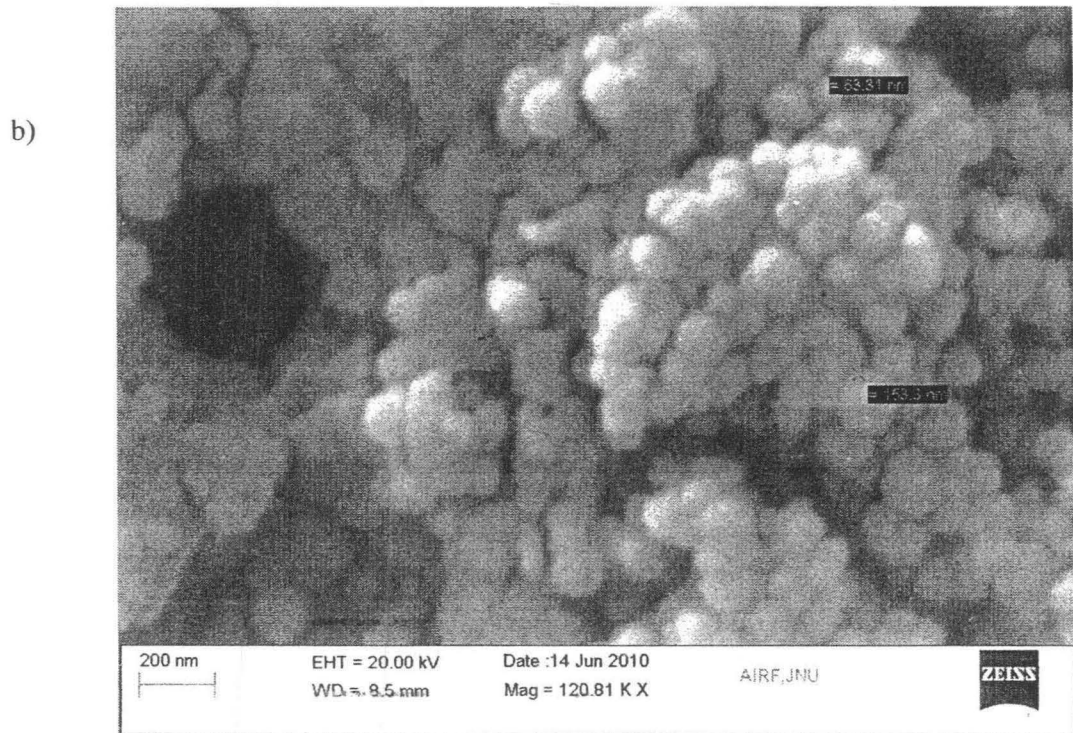


Figure-4.4 (b) SEM micrographs of HAP nanoparticles at mag= 120.81 KX

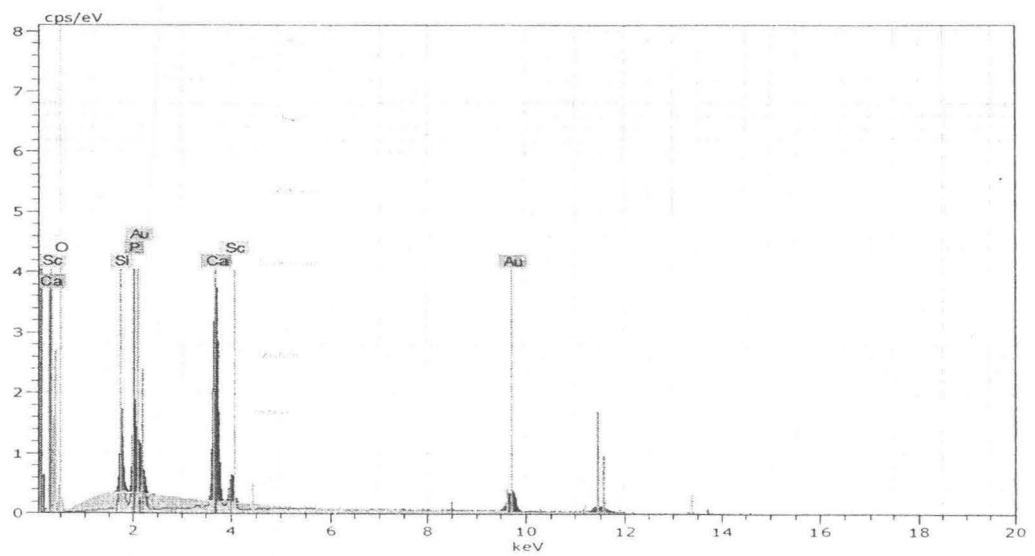


Figure-4.5.SEM-EDX pattern of hydroxyapatite nanoparticle.

Table-4.8. Elemental analysis of HAP nanoparticles by SEM-EDX.

