4. SUMMARY AND CONCLUSIONS

Water is essential for sustenance of all living organisms including plants, animals and human beings. If water is precious, water quality is more precious. Metal pollution of water has been receiving considerable attention of late due to the increasing amount of industrial pollution and these metal ions possess toxicity, causing health hazards to living beings including humans. The impact of heavy metal in trace amounts present in drinking water is dangerous for health in the long term. The presence of metals and metalloids in potable waters, domestic waters and industrial effluents is a subject of serious concern due to their toxic properties. Heavy metals are persistent contaminants and most frequently occur in the environment in trace amounts. Only a small number of heavy metals such as Cd, Cu, Fe, Co, Zn, Hg, V, Pb, Ni, Cr, Mn, Mo, Ag and Sn are associated with environmental, plant, animal or human health problems.

All these metals are chalcophillic, hence they exert toxic effects by attacking the sulphur bonds present in the enzymes and thus inhibit various metabolic activities that are taking place in the organisms. Some of these metals act as micro-nutrients at smaller concentrations in living organisms but accumulation even at ppb level is toxic to most of the life forms. Sometimes at acute level, these metals may even cause death. Heavy metals find their way into the water cycle by (i) natural process: corrosion, geological weathering and volcanic activity, (ii) Anthropogenic sources which include direct addition through industrial processing of ores and metals, use of metals and metal components, bleaching of metal from garbage and solid waste dumps, animals and human excretions which contain heavy metals and agricultural practices through the atmospheric precipitations of industrial pollutants and automobile emissions.
The necessity for the removal of heavy metal ions in waste water streams of the industries and subsequent possible reuse of these valuable metal ions has led to an increasing interest in selective sorbents. Hence from an environmental and economical view point, there remains a challenge to discover more selective and effective methods for toxic heavy metal removal from drinking water as well as industrial effluents. A number of materials are found to form complexes with toxic trace metals and they function through adsorption, ion exchange, precipitation, electrochemical, hydrolytic and oxidation reactions etc.

As a part of the objective to identify heavy metal removing materials which would be low cost material, indigenously synthesized and environmentally friendly and having the potential of field applicability, this study has been carried out. In the present study several sorbents have been studied for heavy metal removal in order to select suitable sorbent and to propose suitable mechanism for heavy metal sorption. The suitability of the sorbents for metal removal was assessed based on the merits and demerits of the sorbents studied.

Chapter I deals with the occurrence of heavy metal pollution, its impact on the humanity and gives a detailed review of the literature regarding heavy metal removal methods, merits and demerits of various sorbents.

Chapter II deals with the experimental methods to analyze the water samples and characterize the sorbents with standard references and the procedure adopted to carry out the adsorption and the kinetic studies that have been carried out.
Chapter III presents the results and discussion of the bio-polymeric materials and nanocomposites prepared and used for heavy metal removal studies in four phases and the results have been presented under the following sub-headings:

III.1 Sorption studies of Cu(II), Fe(III) and Cr(VI) using modified chitin

III.2 Sorption studies of Cu(II), Fe(III) and Cr(VI) using modified chitosan

III.3 Sorption studies of Cu(II), Fe(III) and Cr(VI) using bioinorganic hybrid composites

III.4 Influence of co-cations on sorption capacity of the sorbents. Suitable mechanism, isotherm and kinetic models for sorption of heavy metals on the sorbents have been proposed.

Chapter IV Presents the contribution of the researcher for the removal of heavy metal form water which forms the concluding part of the work.

III.1 Sorption studies of Cu(II), Fe(III) and Cr(VI) using modified chitin

This chapter deals with the results obtained in the sorption studies on the biopolymeric material chitin and its modified forms viz., protonated (PC), Carboxylated (CC) and grafted (GC) chitin. The PC, CC and GC possess high SC than the raw chitin.

