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Chelation Ion-Exchange Properties of Organic Copolymer Resin-III Synthesized from 2, 4-Dihydroxypropiophenone, 1, 5-Diaminonaphthalene and Formaldehyde

N. C. Das

Department of Chemistry, Dr. Ambedkar College of Arts, Commerce and Science, Chandrapur-442401 (M. S.), India

ABSTRACT: The copolymer 2, 4-DHP-1,5-DANF-III has been prepared by condensation of 2,4-dihydroxypropiophenone, 1,5-diaminonaphthalene and formaldehyde in the presence of acid catalyst using 3:1:5 molar ratios of reactants. The resin has been characterized by elemental analysis, UV-Visible, FT-IR, ^{1}H-NMR and SEM analysis. The chelation cation-exchange properties of the copolymer resin has been studied for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} ions. In the study of the selectivity of metal-ion uptake involving the measurements of the distribution of a given metal ion between the copolymer sample and a solution containing the metal ion, a batch equilibrium method was used. The study was carried out over a wide pH range and in medium of different ionic strengths. Copolymer showed a higher selectivity for Ni^{2+} and Cu^{2+} ion than for Zn^{2+} , Co^{2+}, and Pb^{2+} ions.

KEYWORDS: Copolymer, Ion-exchange properties, Batch equilibrium, Chelating, distribution ratio, metal ion uptake.

I.INTRODUCTION

The toxicity of heavy metal ions have increased strongly and rapidly because of many industries catalyst contains metal ions. For the removal of metal ions many techniques have been developed and such as electro-deposition, solid liquid extraction and co-precipitation. To remove the toxic metal ions from aqueous solution, chelating resins have been used widely for this purpose. Toxic metal ions are well known for their harmful effect to human health. The materials and energy require of the waste water treatment process can be simple if the toxic metal ion can be recovered. The use of chelating resins for removal metal ions, is the method choice due to its high loading capacity, high efficiency separation and high degree of selectivity [1].

Gurnule et al [2] prepared chelating ion-exchange resin from phallic acid - melamine - formaldehyde and characterized by elemental analysis, FT-IR and ^{1}H-NMR spectra. Metal ion uptake capacity of synthesized copolymer has been carried out by Batch equilibration method for different metal ions at different concentrations. Dhote et al [3] synthesized a ion exchange resin from 4-hydroxybenzophenone and melamine with formaldehyde which was characterized and chelating nature of prepared resin was studied with Cd (II), Ni (II), Zn (II), Cu (II), and Pb (II) metal ions. Comparative study of strong anion exchange poly (Styrene-co-EGDMA-co-VBC) and strong anion exchange hyper crosslinked poly (HEMA-co-EGDMA-co-VBC) was carried out by N. Abdullah et al [4]. Masram et al have been prepared the copolymer resin from salicylic acid and diaminobenzoic acid with formaldehyde and studied the chelating ion-exchange properties. The resin was found to be, selectivity for Cu^{2+} , Fe^{+3} and Ni^{2+} ion than for Co^{2+} , Zn^{2+} and Pb^{2+} ions [5]. Synthesis, antimicrobial and ion-exchange studies of copolymer resin derived from substituted resorcinol, biuret and formaldehyde have been studied by Ravichander et al [6].

Nandekar et al [7] synthesized a copolymer resin by condensation of salicylic acid, semicarbazide and formaldehyde and studied its ion-exchange properties for Zn (II), Cu (II), Co (II), Ni (II), and Pb (II) ions. The study was carried out at over a wide pH range, different shaking time, in the medium of different ionic strengths and reported that higher selectivity for Cu (II) and Ni (II) than for Zn (II), Co (II) and Pb (II) ions.

However, the literature survey have revealed that no copolymer has been synthesized using monomer of 1,5-diaminonaphthalene, 2,4-dihydroxypropiophenone, and formaldehyde. The present investigation deals with chelating ion-exchange studies of 2,4-DHP-1,5-DAF-III copolymer resin for Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} , and Pb^{2+} ions.

II. MATERIALS AND METHODS

All the chemicals were AR grade. The 1,5-diaminonaphthalene , 2,4-dihydroxypropiophenone, formaldehyde and the solvents like DMF, DMSO, THF, acetone and dimethylether were purchased from Merck, India.

