

## Synthesis, Characterization and Metal Ion Binding Capacities of Resin Derived From P-Nitro Phenol, Hexamine and Formaldehyde

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### ABSTRACT

A chelating ion exchange terpolymer resin p-NPHXF was synthesized by the condensation of p-nitro phenol and hexamine using formaldehyde as a cross linking agent at  $140 \pm 2^\circ\text{C}$  in 2:1:4 molar ratios in presence of glacial acetic acid as catalyst. The resin was characterized by FTIR and elemental analysis. Ion exchange study was carried out with  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  by batch equilibrium method.

**KEYWORDS:** Terpolymeric resins, batch equilibrium method, effect of electrolyte, cadmium, lead.

### Introduction:

Pollution is the unsought, unexpected and unforeseen consequences of the entire phenomena of civilization (WHO 1972). Heavy metal ions dissolved in water are one of the most pollutants of the environment as it accumulates in living tissues, causing many harmful effects. Many industries are responsible for polluting the environment with heavy metal ions contained in their waste water. The effluent generated by industries as petroleum refineries, non-ferrous metal works, aircrafts plating, etc. generally have a complex composition which includes metals (ions or complexes), suspended solids and other components. Many methods have been developed for the removal of metal ions such as electro deposition, co-precipitation and solvent extraction. However the metal ion removal by chelating ion exchange resin using Batch equilibrium method has gained rapid acceptance because of its wide variety of sorbent phases, high degree of selectivity, high loading capacity and enhanced hydrophilicity<sup>1,2,3</sup>.

The extraction of metal ions using chelating ion exchange resins is a green analytical method since it does not involve the use of toxic chlorinated organic solvents, which are very frequently used in conventional liquid-liquid extraction technique or other methods<sup>4</sup>. The main objective of the most of the research works on chelating resins is preparation of insoluble functionalized polymers which can provide more flexible working conditions together with good stability and high capacity for certain metal ions<sup>5,6,7</sup>. The interest in this type of chelating resins are due to the rapid adsorption of metal ions, higher selectivity and less swelling, in comparison with the analogous organic polymers<sup>8,9</sup>.

Polymeric chelating ion exchange materials open a wide hope of opportunities in industrial, environmental and biological application owing to their metal ion exchange selectivity and low cost of production and easy regeneration. Terpolymer plays a major role in fulfilling the task as chelation ion-exchange resin<sup>4,10,11,12</sup>. Terpolymers find very useful applications as adhesives, high temperature flame resistant fibres, coating materials, semiconductors, catalysts and ion exchange resins. Resins synthesised by condensation of a mixture of phenol or hydroxyl benzoic acid with formaldehyde and various amines have been reported. The metal ion uptake

increases with increasing mole proportions of copolymer synthesised from substituted benzoic acid.

A number of terpolymers derived from phenol derivatives have been studied and reported along with their chelating ion-exchange properties. For example, Karunakaran et al.<sup>13</sup> have synthesized terpolymer from *o*-nitrophenol-thiourea-formaldehyde and Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> were used for chelation. Das<sup>14</sup> has derived copolymer from thiosemicarbazone derivatives of phenolic compound. Terpolymers of 8-hydroxy quinoline-formaldehyde-resorcinol/catechol were reported by Shah et al.<sup>15,16</sup> and chromatographic column separation for various metal ions such as Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> have carried out using the quinoline base resins. Mubarak et al.<sup>17</sup> have studied the chelation behaviour of the phenolic-formaldehyde polymers, poly(2,4-dihydroxybenzoic acid-3,5-dimethylene), poly(2-hydroxybenzoic acid-3,5-dimethylene) and poly(3-hydroxybenzoic acid-4,6-dimethylene) towards the trivalent lanthanide metal ions such as La<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup> and Tb<sup>3+</sup> by a static batch equilibrium technique at 25°C as a function of contact time, pH, and concentration. Polymer supported reagents<sup>18</sup> containing various ligands have been studied for their selective complexation towards various metal ions. Dabrowski et al.<sup>19</sup> have efficiently removed trace impurities and toxic metals from industrial waste water by various ion exchangers. *o*-Nitro phenol and thiourea with para-formaldehyde copolymer was identified as an excellent cation exchanger for Zn<sup>2+</sup> and Co<sup>2+</sup> ions<sup>20</sup>.

The present work deals with the synthesis of a terpolymer derived from *p*-nitro phenol, hexamine and formaldehyde. The synthesised polymer is characterized by elemental analysis and spectral studies (FTIR). The metal ion uptake capacity of terpolymer resin by Batch equilibrium method for Pb<sup>2+</sup> and Cd<sup>2+</sup> ions in different electrolytes and different concentrations are examined.

