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Electrical Conductivity, Biological Activity, SEM Studies and Analytical Application of Terpolymer Derived From 2,6-Dihydroxyacetophenone, Paraphenylene diamine and Formaldehyde

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Abstract

The terpolymer resin used for present study (2,6-DHAPDF-I) was already synthesized by condensation of 2,6-dihydroxyacetophenone, paraphenylenediamine and formaldehyde in 1:1:2 ratio and characterized by spectral studies. The DC electrical conductivity was measured as a function of temperature from 303 - 423 K. The results of DC conductivities shows that studied terpolymer can be ranked as semiconductor. Terpolymer has been screened against various bacterias. The terpolymer shows no antibacterial and antifungal activities. The surface morphology was examined by scanning electron microscopy. From this study it is found that it can be used as ion exchanger. Ion exchange properties of the terpolymer resin have been studied for hazardous metal ion like Co^{+2}, Pb^{+2}, Hg^{+2} and Cd^{+2} ions. A batch equilibrium method was employed for the study of selectivity of metal ion uptake. The study was carried out over a wide range of pH and ionic strength of different electrolytes. Rate of metal ion uptake follows the order $Co^{+2} > Cd^{+2} > Pb^{+2} > Hg^{+2}$.

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Keywords: Electrical conductivity, activation energy, antibacterial and antifungal activities, surface morphology, ion exchange properties, batch equilibrium

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Introduction

Polymers are model materials for many of the industrial applications as they have desirable properties such as durability, process ability, transparency, electrical and thermal resistance [1-4]. Phenolic resins have been the workhorse as matrix resins, in composites for structural and thermal structural applications in aerospace because of their ease of processing-ability, thermal stability and cost effectiveness [5]. 2-hydroxy-acetophenone and its substituted derivatives have been condensed with formaldehyde to produce heat and light stabilizers [6]. It is also found to exhibits liquid crystalline behaviour, which depends upon the chain link formation in the structure. Parrish [7,8] has showed that the o-aminophenol resin reported by Gregor *et al.*[9] would be expected to contain substituted amino groups, and prepared a resorcinol formaldehyde-oxine resin which also exhibits chelating properties. The authors have studied ion-exchange capacity of this polymer for eight cations at the minimum pH of a solution. Pancholi *et al.*[10] have synthesized 2-hydroxy-4-methoxyacetophenoneoxime-thiourea-trioxane terpolymer resin; and studied their thermal and kinetic parameters which are reported.

A new resin prepared using 2-hydroxyacetophenone with thiourea and trioxane in presence of 2M HCl as a catalyst is reported by Pancholi and Patel [11]. Various methods *viz.* Broido's [12], Roger's [13], Freeman Anderson's [14], Coats and Redfern's [15], Sharp Wentworth [16] and Freeman Carroll's [17] etc. can be applied to find out the kinetic parameters of thermal decomposition reaction. One or other of these methods have been applied by various researchers [18-27]. Terpolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials [28-29]. Metal ion removal by chelating ion-exchange resins using batch equilibrium methods has gained rapid acceptance because of

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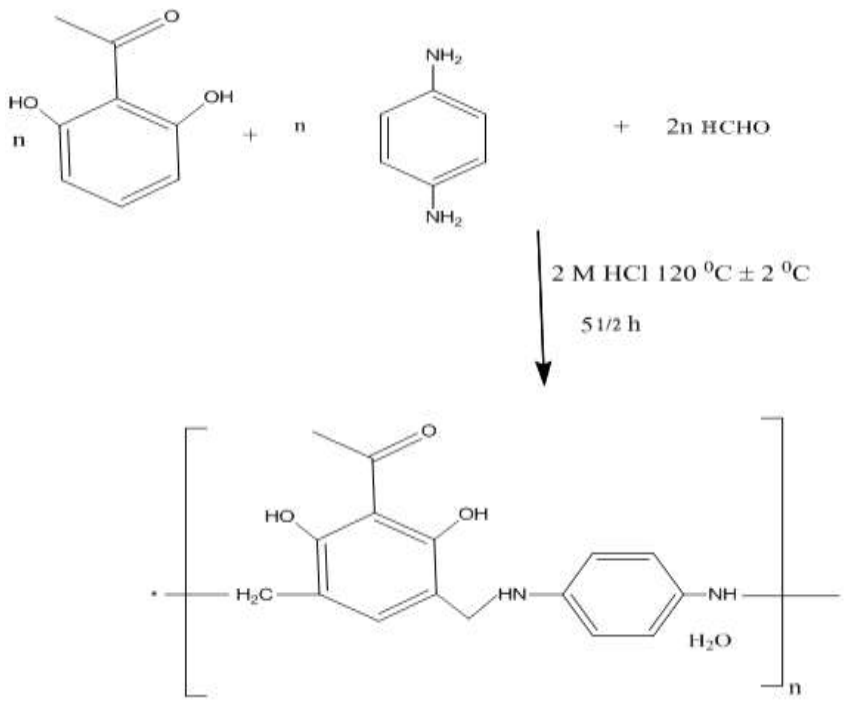
its wide variety of sorbent phases, high degree of selectivity, high loading capacity and enhanced hydrophilicity [30-32].

