Synopsis

The contamination of groundwater by heavy metals originating either from natural soil sources or from anthropogenic sources is a matter of utmost concern to the public health. Remediation of contaminated groundwater is of highest priority since billions of people all over the world use it for drinking purpose. Depending on local geology, groundwater contains heavy metals (including radioactive elements) in low levels, but sometimes in concentrations which are not acceptable for drinking water. These heavy metals may be radioactive or even nanoparticles. They are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Treatment processes for contaminated ground water include filtration, centrifugation, chemical precipitation, coprecipitation, micro- and ultra filtration, sedimentation and gravity separation, flotation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange, electrolysis, adsorption etc. Adsorption is considered as one of the suitable water treatment methods due to the availability of a wide range of adsorbents and its ease of operation. Adsorption can be applied for the removal of organic, inorganic, and biological pollutants both in soluble and insoluble forms. Generally, packed bed columns, with a stable, porous material that has a specific grain size, are used. In spite of these facts, adsorption has certain limitations such as it could not achieve a good status at commercial levels. Probably, it is due to the lack of suitable adsorbents of high capacity to prepare commercial scale columns and a single adsorbent cannot be used for all kind of contaminants. Moreover, tailored materials must be stable and resistant to the medium that is investigated so that there is no release of constituent components. Therefore cost effective alternative technologies or sorbents for treatment of contaminated groundwater are need of the modern days. The high
sorption capability exhibited by many biogenic material such as algae, bacteria, and yeasts or geological materials like silicate and aluminate could be exploited to develop a cost effective method for treating such waters. These geogenic and biogenic matrices can be tailored by chemical modification or by incorporation of suitable material in the matrix. This will not only make them specific to some metal ions or radionuclides but will also enhance their sorption capacity. Composites consisting of two different components are called hybrid materials. Normally one component is inorganic in nature and the other is organic. Combining an inorganic matrix with biological systems offers important advantages. Algae appear to be one of the very promising materials in this regard. Dried algae or even algal extraction residues can be used as sorption material or for immobilizing the specific sorbent. The hybrid materials synthesis by impregnating inorganic material in organic matrices or vice versa shows enhances applicability in wastewater treatment. Hybrid materials could not only be effective in the removal of inorganic pollutants but also show fair affinity towards the radioactive and nanoparticle impurities as well. In general, these materials possess two different sorption sites enabling enhanced capability for removal. Another major advantage associated with these hybrid materials is that they will not leach into experimental solution as they do not have sufficient solubility in ground water in the pH range of 5-8. In view of this they can easily be separated from the process water. This can be verified by quantifying various drinking water quality parameters after decontamination. This will ensure the safe consumption of drinking water by human beings. During this thesis work displacement reaction was used for immobilizing different materials in biogenic matrices. The porosity and the degree of immobilization of the embedded materials was controlled over a wide range of concentration. Core-shell types of hybrid materials were synthesized using sol-gel route. A
third category of hybrid material i.e. organic coating on inorganic substrate was also prepared. The resultant hybrid materials were characterized by using various techniques like Zeta-sizer for size characterization, SEM-EDS, FTIR, BET surface area analysis and XRD for the surface and structural characterization. The stability of the prepared hybrid material and changes in the properties were observed with time. The structure and binding capacity of different types of hybrid material was investigated with regard to their practical use for the selective and reversible accumulation of heavy metals and radionuclides. Detailed analysis of various metal ions was done by using absorption/emission spectroscopy while the ultra trace level of radionuclides was measured by using gamma and alpha spectrometry.

This thesis aims at: (i) Development of highly efficient hybrid materials of different types (impregnation of suitable inorganic material into alginate matrix as well as core shell types), (ii) characterization of the newly developed hybrid material, (iii) removal of contaminants (conventional, radionuclides and nanoparticles) using the hybrid materials, (iv) practical field application of the developed hybrid materials. The hybrid materials developed and investigated in this thesis are: chitosan impregnated calcium alginate (for uranium); silica microspheres (for uranium, thorium); pure calcium alginate beads (for americium) and humic coated goethite (for americium and plutonium); silica microsphere impregnated calcium alginate (for titanium oxide nanoparticle); goethite impregnated calcium alginate (for arsenic); alumina impregnated calcium alginate (for fluoride). The work done and the obtained results are organised in following seven chapters.