## Materials and Methods:

### Synthesis:

The *p*-NPHXF terpolymer resin was synthesized by the solution condensation polymerization *p*-nitro phenol (0.2 mol) and hexamine (0.1 mol) with formaldehyde (0.4 mol) in glacial acetic acid medium at 140°C ± 2 °C in an oil bath for 6 h<sup>21</sup>. The resultant product was then cooled, poured into crushed ice with constant stirring and left overnight. The resin thus obtained was separated and washed with warm water, ethanol and ether and air dried. The yield of the terpolymer was found to be 82%. The dried resin sample was finely grounded and sieved to obtain uniform particle of 100 mesh size and stored in a polyethylene container. The proposed structure of *p*-NPHXF terpolymer resin is shown in Fig 1.

This sieved resin was then characterized using different instrumental analysis techniques and was used for all of the experiments during the research period. The solubility tests of resin in different solvent were performed at room temperature with intermittent shaking. The resin was found to be insoluble in all common organic solvents like acetone, ethanol, benzene, DMF, DMSO, chloroform etc. Infra-red spectra of the synthesized resin sample had been obtained using KBr pallets on a Perkin-Elmer FTIR spectrophotometer. The FTIR spectrum is shown in Fig. 2. The elemental analysis was carried out on Elementar- Vario EL III elemental analyser. The results of elemental analysis are in good agreement with calculated values of %C, %H and %N.

**Metal ion binding capacity of resin:**

The synthesized p-NPHXF terpolymer (25 mg) was taken in a pre-cleaned glass bottles with each of the electrolytes (25 mL) such as KCl, KNO<sub>3</sub>, KI and K<sub>2</sub>SO<sub>4</sub> in different concentrations viz. 0.01, 0.05 and 0.1 M. The pH of the suspensions was adjusted to the desired value by adding required amounts of either 0.1 M HCl or 0.1 M NaOH solutions. The suspensions were mechanically stirred for 24 h at 25°C for the swelling of the terpolymer. To each suspension, 0.1 M of specific metal ion solution (2 mL) was added and vigorously stirred for another 24 h at 25°C. The mixture was then filtered off and washed with distilled water. The filtrate and the washings were collected and then the amount of metal ion was estimated by titrating against standard Na<sub>2</sub>EDTA solution. A blank experiment was also performed following the same procedure without the polymer sample. The amount of metal ions taken up by the polymer in the presence of a given electrolyte can be calculated from the difference between the actual titration value and that of the blank.

**Results and discussion:****Spectral characterization of resin:**

The FTIR spectrum of the resin is shown in Fig. 2. A strong band at 3450 cm<sup>-1</sup> is due to the -OH of phenolic group and a band at 3074 cm<sup>-1</sup> is due to the presence of -NH group. A band at 2924 cm<sup>-1</sup> is due to the methylene group (-CH<sub>2</sub>). The band at 1518 cm<sup>-1</sup> can be assigned to -C=C and at 1338 cm<sup>-1</sup> is due to -NO<sub>2</sub> group. A sharp single band at 755 cm<sup>-1</sup>, which can be assigned to the presence of 1,2,3,4-tetra substituted benzene ring<sup>22</sup>, confirms the polymerization of monomers.

**Elemental analysis:**

Theoretical percentage of carbon, nitrogen and hydrogen content of the resin were calculated from the general formula (C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>O<sub>6</sub>) of the repeating unit of the probable structure (Fig 1). Table 1 show that the results of the elemental analysis are in good agreement with calculated values. The elemental analysis results are in support of the proposed structure of the resin presented in Fig 1.

**Metal ion binding capacity:**

The chelating ion-exchange property of the p-NPHXF terpolymer resin was measured by batch equilibrium method involving Pb<sup>2+</sup> and Cd<sup>2+</sup> ions in various electrolytes viz. KCl, KNO<sub>3</sub>, KI and K<sub>2</sub>SO<sub>4</sub> with different concentrations of 0.01, 0.05, and 0.1 M. The results are presented in Table 2.

The increase in the metal ion uptake with the increase of concentration may be explained on the basis of the stability constants of the complexes. From the results, it is observed that the amount of uptake of metal ion by the terpolymer resin increases with the increasing concentration of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and I<sup>-</sup> and decreases with the increased SO<sub>4</sub><sup>2-</sup> concentration. This may be due to the sulphate ion forming strong chelates with metal ions, while other anions form weak chelates. The influence of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and I<sup>-</sup> ions is less than that of SO<sub>4</sub><sup>2-</sup> ion on the position of the equilibrium of metal chelates.

**Conclusion:**

p-NPHXF terpolymer was synthesized by solution condensation polymerisation technique in acid medium. The structure of the resin was confirmed by spectral studies. From the batch equilibrium studies, the resin has good binding capacity with the selective metal ions and proved as an excellent ion-exchanger.

