

Semiconducting and Chelating Applications of newly Synthesized Terpolymer

Rajesh N. Singru

Department of Chemistry, R.D College of Science, Aheri, Gadchiroli, Maharashtra, India

ABSTRACT

Terpolymer resin p-COF-II was synthesized by the condensation of p-Cresol (p-C) and oxamide (O) with formaldehyde (F) in the presence of 2M HCl as catalyst with 2:1:3 molar ratios of reacting monomers. The electrical properties of p-COF-II terpolymer were measured over a wide range of temperature (313-423K), activation energy of electrical conduction has been evaluated and plot of $\log \sigma$ vs $10^3/T$ is found to be linear over a wide range of temperature, which can be ranked it as semiconductor. The chelating ion-exchange properties of this terpolymer was studied for Fe (III), Cu (II), Ni (II), Co (II), Zn (II), Cd (II) and Pb (II) ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake. The study was carried out over a wide pH range, shaking time and in media of various ionic strengths. The terpolymer showed a higher selectivity for Fe (III), Cu (II), and Ni (II) ions than for Co (II), Zn (II), Cd (II) and Pb (II) ions.

Keywords: Semiconductor, Conductivity, ion-exchanger, adsorption, Chelating, synthesis.

INTRODUCTION

The synthesized terpolymer resins, showing versatile applications and properties, attracted the attention of scientist and introduce the recent innovations in the polymer chemistry. These terpolymers can be used as high energy material [1], ion-exchanger [2], semiconductors [3], antioxidants, fire proofing agent, optical storage data, binders, molding materials etc.

The semiconducting properties of terpolymer resins have gained sufficient ground in recent years. Work on organic conducting polymers is carried out extensively due to their wide applications, [4, 5] in areas such as chemically modified electrodes, sensors etc. An industrially useful semiconducting material has been reported by Dewar et al [6]. The conductivity of an 8-hydroxyquinoline – oxamide-formaldehyde terpolymer resins have been reported over a wide range of temperature [7]. Pal et al [8] has reported electrical conductivity of salicylic acid-biuret / dithiooxamide / dithibiuret-trioxane terpolymer resins.

Ion-exchange technique can remove traces of ionic impurities from water/process liquors and gives out a product of ultra pure quality in a simple efficient and techno-economically viable manner. Ion exchangers are widely used in water treatment and pollution control [9, 10]. Various

hydroxybenzoic acid-formaldehyde and 4-hydroxyacetophenone- biuret - formaldehyde copolymers have been reported and found use as ion-exchangers [11, 12].

MATERIALS AND METHODS

Starting Materials:

The chemicals (starting materials) were of Analar or Chemically pure grade, and wherever necessary the purity was tested and confirmed by TLC.

Synthesis of p-COF-II terpolymer resin

The new terpolymer resin p-COF-II was synthesized by condensing p-cresol (2.16g, 0.2 mol) and oxamide (0.88g, 0.1 mol) with 37 % formaldehyde (11.1 ml, 0.3 mol) in a mol ratio of 2:1:3 in the presence of 2M 200 ml HCl as a catalyst at $130^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 5h in an oil bath with occasional shaking to ensure thorough mixing. The separated terpolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove p-cresol-formaldehyde terpolymer which might be present along with p-COF copolymer. The terpolymer was purified further by dissolving in 8% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The copolymer sample p-COF-II thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel. The yield of the copolymer resin was found to be 80%. The reaction and suggested structure has been given in Fig. 1.