**Chapter 1: Introduction**

In this chapter, concept of hybrid materials was introduced along with their unique advantage for the selective uptake of metal ions from aquatic medium. Categorization of hybrid
materials based on types of formation and interaction among the components are discussed in
details. It also includes a brief discussion about the possible natural and anthropogenic
reasons for elevated level of certain conventional and radioactive elements in groundwater.
Advantages of present work for remediation of groundwater over the existing techniques are
discussed. Literature pertaining to the decontamination of groundwater from different
conventional and radioactive pollutants and earlier work carried out by various researchers in
understanding the interaction of metal ions with hybrid materials are summarized. Finally the
scope of the thesis is presented in brief.

**Chapter 2: Synthesis and characterization of hybrid materials**

This chapter describes the details of experimental methods used for the synthesis and
characterization of different types of hybrid materials along with optimisation of different
parameters and composition of the hybrid materials. Three different categories of hybrid
materials were mainly dealt with in this thesis. Inorganic material impregnated calcium
alginate were synthesised by ionotropic gelation method. Core-shell type hybrid material
silica microspheres were synthesized based on a polyvinylpyrrolidone involved emulsion
polymerization and subsequent sol–gel process. Details of the process of the synthesis as well
as the composition, morphological and structural characterization are discussed. Various
characterization techniques used in the thesis work include Fourier transformed infra red
spectroscopy (FTIR), X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron
microscope (SEM) and energy dispersive X-ray analysis (EDX) etc. The techniques used for
determination of the concentration of the metal ions [flame atomic absorption spectroscopy
(FAAS) and inductively coupled plasma optical emission spectroscopy (ICP-OES)] and
radionuclides [alpha and gamma spectrometry] are also briefed in this section.
Chapter 3: Decontamination of groundwater from radionuclides (U, Th, Pu, Am) using hybrid materials

Wide spread drinking water resources contamination by radioactive constituents can result either from catastrophic incidents (Chernobyl in 1986 and Fukushima in 2012) or natural geological processes like uranium in groundwater of certain district of Punjab, India. In this chapter, the uptake studies of the radionuclides are described. All three categories of the hybrid materials [alginate based; core-shell type; organic coating on inorganic substrate] were utilised for the removal of radioactive contaminants. The results obtained are summarized below.

**Uranium (U) and thorium (Th) removal:** Alginate based hybrid material chitosan impregnated calcium alginate (Cal-Alg-Chi) bead [7% loading of chitosan into 4% Ca-alginate] was used to sorb uranium from potable water without compromising primary water quality parameters. Results from the uptake study, carried out in batch mode, showed more than 98% sorption of uranium in the concentration range of 0.1–50 μgmL⁻¹. Optimum pH for sorption was 3-5. The sorption capacity was evaluated as 36.04 mgg⁻¹ from Langmuir model. The sorption kinetics was also tested. The FTIR spectra were used as a tool for understanding the interaction between uranium and chitosan impregnated into Ca-alginate.

Silica microspheres (SM) were also used to remove the traces of U and Th in different water. Ultra-filtration technique was used to isolate the SM from the water samples. The results of batch sorption experiments suggest that SM is very effective at pH 3, and sorption is more than 99 %. The maximum U and Th uptake were 30 and 36 mg g⁻¹, respectively.
Plutonium (Pu) and americium (Am) removal: Humic coated colloidal suspension of goethite (α-FeO(OH)) followed by ultrafiltration were used to decontaminate the water having $^{239+240}$Pu and $^{241}$Am in the concentration range of 10–100 Bq L$^{-1}$. Experimental results clearly indicate preferential association of Pu and Am with goethite suspension dominated with 30 nm colloids. The impact of humus material on selectivity of Pu and Am by goethite was studied in the concentration range of 10–100 μg mL$^{-1}$ of humic acid. This selectivity was further enhanced linearly with the increase in concentration of humic acid from 10 to 60 μg mL$^{-1}$ and thereafter it remained constant. Laboratory simulated experiments were also carried out for the removal of low level of $^{241}$Am using calcium alginate (Ca-Alg) beads followed by treatment with activated charcoal. It was observed that the variation of carbonate, bicarbonate, does not influence the sorption capacity of calcium alginate whereas the dissolved organic carbon (DOC) decreased the sorption capacity. 98-99% of Am is recovered from Ca-Alg beads by using 0.6 M HNO3.