Experimental

Material and Methods:

All chemicals and solvents used were of AR grade. The procedure of synthesis and characterization of 2,6-DHAPDF - I was published [33] and scheme of reaction is as follows:



Measurement of electrical conductivity:

The resistance of sample of synthesized resin in the temperature range of 303 K to 423 K at a constant voltage of 50 volts across the pallets prepared from terpolymer resin was measured using two probe method adopted by Yawale [34].

The resistivity ρ (rho) and conductivity (σ) of the sample was calculated using the relations, $\rho = R\frac{A}{L}$ and $\sigma = {}^{1}\!/\!_{\rho} = {}^{1}\!/\!_{A.R.}$, respectively, where, R = resistance of pellet, A = surface area of pellet, L = thickness of pellet, ρ = resistivity

The D. C. electrical conductivity (σdc) varies with absolute temperature and the temperature dependence of conductivity was fitted to an Arrehenius type equation.

$$\sigma = \sigma_0 . \exp^{\left[{}^{-\Delta E_a}\!/\!_{KT}\right]} \qquad \ldots.(1)$$

where, σ = Electrical conductivity at temperature T, σ_o = Electrical conductivity at temperature T_∞ i.e. constant (Pre-exponential conductivity), E_a = Activation energy of electrical conductance,
K = Boltzmann constant = 1.38 x 10^{-23} J/K/mol, T = Absolute temperature
The logarithmic form of equation (1) is written as

$$\log\sigma = \log\sigma_o + \frac{-Ea}{2.303K}\cdot\frac{1}{T}$$

It is the equation of straight line. According to this equation, a plot of logσ versus 1/T would be linear i.e. straight line with the slope.

$$\text{Slope} = \frac{-\text{Ea}}{2.303\text{K}}$$

The activation energy was estimated by

Ea = -2.303 x K x slope J, (1ev = 1.6x10^{-19}J)

The temperature dependence of electrical conductivity for polymers was estimated in the range of applicability of Arrhenius type equation. The measured values were plotted as a function of reciprocal of temperature. The plots between log σ versus 1/T were plotted for newly synthesized 2,6-DHAPDF-I terpolymer resins which is under investigation and the activation energy of electrical conductance for 2,6-DHAPDF-I terpolymer resin was calculated.

Biological activity: Experimental procedure for antibacterial analysis:

The 2,6-DHAPDF-I terpolymer was screened for activity against four bacterial strains E.coli, P. aeruginosa, S. aureus and B. subtilis, where B. subtilis and S. aureus are Gram-positive bacteria and E. coli and P. aeruginosa is Gram-negative bacteria. Aspergillus niger and candida albicans were used for

antifungal activities. Pure culture of these pathogenic bacteria and fungi was taken for analysis by Agar diffusion method.

Scanning electron microscopy (SEM):

Surface morphology of the terpolymers was studied by Scanning Electron Microscopy (SEM) using Jeol 6390LV Scanning Electron Microscope at Sophisticated Analytical Instrument Facility, (STIC) Cochin. SEM study provides the exact morphology of the terpolymer resin sample.