In the case of Cu(II), metal ion removal from the SCs of C, PC, CC and GC were found to be 2472, 2810, 3335 and 4035 mg/kg respectively and the contact time for maximum sorption was found to be 30 minutes for all the sorbents. The grafted chitin possesses higher SC than the C, PC, CC. The SCs of the modified chitin were highly dependent on pH and are not influenced by the presence of other ions. The maximum SC was observed at pH 6-8 and a slight decline in SC at both acidic and alkaline medium. The adsorption pattern of the sorbents follows Freundlich isotherm. The values of
thermodynamic parameters confirm the spontaneous and endothermic nature of metal ion sorption. The rate of the reaction follows pseudo second order kinetics. The sorption of metal ion on the sorbents follows intraparticle diffusion pattern.

The SC of C, PC, CC and GC in Fe(III) removal were found to be 3112, 3774, 3940 and 4637 mg/kg respectively at 10 minutes contact time. GC has higher SC than the modified forms. The sorption capacity is slightly influenced by the pH and the maximum sorption was observed at pH 6-8. The co-anions do not have much significant effect on SC of all the sorbents. The adsorption pattern follows Freundlich isotherm. In this case too, the thermodynamic factors confirm spontaneous and endothermic nature and the rate of the reaction follows pseudo second order kinetics. The SC of the metal ion follows intraparticle diffusion pattern.

In Cr(VI) ion removal, the maximum SC at 10 minutes for C, PC, CC and GC were found to be 2316, 2812, 3010 and 3770 mg/kg respectively. The pH of the solution slightly influences the sorption capacity of the sorbents and the maximum SC was observed at pH 5-7. The adsorption pattern shows that it follows Langmuir isotherm. The thermodynamic factors confirm spontaneous and endothermic nature of sorption. Pseudo second order kinetics is followed in the rate of the reaction. It also follows intraparticle diffusion pattern.

Both chitin and modified forms of chitin removes copper and iron by adsorption, ion exchange and chelation mechanism while chromium removal follows electrostatic adsorption coupled reduction and complexation mechanism.
Table 4.1 – The SCs of modified chitin

<table>
<thead>
<tr>
<th>S.No</th>
<th>Materials/ Sorbents</th>
<th>Sorption Capacity (mg/kg)</th>
<th>Cu(II)</th>
<th>Fe(III)</th>
<th>Cr(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PC</td>
<td>2810</td>
<td>3774</td>
<td>2812</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CC</td>
<td>3335</td>
<td>3950</td>
<td>3010</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>GC</td>
<td>4035</td>
<td>4637</td>
<td>3770</td>
<td></td>
</tr>
</tbody>
</table>

All the modified forms of chitin showed an enhanced metal sorption capacity than the raw chitin. Among the modified forms grafted chitin possesses relatively higher SC than the other two forms viz., protonated and carboxylated polymers. As is evident from the above table, among the metal ions chitin preferentially removes iron than the other two ions. Similar trend was reported by many authors. \(^{182, 215-217}\)

The field trials indicated that all the sorbents can be utilized for metal ion removal. Though the modified forms showed higher capacity for metal sorption, its flake forms limit its application at the field condition as this form significantly causes pressure drop and hence cannot be utilized for the development of technology.

III.2. Sorption studies of Cu(II), Fe(III) and Cr(VI) using chitosan beads

The results and analysis of the raw and modified chitosan beads viz., protonated Chitosan Beads (PCB), Carboxylated Chitosan Beads (CCB) and grafted chitosan beads (GCB) have been focused in this study.

PCB, CCB and GCB possess higher SC than the raw chitosan beads. Now a days biosorption has become a promising technique in removing toxic ions. Hence abundant biopolymer chitosan has been suitably modified in order to effectively utilize both amino
and hydroxyl groups of chitosan and employed for the metal sorption. As these modified sorbents are inexpensive, stable, selective, effective and eco-friendly, these modified sorbents could be employed in the development of metal ion removal technology.

