Chapter 5

SUMMARY AND CONCLUSION
Industrial and residential wastewater containing heavy metals, such as cadmium, chromium, copper, lead, and mercury is polluting lakes, rivers, and sea. It causes health problems in both animals and humans. The removal of heavy metal ions from water would play a vital role in reducing health problems and accelerating the biodegradation process in sludge. Molecular imprinting is an emerging technology for the creation of selective binding sites in synthetic polymers. Many biopolymers are known to have a strong binding on metals, and its use of biopolymers as sorbents for the recovery of valuable metals or toxic metals is significant. A variety of investigations demonstrated that biosorption is a useful alternative to the conventional systems for the removal of heavy metal ions from aqueous solution.

Ion imprinted polymers were first developed for an extraction purpose as sorbents for solid phase extraction applications. A recent and increasing interest now lies in the elaboration of metal ion sensors using IIPs as the sensing phase. Ion imprinted polymers find broad applications as preconcentration and separation matrices for metal ions. Ion selective sensors have the advantages of being simple, rapid, and inexpensive. Although bulk polymerization has been extensively used to produce IIPs in a very easy fashion, it clearly appears that the control of their shaping is a crucial issue.

This research explores the utilization of metal ion imprinted interpenetrating polymer networks as selective metal ion binding agent. The polymers are made specific, by imprinting the corresponding metal ions and can be used in wastewater treatment with a specific heavy metal ion. Non-imprinted polymers were also prepared for comparative study. The macromolecular parameters of the polymer matrix and the structure of the ligand functions have a definite influence in the specific and selective removal of metal ions. The results of the investigations of the metal ion imprinted interpenetrating polymer
networks based on alginic acid and metal ion imprinted polymers based on 4-vinylpyridine are summarized as hereunder.

(i) **Metal ion imprinted interpenetrating polymer networks based on alginic acid**

Metal ion imprinted and non-imprinted polymers were prepared and characterized by spectral and thermal methods. The template metal ions selected in the present study are toxic metal ions such as Pb(II), Cd(II) and transition metal ions such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions. The polymer matrix was obtained by interpenetrating alginic acid which is a natural biopolymer with NNMBAA-crosslinked polyacrylamide. All the polymers were characterized by FT-IR which indicated the involvement of carboxyl group in metal ion binding. Surface morphology of the metal ion bound and unbound polymers were followed by SEM and metal composition was confirmed by XRD and SEM-EDAX analysis which proved the crystalline nature of metal bound polymers. The swelling characteristics were measured as equilibrium water content (EWC) to follow the swellability of the studied systems in water. Swelling of imprinted polymer is higher than non-imprinted polymer and decreased on complexation.

Metal ion binding studies of both imprinted and non-imprinted polymer networks were carried out which led to the identification of optimal binding condition. Binding studies were analysed by UV-vis. and AAS techniques. Binding studies clearly revealed that IIP has much higher sorption capacity compared to non-imprinted polymer and also IIP specifically rebind the imprinted metal ion. Also binding increases with increase in concentration. Specific rebinding can be assessed due to the memory effect of the imprinted polymer. The optimum time for maximum binding of metal ions by imprinted and non-imprinted polymers varies with different template metal ions. For ion
imprinted polymers time taken for maximum binding is more compared to non-imprinted polymers. The target metal ion has to penetrate through the highly crosslinked polymer networks to access the imprinted cavity for binding in IIP while in NIP no such predesigned cavity is present which resulted in non-specific binding. The investigation of pH dependence on metal ion binding revealed that the metal ion uptake increased with increase in pH and decreased after reaching saturation point. The sorption characteristics were assessed by plotting both Langmuir and Freundlich isotherms. In all the cases metal ion binding was in agreement with Langmuir, indicating a monolayer sorption on a heterogeneous surface. The effect of temperature on the sorption process was investigated for the sorption of metal ion upon the IPN. The negative value of free energy change indicates the feasibility and spontaneous nature of sorption process. The value of $\Delta H^0$ was positive indicating that the binding was endothermic in nature and the positive value of entropy change suggested an increase in randomness during the sorption process. The pseudo second-order Lagergren equation was used to describe the sorption kinetics of ion imprinted interpenetrating polymer networks.

The selectivity of the imprinted polymer for metal ion was investigated by rebinding the imprinted metal ion in presence of various competitor metal ions. Some important parameters including sorption capacity, distribution ratio, selectivity factor of metal ion with respect to other ions and relative selectivity factor was calculated. Ion imprinted interpenetrating polymer networks exhibited much higher efficiency in selectivity than non-imprinted polymer networks. The analytical results obtained in these investigations suggested the future potential application of the developed systems in metal ion removal from aqueous solution and also for the selective removal of metal ions from environmental water samples.
(ii) Metal ion imprinted and non-imprinted polymers based on 4-vinylpyridine

The metal ion specificity studies of copper ion imprinted polymer based on TTEGDA- and EGDMA-crosslinked poly(4-vinylpyridine) by template polymerization revealed that the vinylpyridine group of the polymer chains were placed in the coordination geometry of the Cu(II) ion and were fixed during crosslinking polymerization which helped in specific rebinding of imprinted metal ion. The synthesized polymers were characterized by various analytical techniques. The interdependence of nature and degree of crosslinking agent and the binding capacity of copper ion imprinted and non-imprinted polymers towards various metal ions were also investigated and found that IIP specifically rebind Cu(II) ion much higher than that of other metal ions. As the degree of crosslinking increases copper ion binding decreases and TTEGDA-crosslinked system showed high binding capacity. The investigation of dependence of pH of the medium on the specific rebinding of the imprinted metal ion revealed that copper ion uptake increased with increase in pH and decreased. The dependence of time on metal ion binding was also investigated. The selectivity studies from mixture of metal ions proved that IIP selectively bind Cu(II) ion than other metal ions, in both crosslinked systems.

In summary, the investigations made in the present work include the development of metal ion selective ion imprinted polymers which can be successfully applied for the removal of toxic metal ions from environmental samples of water. The tailored systems have memory for initially present metal ions which in turn depend on a number of factors characteristics of polymer matrix. Besides possessing mild imprinting polymerization condition, low price, superior stability and reusability, the imprinted sorbents showed several positive characteristics, such as fast sorption kinetics, high affinity, selectivity and accessibility for metal ions. The nature and degree of crosslinking agent
have a remarkable role in providing stability to the tailored system. Imprinting polymerization is used to make polymers with a high capacity for hazardous as well as transition metal ions for environmental treatment. Imprinting polymerization provides a flexible, new approach that can be used for the removal of a variety of water pollutants. Only the imprinting molecule has to be changed to create different imprinted polymers.