CHAPTER - V
METHODS AND MATERIALS

The monomers used, methyl methacrylate, divinyl benzene (Aldrich), ethyleneglycol dimethacrylate, 2-hydroxyethyl methacrylate (Fluka) were purified by low pressure distillation. Polymerisation reactions were done using procedures reported in literature. Chloromethylated polystyrene beads were obtained as gift from Thermax Ltd., Pune. Solvents used were of reagent grade and were distilled and purified by standard procedures. The metal salt solutions were prepared in doubly distilled water. Metal ion concentrations were determined by standard volumetric, complexometric, colorimetric and gravimetric procedures. ESR spectra were recorded on a Varian E-112 ESR spectrometer at room temperature and at liquid nitrogen temperature at SAIF, IIT Chennai. Microanalyses were also performed at SAIF, IIT Chennai. The IR spectra were recorded on a Perkin Elmer 397 spectrophotometer using KBr pellets. The magnetic susceptibility measurements were measured on a Guoy balance at room temperature, using Mercury(II) tetrathiocynato cobaltate(II) Hg[Co(NCS)₄] as the calibrant. Thermal analysis was done using a Schimadzu 2000 TGA V5 thermobalance at Regional Research Laboratory, Thiruvanthapuram. The electronic spectral measurements were done on a Schimadzu model UV-2000 Spectrophotometer using diffuse reflectance technique.
1. Preparation of Divinyl Benzene Crosslinked PMMA Resin

The monomers were washed with NaOH solution (1%, 3 times) and water (3 times) to remove the inhibitors. The crosslinked polymers were prepared by suspension polymerisation. Poly(vinyl pyrrolidone) (150 mg) was dissolved in water (100 ml) and heated to 80-90 °C. The mixture of monomers, MMA (25 g) and DVB (1.32 g) for 2% crosslinked polymer and benzoyl peroxide (150 mg) as initiator were added to the hot solution with vigorous stirring for 6 h. The precipitated polymer was filtered, washed with hot water (20 ml x 3 times), methanol (20 ml x 3 times), acetone (20 ml x 3 times) and dried at 60 °C in vacuum. Polymers with degree of crosslinking 5, 10 and 15 mole percent were prepared by varying the monomer ratio.

Yield: 25.9g.

2. Preparation of Ethyleneglycol Dimethacrylate Crosslinked PMMA Resin

The monomers, MMA and EGDMA were washed with NaOH solution (1%, 3 times) and with water (3 times) to remove the inhibitors. The crosslinked polymers were prepared by suspension polymerisation technique. Poly(vinyl pyrrolidone) (150 mg) was dissolved in water (100 ml) and heated to 80 °C. The mixture of monomers, methyl methacrylate (20 g) and ethyleneglycol dimethacrylate (0.72 g) for 2% crosslinked polymer (mole percent) and benzoyl peroxide (150 mg) as initiator were added to the hot
solution with vigorous stirring. The mixture was heated at 80 °C with stirring for 12 h. The polymer so obtained was filtered, washed with hot water, CCl₄, benzene, ethanol and methanol (20 ml x 3 times) and dried at 60 °C in vacuum. Polymers with degree of crosslinking 5, 10, 15 mole percent were prepared by varying the monomer ratio.

Yield 20.2g.

3. Conversion of Crosslinked Poly(methyl methacrylate) to Poly(2-aminoethyl methacrylamide)

The crosslinked PMMA, (PMMA-DVB and PMMA-EGDMA) resins (5g) were preswollen in acetonitrile and suspended in toluene (30 ml) in an RB flask. Ethylene diamine (15ml) was carefully added and refluxed in an oil bath at 110 °C for about 36 h. The resin was washed with toluene (10ml x 3 times) and then with acetonitrile and water and dried in vacuum. The resin gave a deep blue colour with ninhydrin reagent indicating free-NH₂ groups.

Yield 4g.

4. Estimation of Amine Capacity of PMMA Supported Amines, Poly(2-aminoethyl methacrylamide)

The polymer amine, poly(2-aminoethyl methacrylamide) (200 mg) was suspended in dil. HCl (40 ml, 0.1 N) for 24 h. The resin was then filtered off
and titrated against NaOH solution (0.1 N) using phenolphthalein indicator. From this the value of amine capacity was estimated. Amine capacity of the resin, 4.3 meq/g.