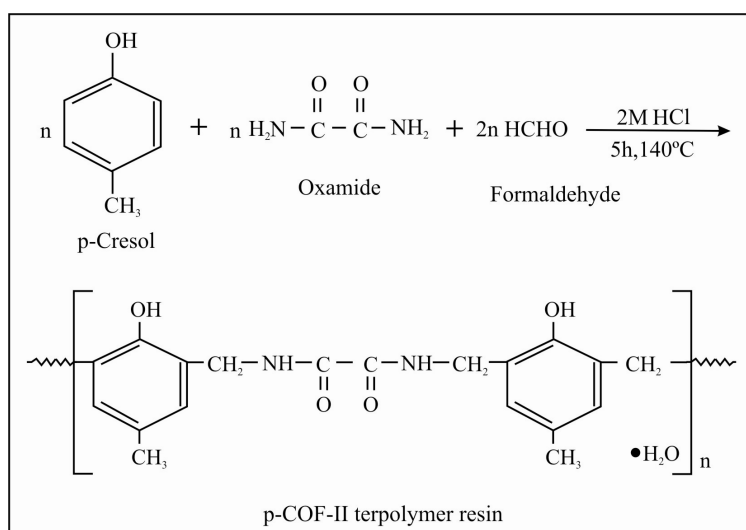


Fig. 1 Suggested structure of p-COF-II terpolymer resin

Conductivity Measurement

The DC electrical conductivity measurements in solid state were carried out in a suitable sample holder designed for the purpose, by finding out the resistance of the sample, in the temperature range of 313K to 463K at constant voltage of 50 volts across the pellets prepared from terpolymer resins. The measurements were made by Auto Compact LCR-Q tester model 4910.

To prepare the pellets, the purified terpolymer resins were thoroughly ground with an agate pestle and mortar. The well powdered terpolymer was palatalized in a steel die at 5 t/cm^2

pressure with the help of a hydraulic press. Pellets of 1.2 cm in diameter and nearly 0.2 to 0.3 cm thickness were prepared. The pellet of the test samples was put in a typical sample holder fabricated in this laboratory and resistance was measured using conductivity bridge over wide range of temperature.

For this purpose, the sample pellet was heated in a tubular furnace in which the temperature of the furnace being increased by steps from room temperature to about 423 K.

Ion-exchange properties:

The copolymer sample (25mg) was suspended in an electrolyte solution (25ml) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1M HNO₃ or 0.1M NaOH. The suspension was stirred for 24hrs at 30°C. To this suspension 2 ml of 0.1M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 30°C for 24 hrs. The polymer was then filtered off and washed with distilled water. The filtrate and the washing were collected and then the amount of metal ion was estimated by titrating against standard EDTA (ethylene diamine tetra-acetic acid) at the same pH (experimental reading). The same titration has been carried out without polymer (blank reading). The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments. The experiment was repeated in the presence of several electrolytes at various pH and different time intervals ^[14].

Ion-Exchange Capacity

The term ion exchange capacity is intended to describe the total available exchanged capacity of an exchange resin, as described by the number of functional group on it. Ion exchange capacity was determined by following experimental procedure.

25 mg of resin sample was suspended in 50 ml of double distilled water; to this add 25 ml of 0.5 M sodium acetate solution. The mixture has been stirred for 2 to 5 min. when H⁺ from resin liberated in the solution to form acetic acid and adsorbed sodium ion (Na⁺). Then the solution was filtered and the filtered is titrated with 0.5 M NaOH solution.

The ion-exchange capacity can be calculated by using following equation, in mill mol per gram (mmol.g⁻¹)

Ion-exchange capacity of terpolymer resin = XY / Z

Where, X = molarity of NaOH

Y = volume of NaOH required during titration

Z = Weight of the exchanger

The ion-exchange capacity of representative sample of each terpolymer resin has been determined and compared it with commercial ion-exchangers.

RESULTS AND DISCUSSION

Electrical conductivity

The thermal activation energy and the values of electrical conductivity at different temperatures are given in Table 1. The resistance values of the pellets of the terpolymers ranging from 313 K to 423 K were converted into conductivity values (σ) by taking into account the thickness of the pellet and its diameter and evaluating thickness area parameters of the pellet of a particular

terpolymer. The temperature dependence of the electrical conductivity of the terpolymers is shown in Fig. 2. In the electrical conduction domain, the temperature dependence of the electrical conductivity obeys the well known equation [4].

$$\sigma = \sigma_0 \exp(\Delta E/kT)$$

Where,

k = Boltzmann constant

σ_0 = electrical conductivity at temperature $T \rightarrow \infty$

σ = electrical conductivity at temperature T

ΔE = electrical conductivity energy of electrical conduction.