A. *Synthesis of 2, 4-DHP-1, 5-DANF-III copolymer*

The copolymer was prepared by condensing 2,4-dihydroxypropiophenone, 1,5-diaminonaphthalene and formaldehyde in the presence of acid catalyst in 3:1:5 molar ratios of monomers at temperature 126 ± 2 ^{0}C for about 5hrs. The solid product was obtained and to remove 2,4-dihydroxypropiophenone formaldehyde copolymer, the product obtained was extracted with diethyl ether which might be present along with 2,4-DHP-1,5-DANF-III copolymer. Copolymer was further purified by dissolving in 8% NaOH and then filtered. It was then reprecipitate by drop wise addition of 1:1 con. HCl and water with rapid stirring to avoid the lumping formation. The sample was dried, powdered and kept in vaccum desicator. The yield of the resin was found to be 78%. The reaction of the above synthesis has been presented in Figure-1.

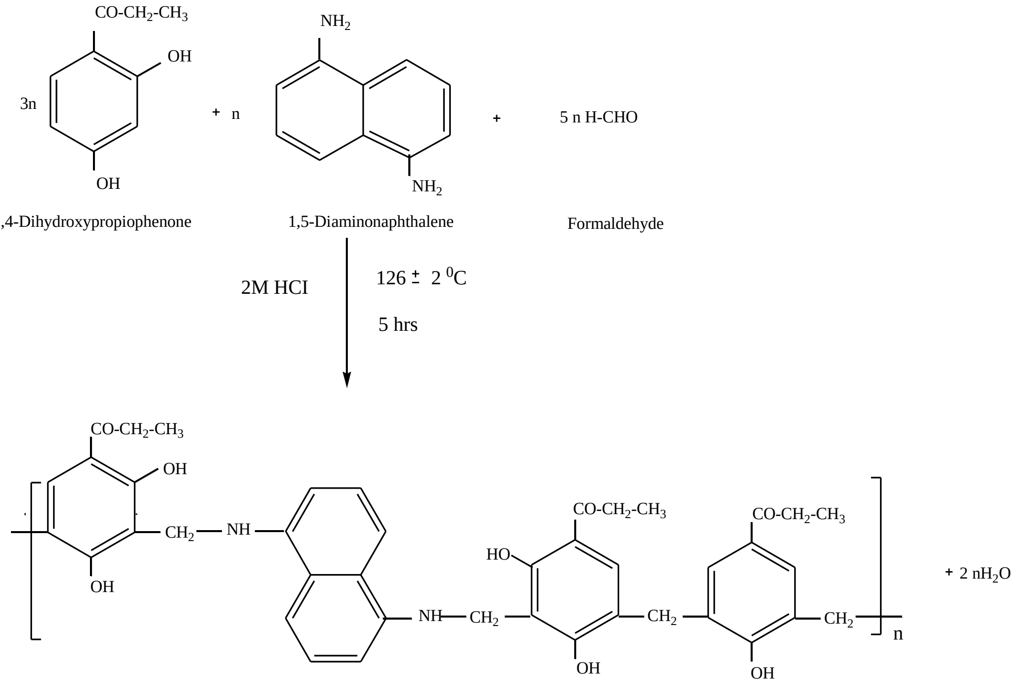

Figure 1: Synthesis of 2,4-DHP-1,5-DANF-III copolymer resin

B. *Physico-chemical and analytical studies*

The elemental analysis of copolymer resin was carried out on Elemental Vario EL III Carlo Erba 1108. Infrared spectra has been scanned in najol mull on Perkin-Elmer-Spectrum RX-I, FT-IR Spectrophotometer in the range of 4000-

500 cm^{-1} in KBr pellets. The ^{1}H-NMR spectrum of copolymer was scanned on Bruker Advance -II 400 MHz NMR spectrophotometer using DMSO-d$_6$ as a solvent. All the spectral studies for the synthesized copolymer were carried out at STIC, Cochin University, Cochin, India.

C. Ion-exchange properties

To decide the selectivity of copolymer 2,4-DHP-1,5-DANF-III as an ion exchanger study was carried out by the influence of various electrolytes at different pH and concentration, the rate of metal ion uptake and distribution of metal ion between the solution and copolymer phase. The chelating ion exchange properties was carried out with the copolymer sample by the batch equilibrium method.