Experimental of ion exchange:

The ion-exchange properties of synthesized 2,6-DHAPDF - I terpolymer resin was determined by batch equilibrium method developed by Gregor and De-Geiso *et al.*

Determination of metal ion uptake in the presence of electrolyte of different concentration:

The terpolymer sample (25 mg) was suspended in an electrolyte solution (25mL) of known concentration. The pH of the suspension was adjusted to required value by using either 0.1 M HNO_3 or 0.1 M NaOH. The suspension was stirred for 24 h at 25 °C. To this suspension 2 mL of 0.1 M solution of metal ion was added and pH was adjusted to required value for particular metal ion. The mixture was again stirred at 25 °C for 24 Hrs and filtered. The terpolymer was washed and washings were combined with filtrate and metal ion content was determined by titrating against standard EDTA, using appropriate buffer and suitable indicator (Table – 1). A blank experiment was also carried out in the same manner without adding the polymer sample. The blank solution was again estimated for the metal ion content. The amount of metal ion taken up by polymer was calculated from the difference between a blank experiment and the reading in the actual experiments. The experiment was repeated in the presence of several electrolytes of known concentration with four different metal ions *viz.* Pb^{2+}, Co^{2+}, Cd^{2+} and Hg^{2+}. The same procedure was applied to all molar ratios of the terpolymer samples.

Table 1: Summarized Procedures for EDTA Titration of cations under investigation

Metal Ion	Type of titration	pH	Buffer	Indicator	Colour change
Pb^{2+}	Direct	5.5	Hexamine	Xylenol orange	Red-yellow
Co^{2+}	Direct	5.0	Hexamine	Xylenol orange	Red-yellow
Hg^{2+}	Direct	6.0	Hexamine	Xylenol orange	Red-yellow
Cd^{2+}	Direct	5.5	Hexamine	Xylenol orange	Red-yellow

Evaluation of the rate of metal ion uptake:

In order to estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type described above were carried out, in which the metal ion taken up by the chelating resins was determined from time to time at 298.15K [in the presence of 25 mL of 1 M $NaNO_3$ solution]. It was assumed that, under the given conditions, the state of equilibrium was established within 24 hrs.

The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that at the state of equilibrium [35].

$$\text{\% of amount of metal ions taken up at different time} = \frac{\text{Amount of metal ion adsorbed x 100}}{\text{Amount of metal ion adsorbed at equilibrium}}$$

Evaluation of the distribution of metal ions at different pH:

The distribution of each one of the four metal ions i.e. Pb^{2+}, Co^{2+}, Hg^{2+} and Cd^{2+} between the polymer phase and the aqueous phase was determined at 298.15K and in the presence of a 1M $NaNO_3$ solution. The experiments were carried out at different pH range 2.5-6.0. The distribution ratio (D), is defined by the following relationship:

$$D = \frac{\text{Amount of metal ion on resin}}{\text{Amount of metal ion in solution}} \text{ X } \frac{\text{Volume of solution (mL)}}{\text{Weight of resin (g)}}$$

Result and Discussion

Electrical conductivity:

The DC resistivity of 2,6-DHAPDF - I terpolymer resin was measured in the temperature range of 303 – 423 K by applying a constant voltage (50 Volts) across the pellet. Data of D. C. resistivity of terpolymer resin presented in Table – 2.

The electrical conductivity of the terpolymer sample at room temperature is 3.702 x 10^{-12} $ohm^{-1}.cm^{-1}$. The plot of log σ versus $1/T$ is depicted in Figure 1. It can be seen from the Fig. 1, that the plot is linear in the temperature range under study. Besides, the data reveals that electrical conductivity of studied terpolymer increases with the increase in temperature. Hence, the terpolymer can be ranked as semiconductor [36]. The activation energy calculated from the slope of the plots was found to be 6.197 x10^{-23} $JK^{-1}.mol^{-1}$. This low magnitude of activation energy may be due to the presence of large number of pi- electrons present in the terpolymers.

Table-2: Evaluation of activation energy of electrical conduction from resistivity measurement of 2,6-DHAPDF-I terpolymer resin.