In the case of Cu(II), metal ion removal the SCs of CB, PCB, CCB and GCB were found to be 1275, 3264, 4363 and 4900 mg/kg respectively after 10 minutes as contact time. The grafted chitosan beads possess higher SC than the C, PC, and CC. The SCs of the modified chitosan were slightly influenced by the pH and the maximum SC was observed at pH 6-8. The adsorption pattern of the sorbents follows Freundlich isotherm. The values of thermodynamic parameters confirm the spontaneous and endothermic nature of metal ion sorption. The rate of the reaction follows pseudo second order kinetics. The sorption of metal ion on the sorbents follows intraparticle diffusion pattern.

In Fe(III), metal ion removal the SCs of CB, PCB, CCB and GCB were found to be 2913, 3533, 3905 and 4203 mg/kg respectively at 10 minutes of contact time. The grafted chitosan beads possess higher SC than the C, PC, and CC. In the case of Fe(III) also, the SCs of the modified chitosan were slightly influenced by the pH and maximum SC was observed at pH 6-8. Freundlich isotherm is followed in the adsorption pattern of the sorbents. Spontaneous and endothermic nature of metal ion sorption is confirmed by the values of thermodynamic parameters. Pseudo second order kinetics is followed in the rate of the reaction and intraparticle diffusion pattern is followed in the sorption of the metal ion.

In Cr(VI), metal ion removal the SCs of CB, PCB, CCB and GCB were found to be 1298, 3239, 3647 and 4057 mg/kg respectively at 10 minutes as contact time. The
grafted chitosan beads possess higher SC than the C, PC, and CC. In the case of Fe(III) also, the SCs of the modified chitosan were influenced by the pH and maximum SC was observed at pH 5-7. Langmuir isotherm is followed in the adsorption pattern of the sorbents. Spontaneous and endothermic nature of metal ion sorption is confirmed by the values of thermodynamic parameters. Intraparticle diffusion pattern is followed in the sorption of the metal ion and pseudo second order kinetics is followed in the rate of the reaction.

As it is in the case of chitin, both chitosan and modified forms of chitosan removes copper and iron by adsorption, ion exchange and chelation mechanism, while chromium mechanism follows electrostatic adsorption coupled reduction and complexation. The effect of co-anions on the SC was found to be negligible and conforms the selectivity of the metal ions.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Materials/ Sorbents</th>
<th>Sorption Capacity (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu(II)</td>
</tr>
<tr>
<td>1</td>
<td>PCB</td>
<td>3264</td>
</tr>
<tr>
<td>2</td>
<td>CCB</td>
<td>4363</td>
</tr>
<tr>
<td>3</td>
<td>GCB</td>
<td>4900</td>
</tr>
</tbody>
</table>

Table 4.2 – The SCs of modified chitosan beads

All the modified forms of chitosan showed an enhanced metal sorption capacity than the raw chitosan. Among the modified forms grafted biopolymers possesses relatively higher SC than the other two forms viz., protonated and carboxylated polymers.
The sorption ability of chitosan is comparably higher than that of chitin. Such trend while studying the sorption of heavy metals has been reported by many authors.²¹,²²,²³ A significant increase in the sorption capacity of the order of three to six times was observed in the removal of dyes by chitosan.²⁴ This is believed to be due to the higher number of free amino groups in the chitosan molecule. This suggests that in chitin and chitosan, the degree of deacetylation, a proportion between amine and acetylamino groups could be a key factor in controlling the sorption of metal ions.

Field trial results indicate that these sorbents could be employed for metal ion removal. All the modified chitosan beads, particularly grafted chitosan bead, showed higher selectivity towards metal sorption. As these sorbents are in the bead form, they can be utilized for the development of sorption technology which would not affect the filtration ability. Since these modified chitosan beads are inexpensive, stable, selective, effective and eco-friendly, these could be employed as promising sorption agents.

III.3. Sorption studies of Cu(II), Fe(III) and Cr(VI) using biopolymeric composites

This chapter presents the result and analysis of polymeric composites viz., nano-hydroxyapatite (n-HAp), nano-hydroxyapatite/chitin (n-HApC) composite and nano-hydraxyapatite/chitosan (n-HApCs) composites. Polymeric composites are a new class of materials with ultrafine phase dimensions. These compounds were prepared by mixing low cost inorganic materials/ exchangers and chitin/chitosan.

