SUMMARY

Natural water is being contaminated with several heavy metals arising from mining wastes and industrial discharges. Commonly encountered metals of concern include Pb, Cu, Zn, Co etc. These metals are toxic in both, their chemically combined forms as well as in elemental form. Exposure to these contaminants, present even in low concentration in the environment, can be harmful to the human health. In order to solve heavy metal pollution in the environment, it is important to bring applicable solutions. Among various treatment technologies available for removal of heavy metal ions from aqueous solutions are chemical precipitation, ion exchange, coagulation, bioremediation and sorption/adsorption. Of all these techniques adsorption on solid substrate is preferred because of its high efficiency, easy handling and cost effectiveness as well as availability of different adsorbents.

The common adsorbents primarily include activated carbons, zeolites, clays, biomass and polymeric materials. However, above described adsorbents suffer from low adsorption capacities and separation inconvenience. Therefore, efforts are still needed to exploit new promising adsorbents.

Hydroxyapatite (HA) is a mineral, from the group of apatites, having the chemical formula: \(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\). HA has been used to prepare biomaterials for hard tissues repair and replacement, because of its excellent biocompatibility with human organs as well as its close similarities to the main inorganic constituent of bone in both composition and structure. The structure of hydroxyapatite consists of two subsystems, e.g. Ca channels in which OH groups are arranged and main frameworks of calcium phosphate.

In addition to its similarity to natural bone mineral, HA is an osteoconductive
material that provides a temporary scaffold for bone growth. HA appears to form a direct chemical bond with hard tissues. On implantation of HA particles or porous blocks in bone, new lamellar cancellous bone forms within 4 to 8 weeks.

HA crystals are best described as hexagonal rhombic prisms. The lattice parameters for HA are $a=9.432$ Å and $c=6.881$ Å. Hydroxyl ions (OH\(^-\)) occur at the corners of the basal plane. These ions are positioned at every 3.44 Å (one half the unit cell), parallel to the c-axis and perpendicular to the basal plane. Thus, 60% of calcium ions in the unit cell are associated with the hydroxyl ions and density of this material is 3.219 g/cm\(^3\).

In recent years, HA has received attentions as an advanced material for various applications such as sensors, catalysts, immobilization reagents, conductors, protein delivery agents and adsorbents. HA is tolerant of vacancies and substitutions because of its complex composition and crystal structure. Fundamentally, HA has the very marked ability to adsorb various ions, organic molecules and polymers by ion exchange. Also in addition to high adsorption capacity, it has low water solubility, high stability under reducing and oxidizing conditions. Because of the high stability and flexibility of the apatite structure, many cationic and anionic substitutions are possible. Various mechanisms have been suggested for the substitutions, ion exchange and complex formation. Ca\(^{2+}\) can be substituted by monovalent, divalent and trivalent cations. OH\(^-\) and PO\(_4\)^{3-} can be replaced by some anions and can provide surface complexation. Furthermore, HA is abundant in nature, available easily, low in cost and have minimal environmental impact for restoration or remediation of natural resources.
Extensive efforts have been made to produce synthetic HA nanoparticles. As per our literature review, several techniques have been utilized for HA preparation such as chemical precipitation, sol-gel, hydrothermal, microwave assisted, flame synthesis and hydrolysis, which can be divided into solid-state reactions and wet methods. Among these processes, chemical precipitation is the most promising method because of its simplicity of experimental operations, low operating temperature and high yields of pure products.

HA nanoparticles have key physico-chemical properties. They have larger surface area than bulk particles and can effectively, inexpensively and rapidly adsorb heavy metals. Therefore, HA nanoparticles have been applied to the research related to the removal of heavy metals.

The present research work was undertaken to develop HA nanoparticles with high surface area by chemical precipitation method. HA was characterized for its physical, surface and adsorption properties. Adsorption studies of heavy metals having different ionic radius (lead, copper, zinc and cadmium) using HA nanoparticles were carried out by varying the parameters.