5. Preparation of PMMA Supported Schiff Base Resins I and III (acac based)

The PMMA supported amine, Poly(2-aminoethyl methacrylamide) (2 g) was taken in an R.B. flask. Ethanol (15 ml) was added as the solvent. Acetyl acetone (2 ml) was added and refluxed at 70 °C for 6 h. The resin was filtered, washed with ethanol and methanol (20 ml x 3 times) and dried in vacuum,

Yield 1.9 g.

6. Preparation of PMMA Supported Schiff Base Resins II and IV (2-HAP based)

The PMMA supported amine, poly(2-aminoethyl methacrylamide) (2 g) was taken in an R.B. flask. Ethanol (15 ml) was added as the solvent. 2-Hydroxy acetophenone (1.7 ml) was added and refluxed at 70 °C for 6 h. The resin was filtered, washed with ethanol and methanol (20 ml x 3 times) and dried in vacuum,

Yield - 1.9 g.
7. Estimation of Enol and Phenol Capacities of Schiff Base Resins I-IV

The Schiff base resins (200 mg) were pre-swollen in acetonitrile and were mixed with acetylating mixture (10 ml) containing acetic anhydride and pyridine and were refluxed for 5 h. After acetylation, excess acetic anhydride remaining was hydrolysed to acetic acid by adding water. The liberated acetic acid was then titrated against alcoholic KOH (0.5 N) using phenolphthalein as indicator. A blank was also conducted. The enol and phenol capacities of the resins were determined.

enol capacities-3.1 and 3.2 (meq/g) (Resins I and III)
phenol capacities - 3.4, 3.5 (meq/g) (Resins II and IV)

8. Preparation of PMMA Supported Schiff Base Chelates

Solutions of metal salts of Fe(III), Co(II), Cu(II), Mn(II), Zn(II), Ni(II), Th(IV) and Zr(IV) (0.02 M, 40 ml) were shaken on a mechanical shaker with 500 mg each of the crosslinked PMMA bound Schiff bases at room temperature in aqueous medium and natural pH for 24 h and the metal intake capacity in each case was determined by volumetric, gravimetric and colourimetric procedures.
9. Preparation of Divinyl Benzene Crosslinked PHEMA Resin

The monomers, HEMA and DVB were purified by washing with 1% NaOH solution. After purification the monomers were stored in a refrigerator, Azobisisobutyronitrile (AIBN) was recrystallised from methanol.

The DVB crosslinked PHEMA resin was prepared by suspension polymerisation. HEMA (25 g), DVB (1.09 g), AIBN (150 mg) and benzyl alcohol (25 ml) were mixed in a 250 ml polymerisation flask. A solution of 35% NaCl (80 ml) and IM NaOH (15 ml) containing MgCl$_2$·6H$_2$O (0.8 g) were separately prepared and charged into the flask containing the monomers. The contents were stirred at 500 rpm at 75 °C on a water bath. After 10 h the flask was cooled to room temperature, the polymer beads were collected by filtration and washed thoroughly with methanol to remove Mg(OH)$_2$ and finally with distilled water. The PHEMA beads were dried in vacuum. Yield 26g.

10. Preparation of Ethyleneglycol Dimethacrylate Crosslinked PHEMA Resin

The monomers, HEMA and EGDMA were purified by washing with 1% NaOH solution. After purification, the monomers were stored in a refrigerator. Azobisisobutyronitrile (AIBN) was recrystallised from
methanol. The ethyleneglycol dimethacrylate crosslinked PHEMA resin was prepared by suspension polymerisation. HEMA (20 g), EGDMA (0.62 g), AIBN (150 mg) and Benzyl alcohol (25 ml) were mixed in a polymerisation flask. A solution of 35% NaCl (80 ml) and IM NaOH (15 ml) containing MgCl$_2$•6 H$_2$O (0.8 g) were separately prepared and charged into the flask containing the monomers. The contents were stirred at 500 rpm at 75 °C on a water bath. After 10 h the flask was cooled to room temperature, the polymer beads were collected by filtration and washed thoroughly with methanol to remove Mg(OH)$_2$ and finally with distilled water. The EGDMA crosslinked PHEMA beads were then dried in vacuum.