Diameter of the pellet: = 0.678cm

Thickness of the pellet (l) = 0.156cm

Surface area of the pellet (A) = 0.487cm^2

A/I = 3.12cm

Temp (*T*) (K)	**$1/T$ x 10^3 (K^{-1})**	**Resistance (*R*) ohm**	**Resistivity $\rho = R \times A/l$**	**Conductivity $\sigma = 1/\rho$ $(ohm.cm.)^{-1}$**	***log σ***
303	3.3	8.657 x10^{10}	2.700x10^{11}	3.702x10^{-12}	-11.43
308	3.24	8.564 x10^{10}	2.671 x10^{11}	3.742x10^{-12}	-11.42
313	3.19	6.245 x10^{10}	1.948 x10^{11}	5.132x10^{-12}	-11.26
318	3.14	5.034 x10^{10}	1.570 x10^{11}	6.367x10^{-12}	-11.19
323	3.11	4.123 x10^{10}	1.286 x10^{11}	7.774x10^{-12}	-11.10
328	3.05	3.465 x10^{10}	1.081 x10^{11}	9.250x10^{-11}	-11.03
333	3.33	3.098 x10^{10}	9.665 x10^{10}	1.030x10^{-11}	-10.98
338	2.96	2.345 x10^{10}	7.316 x10^{10}	1.366x10^{-11}	-10.86
343	2.91	1.876 x10^{10}	5.853 x10^{10}	1.708x10^{-11}	-10.76
348	2.87	1.643 x10^{10}	5.126 x10^{10}	1.950x10^{-11}	-10.70

353	2.83	1.234×10^{10}	3.850×10^{10}	2.597×10^{-11}	-10.58
358	2.79	9.243×10^{9}	2.883×10^{10}	3.467×10^{-11}	-10.46
363	2.75	7.243×10^{9}	2.259×10^{10}	4.425×10^{-11}	-10.35
368	2.72	6.254×10^{9}	1.951×10^{10}	5.125×10^{-11}	-10.29
373	2.68	5.215×10^{9}	1.627×10^{10}	6.146×10^{-11}	-10.21
378	2.65	4.134×10^{9}	1.289×10^{10}	7.758×10^{-11}	-10.11
383	2.61	3.215×10^{9}	1.003×10^{10}	9.969×10^{-11}	-10.00
388	2.58	3.012×10^{9}	9.397×10^{9}	1.064×10^{-10}	-9.97
393	2.55	2.512×10^{9}	7.837×10^{9}	1.275×10^{-10}	-9.89
398	2.51	2.134×10^{9}	6.658×10^{9}	1.501×10^{-10}	-9.82
403	2.48	2.012×10^{9}	6.277×10^{9}	1.593×10^{-10}	-9.79
408	2.45	1.845×10^{9}	5.756×10^{9}	1.737×10^{-10}	-9.76
413	2.42	1.423×10^{9}	4.439×10^{9}	2.252×10^{-10}	-9.64
418	2.39	1.261×10^{9}	3.934×10^{9}	2.541×10^{-10}	-9.59
423	2.36	1.562×10^{9}	4.873×10^{9}	2.051×10^{-10}	-9.68

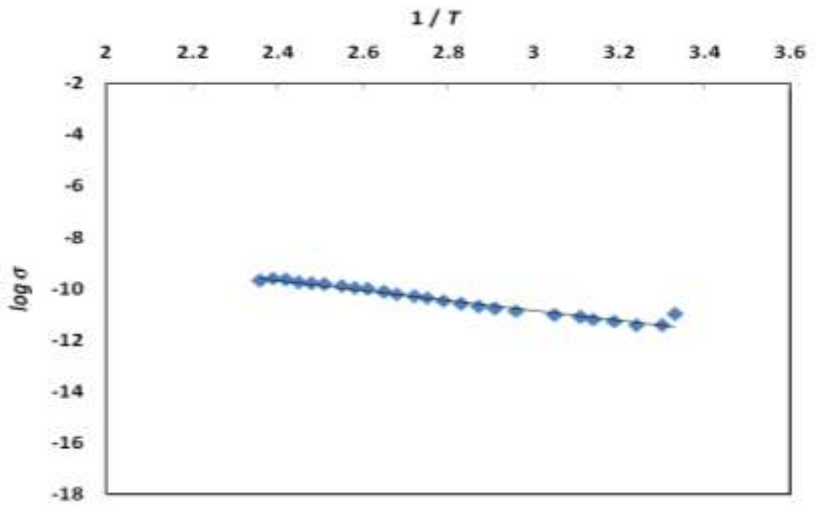


Fig. 1: Plot of log σ versus 1/T for 2,6-DHAPDF-I terpolymer

Biological activity:

The synthesized 2,6-DHAPDF - I terpolymer resins screened against all the four bacteria Bacillus substilis, Escherchia coli, Staphylococcus aureus and Pseudomonas aeruginosa. Zone of inhibition obtained with respect to standard antibacterial drug (Ciprofloxacin) were given in Table-3 and relative antibacterial activity of 2,6-DHAPDF-I terpolymer shown in Fig. 2. Terpolymers 2,6-DHAPDF-I does not shows any antibacterial activity against above bacteria.