Systematic studies have been performed for adsorption study of heavy metals by varying different parameters like HA dosage, equilibrium time, pH of initial solution, reaction temperature as well as metal ions concentration. Studies on all these aspects, i.e. thermodynamic study, adsorption mechanism, adsorption kinetics and isotherms have been compiled in the form of the present thesis.
The research work carried out, has been divided into eight chapters.

Chapter I gives an introduction to structure, properties and preparation methods of HA. It gives an introduction to adsorption process, factors that affect the adsorption process, adsorption isotherms and various adsorption equations. It also contains literature survey and elucidates the necessity of undertaking the present work.

Chapter II comprises of experimental methods and instrumentations used for preparation and characterization of HA nanoparticles as well as nanostructured HA.

Chemical precipitation method was used to prepare HA nanoparticles using Ca(NO$_3$)$_2$·4H$_2$O and (NH$_4$)$_2$HPO$_4$ aqueous solutions as starting reactants. The pH of these solutions was adjusted to desired value by adding concentrated NH$_4$OH. After completing the reaction, the resulting precipitate was aged under stirring for the desired time. The resulting material was oven-dried and calcined in air.

After optimizing values of pH value, preparation method was used to prepare adequate amount of HA nanoparticles to be used for further studies. Green samples of the prepared HA nanoparticles were made with different dimensions using steel dies and hydraulic press. Samples were sintered at high temperature, i.e. 800°C.

HA powders were characterized by powder X-ray diffraction and phase identification was carried out by comparing the diffraction data with JCPDS standards. The morphology and size of prepared nanoparticles were studied from transmission electron microscopy (TEM) micrograph.

The specific surface area of the calcined-HA nanoparticles was determined by nitrogen adsorption analysis (BET) using Gemini-2375 surface area and pore size analyzer. The calcium to phosphate molar ratio of the prepared HA nanoparticles were
measured by inductively coupled plasma (ICP) technique.

Chapter III includes results of the study on optimizing parameters affecting the chemical precipitation method used to prepare HA nanoparticles, namely the pH. XRD patterns of this sample were in agreement with the corresponding values reported for hexagonal HA.

The absorptions due to the vibration modes from phosphates and hydroxyl groups, which represents the HA structure in IR spectra, were noticed in FT-IR spectra of the prepared powders before and after calcination. ICP result showed that the final molar ratio of Ca/P obtained was 1.6787 close to the theoretical molar ratio (1.6667).

The powder sample was prepared to form pellets under different applied pressure. Physical and mechanical properties of these pellets were determined. These properties have been correlated with the applied pressure used for pellet formation.

The physical testing showed that the sintered HA samples consist of solid parts and porous part. The mechanical characterizations showed that as the pressure increases from 50 kg/cm$^3$ to 125 kg/cm$^3$ compressive strength increases from 27.92 MPa to 128.96 MPa. This difference belongs to the different porosity of the samples.

In chapter IV, lead adsorption studies using HA samples in powder form are given. Here adsorption experiments were carried out to prefix amount of the HA along with the lead ions solution. The effect of contact time, pH of initial solution, reaction temperature, HA dosage and lead ions concentration was studied to optimize experimental conditions. The concentration of lead ions, both before and after adsorption studies were measured using UV-visible spectrophotometer Shimadzu UV-1601.
Langmuir and Freundlich isotherms were used to analyze the equilibrium data. The pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models were applied to study the kinetics of the sorption processes. In addition, various thermodynamic parameters, such as standard Gibbs free energy ($\Delta G^\circ$), standard enthalpy ($\Delta H^\circ$) and standard entropy ($\Delta S^\circ$) were calculated. The adsorption mechanism was investigated by the X-ray Diffraction (XRD) and FT-IR spectra.

The maximum uptake of lead ions was obtained at pH 6. The pseudo-second order kinetic model provided the best correlation of the used experimental data compared to the pseudo-first order. This suggests that the rate-limiting step of this system may be adsorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate.

