APPLICATIONS OF FUNCTIONALIZED POLYMERS AS METAL ION EXTRACTANTS AND CATALYSTS

BY

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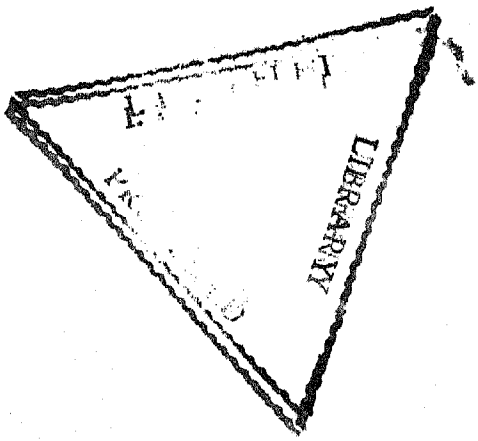

CERTIFICATE

This is to certify that the thesis entitled **"APPLICATIONS OF FUNCTIONALIZED POLYMERS AS METAL ION EXTRACTANTS AND CATALYSTS"** being submitted by **Rita Pathak** to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. Rita Pathak has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

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Rita Pathak

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ABSTRACT

A brief review of previous work, involving various types of chelating ligands and polymeric supports used is described in the first chapter. The use of functionalized polymers having transition metal complexes as catalysts for oxidation reaction has been studied. The scope of the present work has been indicated at the end of this chapter.

Second chapter of the thesis gives the details about the nature and source of various starting materials, namely, metal salts, ligands and polymer employed in the synthesis of homogeneous and anchored metal complexes. General method for functionalization of poly-styrene divinyl benzene and the preparation of homogeneous and anchored metal complexes have also been described in this chapter along with the procedure for the oxidation of 2,6-di-tert-butyl phenol. A brief account of various physico-chemical methods employed in characterizing the catalysts and oxidation products are also given.

Third chapter deals with the synthesis and analytical properties of XAD_4-1-hydrazinophthalazine resin[1]. The resin has been characterized on the basis of infrared spectral studies and elemental analysis. Sorption behaviour of various

metal ions [Copper(II), Nickel(II), Cobalt(II), Zinc(II), Iron(III), Chromium(III), Lead(II) and Cadmium(II)] was studied as a function of pH. Concentration of Cu(II), Ni(II), Co(II), Fe(III), Cr(III), Pb(II) and Cd(II) was monitored by flame atomic absorption spectrometry. Results of various experiments like optimum pH of metal ion uptake, resin capacity, pH dependence of trace metal ion uptake and equilibration time are discussed. Based on these studies, methods for preconcentration and separation of some metal ions were developed of which the one of separation of Fe(III) from some other metal ions is more interesting. Both batch as well as column techniques were used. Recoveries of metal ions were also checked in the presence of excess amounts of sodium(I), magnesium(II) and calcium(II) salts. XAD_4-1-hydrazino-phthalazine resin was also checked for its stability towards acids and bases. The chelating ion exchange resin was used for the separation of metal ions in some real samples.

Fourth chapter describes the synthesis, characterization and analytical properties of XAD_4- p-tert-butyl-calix[4]arene resin. Sorption behaviour of Copper(II), Nickel(II), Zinc(II), Cobalt(II), Cadmium(II), Lead(II), Iron(II), Uranium(VI), Thorium(IV), Lanthanum(III), Terbium(III) and Neodymium(III) as a function of pH has been studied on this resin . Concentration of Lanthanum(III), Neodymium(III),

Chapter six deals with the catalytic activity of anchored metal complexes[3]. The oxidation of 2,6-di-tert-butyl phenol with tert-butylhydroperoxide (Bu^tO_2H) has been studied using polymer (XAD-4) anchored salicylaldoxime (sal-H), 1,3-propylene-bis-salicylaldimine (salpen) and o-phenylene-bis-salicylaldimine (salphen) complexes of molybdenum and vanadium. The predominant products formed in the oxidation reactions were 2,6-di-tert-butyl benzoquinone (BQ) and 3,3'-5,5'-tetra-tert-butyl diphenoquinone (dPQ), whereas with some only 2,6-di-tert-butyl benzoquinone was formed. The effects of varying the ligand, metal and the support on the catalytic activity in the oxidation of 2,6-di-tert-butyl phenol have been studied. It also describes the efficacy of the catalyst after recycling.

Summary and further scope of the work have been described in the seventh chapter.

References

1) R.Pathak and G.N.Rao, *Talanta,* 1997, **44**, 1447.

2) R.Pathak and G.N.Rao, *Anal. Chim. Acta*, 1996, **335**, 283.

3) R.Pathak and G.N.Rao, *J. Mol. Catal.*, 1997, in press.

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