Yield - 20.4 g.

11. Estimation of Hydroxyl Group in PHEMA Resin

The PHEMA resin (200 mg) was pre-swollen in acetonitrile and was mixed with acetylating mixture (10 ml) containing acetic anhydride and pyridine and was refluxed for 5 h. After acetylation, the excess acetic anhydride remaining was hydrolysed to acetic acid by adding water. The liberated acetic acid was then titrated against alcoholic KOH (0.5 N) using phenolphthalein as indicitor. A blank was also conducted. The hydroxyl group capacity of the resin was determined.

Hydroxyl group capacity, 4.8 meq/g.
12. Conversion of Crosslinked PHEMA Beads to Poly(2-aminoethyl methacrylate resin)-Delepine Reaction

The crosslinked PHEMA resin (11 g) was suspended in DMF (200 ml) Hexamethylene tetramine (11.2 g) and Potassium iodide (13.2 g) were added to this suspension and heated with stirring under reflux at 110 °C in an oil bath for 10 h.

The resin was filtered, washed with 6 N HCl and water. It was then stirred with a solution of NaOH (10%, 15 ml) for 2 h, filtered, washed several times with water and methanol (50 ml x 3 minutes x 4 times) and dried in vacuum to constant weight.

The resins gave a deep blue colour with ninhydrin reagent indicating the presence of free-NH₂ groups. The amine capacity of the resins were estimated by a procedure similar to the one described earlier. Yield 9.9 g, 9.6 g (DVB and EGDMA crosslinked amino resins). Amine capacity of the resins 4.6, 4.7 meq/g (DVB and EGDMA crosslinked amino resins).

13. Preparation of PHEMA Supported Schiff Base Resins V and VII (acac based)

The PHEMA bound amine, poly(2-aminoethyl methacrylate) (2 g) was taken in an RB flask. Ethanol (15 ml) was added as the solvent. 2 ml acetyl acetone was added and refluxed at 70 °C for 6 h. The resin was filtered,
washed with ethanol and methanol (20ml x 3 times) and dried in vacuum.

Yield - 1.8 g, 1.9 g (Resins V and VII)

The enol capacity of the resins were determined by acetylation method as described earlier.

Enol capacities - 3.4 and 3.5 meq/g (Resins V and VII)

14. Preparation of PHEMA Supported Schiff Base Resin VI and VIII (2-HAP based)

The PHEMA bound amine, poly (2-aminoethyl methacrylate) (2 g) was taken in an RB flask. Ethanol (15 ml) was added as the solvent. 2 ml 2-hydroxy acetophenone was added and refluxed at 70 °C for 6 h. The resin was filtered, washed with ethanol and methanol (20ml x 5 times) and dried in vacuum. Yield - 1.9 g.

The phenol capacity of the Schiff base resins VI and VIII were determined by acetylation method. Phenol capacity, 3.6 and 3.4 meq/g (Resins VI and VIII)

15. Preparation of PHEMA Supported Schiff Base Chelates

Solutions of metal salts of Fe(III), Co(II), Ni(II), Cu(II), Mn(II), Zn(II), Th(IV) and Zr(IV) (0.02 M, 40 ml) were shaken on a mechanical shaker with 500 mg each of the crosslinked PHEMA bound Schiff bases at room
temperature in aqueous medium and natural pH for 24 h. The metal intake capacity in each case was estimated by standard volumetric, gravimetric and colorimetric procedures.


A weighed amount of Chloromethyl polystyrene resin (300 mg) was heated with pyridine (3 ml) in a Kjeldahl flask for 4 h at 100°C. It was quantitatively transferred to a 250ml conical flask containing 50% acetic acid (30 ml). Conc. HNO₃ (5 ml), was added, followed by slow addition of AgNO₃ (10 ml, 0.1 N), during magnetic stirring. The suspension was mixed well. The excess of Ag NO₃ was back titrated with standard ammonium thiocyanate solution using ferric alum as indicator. A blank was also conducted. The chlorine capacity of the Chloromethyl polystyrene was thus determined. Chlorine capacity - 4.2 meq/g.