Chapter 4: Removal of TiO$_2$ nanoparticles (TiO$_2$ NP) from aquatic medium using hybrid materials

Concerns have been raised in recent times that TiO$_2$ NP may throw challenges to human health because of its unique bioactivity as many in vitro and in vivo toxicological studies showed adverse effect of TiO$_2$ NPs on living organisms. This chapter discussed about the utilization of the core-shell type of hybrid material silica microspheres for the isolation of nanoparticles from aquatic medium. Calcium–alginate–silica microsphere (Cal-Alg-SM) bead [10 % (wt/vol) SM loaded in 4% calcium alginate] was developed by calcium alginate impregnation of silica microspheres prepared through sol-gel route. These beads were highly efficient in the removal of TiO$_2$ NP from aquatic bodies. Uptake studies carried out in batch
mode, showed that Cal-Alg-SM beads are very effective for removal of TiO$_2$ NP in the pH range of 3-5 and the sorption was more than 90% in the concentration range of 10–500 μg mL$^{-1}$. Sorption isotherm was seen to follow Langmuir model and the uptake capacity evaluated was 29.9 mg g$^{-1}$. Mechanism of sorption was proposed based on the zeta potential values of the silica microspheres and TiO$_2$ NP at different pH.

**Chapter 5: Hybrid materials for decontamination of groundwater from conventional pollutants (As, F)**

In recent years, arsenic and fluoride contamination of drinking water has become a major concern on a global scale. In this Chapter, the uptake studies of arsenic and fluoride are described. The results obtained are summarized below.

**Arsenic (As) uptake:** Goethite ($\alpha$ FeO(OH)) impregnated calcium alginate (Cal-Alg-Goe) beads [18% goethite loaded in 4% calcium alginate] were used to sorb the arsenic from groundwater without disturbing its physicochemical characteristics. The results of batch sorption experiments suggest that Cal-Alg-Goe beads are very effective for removal of arsenic in the concentration range of 10 – 10000 ng mL$^{-1}$. The sorption at different pH was explained based on the species of arsenic present and the zeta potential values of goethite. Isotherm and kinetic models were tested and the sorption capacity was 30.4 mg g$^{-1}$.

**Fluoride (F) uptake:** The feasibility of alumina impregnated calcium alginate (Cal-Alg-Alu) beads [22 % (wt/vol) alumina loaded in 2% calcium alginate] was tested to sorb the excess fluoride ions from the potable water without disturbing the drinking water qualities. The results of batch sorption experiments suggest that Cal-Alg-Alu beads is very effective for defluoridation in the pH range of 3.5 to 9.0 and sorption is more than 99% in the concentration range of 1 – 100 mg L$^{-1}$. Equilibrium sorption follows Langmuir isotherms.
well and the maximum fluoride uptake calculated was 17.0 mg g$^{-1}$. Equilibrium time was 300 minutes and both the pseudo-first-order and pseudo-second-order kinetic models were tested.

**Chapter 6: Application of the hybrid materials developed under this study for decontamination of Uranium, Fluoride and Arsenic contaminated groundwater under field conditions**

This chapter discusses the effectiveness of the newly developed hybrid materials for contaminated water samples collected from the various parts of India. In case of uranium, samples were from the state of Punjab; while fluoride and arsenic contaminated samples were collected from Andhra Pradesh and the state of West Bengal, India respectively. Various measured physicochemical parameters of groundwater before and after the treatment with hybrid material were studied and presented in details. It is clear from the result that there is no elevated level of concentration of any particular property after the treatment assuring the drinkability of the water. Special care had been taken to check the leachability of the constituent from the hybrid materials.

Integrity of the hybrid materials were checked by studying the morphological, structural characteristics, reusability and quantification of various constituents of the hybrid material after the decontamination processes. Various experimental results clearly indicate that the newly developed materials in field condition are as effective as in case of laboratory spiked samples. In all three cases a flow process diagram was proposed for effective online removal of U, F and As.

**Chapter 7: Work summary**

In this chapter, we summarize the main conclusions of the thesis. It has been conclusively demonstrated that specificity of the material can be enhanced by incorporation of geogenic or
biogenic materials into the biogenic matrix. Core-shell hybrid materials showed enhanced sorption because of the higher surface area. Evaluation of composite structure and metal-binding capacity of different types of immobilized materials with regard to their use for the selective and reversible accumulation of metal ions were carried out. In addition, we have emphasized that the leaching of the components doesn’t take place and also there is no uptake of essential elements from potable water and suitable for human consumption. Demonstration of the newly developed hybrid materials for efficient removal of the contaminants in the field conditions was successfully carried out. This Chapter is concluded with future scope of the work which stress the needs for strengthening the certain areas for highly efficient use of hybrid materials.