2.1 LITERATURE REVIEW

Metal chelating polymers have attracted attention in environmental remediation and separation of trace heavy metal ions from aqueous solutions. Besides, they show good physical, chemical and mechanical properties such as high mechanical strength, adsorption capacity, selectivity, porosity, high surface area, and durability. Heavy metal ion selectivity of a chelating resin is mainly dependent on the nature of the chelating group immobilized on the polymeric backbone (Llosa Tanco et al 2002). These Chelating polymers are normally synthesized by the incorporation of active chelating groups with O, N, and S into a polymeric matrix. Such chelating groups may be incorporated into the repeating units of the polymer matrix or covalently bound to a polymer backbone as pendent groups by the polymerization of suitable monomers. Due to the strong electrostatic exchange between a chelating resin and metal ions or the electrostatic exchange accomplished by a rapid chemical reaction, lead to strong metal ligand bonds. The strength of the chelating interaction is governed by the metal ion properties such as, its electronic configuration, oxidation state, basicity, stereochemistry, and polarization of the ligand on the resin (Zalloum & Mubarak 2008).

Reddy & Reddy (2006) have found that polymers containing azomethine group are most efficient in the removal of metal ions such as Pb(II), Hg(II), Cr(VI) and Cd(II).
Duran et al (2008) investigated adsorption of different heavy metals such as lead, cadmium, chromium and copper ions on poly(VP-PEGMA-EGDMA) beads and suggested that the polymeric adsorbent has higher adsorption capacity than other adsorbents.

Monier et al (2010) has reported that chemically modified wool chelating fiber wool-g-PCA\(\text{H}\) show good adsorption affinity towards Mg(II), Cu(II), and Co(II) ions.

Marin et al (2006) synthesized polyazomethine-ether and investigated the same by elemental analysis and spectroscopic methods (IR, UV, \(^1\)H NMR) and studied their thermal behaviour by differential scanning calorimetry (DSC), optical microscopy, and thermo gravimetical analysis.

Vasanthi & Ravikumar (2007) have synthesized new polyesters having azomethine and phenylthiourea groups in their polymer backbone by interfacial polycondensation method. The resulting polyesters were characterized by viscosity, IR, NMR and TGA analysis.

Kaya et al (2009) have synthesized new polyphenols derived from o-dianisidine and characterized the structures of the obtained polymer compounds by FTIR, UV–vis, \(^1\)H NMR and \(^{13}\)C NMR techniques.


Iwan et al (2010) synthesized aliphatic–aromatic poly(azomethine)s with ester groups and these polymers were characterized by FTIR, \(^1\)H, \(^{13}\)C NMR spectroscopy, and elemental analysis. They have
found the material as thermotropic which can be used in opto(electronic) applications.

Baraka et al (2007) synthesized and characterized Melamine–formaldehyde–diethylenetriaminepentaacetic acid (MF–DTPA) resin, and used them as adsorbent for the removal of Cd(II), Co(II), Zn(II), and Cu(II) ions.

Zalloum and Mubarak (2008) synthesized poly(2-hydroxy-4-acryloyloxybenzophenone) (poly(2H4ABP)) and examined its chelation properties towards divalent heavy metal ions Cu(II), Zn(II), Ni(II), and Pb(II) in aqueous solution under different experimental conditions. Different amounts of crosslinked divinylbenzene was added to the poly(2H4ABP) and its adsorption capacity was compared with the uncross-linked one.

Murugesan et al (2011) studied the removal of Cd(II), Pb(II) and Cu(II) ions from aqueous solution using poly(azomethineamide)s polymer as adsorbent. The newly synthesized polymer has been characterized using NMR, FTIR and SEM analyses. Ji et al (2007) synthesized and characterized a new chelating resin containing bis[2-(2-benzothiazolylthioethyl)sulfoxide]. The adsorption capacities of the resin for Hg(II), Ag(I), Cu(II), Zn(II), Pb(II), Mn(II), Ni(II), Cd(II) and Fe(III) ions has been investigated.

Thermoresponsive polymers, poly(N-isopropylacrylamide) (PNIPAAm), having chelating functionalities have been synthesized and used for the removal of Cu(II), Ni(II), Co(II), and Pb(II) ions (Saitoh et al 2003)

Abia & Asuquo (2006) have used modified and un-modified agricultural waste as adsorbent for the removal of lead and nickel ions from aqueous solution. The synthesized adsorbents were characterized using FTIR, NMR and DSC techniques.
Ahamed et al (2008) have synthesized modified PVC resin and used for the removal of heavy metal ions from waste water. The polymer was characterized using FTIR and NMR techniques. The investigation of variables affecting adsorption such as pH, concentration and time variation studies were carried out.

Ahmetli & Tarlan (2007) studied the effectiveness of two styrene/divinyl benzene (SDB) compounds for the removal of Fe(II) and Fe(III) ions from aqueous solutions. The first compound styrene/divinyl benzene sulfonate (SDB-S) was a commercial sample used as an ion-exchange resin. The second compound was a terpolymer, styrene/divinyl benzene/allyl methacrylate (SDBAM), which was synthesized from the corresponding monomers and used as an adsorbent.

Nasser Arsalani et al (2009) have synthesized amine containing resins using polyacrylonitrile with diethylenetriamine (DTA) or triethylenetetramine (TETA) by a rapid, simple, and economically feasible route. The prepared resins, completely insoluble in water and common organic solvents, which were used to remove Ni(II) ion from aqueous solutions.