The adsorption of lead ions by HA was increased as the initial concentration of lead ions increased in the medium. The maximum lead ions adsorption achieved to be 86.73 miligram per gram HA. It was found that the adsorption of lead ions on HA was correlated well with the Langmuir equation as compared to other isotherm equations under the concentration range studied. Thermodynamic calculations showed that the lead ions adsorption process of HA has endothermic and spontaneous nature. This study indicated that HA could be used as an efficient adsorbent for removal of lead ions from aqueous solution.

Chapter V deals with adsorption study on the removal of copper ions from aqueous solutions by synthetic HA. In order to determine the adsorption capacity of HA for copper ions as well as the influence of the contact time, aqueous copper ions concentration, the amount of HA, solution pH, adsorption experiments were performed.
by batch equilibration technique. The concentrations of copper ions were measured using UV-visible spectrophotometer. The kinetics of the adsorption process, adsorption isotherms and various thermodynamics parameters have been studied as shown in chapter IV. The adsorption mechanism was investigated by the X-ray Diffraction (XRD) and FT-IR spectra.

The efficiency of copper ions adsorption increased with increase in the adsorbent dosage. Isotherm studies indicate that Langmuir model fits the experimental data better than Freundlich model. The adsorption of copper ions increases as pH value enhanced from 5 to 7. The thermodynamic parameters of the adsorption indicate that within 283–323 K the adsorption is spontaneous and endothermic.

Chapter VI contains adsorption study on the removal of cadmium ions from aqueous solutions by synthetic HA. In order to determine the adsorption capacity of HA for cadmium ions as well as the influence of the contact time, aqueous cadmium ions concentration, the amount of HA, solution pH, adsorption experiments were performed by batch equilibration technique. The concentration of cadmium ions were measured using UV-visible spectrophotometer. The kinetics of the adsorption process, adsorption isotherms and various thermodynamics parameters have been studied as shown in chapter IV. The adsorption mechanism was investigated by the X-ray Diffraction (XRD) and FT-IR spectra.

The kinetic adsorption of cadmium ions on HA can be described well by a pseudo-second-order model. Adsorption of cadmium ions on HA is strongly dependent on pH values. The adsorption increases with increasing pH values. The adsorption isotherms of cadmium ions on HA can be described well by the Langmuir model. The
thermodynamic parameters calculated from the temperature dependent adsorption isotherms indicate that the adsorption process is spontaneous and endothermic.

Chapter VII comprises adsorption study on the removal of zinc ions from aqueous solutions by synthetic HA. In order to determine the adsorption capacity of HA for zinc ions as well as the influence of the contact time, aqueous zinc concentration, the amount of HA, solution pH, adsorption experiments were performed by batch equilibration technique. The concentration of zinc ions were measured using UV-visible spectrophotometer. The kinetics of the adsorption process, adsorption isotherms and various thermodynamics parameters have been studied as shown in chapter IV. The adsorption mechanism was investigated by the X-ray Diffraction (XRD) and FT-IR spectra.

Kinetic studies suggest that zinc ions adsorption on HA could be described more favorably by the pseudo-second-order kinetic model. The Gibbs free energy was determined to be negative, indicating the spontaneous nature of the adsorption process. The maximum uptake of zinc ions were obtained at pH 7. The adsorption of zinc ions by HA was increased as the initial concentration of zinc ions increased in the medium. The maximum zinc ions adsorbed were achieved to be 22.17 miligram per gram HA. It was found that the adsorption of zinc ions on HA was correlated well with the Langmuir equation as compared to other isotherm equations under the concentration range studied.

The important conclusions and outcome of the thesis are discussed in the chapter VIII. These results showed that HA nanoparticles with high surface area and mesoporosity can be made by using chemical precipitation method. Removal of heavy metal ions (lead, cadmium, copper and zinc) from aqueous solution is possible using HA.
powder. The adsorption of metal ions by HA increased as the initial concentration of metal ions increased in the medium. The solution pH is an important parameter in controlling metals ions sorption onto the HA. The percentage adsorption increased with temperature which may be result of increase in the mobility of the metal ions.