CHAPTER 5

CONCLUSION AND OUTLOOK

Molecular imprinting is an emerging technology which enables us to synthesize the materials with highly specific binding sites towards the target molecules. Molecularly imprinted polymers (MIPs) are a class of highly crosslinked polymer that can bind certain target compound with high specificity. The polymers are prepared in the presence of the target molecule itself as the template. This procedure can be accomplished via either reversible covalent bonding or non-covalent interactions between monomers and imprinting molecules. After removal of the template, the polymer can be used as a selective binding medium for the print molecule. The chemical, mechanical and thermal stability with high selectivity and specificity of the imprinted polymers made them very promising in the reach field. The selectivity of imprinted polymers arises because the polymer synthesized in the presence of a template molecule or ion and a functional monomer. Then, template ions or molecules are removed from the polymer matrix. As a consequence, the ion or imprinted polymer is able to selectively recognize the template ion or molecule from other components in a sample. The selectivity is as a result of the combination of the cavity shape fixing and the exactness of the arrangement of the functional group. The interaction between functional monomer, template and the crosslinker is responsible for this successful imprint.

The foregoing investigations on the development of metal ion selective polymers by metal ion imprinting technology revealed the possibility to design desired system with enhanced selectivity towards the template metal
ion. The study was conducted with optimized 25-65% DVB-, EGDMA- and BDDMA-crosslinked poly(4-vinyl pyridine). The templates used in this study are Cu(II), Co(II) and Ni(II) ions. The developed polymers were characterized by FT-IR, UV-vis., EPR, and SEM-EDAX and powder-XRD spectral analysis. Various factors affecting the binding studies were analyzed and optimized.

The principle of molecular imprinting is based on the preservation of host-guest geometry in the polymer matrix. The spectroanalytical techniques used for characterization are FT-IR, UV-vis., EPR, SEM-EDAX and powder-XRD. The FT-IR spectra of the metal ion imprinted and non-imprinted polymers showed characteristic peaks of the respective crosslinking agent in addition to those of the functional monomer. Electronic spectra provide an accurate and simple method for determining geometry around the transitional metal ions. The absorption maxima of the UV-vis. spectra of DVB-, EGDMA-and BDDMA-crosslinked Cu(II) ion imprinted polymers suggests a tetragonal structure. Whereas for the Co(II) and Ni(II) ion complexes octahedral coordination geometries are observed. The scanning electron microscopy is most widely used technique to study the shape, size, morphology and porosity of polymers. The change in surface morphology of the imprinted and non-imprinted polymers has been investigated using this technique. The chemical composition and metal content of the polymer could be confirmed by SEM-EDAX. The powder-XRD data gives the texture of the imprinted and non-imprinted polymers and it is ideally suited for the characterization and identification of polymers. Powder-XRD data showed the amorphous and crystalline nature of imprinted polymers. The amorphous component suggests a very broad halo peaks. The crystalline parts showed sharp narrow diffraction peaks and this supported
the incorporation of metal ions in the bound imprinted polymer. The EPR parameters of Cu(II) complexes were calculated and the values indicates the tetragonal type geometry of Cu(II) complexes. The bonding parameter ($\alpha^2_{Cu}$) of Cu(II) complexes were calculated by the Kivelson and Neimen equation and the results suggested the covalency of the ligand group with the coordinating Cu(II) ion. Surface area measurements of EGDMA-crosslinked Cu(II) ion imprinted polymers by methylene blue adsorption experiments revealed the formation of high surface area for imprinted polymer than that of non-imprinted polymer.

The swelling characteristics of the polymers in water were investigated. The results revealed the fact that the equilibrium water content (EWC) of the imprinted polymers is higher than that of non-imprinted polymers. The EWC values are low for DVB-crosslinked system due to the rigid and hydrophobic nature. The flexible EGDMA-and BDDMA-crosslinked systems have high swelling properties. The metal ion complexed systems have low swelling properties than the non-complexed systems.

Binding studies of the polymeric systems revealed that the imprinting of metal ions resulted in high specificity and selectivity. The metal ion specificity studies of DVB-, EGDMA- and BDDMA-crosslinked Cu(II), Co(II) and Ni(II) ions imprinted polymers were investigated. In all cases the metal ion imprinted system rebind its own desorbed metal ions specifically than the other metal ions and the amount of metal ions bound was higher than that of the non-imprinted polymer. In contrast to the previous reports, the low crosslinked systems showed high specific binding. Further, the metal ion binding conditions were optimized by effect of concentration, time and pH. The effect of concentration of metal ion solution plays an important role on metal ion rebinding of imprinted and non-imprinted polymers. When the
concentration of template metal ion solution increased the amount of metal ions bound to the polymer also increased. In all cases the amount of metal ions bound by the imprinted polymer is higher than that of non-imprinted polymer. The effect of extent of crosslinking on metal ion binding was also investigated. The results suggests that the Cu(II), Co(II) and Ni(II) ion binding on DVB-, EGDMA- and BDDMA-crosslinked polymers decreases with increase in percentage of crosslinking.

The dependence of time on metal ion binding by DVB-, EGDMA- and BDDMA-crosslinked Cu(II), Co(II) and Ni(II) imprinted and non-imprinted systems was investigated. The pH dependence on the metal ion binding by DVB-, EGDMA- and BDDMA-crosslinked metal ion imprinted and non-imprinted polymers were followed. The adsorption characteristics of EGDMA-crosslinked Cu(II) ion imprinted polymers were studied and the results are in agreement with the Langmuir adsorption isotherm. In the kinetic study, the effect of temperature on metal ion binding by the EGDMA-crosslinked Cu(II) ion imprinted polymer was studied at temperatures between 30 and 60 °C. The obtained results showed that the increase in temperature favors the adsorption of metal ion quantitatively up to a temperature range of 40-50 °C and decreases further. From the results the thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°), entropy change (ΔS°) were determined using the van’t Hoff plots. The results revealed that the metal ion binding is a second order process.

The metal ion selectivity studies of DVB-, EGDMA- and BDDMA-crosslinked Cu(II), Co(II) and Ni(II) ion imprinted and non-imprinted polymers were investigated. The results revealed that the Cu(II) ion
imprinted system selectively rebound Cu(II) ion from a mixture of Cu(II) and Co(II) ions. Similarly the Ni(II) ion imprinted system showed expected selectivity towards Ni(II) ions from a mixture of Ni(II) and Cd(II). In the case of Co(II) ion imprinted polymers, the selective binding was towards Co(II) ion from Co(II) and Ni(II) mixture. Among the various crosslinked systems, the EGDMA-crosslinked system showed high selectivity.

The metal ion imprinted polymers showed enhanced specificity and selectivity towards the metal ion which was used as the template. Thus by metal ion imprinting approach imprinted polymers with high specificity and selectivity towards Cu(II), Ni(II) and Co(II) ions could be developed and optimized. The versatility and flexibility of this technology is very useful as the polymers can be easily tailored to the needs of specific applications. Additionally, since molecular imprinted polymers are stable, and robust, these can be applied to measurements in harsh environments in different areas such as chemical, pharmaceutical, and food industries. The explosive growth of research activity within the field of molecular imprinting is remarkable. Accordingly, we envisage a continued growth in research activity in the area over the coming years and a concomitant increase in the application for the science and technology of molecular imprinting.