D. Determination of metal ion uptake in the presence of electrolytes of different concentrations

Copolymer sample 25 mg was suspended in 25 ml NaNO3 electrolyte solution of known concentration. The pH of the solution was adjusted by using either 0.1 N NaOH or 0.1 N HCl. The suspension was stirred at temperature 25 ^{0}C for of 24 hrs. To this suspension 2 ml of 0.1M solution of the metal ion was added and the required pH was adjusted. The mixture was again stirred for 24 hr at 25 ^{0}C and filtered. The solid was washed and the filtrate and washings were combined and the metal ion content was determined by titration against standard EDTA [8]. The amount of metal ion uptake of the polymer was calculated from the difference between the reading in actual experiments and a blank experiment without polymer. Same experiment was repeated in presence of other three electrolytes such as NaCl and $NaClO_4$, Na_2SO_4 at different concentrations.

E. Evaluation of the Rate of Metal Uptake

A series of experiments of the type described above were carried out in order to evaluate the time required to reach the state of equilibrium under given experimental conditions, in which the metal ion taken up by chelating resins was determined from time to time in the presence of 25 ml of 1M NaNO3 solution at 25 ^{0}C. It was assumed that the state of equilibrium was established within 24 hrs under given conditions. Rate of metal ions uptake is expressed as percentage of the amount of metal ions taken up after a certain time.

F. *Evaluation of the distribution of metal ions at different pH*

The distribution of each one of the five metal ions Cu(II), Co(II), Ni(II), Zn(II) and Pb(II) between the copolymer phase and aqueous phase was estimated at 25 ^{0}C in the presence of a solution of 1M, $NaNO_3$. The experiments were carried out at different pH values as described earlier. The Distribution ratio (D) was calculated with the following relationship

$$D = \frac{\text{Weight of metal ion taken up by 1 g of resin sample}}{\text{Weight of metal ion present in 1 ml solution}}$$

III. RESULTS AND DISCUSSION

A. Elemental analysis

The prepared resin was found to soluble DMF, DMSO and THF but insoluble in almost all other organic and inorganic solvents. The copolymer 2,4-DHP-1,5-DANF-III was analyzed for carbon, hydrogen and nitrogen content and found to be good agreement with calculated value. The empirical formula and empirical formula weight, which is shown in the Table 1.

Table1: Elemental analysis and empirical formula of copolymer resin

Copolymer resins	% of ‘C’ observed calculated	% of ‘H’ observed calculated	% of ‘N’ observed calculated	Empirical formula of repeat unit	Empirical formula Weight
2,4-DHP-1,5-DANF-III	68.32 69.88	6.20 5.68	4.32 3.97	$C_{41}H_{40}N_2O_9$	704

B. FT-IR spectra

The FT-IR spectra of copolymer 2, 4-DHP-1, 5-DANF-III is presented in Figure 2. A broad band displayed at 3243 cm^{-1} may be due to the stretching vibration of phenolic –OH group which exhibiting intramolecular hydrogen bonding. The sharp and strong band at 1626 cm^{-1}may be on account of stretching vibration of carbonyl group (Ar-CO group). The medium band appeared at 2938 cm^{-1}may be due to –NH- group in pyridine moiety. The presence of methyl and methylene vibration has been indicated by the medium band at 2978 cm^{-1}. A weak band at 1458 cm^{-1} describes the presence of >C=C< (aromatic) group. The sharp and strong band at 1373 cm^{-1}, suggested the presence of $–CH_2-$ methylene bridge in copolymer chain [9, 10].