17. Conversion of DVB Crosslinked Chloromethylated Polystyrene Resin to Aminomethyl Polystyrene (Delepine Reaction)

The crosslinked Chloromethylated PS resin (11 g) was suspended in DMF (200 ml). Hexamethylene tetramine (11.2 g) and potassium iodide (13.2 g) were added to this suspension and heated with stirring under reflux at 110 °C in an oil bath for 10h. The resin was filtered, washed with 6 N HCl.
It was stirred with a solution of NaOH (10%, 15 ml) for 2 h, filtered, washed several times with water and methanol (50 ml x 3 minutes x 4 times) and dried in vacuum to constant weight.

Yield 10.2 g. Amine capacity 4.1 meq/g.

18. Preparation of PS Supported Schiff Base Resin IX (acac based)

The PS immobilised amine, aminomethyl polystyrene (2 g) was taken in an R. B. Flask. Ethanol (15 ml) was taken as solvent. 2 ml acetyl acetone was added and refluxed at 70°C for 6 h. The resin was filtered, washed with ethanol and methanol (20 ml x 3 times) and dried in vacuum.

Yield 1.8 g.

The enol capacity of the Schiff base resin (IX) was estimated by acetylation method using acetic anhydride, Enol capacity, 3.2 meq/g.

19. Preparation of PS Supported Schiff Base Resin X (2-HAP based)

The PS anchored amine, aminomethyl polystyrene (2 g) was taken in an R.B. flask. Ethanol (15 ml) was added as the solvent. 2ml 2-hydroxy acetophenone was added and refluxed at 70°C for 6 h. The resin was filtered, washed with ethanol and methanol (20 ml x 3 times) and dried in vacuum. Yield 1.9 g.
The phenol capacity of the resin (X) was determined by acetylation method. Phenol capacity - 3.4 meq/g.

20. Preparation of PS Supported Schiff Base Chelates

Solutions of metal salts of Fe(III), Co(II), Cu(II), Ni(II), Mn(II), Zn(II), Th(IV) and Zr(IV) (0.2 M, 40 ml) were shaken on a mechanical shaker with 500 mg each of crosslinked PS immobilised Schiff bases at room temperature in aqueous medium and natural pH for 24 h and the metal capacity in each case was estimated by volumetric, gravimetric and colorimetric procedures.

21. Preparation of Divinyl Benzene Crosslinked Polyacrylamide Resin

Acrylamide (10 g) was dissolved in a mixture of chloroform and ethanol (2:1 v/v). Purified DVB (1.09 g) and benzoyl peroxide (50 mg) were added and the contents were heated over a steam bath for about 2 h with constant stirring. The solid polymer separated out was filtered and washed with benzene and toluene (20 ml x 5 times each) and finally with methanol. Yield 8.2 g.

22. Conversion of Polyacrylamide into Poly(2-aminoethyl acrylamide)

The DVB crosslinked polyacrylamide resin (10 g) was refluxed in an RB flask with ethylene diamine (15 ml) and toluene (20 ml) at 110 °C for
about 20 h with constant stirring. The product was collected by filtration, washed with toluene (20 ml x 5 times) and finally with methanol. A test portion of the resin on treatment with ninhydrin reagent gave a deep blue colour characteristic of free amino group.

Yield - 9.9 g.

23. Estimation of Amino Group Capacity of Poly(2-Aminoethyl acrylamide)

The polymer bound amine, poly(2aminoethyl acrylamide)(200 mg) was suspended in dil. HCl (40ml, 0.1 N) for 24 h. The resin was filetered off and titrated against NaOH solution (0.1 N) using phenolphthalein indicator. From this the amine capacity was estimated. Amino group capacity of the resin, 1.52 meq/g.

24. Preparation of Polyacrylamide Supported Schiff Base Resin XI (Salicyldehyde based)

Poly(2-aminoethyl acrylamide) (5 g) was refluxed with salicylaldehyde (5 g) in ethanol (25 ml) in an RB flask for 2 h. The product obtained was washed with methanol (20 ml x 10 times) and finally with ethanol and dried in vacuum.