Table-3: Relative antibacterial activity of 2,6-DHAPDF-I terpolymer.

S. N.	Terpolymers	Concentration screened (µg/mL)	Diameter of inhibition zones in mm			
			E. coli	P. aeruginosa	S. aureus	B. subtilis
1	2,6-DHAPDF -I	100	NF	NF	NF	NF
		250	NF	NF	NF	NF
		500	NF	NF	NF	NF
		1000	NF	NF	NF	NF
2	Ciprofloxacin (Standard)	100	23	01	21	15
		250	26	03	25	19
		500	28	08	27	22
		1000	31	14	34	25

NF- Not found

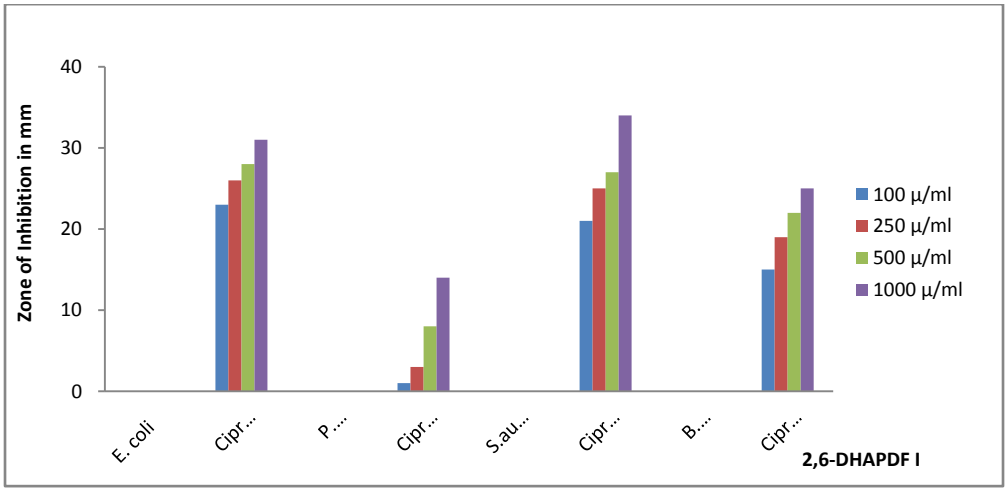
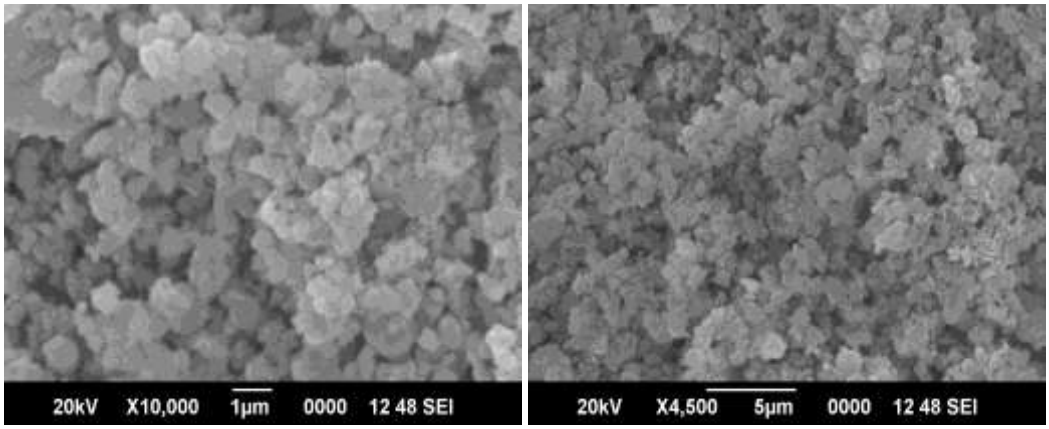


Fig. 2 : Relative antibacterial activity of 2,6-DHAPDF-I terpolymer

SEM Analysis:

A surface Morphological study of synthesized and purified terpolymer resin has been reported by scanning electron microscopy and is shown in Fig. 3. The SEM images show the microporous structure and the transition state between amorphous to crystalline states. The crystalline character found in the terpolymer may be because of the acidic nature of the monomer 2,6-dihydroxyacetophenone. However the terpolymer is predominantly amorphous because of the polycondensation reaction. The surface morphological studies reveal the ion exchange property and therefore can be used as ion exchanger in the purification of water and waste water by removing the hazardous ions.