Element	Series	Umn.C (wt.-%)	Norm.C (wt.-%)	Atom.C (at.-%)	Error (%)
Calcium	K-series	6.46	6.46	2.77	0.2
Silicon	K-series	1.13	1.13	0.69	0.1
Phosphorus	K-series	1.65	1.65	0.92	0.1
Scandium	K-series	0	0	0	0
Gold	K-series	2.02	2.02	0.18	0.1
Oxygen	K-series	88.74	88.74	95.44	0.4

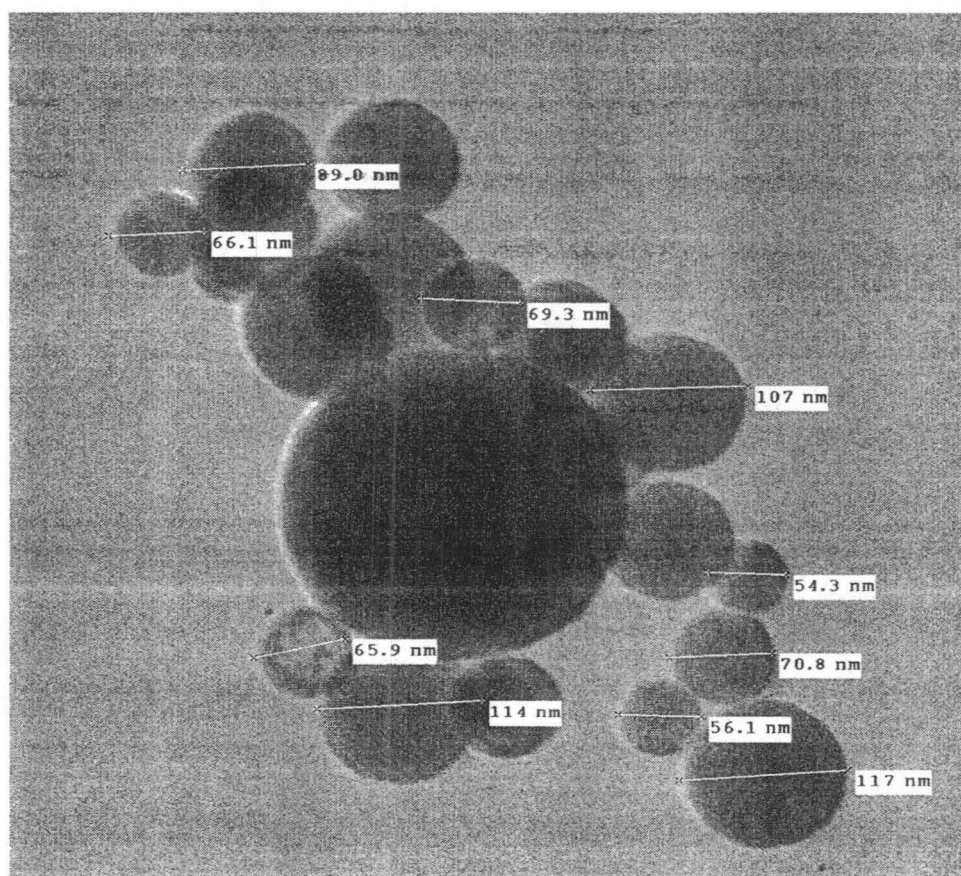


Figure-4.6. TEM image of a cluster of hydroxyapatite nanoparticles at 20,000 magnification

#### 4.4 EFFECTS OF NANO-HAP ON SALT-AFFECTED SOIL PROPERTIES

##### 4.4.1 pH, EC and TDS

Table-4.9 shows pH, EC and TDS before and after the application of HAP nanoparticles to the affected soils. With increase in the nanoparticle concentration, it was found that the average pH dropped. The decrease in pH may be due to metal uptake by HAP. Surface complexation of heavy metals on HAP surface results in partial displacement of  $H^+$  which results in pH reduction. This result is in agreement with the previous results (Cao et al., 2004; Xu et al., 1994 and Wu et al., 1991). EC and TDS increased with increasing the nanoparticle concentration. EC indicates the concentration of soluble salts while TDS is the total dissolved solids in soil solution. As the level of TDS increases, conductivity also increases. The increase in the EC and TDS value was mainly due to increase in the soluble ions in the soil solution after the nanoparticle application. This result is similar to that obtained by Ilyas et al (1990). High EC has been proved better during early phase of reclaiming saline-sodic soil because of positive effect of electrolytes on soil infiltration (Shainberg & Letey, 1984.; Ghafoor et al., 1985a & b, 1990a.; Girdhar, 1996; Gupta, 1990.; Murtaza et al., 1996.; Oster & Jayawardane, 1999). The variation in pH, EC and TDS of sodic soil at different HAP nanoparticle concentrations is shown in fig-4.7, fig-4.8 and fig-4.9 respectively.

Table-4.9. pH, EC and TDS before and after the application of HAP nanoparticles to affected soils.