Yield 5.7 g.
25. Preparation of Polyacrylamide Supported Schiff Base Resin XII
(2-Hydroxy naphthaldehyde based)

Poly(2-aminoethyl acrylamide) (5 g) was refluxed with 2-hydroxy naphthaldehyde (5 g) in a mixture of hot methanol and ethanol (25 ml each) in an R.B. flask for 6 h. The product obtained was washed with methanol (20 ml x 10 times) and dried in vacuum.

Yield 6.2 g.

26. Estimation of Phenol Group Capacities of Schiff Bases XI and XII

Phenol capacities of the Schiff base resins XI and XII were determined by acetylation method. The Schiff base resins (200 mg) was pre-swollen in acetonitrile and was mixed with acetylation mixture (10 ml) containing acetic anhydride and pyridine and was refluxed for 5 h. After acetylation, excess acetic anhydride remaining was hydrolysed to acetic acid by adding water. The liberated acetic acid was then titrated against alcoholic KOH (0.5 N) using phenolphthalein as indicator. A blank was also conducted. The phenol capacities of the resins (XI and XII) were estimated.

Phenol Capacities, 3.4 and 3.3 meq/g.
27. Preparation of PA Supported Schiff Base Chelates

Solutions of metal salts of Fe(III), Co(II), Cu(II), Mn(II), Zn(II), Ni(II), Th(IV) and Zr(IV) (0.02M, 40 ml) were shaken on a mechanical shaker with 500 mg each of the crosslinked PA immobilised Schiff bases X1 and XII at room temperature and natural pH for 24 h and the metal intake capacity in each case was estimated by volumetric, gravimetric and colorimetric procedures.

28. Estimation of Iron

The residual Fe$^{3+}$ was estimated both by volumetric analysis and colorimetry. In titration method, the reduction of Fe$^{3+}$ to Fe$^{2+}$ was effected by SnCl$_2$. The reduced Fe$^{2+}$ was determined, by titration with K$_2$Cr$_2$O$_7$ (0.01 N) using N-Phenyl anthranillic acid as internal indicator.

In colorimetric procedure, 2 ml from a definite made up volume of iron filtrate was taken in a 100 ml standard flask and con HNO$_3$ (2 ml) was added. Ammonium thiocynate (5 ml, 2M) was added to develop the colour. The solution was made upto 100 ml. The absorbance was measured using a photoelectric colorimeter at 480 nm. The concentration of the solution was determined in comparison with values on a reference curve.
29. Estimation of Cobalt

The cobalt filtrate was made up to 250 ml. Definite volume (20 ml) of the solution was pipetted out into a conical flask. Excess of standard EDTA solution (20 ml, 0.02 M) was added followed by 0.5 ml NH₄Cl - NH₄OH buffer to maintain pH at 7. The excess of EDTA was back titrated against standard ZnSO₄ solution (0.02M) using Eriochrome black-T indicator. The end point was the color change from blue to violet.

30. Estimation of Zinc

The Zn filtrate was made up to 250 ml. Definite volume (20 ml) of this solution was pipetted out into a conical flask. The solution was diluted to 100 ml with deionised water. NH₄OH-NH₄Cl buffer (2 ml, pH=10) was added. The solution was titrated against standard EDTA solution (0.01M) until the colour changed from wine red to blue.

31. Estimation of Nickel

A back titration procedure was adopted for the estimation of Nickel. Definite volume (20 ml) of the made up nickel ion filtrate was added to known excess (30 ml) of standard EDTA (0.01 M). The solution was diluted to 200 ml with deionised water. Aqueous NH₄OH - NH₄Cl buffer (4 ml, pH=10) was added. Eriochrome black-T indicator (30-40 mg) was added.
The excess EDTA remaining was titrated with standard 0.01M Zn\(^{2+}\) solution until the colour changed from blue to wine red.