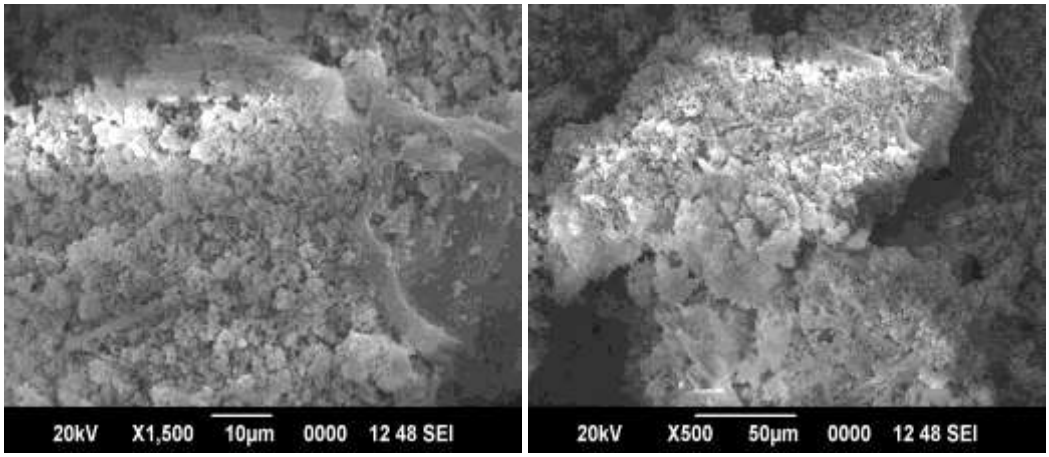


Fig.3: SEM images of 2,6-DHAPDF-I Terpolymer resin

Analytical application (Ion-exchange application):

The chelation ion-exchange property of the 2,6-DHAPDF-I terpolymer was measured by batch equilibrium method involving Co^{2+}, Cd^{2+}, Pd^{2+} and Hg^{2+} metal ions in various electrolyte viz. NaCl, $NaNO_3$ and Na_2SO_4 in different concentration such as, (0.01, 0.05, 0.1, 0.5 and 1.0) $mol.L^{-1.}$ The results are presented in Table-4.

Table - 4: Evaluation of the influence of different electrolyte on the uptake of several metal ions of 2,6-DHAPDF-I terpolymer resins

Metal Ion	Electrolyte conc. (mol/lit)	Weight of the metal ion (mg) taken up in presence of		
		NaCl	$NaNO_3$	Na_2SO_4
Co^{2+}	0.01	1.94	2.01	1.57
	0.05	1.69	1.72	1.42
	0.1	1.33	1.45	1.32
	0.5	1.21	1.24	1.20
	1.0	0.87	1.08	0.78
	0.01	1.69	1.78	1.57
	0.05	1.61	1.71	1.24

Cd^{2+}	0.1	1.36	1.48	1.02
	0.5	1.24	1.34	0.94
	1.0	0.97	1.09	0.79
	0.01	1.21	1.34	-
	0.05	1.11	1.28	-
	0.1	0.97	1.22	-
Pb^{2+}	0.5	0.81	0.97	-
	1.0	0.70	0.76	-
	0.01	0.58	0.79	-
	0.05	0.34	0.45	-
	0.1	0.22	0.25	-
Hg^{2+}	0.5	0.15	0.18	-
	1.0	0.09	0.12	-

Effect of electrolytes on the metal ion uptake:

Examination of the data in Table-4 revels that the amount of metal ions taken up by a given amount terpolymer depends on the nature and concentration of the electrolyte present in the solution. In case of the metal ions Co^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+} the amount of metal ions taken up by the terpolymer samples increases with decreasing concentration of the Cl^-, NO_3^- and SO_4^{2-}. This observation can be explained on the basis of stability constant with these metal ions. This type of trend has been observed by Butolia *et al.* [37].