Sample No.	Parameter	Conc. Of Hap (w/w)					
		0%	2%	4%	6%	8%	10%
S1	pH	8.96	8.76	8.74	8.7	8.66	8.64
S2		8.95	8.72	8.7	8.7	8.62	8.6
Average		8.96	8.74	8.72	8.7	8.64	8.62
S1	EC dS/m	0.75	0.79	0.79	0.91	0.96	0.96
S2		0.87	0.88	0.89	0.9	0.92	0.99
Average		0.81	0.83	0.84	0.9	0.94	0.98
S1	TDS (ppm)	358	375	382	394	400	404
S2		432	442	445	449	462	486
Average		395	408.5	413.5	421.5	431	445

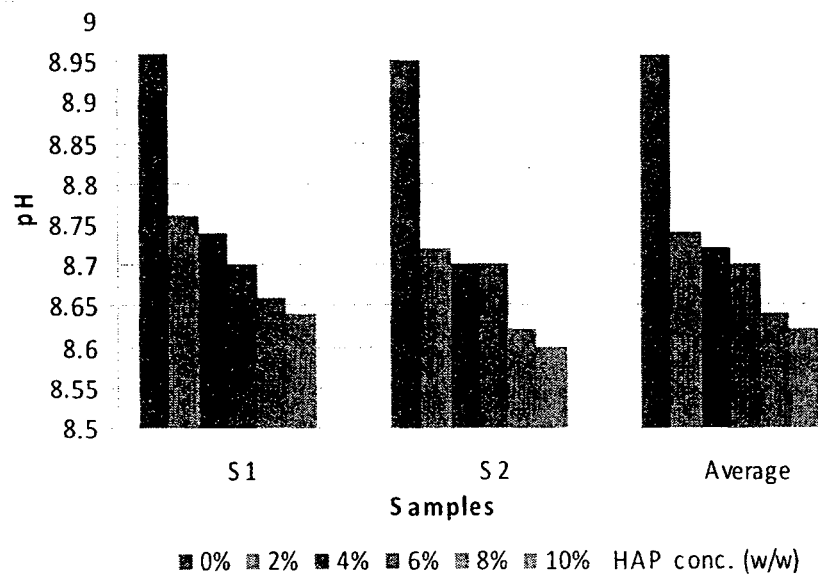


Figure-4.7 .Changes in soil pH at different concentration of HAP nanoparticles.

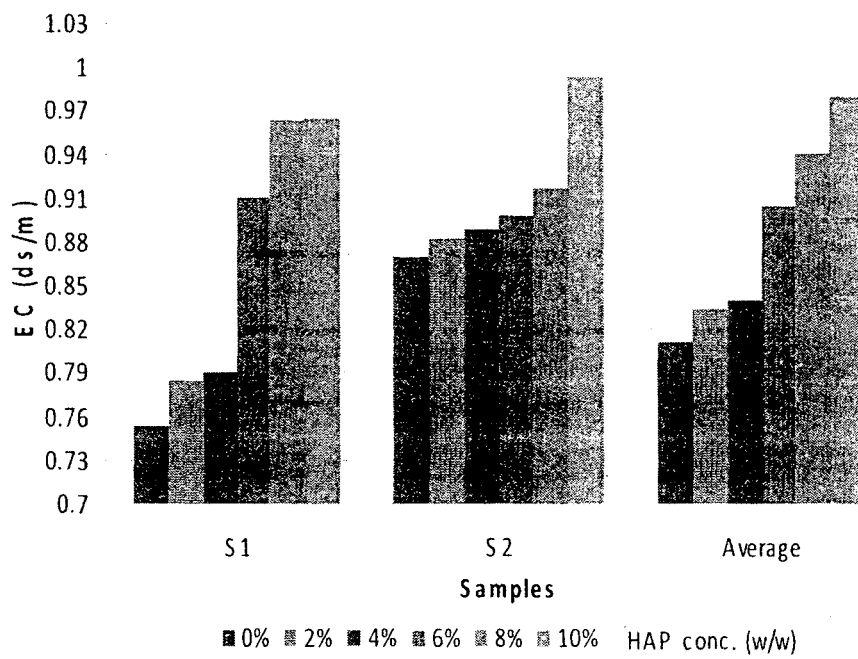


Figure-4.8 Changes in soil EC after application of HAP nanoparticle at different concentration.

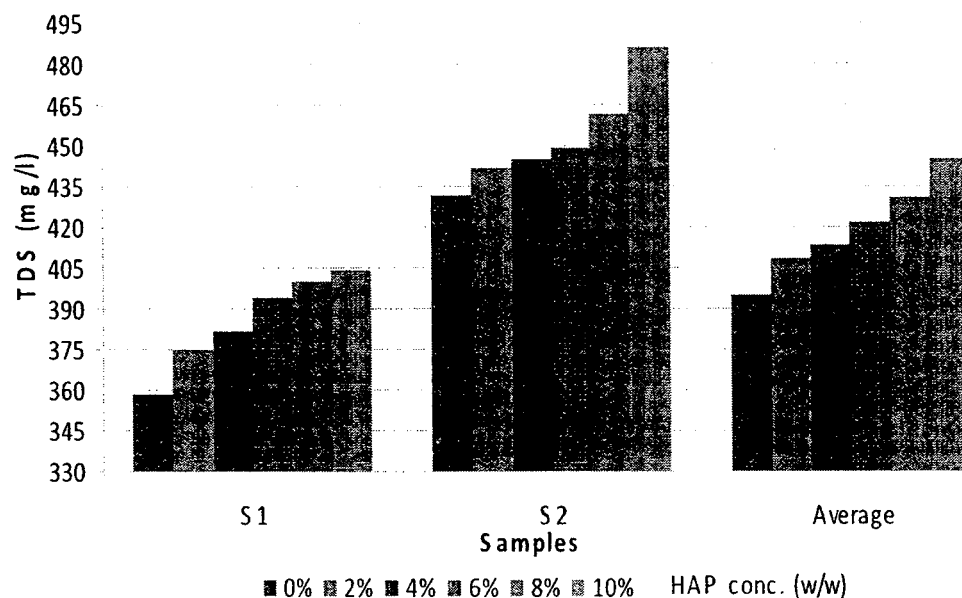


Figure-4.9 TDS of soil after HAP nanoparticle application at different concentration.