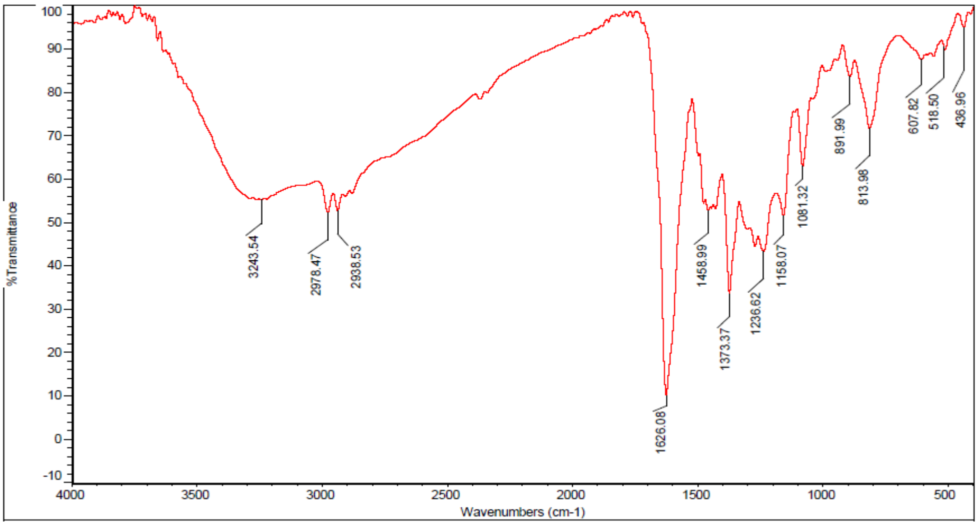

Figure 2: FT-IR-spectra of 2,4-DHP-1,5-DANF-III copolymer resin

C. ^{1}H-NMR Spectra

The ^{1}H-NMR spectra of 2,4-DHP-1,5-DANF-III is dipected in Figure 3. NMR spectra shows weak multiplicity signal in the region 6.3 (δ) ppm which indicates aromatic protons (Ar-H). A singlet signal observed at 7.1(δ) ppm is due to presence of phenolic-OH proton in intramolecular hydrogen bonding . The methyl proton of $Ar-CO-CH_2-CH_3$ moiety is identified by the triplet signal at 1.1 (δ) ppm. The quartet peaks appeared in the region 2.9 (δ) ppm indicates the presence of methylenic proton of $Ar-CO-CH_2-CH_3$ group. The proton of methylenic bridge$Ar-CH_2-NH-$ may be recognized as doublet signal observed at 2.5 (δ) ppm. The triplet signal in the region 7.6 (δ) ppm may be due to proton of –NH- bridge (amido) of copolymer chain [11, 12].

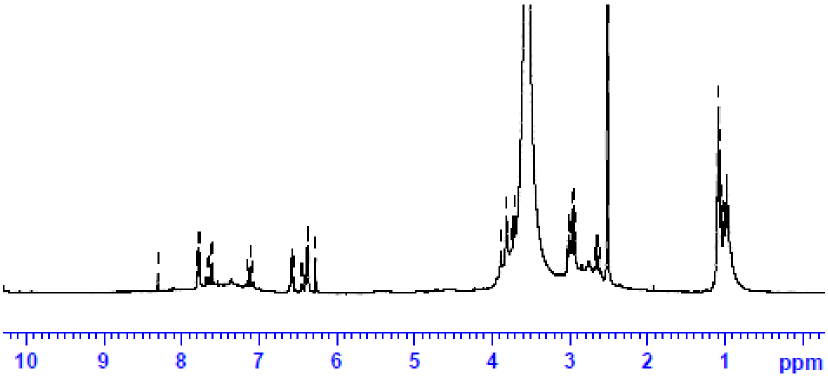

Figure 3: H^1-NMR-spectra of 2,4-DHP-1,5-DANF-III copolymer resin

D. Scanning electron microscopy

The surface features of the resin were studied by scanning electron micrograph at different magnification which is presented in Figure-4. It gives information of defects in structure and surface topography. The morphology shows spherulites and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of copolymer 2, 4-DHP-1, 5 DANF-III sample. It also shows the fringes model of crystalline and amorphous structure. Thus the resin is crystalline as well as amorphous or transition between amorphous and crystalline [13].