This relation has been modified as Electrical Properties of...Terpolymers.

$$\log \sigma = \log \sigma_0 + \frac{-\Delta E}{2.303kT}$$

According to this relation, a plot of $\log \sigma$ Vs. $1000/T$ would be linear with a negative slope. The result of the D.C. conductivities are presented here in the form of plots of $\log \sigma$ Vs. $1000/T$, as the range of conductivities was found to be 1.29×10^{-9} to $2.91 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$.

It will be seen from the plots (Fig. 2) of terpolymer that there is a consistent increase in electrical conductivity as the temperature rises roughly from 313 K to 423 K. these trend is a characteristic of semiconduction [5]. The activation energy was determined from the curves $\log \sigma$ Vs. $(10^3/T)$. The plot of $\log \sigma$ Vs. $10^3/T$ are found to be linear (Fig.2) over wide range of temperature which indicates the semiconducting nature of terpolymer [5, 6].

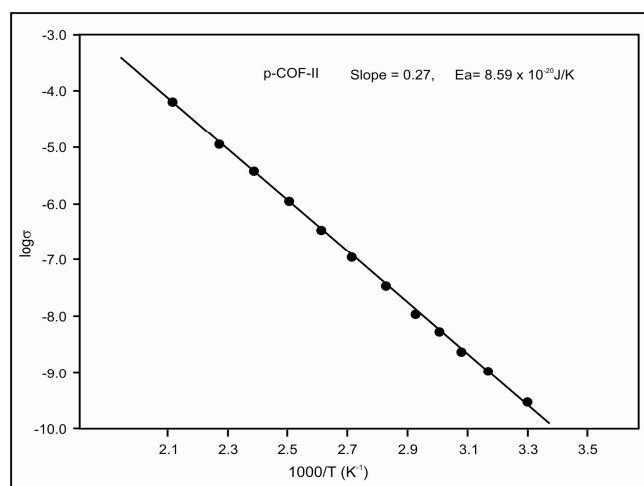


Fig. 2 Electrical conductivity plot of p-COF-II terpolymer resin

Table 1 Electrical conductivity data of p-COF terpolymer resin

Terpolymer	Electrical Conductivity $\text{ohm}^{-1} \text{ cm}^{-1}$		ΔT (K)	ΔE (ev)
	313 K	423 K		
p-COF -II	1.29×10^{-9}	2.91×10^{-6}	313 – 423	0.85×10^{-4}

Table 2 Effect of different electrolytes on the uptake of several metal ions ^a by p-COF-II terpolymer resin

Metal ion	Electrolyte (mol/l)	pH	Weight of the metal uptake (mmol.g ⁻¹) in the presence of electrolyte			
			NaNO ₃	NaCl	NaClO ₄	Na ₂ SO ₄
Fe(III)	0.01	2.5	1.06	0.56	1.18	3.17
	0.05		1.24	0.84	1.70	2.52
	0.10		1.45	1.06	1.92	1.99
	0.50		1.75	1.45	2.42	1.16
	1.00		2.23	2.06	3.01	0.73
Cu(II)	0.01	4.5	1.99	1.21	1.73	3.45
	0.05		2.17	1.86	2.36	2.81
	0.10		2.41	2.43	3.01	2.18
	0.50		2.73	3.01	3.69	1.35
	1.00		2.88	3.71	4.27	0.65
Ni(II)	0.01	4.5	0.87	0.74	1.33	2.92
	0.05		1.46	1.22	1.92	2.33
	0.10		2.02	1.69	2.51	1.74
	0.50		2.50	2.21	3.09	1.16
	1.00		3.22	2.98	3.68	0.57
Co(II)	0.01	5.00	1.40	1.33	1.16	1.87
	0.05		1.16	1.14	1.04	1.23
	0.10		0.92	0.97	0.86	0.92
	0.50		0.69	0.79	0.69	0.75
	1.00		0.45	0.57	0.41	0.51
Zn(II)	0.01	5.00	2.41	1.74	1.79	2.08
	0.05		2.02	1.47	1.66	1.42
	0.10		1.56	1.10	1.40	1.28
	0.50		1.17	0.84	1.16	0.89
	1.00		0.64	0.51	0.71	0.57
Cd(II)	0.01	5.00	2.43	2.30	1.95	1.66
	0.05		1.98	1.82	1.55	1.28
	0.10		1.49	1.42	1.11	1.02
	0.50		0.98	0.97	0.92	0.79
	1.00		0.77	0.66	0.68	0.57
Pb(II)	0.01	6.00	2.41	2.24	1.87	3.47
	0.05		1.77	1.67	1.52	2.84
	0.10		1.12	1.40	1.21	2.18
	0.50		0.45	1.21	0.93	1.56
	1.00		0.17	0.92	0.59	0.91