#### 4.4.2 Soluble cations and anions

Table-4.10 indicates the concentration of major soluble cations in the soil solution after the application of the nanoparticle at different concentrations. The AAS results showed an increase in the average concentration of all the major cations.  $\text{Na}^+$  increased from 162.47 (0%) to 223.63 ppm (10% application).  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  also increased from 43.37 (0%) to 62.65 ppm (10% application), 7.06 (0%) to 22.78 ppm (10% application) and 16.19 (0%) to 38.69 ppm (10% application) respectively after applying the nanoparticles. This means that the  $\text{Ca}^{2+}$  in the applied HAP nanoparticle replaced the  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  present on the exchange sites and the cations went into solution. This may account for the increase in sodium, magnesium and potassium ion concentrations in the solution. The effect of HAP nanoparticles on cation concentration is shown in fig-4.10.

Table-4.11 shows major anion concentration before and after the nanoparticle application. In sodic soils, carbonates and bicarbonates are dominant which constrains plant growth. HAP application decreased carbonate and bicarbonate concentration in



soil solution which may result in decrease in soil sodicity. While the concentration of major soluble anions, chloride and sulphate increased, but the increase was not significant enough to interfere with plant growth as the simultaneous increase in EC was less than one. Variations in anion concentration at different nanoparticle concentrations is shown in fig.-4.11.

Table-4.10. Concentration of major cations after HAP nanoparticle application.

Sample No.	Cations (ppm)	Conc. Of Hap (w/w)					
		0%	2%	4%	6%	8%	10%
S1	Na	147.96	187.3	213.29	224.65	227.26	228.69
S2		176.98	183.34	184.81	204.69	209.34	218.57
Average		162.47	185.32	199.05	214.67	218.3	223.63
S1	K	14.6	30.69	33.48	34.56	36.53	37.62
S2		17.78	26.17	32.74	34.17	38.28	39.76
Average		16.19	28.43	33.11	34.37	37.41	38.69
S1	Ca	43.64	52.23	61.65	64	66.61	68.77
S2		43.1	43.85	44.31	46.36	51.76	56.54
Average		43.37	48.04	52.98	55.18	59.18	62.65
S1	Mg	9.95	13.88	24.42	26.91	28.19	28.34
S2		4.16	5.78	6.75	13.18	16.45	17.22
Average		7.06	9.83	15.59	20.05	22.32	22.78

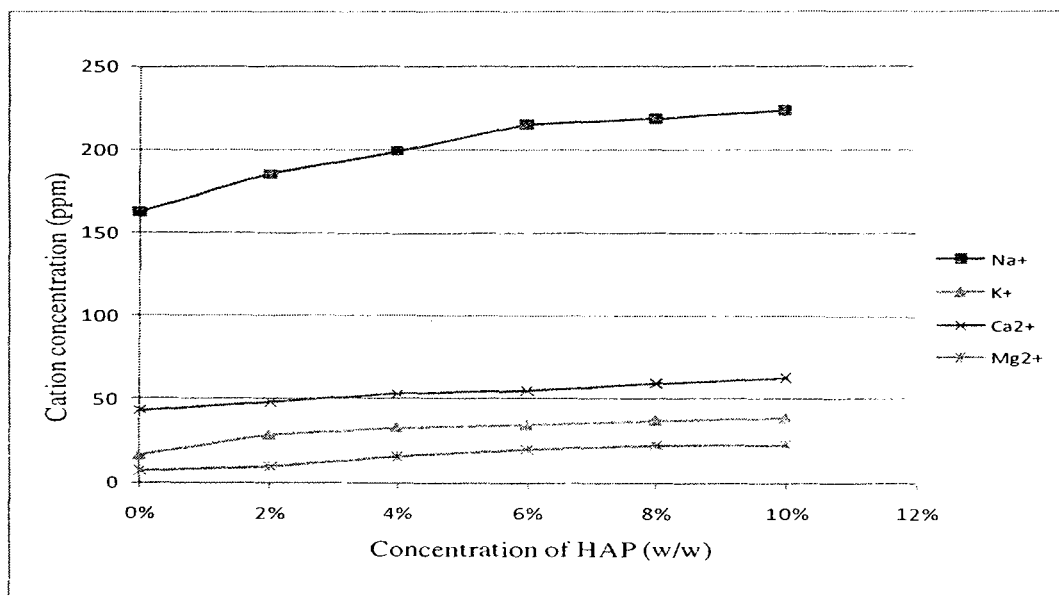


Figure-10. Variation in cation concentration after HAP nanoparticle application.

Table-4.11. Concentration of major anions after HAP nanoparticle application.