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Table 1: Elemental analysis results of p-NPHXF

Element	Calculated (%)	Found (%)
Carbon (C)	53.33	53.29
Hydrogen (H)	4.40	3.911
Nitrogen (N)	11.02	10.30

Table 2: Metal ion uptake of p-NPHXF terpolymer resin.

Metal ions	Conc. of electrolytes (mol L <sup>-1</sup> )	Metal ion uptake in presence of electrolyte (mg)			
		KI	KNO <sub>3</sub>	KCl	K <sub>2</sub> SO <sub>4</sub>
Pb <sup>2+</sup>	0.01	5.18	5.05	4.50	3.36
	0.05	25.9	15.54	11.9	2.08
	0.1	36.26	18.65	15.2	1.49
Cd <sup>2+</sup>	0.01	2.81	5.62	4.16	2.09
	0.05	5.62	8.99	5.62	1.54
	0.1	8.43	10.12	8.43	0.90

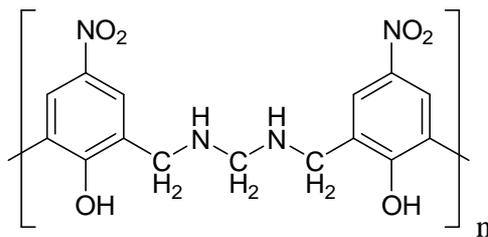


Fig. 1: Proposed structure of polymer

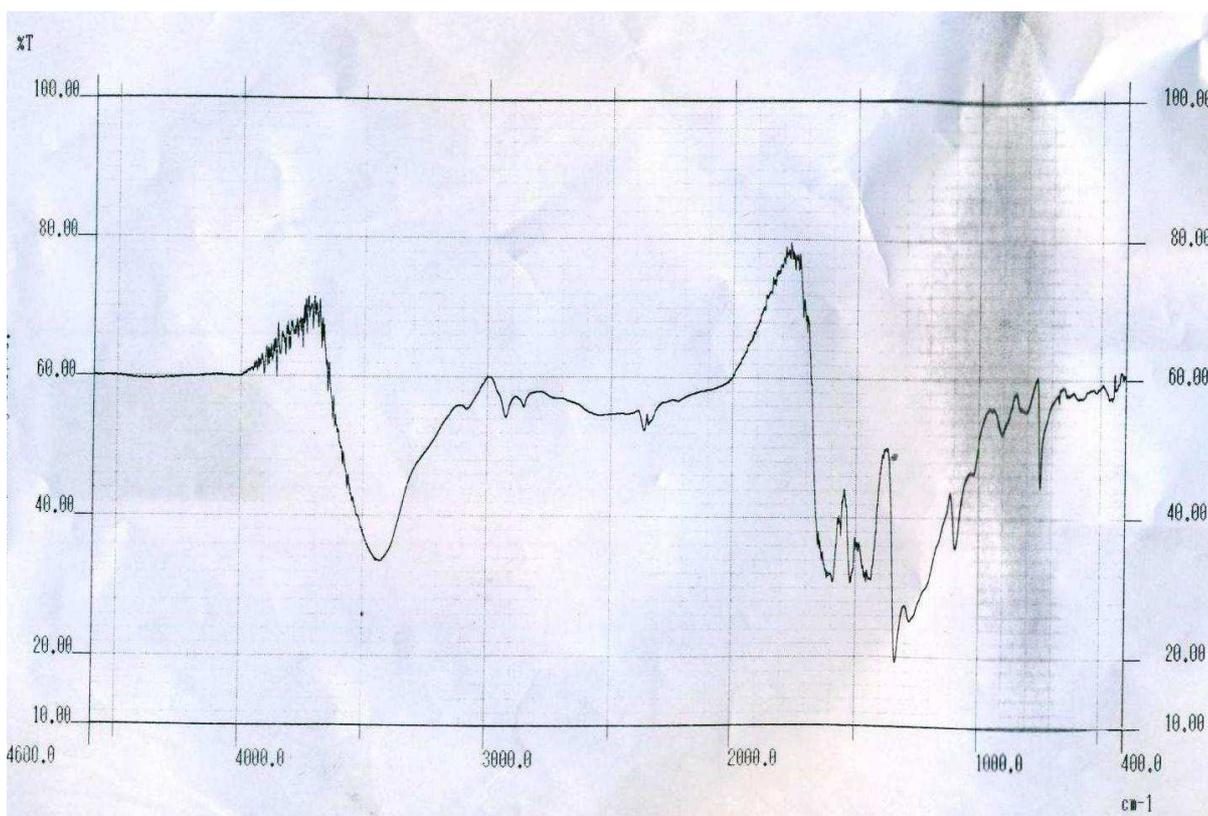


Fig 2: IR spectrum of p-NPHXF