Srinivasan & Tharanitharan (2009) synthesised new modified polymeric Duolite XAD-761 resin and used in batch adsorption experiments for the removal of Ni(II) ions.

Emine Malkoc et al (2006) have studied the biosorption capacity of the cone biomass of Thuja orientalis on Ni(II) removal in the batch mode. The biosorption equilibrium level have been determined as a function of contact time, pH, temperature, agitation speed at several initial metal ion and adsorbent concentrations.
Kausar et al (2011) studied the fabrication of high-performance thiourea-substituted poly(thiourea-ether-imide)s (PTEIs) with good retention of thermal properties along with flame retardancy. New aromatic monomer, 4,4′-oxydiphenyl-bis(thiourea) (ODPBT), has been efficiently synthesized and polymerized with various dianhydrides (pyromellitic dianhydride, 3,3′,4,4′-benzophenone tetracarboxylic dianhydride and 4,4′-(hexafluoroisopropylidene)diphthalic dianhydride) via two-stage chemical imidization to fabricate a series of PTEIs.

Oximes are one among the selective chelating agents used to remove number of heavy metal ions. Ebraheem et al (2000) reported that chelation properties of Poly(8-Hydroxyquinoline 5,7-diylmethylene) crosslinked with Bisphenol–A toward La(III), Ce(III), Nd(III), Sm(III) and Gd(III) ions. Shafa-Amry et al (2006) studied the chelating properties of two chelate-forming polymers derived from piperazine and each of benzaldoxime and 2, 4-dihydroxy-benzaldoxime towards certain trivalent lanthanide metal ions in aqueous solution.

Eisazadeh (2008) studied the removal of arsenic from water using polypyrrole and its composites. In their research various adsorbents such as bentonite, activated carbon, and conductive electroactive polypyrrole composites were employed. Conductive polypyrrole composites were prepared using different surfactants such as sodium dodecylbenzenesulfonate, hydroxypropylcellulose, polyvinyl alcohol and polyethylene glycol in the presence of FeCl₃ as an oxidant. The results indicate that the type of adsorbents and surfactants have a great effect on the removal of arsenic.

Moyers & Fritz (1977), anchored two hydroxyiminodiaceticacid functional groups onto benzene ring by condensing resorcinol, m-phenyl-enediamine tetraacetic acid with formaldehyde and used it to separate Co(II)
from Ni(II) in a gravity flow column. Sakaguchi & Nakajima (1986) studied the recovery of uranium with immobilized polyhydroxyanthraquinone.

Polymeric resin obtained by condensing phenol-formaldehyde and piperazine has been used to remove Cu(II) ions from aqueous solution (Hodgkin & Eibl 1985).

Samal et al (1999) synthesised phenolic Schiff base from 4,4’-diaminodiphenylsulphone and o-hydroxyacetophenone with formaldehyde/furfuraldehyde and used for the adsorption of Ni(II) and Cu(II) ions from aqueous solution.

Bhattacharya et al (2008) investigated the adsorption, kinetics and equilibrium studies on the removal of Cr(VI) from aqueous solutions using different low-cost adsorbents.

Bilgili (2006) studied the adsorption behaviour of 4-chlorophenol from aqueous solutions by XAD-4 resin and evaluated the adsorption isotherm, kinetic, and thermodynamic behaviour.

2.2 SCOPE OF THE PRESENT WORK

The present research work aims to develop and synthesize different types of novel chelating polymeric resins bearing O, N, S donor atoms, by condensation polymerization. These resins can effectively co-ordinate with heavy metal ions in aqueous solution. The heavy metal ions that have been chosen for the present investigation are Ni(II), Cd(II), Zn(II), Hg(II), Th(IV). The scope of the present study is as follows:

- To synthesize monomers containing ligands that can act as Lewis base and synthesize novel polyamides (PA-I & PA-II)
and polyesters (PE-I & PE-II) bearing pendent chelating groups from their respective monomers by condensation polymerization

- To establish the presence of various functional groups present in the monomers and polymers by Fourier Transform Infrared (FT-IR) Spectroscopy and confirm their structures using $^1$H and $^{13}$C Nuclear Magnetic Resonance (NMR) Spectroscopy.

- To evaluate the thermal stability of polymers by Thermo Gravimetric Analysis (TGA) and to study the surface morphology and elemental composition of polymers by Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX) spectroscopy respectively.

- To determine the particle size of polymers, and to verify their amorphous nature, by Dynamic Light Scattering (DLS) and X-Ray diffraction (XRD) methods.

- To determine the adsorption capacity of the polymers towards removal of heavy metal ions from aqueous solutions and to study the various parameters that influence the adsorption process viz,
  - Solution pH
  - Initial metal ion concentration
  - Adsorbent (resin) dosage
  - Contact time
  - Temperature
  - Electrolyte
- Adsorption kinetics and equilibrium studies – to determine the rate of adsorption of metal ions onto various polymeric resins with the help of three different kinetics models, namely pseudo-first order, pseudo-second order and intra particle diffusion model and to predict the adsorption mechanism and to determine the maximum adsorption capacity of polymeric resins, using the Langmuir, Freundlich, Sips and Temkin adsorption isotherm models.

- To examine the competitive adsorption of heavy metal ions in a batch manner, and to determine the adsorption capacities of polymers under competitive and non-competitive conditions.

- Thermodynamic studies and desorption studies – to determine the spontaneity and thermodynamic nature (endothermic or exothermic) of the adsorption processes and to regenerate the spent adsorbent, and to evaluate the possibility of its reuse.