Sample No.	Anions (meq/l)	Conc. Of Hap (w/w)					
		0%	2%	4%	6%	8%	10%
S1	$\text{CO}_3^{2-}$	4.29	3.08	1.91	3.64	1	1
S2		3	3	4	3	3.53	4
Average		3.64	3.04	2.95	3.32	2.27	2.5
S1	$\text{HCO}_3^-$	5.71	5.38	5.71	5.46	3	5
S2		6.5	5.5	3	4.5	5	1
Average		6.1	5.19	4.36	4.98	4.5	3.5
S1	$\text{SO}_4^{2-}$	0.42	0.28	0.29	0.35	0.37	0.36
S2		0.24	0.34	0.29	0.39	0.37	0.38
Average		0.33	0.31	0.29	0.37	0.37	0.37
S1	$\text{Cl}^-$	0.41	0.45	0.53	0.62	0.7	0.75
S2		0.7	0.61	0.69	0.73	0.74	0.81
Average		0.55	0.53	0.61	0.68	0.72	0.78

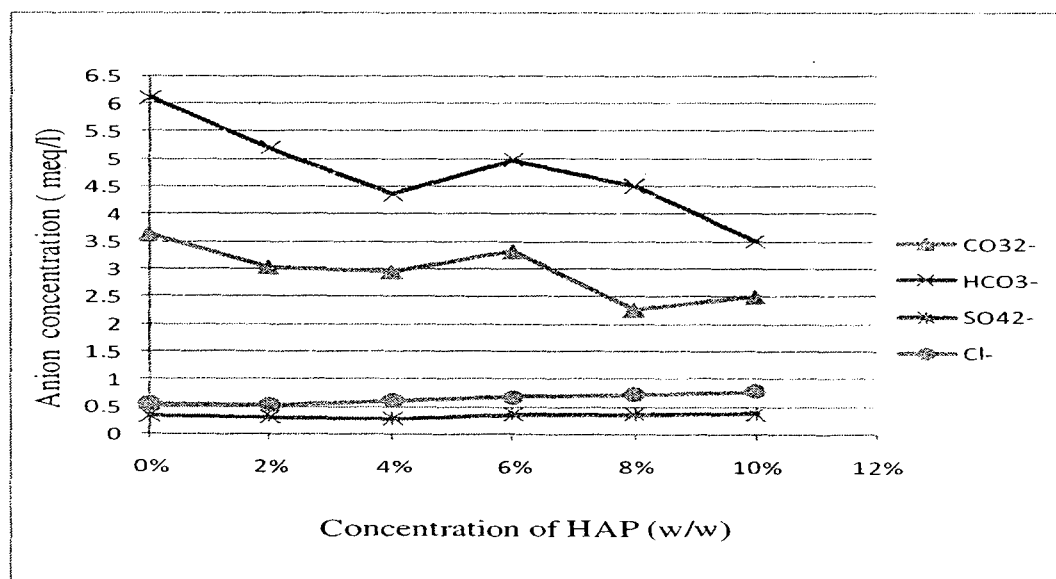


Figure-4.11. Variations in anion concentration after HAP nanoparticle application.

#### 4.4.3. Exchangeable cations

Table-4.12 shows the exchangeable cation concentration of the soil before and after the addition of HAP nanoparticles at different concentrations. The concentration of  $\text{Na}^+$  varied from 5.64 (0%) to 3.27 Cmol/kg (10% HAP application),  $\text{K}^+$  from 0.64 (0%) to

0.55 Cmol<sub>c</sub>/kg (10% HAP application), Ca<sup>2+</sup> from 17.53 (0%) to 24.35 Cmol<sub>c</sub>/kg (10% HAP application) and Mg<sup>2+</sup> from 6.17(0%) to 4.31 Cmol<sub>c</sub>/kg (10% HAP application). Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> are showing a decreasing trend with the increase in HAP concentration whereas Ca<sup>2+</sup> concentration increased with increasing HAP concentration. It indicated that exchangeable Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> ions decreased by 42.04%, 12.1% and 30.08% respectively. 38.97% increase was observed for exchangeable Ca<sup>2+</sup>. This may be the result of increased displacement of exchangeable Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> due to increased soil solution Ca<sup>2+</sup> from the added HAP. In general, higher the charge and smaller the hydrated radius of the cation, the more strongly it will absorb to the exchange sites. So the less tightly held cations like Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> are displaced by Ca<sup>2+</sup> into the soil solution thus increasing the concentration of soluble cations in soil solution. Similar results have been obtained by previous study done by Ilyas et al (1990) using gypsum.

Table-4.12. Concentration of exchangeable cations after the application of HAP nanoparticles.