### 32. Estimation of Copper

Definite volume (20 ml) of made up copper ion filtrate was pipetted into a conical flask. The mineral acid remaining, if any was neutralized by adding dilute solution of ammonium hydroxide in drops until a faint permanent precipitate was formed. The precipitate was dissolved in very dilute acetic acid (1 or 2 drops), KI solution (10 ml, 10%) was added. The liberated iodine was titrated using standard thiosulphate solution (0.01N) using starch as indicator added towards the end point.

### 33. Estimation of Manganese

Hydroxylamine hydrochloride (0.5 g) was added to the Manganese ion filtrate and gently warmed. Requisite amount of dilute NaOH was added to neutralise the solution. It was made up to a definite volume. 20 ml of the solution was pipetted and to it, 5 ml of triethanol amine and 3ml of ammonium chloride-ammonium hydroxide buffer solution was added. It was titrated against standardised EDTA solution (0.02M) using Eriochrome black-T indicator till the colour changed from wine red to blue.
34. Estimation of Thorium

Definite volume of the made up metal ion solution residual metal ion solution (20 ml) was pipetted into a conical flask. The solution was diluted with deionised water (25 ml). The pH of the solution was adjusted to 2-3 by the addition of dil. HNO₃ (2.5 ml, 0.5M) Xylenol orange indicator (3 drops) was added and the solution was titrated with EDTA (0.01 M) until the colour changed from red to lemon yellow.

35. Estimation of Zirconium

The residual Zirconium ion solution was concentrated by evaporation. Freshly prepared diammonium hydrogen phosphate (10%) solution was added in 50-100 fold excess. The solution was diluted to 300 ml and boiled for a few minutes. It was digested on a water bath for 15-30 minutes and was cooled to about 60°C. The solution containing the precipitate was filtered through a quantitative filter paper (Whatman 40). The precipitate was washed with sulphuric acid (150 ml 1 M) containing 2.5 g diammonium hydrogen phosphate and then with cold ammonium nitrate solution (5%) until the filtrate was sulphate free. The precipitate was dried at 120°C and finally ignited for 2 h and weighed as Zr P₂O₇.
36. Effect of pH

Complexation experiments were carried out with different resins for different metal ions Fe(III), Co(II), Ni(II), Cu(II), Zn(II). The complexation was carried out in the pH range 2 to 5.5 for metals like Co(II), Ni(II), Cu(II) and Zn(II). In the case of Fe(III) the study was limited in the pH range 1-3 so as to avoid metal hydroxide precipitation.

37. Effect of Temperature

The study of the influence of temperature was done within a range of 30 to 70 °C. The swollen resins were equilibrated with different metal ions at 30 °C, 50 °C and 70 °C in each case determining the residual metal ion concentration. The metal intake by the polymeric ligand at various temperatures were calculated.

38. Effect of Solvent

Metal complexation in different solvents like DMF, THF, dioxane, acetonitrile, ethanol and methanol were carried out. The polymer was preswollen in a definite volume (20 ml) of solvent and was shaken (12 h) with various metal ions (40 ml, 0.02M). The metal intake by the polymer was determined by standard analytical methods.
39. Adsorption of Metal Ions on Crosslinked PS and PHEMA Schiff Base Resins

The adsorption experiments were done with Cu(II) and Co(II) on the 10% PMMA-DVB and PHEMA-DVB Schiff base resins respectively.

Different volumes of the metal ions Cu(II) and Co(II) (4 ml, 8 ml, 12 ml, 16 ml, 20 ml) of definite concentrations (0.02M) were taken in conical flasks containing 1 g each of the polymer ligand. Distilled water of varying volume 16 ml, 12 ml, 8 ml and 4 ml respectively were added to these flasks, so that the final volume of the solution was 20 ml in each of the flasks. The resulting solution was stirred for a period of 10 h, so that equilibrium of the metal ion with the resin was attained. 5ml portions of the clear supernatant liquid were analysed for determining the equilibrium metal ion concentration (Ce). The metal ion concentration (Co-Ce) was determined in each case by calculating the metal ion adsorbed by 1g of the resin. The metal ion adsorption at different concentrations were processed, so as to fit in Langmuir and Freundlich adsorption isotherms. This was done by plotting Ce/ (x/m) vs Ce or ln (x/m)/Ce vs x/m (for Langmuir adsorption isotherms) and log x/m Vs log Ce (for Freundlich adsorption isotherm). The adsorption experiments were done at 30 °C and 50 °C with the metal ions on 10% PMMA-DVB and 10% PHEMA-DVB Schiff base resins.
40. Kinetics of Complexation

The various metal ions (20 ml, 0.02 M) were equilibrated with crosslinked PMMA, PHEMA and PS Schiff base resins (0.5 g) for a period of 6-24 h at an optimum pH. The time taken for maximum metal intake was determined by analysing the residual metal ion concentration.