^a [M(NO₃)₂] = 0.1 mol/l; Volume = 2 ml; Volume of electrolyte solution : 25 ml, Weight of resin = 25 mg; time: 24 h; Room temperature.

Ion-exchange properties

Batch equilibrium technique developed by Gregor et al and De Geiso et al was used to study ion exchange properties of p-COF-II terpolymer resin. The results of the batch equilibrium study carried out with the copolymer p-COF-II are presented in Table 5, 6 and 7. Seven metal ions Fe³⁺, Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ in the form of aqueous metal nitrate solution were used. The ion exchange study was carried out using three experimental variables : a) Electrolyte and its ionic strength b) uptake time and c) pH of the aqueous medium, Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymers similar to the earlier co-workers [13,14]. The details of experimental procedure are given below.

Effect of electrolyte and its ionic strength on metal uptake

We examined the influence of ClO₄⁻, NO₃⁻, Cl⁻ and SO₄²⁻ at various concentrations on the equilibrium of metal-resin interaction. Table 2 shows that the amount of metal ions taken up by a

given amount of terpolymer depends on the nature and concentration of the electrolyte present in the solution. Generally as concentration increases of the electrolyte, the ionization decreases, the number of ligands decreases in the solution which form the complex with less metal ions and more ions are available for adsorption. Hence on increasing concentration there should be increase in uptake of metal ion. But trend disturbed due to formation of more stable complex with more number of ligands which decrease the number of metal ions available for adsorption, hence uptake decreases. In the presence of perchlorate, chloride and nitrate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increase with increasing concentration of the electrolytes, whereas in the presence of sulphate ions the amount of the above mentioned ions taken up by the terpolymer decreases with increasing concentration of the electrolyte. Moreover, the uptake of Co (II), Zn (II), Cd (II) and Pb (II) ions increase with decreasing concentration of the chloride, nitrate, perchlorate and sulphate ions. This may be explained on the basis of the stability constants of the complexes with those metal ions. The ratio of physical core structure of the resin is significant in the uptake of different metal ions by the resin polymer. The amount of metal ion uptake by the p-COF-II terpolymer resin is found to be higher when comparing to the other polymeric resins [15].

Estimation of the rate of metal ion uptake as a function of time

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried to while operating as close to equilibrium conditions as possible. As shaking time increases the polymer gets more time for adsorption, hence uptake increases. Table 3 shows the dependence of the rate of metal ion uptake on the nature of the metal. 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 result shows 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. It is found that Fe (III) ions require about 3hrs for the establishment of the equilibrium, whereas Cu (II), Ni (II), Co (II) and Zn (II) ions required about 5 or 6 hrs [16]. Thus the rate of metal ions uptake follows the order Cu (II) > Ni (II) > Co (II) \approx Zn (II) > Cd (II) > Pb (II) for all of the terpolymers [16]. The rate of metal uptake may depend upon hydrated radii of metal ions. The rate of uptake for the post transition metal ions exhibit other trend for Cd(II), the rate of uptake is in the comparable that of Pb(II) because of difference in 'd' orbital.