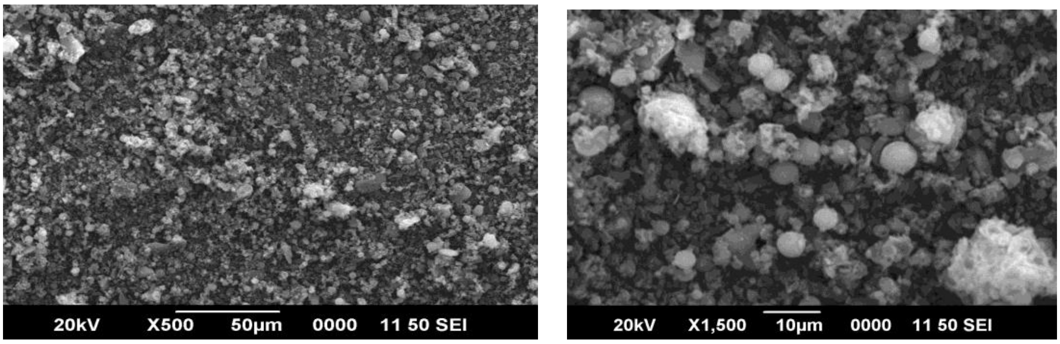

Figure 4: SEM micrograph of 2, 4-DHP-1, 5-DANF-III copolymer resin

E. Determination of metal uptake in the presence of various electrolytes and different concentrations

The influence of chloride, nitrate, perchlorate and sulphate at different concentrations on the equilibrium of metal-copolymer interaction has been examined. The amount of metal ions taken up by a given amount of resin sample depends on the concentrations and nature of the electrolyte present in the solution which is presented in Table 2. In the presence of chloride ions and perchlorate ions, the uptake of Ni(II) and Cu(II) ions increases with increasing electrolyte concentrations, where as the uptake of Co(II), Zn(II) and Pb(II) ions decreases with increasing concentration of the both the electrolytes.

Table 2: Evaluation of the effect of different electrolytes on the uptake[a] of several metal ions by 2, 4-DHP-1, 5-DANF-III copolymer

Metal ion	pH	Conc.	Weight of metal ion (in mg.) taken up in the presence of			
			$NaClO_4$	NaCl	$NaNO_3$	Na_2SO_4
Cu^{2+}	4.5	0.01	2.20	2.07	2.20	3.80
		0.05	2.93	2.51	2.36	3.27
		0.10	3.07	2.90	2.47	2.55
		0.50	3.52	3.20	3.33	1.62
		1.00	4.35	3.54	3.83	1.22
Ni^{2+}	4.5	0.01	2.14	1.34	1.22	3.34
		0.05	2.57	1.48	1.95	2.69
		0.10	3.14	1.65	2.27	1.86
		0.50	3.37	3.13	2.95	1.60
		1.00	4.01	3.40	3.49	0.96
Co^{2+}	5.0	0.01	1.84	1.92	2.01	1.91
		0.05	1.65	1.46	1.81	1.67
		0.10	1.46	1.30	1.56	1.45
		0.50	1.14	1.02	1.32	1.21
		1.00	0.83	0.86	0.91	1.07
Zn^{2+}	5.0	0.01	2.21	1.92	2.63	2.36
		0.05	2.01	1.76	2.21	1.84
		0.10	1.46	1.34	1.84	1.61
		0.50	1.24	1.01	1.51	1.33
		1.00	0.76	0.76	1.05	0.92
Pb^{2+}	6.0	0.01	1.81	2.11	1.94	2.13
		0.05	1.54	1.81	1.79	1.88
		0.10	1.33	1.29	1.45	1.39
		0.50	1.22	1.11	1.11	1.09
		1.00	0.91	0.82	1.00	0.80

[a]$[M(NO_3)_2]$ = 0.1 mol/l; Volume = 2 ml; Volume of electrolyte solution: 25 ml
Weight of resin = 25 mg; time: 24 h : Room temperature

But in the presence of nitrate ions, the uptake of Ni(II) and Cu(II) ions increases with increasing concentration of the electrolyte where as the uptake of Zn(II), Co(II), and Pb(II)ions decreases with increasing concentration of $NaNO_3$ electrolyte. However, in the presence of SO_4^{2-} ions, the uptake of Ni(II), Cu(II), Co(II), Zn(II), and Pb(II) ions decreases with increasing concentration of Na_2SO_4 electrolyte. This is due to perchlorate ions, chloride ions and nitrate ions forms weak complexes with Cu (II) and Ni(II) ion while sulphate forms strong complexes with Cu(II) and Ni(II). But perchlorate, chloride and nitrate ions forms strong complexes with Co(II), Zn(II) and Pb(II) [14-16].