41. Batch Uptake Experiments

The different Schiff base resins of PMMA-DVB, PHEMA-DVB and PS-DVB (0.5 g) were equilibrated (12 h) with different metal ion pairs (40 ml, 0.02 M) at 30 °C in separate experiments at an optimum pH. The capacity of each of the resins were determined by analysing the residual metal ion concentrations.

42. Column Breakthrough Experiments

The chelating resins of PMMA-DVB, PHEMA-DVB and PS-DVB were preswollen and charged into a glass column (30 cm x 1.2 cm diameter) as a slurry. The column was uniformly packed without any air bubbles. The metal solution (different volumes, 0.02 M) at an optimum pH was poured continuously into the column at the rate of 2 cm³ per minute. The addition was continued to have maximum complexation.
HCl of lower concentration (0.02, 0.04 M etc.) was added as eluent to remove the first component. The second component was eluted with HCl of higher concentration (0.2, 0.35 M) followed by washing the column. The eluents were collected quantitatively and assayed to determine the component metal ions.

43. Oxidation of Substituted α-Phenyl ethanols

The substituted α-phenyl ethanols (0.01 mol) were refluxed at 60 °C with \( \text{K}_2\text{Cr}_2\text{O}_7 \) (0.005 mol) in acetonitrile (20 ml) in the presence and absence of polymer (PMMA-DVB, PHEMA-DVB, PS-DVB) anchored Schiff base Mn(II) chelate catalyst (200 mg). The reaction was monitored by TLC. After completion of the reaction the mixture was washed several times with acetonitrile and the products extracted into it. The combined extract was concentrated and the products obtained were dried in vacuum. The conversion of alcohols to carbonyl compounds was ascertained by FTIR and \(^1\)HNMR.

44. Kinetics of Oxidation of Differently Substituted α-Phenyl ethanols Using Polymer Supported Schiff Base Chelates

α-phenyl ethanol or substituted α-phenyl ethanol (1 mmol), \( \text{K}_2\text{Cr}_2\text{O}_7 \) (0.005 mol) and polymer anchored Schiff base Mn(II) chelate catalyst (200 mg) was added to the alcohol and shaken well at 30 °C. An aliquot of
the solution (1 ml) was withdrawn after regular intervals of time, and the concentration of the ketone formed was measured spectrophotometrically. The experiment was repeated at different intervals of time and at refluxing temperature. The rate constant for the reaction was calculated and the kinetic parameters computed.

45. Oxidation of Ascorbic acid to Dehydroascorbic acid by Polymer Supported Metal Chelate Catalysts

A 1 x 10^{-3} mol dm^{-3} solution of ascorbic acid was prepared in water afresh. A 1:1 mixture of methanol and water was used as the solvent. The catalyst concentration was 1.0 x 10^{-6} mol. All kinetic runs were carried out at 27°C. Requisite amounts of all the reagents except ascorbic acid were taken in a reaction bottle. The required amount of ascorbic acid was added to the bottle. The course of the reaction was monitored by following the absorbance of ascorbic acid at 265 nm where it has maximum absorbance and all other substances present in the reaction have negligible absorbance. The kinetic run was performed without the catalyst and then with various polymer anchored chelate catalysts of Cu(II), Fe(III) etc. The solution was transferred to the cuvet using a syringe. The kinetic runs was also performed with varying amounts of ascorbic acid in excess in the range 2.0 - 20.0 x 10^{-5} mol dm^{-3} at constant catalyst concentration of 1.0 x 10^{-6} mol dm^{-3}. 