Evaluation of rate of metal ion uptake:

The rate of metal ion adsorption of 2,6-DHAPDF - I terpolymer resin sample was determined to find out the shortest period of time for which equilibrium could be carried out while operating as close to equilibrium conditions as possible. Table-5 shows the dependence of the rate of metal ion uptake on the nature of the metal ions. The rate refers to the change in the concentration of the metal ions in the aqueous solution, which is in contact with the given polymer. The results show that the time

taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion under given conditions. Examination of data reveals that Co^{2+} ion requires less time (5 Hrs) while Cd^{2+} and Pb^{2+} ions required about 6 hrs for the establishment of equilibrium, and Hg^{2+} required 7 Hrs for establishment of equilibrium Thus, the rate of metal ion uptake follows the order: $Co^{2+} > Cd^{2+} > Pb^{2+} > Hg^{2+}$. This observed order indicates that the rate of metal ion uptake depends on the nature of metal ion i.e. as the size of the metal ion increases the time taken for the uptake of metal ions also increases in order to reach the equilibrium. The above order may be explained on the basis of their stability constants. This type of trend has also been observed by earlier workers.

Table - 5: Comparison of the rate of metal ion uptake of 2,6-DHAPDF-I terpolymer

Metal Ion	Percentage of the amount of metal ion uptake at different (Hr)						
	1	2	3	4	5	6	7
Co^{2+}	38.0	50.2	66.1	71.9	90.6	-	-
Cd^{2+}	28.1	37.2	55.9	60.1	70.4	83.1	-
Pb^{2+}	10.9	28.2	43.9	45.2	73.0	78.2	-
Hg^{2+}	-	-	22.8	60.5	67.0	83.1	90.0

Distribution ratios of metal ions at different pH:

The results of the effect of pH on the amount of metal ion distributed between two phases are summarized in Table-6.

Studies on the effect of pH on the amount of metal ions distributed between two phases indicate that the relative amount of metal ion taken up by the 2,6-DHAPDF - I terpolymer resin increases with increasing of pH of the medium. The magnitude of increase, however, is different for different metal ions.

The study was carried out only up to pH 6.0 in order to prevent hydrolysis of the metal ions at higher pH. From the data of Table-6, we conclude that the out of all the four metal ions Hg^{2+} have low distribution ratio (D) over the pH range 3.5 to 6.0. This could be attributed to low stability constant of the metal complexes.

The reported order of selectivity of a cation exchange resin for divalent metal ions by Irving *et al.* is as: $Pd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+} > Mg^{2+}$.

In the present study the observed order of distribution ratio of divalent ion measured in the pH range 2.5 to 6.0 was found to be $Co^{2+} > Cd^{2+} > Pb^{2+} > Hg^{2+}$. This order partly matches with above trend of this study and is helpful in selecting the optimum pH for a selective uptake of a metal ion from a mixture of different ions.

Table - 6: Distribution ratio (D^a) of different metal ions as function of the pH of 2,6-DHAPDF-I terpolymer resins

Metal Ion	Distribution ratio of metal ions at various pH								
	1.5	1.75	2.0	2.5	3	3.5	4	5	6
Co^{2+}	-	-	-	44.12	92.30	121.12	198.10	120.5	243.2
Cd^{2+}	-	-	-	22.29	33.10	76.90	99.02	110.10	180.24
Pb^{2+}	-	-	-	30.01	37.31	49.02	59.22	98.4	102.61
Hg^{2+}	-	-	-	-	-	11.00	20.11	44.12	99.0

D^a = weight (in mg) of metal ions taken up by 1g of terpolymer/ weight (in mg) of metal ions present in 1 mL of solution.

4. Conclusion

Electrical conductivity of the 2, 6 DHAPDF - I Terpolymer increases with increase in temperature from *T*/K = 303 to 423. Hence it can be treated as semiconductor and does not degrade upto 423 K.

It does not show antibacterial activity against Escherichia coli, Pseudomonas aeruginosa, Staphylococus aureus and Bacillus subtilis in the range of concentration screened and it also doesn't show antifungal activity against the fungi screened.

2, 6 DHAPDF - I terpolymer show the good ion exchange with divalent metal ion (Co^{++}, Cd^{++}, Pb^{++}, Hg^{++}) and SEM study also supported to the crystalline structure of the ion exchange resin. Hence it can be used in the purification of water and pollution control.

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