Sample No.	Exchangeable Cations (Cmolc/Kg)	Conc. Of Hap (w/w)					
		0%	2%	4%	6%	8%	10%
S1	Na	5.53	4.5	3.45	3.32	3.3	3.15
S2		5.75	4.6	3.58	3.57	3.55	3.39
Average		5.64	4.55	3.52	3.44	3.43	3.27
S1	K	0.59	0.57	0.54	0.53	0.53	0.52
S2		0.68	0.67	0.63	0.6	0.59	0.58
Average		0.64	0.62	0.59	0.57	0.56	0.55
S1	Ca	20.55	21.83	23.01	24.13	27.14	27.57
S2		14.5	16.22	17.25	18.49	19	21.14
Average		17.53	19.03	20.13	21.31	23.07	24.35
S1	Mg	5.71	5.37	5.33	5.24	4.97	4.43
S2		6.63	4.8	4.61	4.58	4.5	4.2
Average		6.17	5.09	4.97	4.91	4.74	4.31

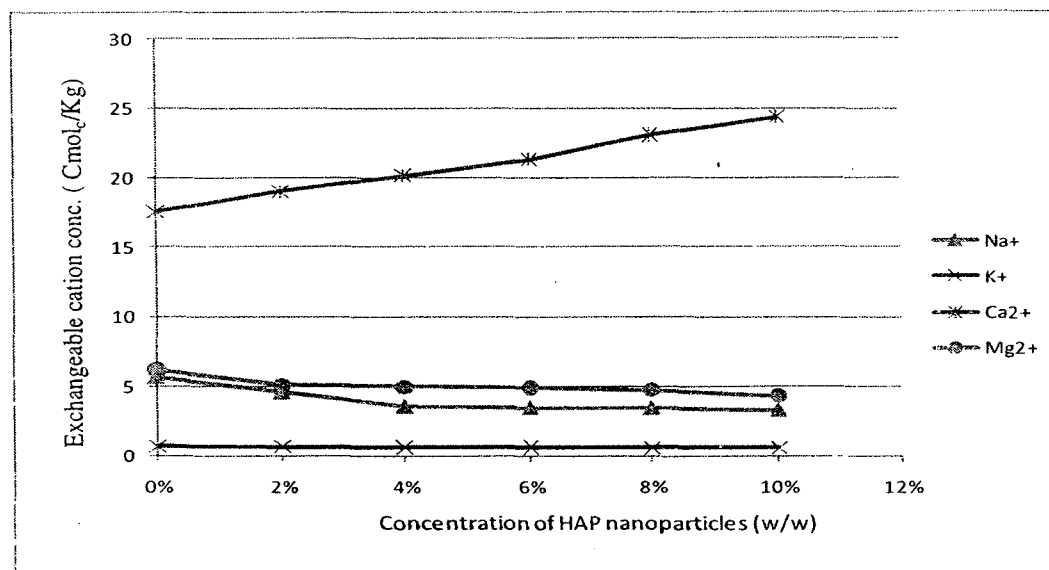


Figure-4.12. Variation in exchangeable cations after HAP nanoparticle application.

#### 4.4.4. CEC, ESP and SAR

Table-4.13 shows CEC, ESP and SAR values before and after the addition of different concentration of HAP. Average CEC and SAR increased from 29.96 to 32.48 Cmolc/Kg and 6.02 to 6.14 mmol/l respectively. ESP levels greater than 15 are associated with severely deteriorated soil physical properties. After the application of HAP nanoparticles, the average ESP values decreased from 18.81% to 10.0%. Variation in ESP with pH at different concentrations of HAP is shown in fig-13. Application of HAP nanoparticles increased the CEC which is in agreement with the results obtained by Suguna Devakumari (2005) and Vijayakumar (2006). This may be due to significant increase in  $\text{Ca}^{2+}$  ions on the exchange sites of the soil. So, increase in CEC suggested that HAP particles help in improving cation exchange capacity. With the application of HAP nanoparticle, ESP decreased by 46.55%. The increasing CEC and decreasing concentration of soil exchangeable  $\text{Na}^+$  resulted in reduction of soil ESP. Choudhary et al (2004) and Makoi and Nadkidemi (2007) reported same results with gypsum and farmyard manure. Table-13 shows a general guide for the desirable proportion of different cations ratio that suits different plants (Abbott 1989). Observed % CEC at 0% and 10% HAP nanoparticle application is also shown in table-4.14. The percentage of

CEC occupied by calcium increased from 58.48 to 74.98 whereas Mg and Na decreased from 20.57 to 13.27 and 18.81 to 10.06 respectively.

Table-4.13. CEC, ESP and SAR values after the application of HAP nanoparticle.

Sample No.	Parameters	Conc. Of Hap (w/w)					
		0%	2%	4%	6%	8%	10%
S1	CEC Cmol/l	32.38	32.27	32.33	33.23	35.95	35.67
S2		27.56	26.29	26.07	27.24	27.64	29.3
Average		29.97	29.33	29.2	30.23	31.8	32.48
S1	ESP (%)	17.09	13.94	10.67	9.99	9.17	8.83
S2		20.85	17.48	13.74	13.11	12.86	11.56
Average		18.82	15.5	12.04	11.39	10.77	10
S1	SAR mmol/l	5.25	5.94	5.8	5.93	5.87	5.84
S2		6.89	5.44	6.83	6.81	6.48	6.51
Average		6.02	6.82	6.16	6.28	6.12	6.14