The SCs of n-HAp, n-HApC and n-HApCs composites in Cu (II) removal were found to be 4800, 4775 and 4851 mg/kg respectively. The sorption capacity is influenced by the pH and the adsorption pattern follows Freundlich isotherm. The thermodynamic factors confirm spontaneous and endothermic nature of the sorption. The rate of the
reaction follows pseudo-second-order kinetics. The SC of the metal ion follows intraparticle diffusion pattern.

The SCs of n-HAp, n-HApC and n-HApCs composites in Fe(III) removal were found to be 4738, 4800 and 4750 mg/kg respectively. The sorption capacity is slightly influenced by the pH and Langmuir isotherm is followed in the adsorption pattern. In the sorption of Fe(III) too, the thermodynamic factors confirm spontaneous and endothermic nature. The rate of the reaction follows pseudo second order kinetics. Intraparticle diffusion pattern is followed in the SC of the metal ion.

The SC of n-HAp, n-HApC and n-HApCs composites in Cr(VI) removal were found to be 2664, 2869 and 3485 mg/kg respectively. The sorption capacity is slightly influenced by the pH and the adsorption pattern follows Freundlich isotherm. The thermodynamic factors confirm spontaneous and endothermic nature. The rate of the reaction follows pseudo-second-order kinetics. The SC of the metal ion follows intraparticle diffusion pattern. The results of field trials of all the composites indicate that these sorbents can be effectively utilized to remove the metal ions from water.

**Table 4.3 – The SCs of biopolymeric composites**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Materials/ Sorbents</th>
<th>Sorption capacity (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu(II)</td>
</tr>
<tr>
<td>1</td>
<td>n-HAp</td>
<td>4800</td>
</tr>
<tr>
<td>2</td>
<td>n-HApC composite</td>
<td>4775</td>
</tr>
<tr>
<td>3</td>
<td>n-HApCs composite</td>
<td>4851</td>
</tr>
</tbody>
</table>
Though there is no significant increase in the sorption capacity of both chitin and chitosan composites than the n-HAp, these composites have been identified as effective and promising sorbents for field application as these composites could be made into any desirable form like membrane, beads and candles etc. Further, these composites showed higher sorption capacity than chitosan which in turn was higher than chitin. This enhancement in sorption capacity of composites than the respective biopolymers may be due to the combined advantages of both biopolymer and n-HAp.

In chapter III.4, the selectivity of a particular metal ion in the admixture of co-cations was discussed. The preferential adsorption is observed for Fe(III) > Cu(II) > Cr(VI) by all the sorbents and are discussed in terms of ionic potential, ionic radius and solvation of metal ions.
SCOPE FOR FURTHER RESEARCH

Heavy metals are non-biodegradable and form complexes with organics in the environment thereby increasing their mobility in the biota and manifest toxic effects. Heavy metal pollution has been identified as one of the major pollutions in the world. Several materials have been tried for the removal of heavy metals. In the present investigation, the suitability of modified chitin and chitosan/composites for the development of heavy metal removal technology has been highlighted. Definitely such type of research work would pave way to the development of a successful technology. The sorbents chitin, chitosan beads and composites showed a significant selectivity towards metal ions.

However, chitin has been used in its normal flakes form which limits its application in the field for the technology development. Hence the sorption capacity of chitin and its chemical modifications can be studied after making them into useful bead form, which provides good scope for future research work. Though all the sorbents can be regenerated using dilute acids, like HCl, H₂SO₄ etc., the concentration and the volume of acid has to be optimized with respect to a particular type of sorbent and metal ion. Further, these materials have to be experimented in actual field conditions in order to know their stability and optimize the factors like regeneration capacity, fixation of dosage, volume of water to be treated, designing of a model, cost factor, etc., before dedicating the technology to the community.