F. Rate of metal ion uptake as a function of time

To determine the time required to reach the equilibrium, the rates of metal ion absorption by 2, 4-DHP-1, 5-DANF-III resin samples were measured for Pb(II), Ni(II), Co(II), Cu(II), Zn(II) ions. The dependence of the rate of metal-ion uptake on the nature of the metal ions which is shown in Table-3. These results indicate that the time taken for the uptake of the different metal ion depended on the nature of the metal ions under the given conditions. A careful examination of the experimental data, shows that Cu(II), Ni(II), Zn(II) and Co(II) ions required about 5 hrs to attain the equilibrium, where as Pb(II) ions required almost 6 hrs for equilibrium. The experimental results revealed that the rate of metal-ion uptake of Cu(II), Ni(II), Co(II), Zn(II) is more than Pb(II). This trends is due to Cu(II), Ni(II), Co(II), Zn(II) have nearly equal ionic size but Pb(II) has comparatively large ionic size [17-19].

Table 3: Comparison of the rates of metal (M) ion uptake[a] by 2, 4-DHP-1, 5-DANF-III copolymer

Metal ion	pH	% of metal ion uptake[b] at different time (hrs.)					
		1	2	3	4	5	6
Cu^{2+}	4.5	61.6	72.5	81.5	88.1	95.3	-
Ni^{2+}	4.5	68.7	78.3	82.3	90.3	95.6	-
Co^{2+}	5	53.6	66.3	77.2	87.4	94.5	-
Zn^{2+}	5	55.0	67.1	77.1	88.5	95.4	-
Pb^{2+}	6	41.4	56.4	67.2	77.6	88.2	96.2

[a] $[M(NO_3)_2]$= 0.1 mol/l; volume : 2ml; $NaNO_3$ = 1.0 mol/l; volume: 25ml, Room temperature.
[b] Metal ion uptake = (Amount of metal ion absorbed x 100) / amount of metal ion absorbed at equilibrium.

G. *Distribution ratios of metal ions at different Ph*

The effect of pH on the distributed of amount of metal ions between two phases is presented in the Table 4. The distribution ratio indicates that the relative amount of metal ions uptake by the 2, 4-DHP-1, 5-DANF-III copolymer increases with increasing pH of the medium [20]. To prevent hydrolysis of the metal ions at higher pH, the study was carried out up to a definite pH value for the particular metal ion. However, the increase magnitude is different for different metal cations. The distribution of metal ions Cu(II) and Ni(II) is selectively more comparatively any other metal ions under investigation. The order of distribution ratio of metal ions is found to be Cu(II) > Ni(II) > Co(II) > Zn(II) > Pb(II). The results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions.

Table 4: Distribution Ratio ‘D’[a] of Different Metal Ions[b] as a function of different pH of 2, 4-DHP-1, 5-DANF-III Copolymer resin

Metal ions	Distribution ratios of different metal ions at different pH							
	1.5	2.0	2.5	3.0	3.5	4	5	6
Cu^{2+}	-	-	88.3	93.6	134.2	184.4	560.6	1313.3
Ni^{2+}	-	-	76.1	80.5	102.2	185.1	375.2	877.4
Co^{2+}	-	-	44.4	77.5	97.4	166.4	244.3	441.6
Zn^{2+}	-	-	42.2	67.7	80.4	94.1	156.1	288.3
Pb^{2+}	-	-	40.1	61.6	81.2	108.1	136.2	244.3

[a] D = weight (in mg) of metal ions taken up by 1g of copolymer/weight (in mg) of metal ions present in 1ml of solution.

[b] $[M(NO_3)_2]$= 0.1 mol/l; volume : 2ml; $NaNO_3$ = 1.0 mol/l; volume: 25ml, time 24h (equilibrium state) at Room temperature.

IV.CONCLUSION

The 2, 4-DHP-1, 5-DANF-III copolymer based on the condensation reaction of 2, 4-dihydroxypropiophenone and 1, 5-diaminonaphthalene with formaldehyde in the presence of 2M, HCL acid as catalyst has been prepared. The structure of the resin has been confirmed by physico-chemical and spectral studies. The 2, 4-DHP-1, 5-DANF-III is a selective chelating ion-exchange copolymer for certain metal ions. Copolymer shows a higher selectivity for Ni^{2+} and Cu^{2+} ion than for Co^{2+}, Zn^{2+} and Pb^{2+} ions.

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