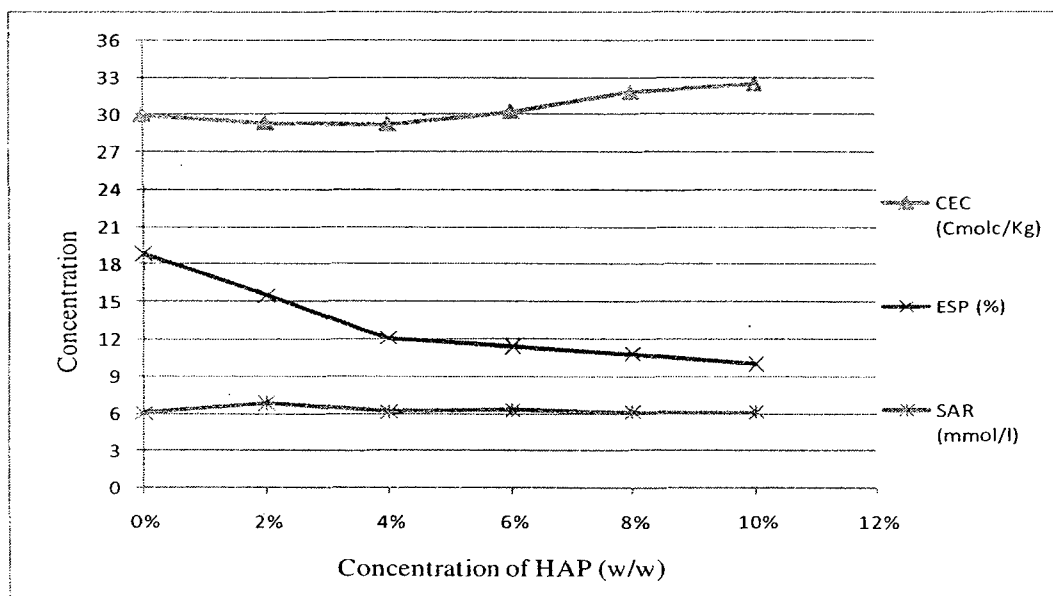


Figure-4.13. Variation in CEC, ESP and SAR values after the application of HAP nanoparticle.

Table-4.14 Desirable proportion of different cation ratio that suits different plants.

Cations	Desirable % CEC	Observed % CEC	
		0 %	10%
Ca	65-80	58.48	74.98
Mg	10-15	20.57	13.27
K	1-5	2.13	1.7
Na	0-1	18.81	10.06

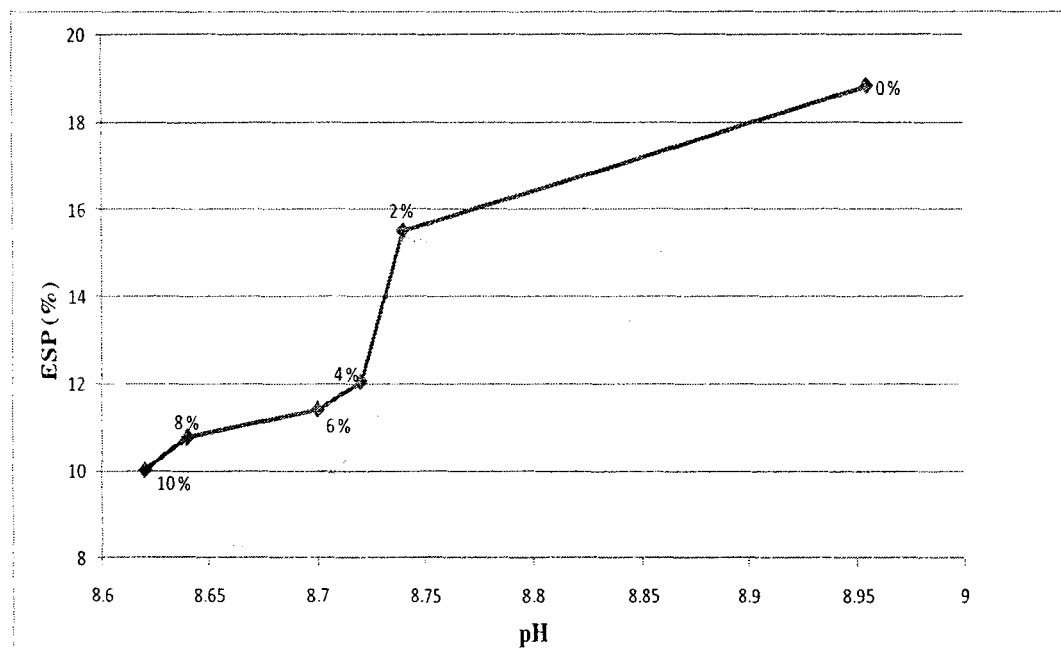
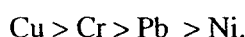


Figure-4.14. Variations in ESP with pH at different nanoparticle concentrations.

#### 4.4.5. Heavy metals

Table-4.15 shows that after treating the soil samples with HAP at different concentrations resulted in significant decrease in heavy metal concentrations. The increase in quantity of HAP nanoparticle resulted in increased removal of metal ions. The concentration decreased from 28.54(0%) to 14.04 (10% addition) for Cr, from

12.84 (0%) to 6.86 (10% addition) for Pb, 7.63 (0%) to 5.54 (10% addition) for Ni and 10.01 (0%) to 4.60 (10% addition) for Cu. After seven days of treatment, the concentration of Cr decreased by 50.82% (10% addition), Pb decreased by 46.61% (10% addition), Ni decreased by 27.31% (10% addition) and Cu decreased by 53.99% (10% addition). From this experiment, the following trend was observed for the heavy metals:



These results are in agreement with the previous study done by Seaman et al (2001) on immobilization of Ni, Pb, Cr and Cu in sediments using HAP. Saxena et al (2006) also reported decline in concentration of lead and copper using low grade rock phosphate of Jhabua (M.P). The exact reaction mechanism responsible for the removal of metal ions by apatite is still unknown but the sorption process generally involves the possible reaction mechanisms for metal immobilization:

- a) Ion-exchange process (Xu., 1994; Gómez del Río et al., 2004 and Chen., 2002).
- b) Surface complexation (Xu., 1994; Leyva., 2001 and Vega., 2003).
- c) Dissolution of HAP and precipitation of new metal phosphates (Ma., 1994 and Xu., 1994)
- d) Substitution of calcium in HAP by other metals during recrystallization (co-precipitation) (Xu., 1994 and Jeanjean., 1994).

The ion exchange mechanism could be described by the following general reaction:

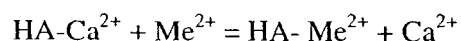


Table-4.15. Heavy metal concentration before and after application of HAP nanoparticles.

Sample No.	Metals	Conc. Of Hap (w/w)					
		0%	2%	4%	6%	8%	10%
S1	Cr (ppm)	28.89	27.54	20.75	18.58	17.64	13.16
S2		28.19	23.93	22.35	18.71	16.88	14.91
Average		28.54	25.74	21.55	18.65	17.26	14.04
S1	Pb (ppm)	13.51	9.94	9.72	9.18	7.41	6.75
S2		12.18	11.49	10.33	9.08	8.15	6.96
Average		12.84	10.71	10.03	9.13	7.78	6.86
S1	Ni (ppm)	7.69	7.52	6.94	6.07	5.53	5.31
S2		7.56	7.13	6.56	6	5.9	5.77
Average		7.62	7.33	6.75	6.04	5.71	5.54
S1	Cu (ppm)	9.28	6.27	5.48	5.42	5.33	4.8
S2		10.74	8.78	5.69	5.24	5.19	4.41
Average		10.01	7.52	5.59	5.33	5.26	4.6

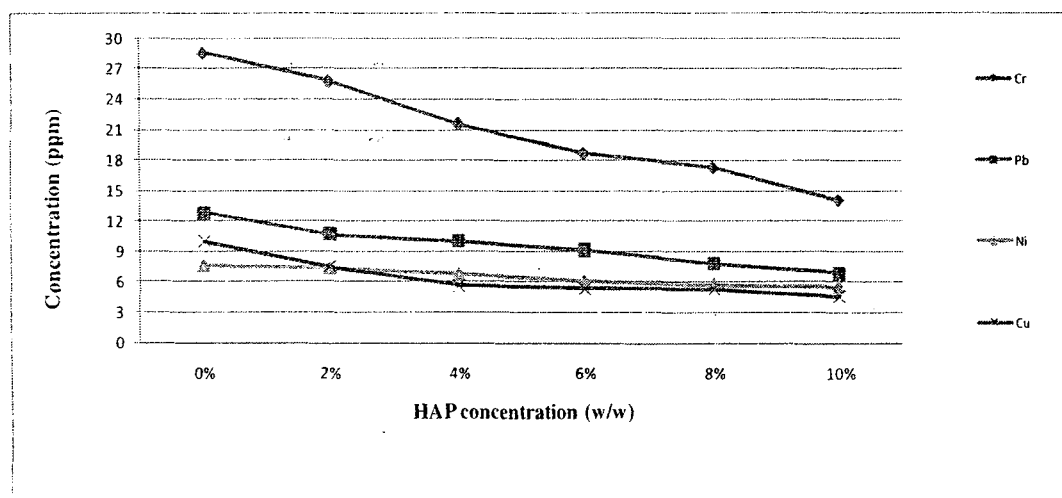


Figure-4.15. Variation in heavy metal concentration after the application of HAP nanoparticles



## *Chapter-5*

*Conclusions*

## CHAPTER-5

### CONCLUSIONS

To achieve the objectives of the present study, sample collected was analysed in duplicates for pH, EC, TDS, major soluble cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ) and anions ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ), exchangeable cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ) and heavy metals (Ni, Cr, Cu and Pb). The analytical data were evaluated for ESP, SAR and CEC. The parameters like ESP and CEC were calculated for assessment of soil quality for agricultural purposes. The following were the major findings of the present study:

- 1) The pH, EC, ESP and prevalence of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  suggested the sodic nature of the soil.
- 2) Mineralogical composition indicated dominance of quartz followed by albite and hornblende.
- 3) HAP nanoparticle application markedly decreased soil pH and increased EC and TDS.
- 4) Application of HAP nanoparticles significantly decreased the ESP value below the typical ESP value for sodic soil.
- 5) HAP nanoparticles substantially removed Ni, Cu, Cr and Pb from soil samples. The removal efficiency for Ni, Cu, Cr and Pb was 27.39%, 53.99%, 50.82% and 46.61% respectively. Hence, it can be concluded that HAP nanoparticles are effective in removing above mentioned heavy metals from soil.
- 6) This study suggested the effectiveness of HAP nanoparticles in decreasing the sodicity of soil and improving its chemical properties.

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