Table 3 Comparison of the rates of metal (M) ion^a uptake by p-COF-II copolymer resin

Metal ion	pH	Percentage of metal ion uptake ^b at different times (h)						
		1	2	3	4	5	6	7
Fe(III)	2.5	53.3	78.6	96.4	-	-	-	-
Cu(II)	4.5	49.5	61.3	68.6	79.9	93.7	-	-
Ni(II)	4.5	50.7	60.6	70.1	86.1	94.6	-	-
Co(II)	5	45.2	59.7	69.1	84.2	94.1	-	-
Zn(II)	5	49.1	59.6	69.5	84.5	96.1	-	-
Cd(II)	5	30.1	50.6	60.2	70.1	85.2	94.1	-
Pb(II)	6	28.5	49.3	57.2	69.2	84.1	95.7	-

^a $[M(NO_3)_2] = 0.1 \text{ mol/l}$; volume : 2ml; $NaNO_3 = 1.0 \text{ mol/L}$; volume: 25ml, Room temperature.

^b Metal ion uptake = (Amount of metal ion absorbed x 100) / amount of metal ion absorbed at equilibrium.

Distribution ratios of metal ions at different pH

The distributions of metal ion depend upon pH of the solution. As pH, increases the H⁺ ion concentration in the solution decrease and only metal ion in the solution available for adsorption which increase uptake.

The effect of pH on the amount of metal ions distributed between two phases can be explained by the data given in Table 4. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ion taken up by the p-COF-II terpolymer increases with increasing pH of the medium [17]. The magnitude of increase, however, is different for different metal cations. The study was carried from 2.5 upto pH 6.5 to prevent hydrolysis of metal ions at higher pH. For Fe^{3+} ion the highest working pH is 3, has lower distribution ratio since Fe^{3+} forms octahedral complex with ligand of electrolyte, which shows crowding effect. This steric hindrance may be lower the distribution ratio of Fe^{3+} ion. Cu^{2+} and Ni^{2+} have higher distribution ratio over pH range of 2.5 to 6.5 which may be due to the less steric hindrance. Thus the value of distribution ratio for given pH depends upon the nature and stability of chelates formation for particular metal ion.

Table 4 Distribution ratio D^a of various metal ions b as function of the pH by p-COF-II terpolymer resin

Metal ion	Distribution ratio a of the metal ion at different pH							
	1.5	2	2.5	3	3.5	4	5	6
Fe(III)	20.2	125.6	237.1	368.2	-	-	-	-
Cu(II)	-	-	-	68.3	93.4	212.1	681.4	1209.4
Ni(II)	-	-	-	52.1	74.8	230.4	462.1	914.1
Co(II)	-	-	-	41.5	65.4	155.8	248.2	445.4
Zn(II)	-	-	-	43.7	73.1	99.3	133.0	225.8
Cd(II)	-	-	-	31.2	65.7	107.1	174.2	234.3
Pb(II)	-	-	-	39.6	63.5	126.2	197.2	273.6

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 $[\text{M}(\text{NO}_3)_2] = 0.1 \text{ mol/l}$; volume : 2ml; $\text{NaNO}_3 = 1.0 \text{ mol/l}$; volume: 25ml, time 24h (equilibrium state) at Room temperature.

The data of distribution ratio shows a random trend in certain cases [18]. This may be due to the amphoteric nature of the p-COF-II resin. Table 7 shows that reported resin provides better selectivity for one metal ion in presence of other metal ions. From the result it reveals that with decrease in atomic number the ion uptake capacity is increasing at that particular pH. In case of Cd (II) and Pb (II) purely electrostatic factors are responsible. The ion uptake capacity of Cd (II) is lower owing to the large size of its hydrated ion than that of Cu (II). The steric influence of the methyl group and hydroxyl group in p-COF-II resin is probably responsible for their observed low binding capacities for various metal ions. Thus the interaction of this resin material with various metal ions in an aqueous environment may largely limit the binding sites, which are suitably, disposed in a conformational favourable manner on the surface layer.

The higher value of distribution ratio for Cu (II) and Ni (II) at pH 2.6 to 6.0 may be due to the formation of most stable complex with chelating ligands. Therefore the polymer under study has more selectivity of Cu^{2+} and Ni^{2+} ions at pH 4.0 to 6.0 than other ions which form rather weak complex. While at pH 3 the terpolymer has more selectivity of Fe^{3+} ions. The p-COF-II terpolymer resin take up Fe (III) ion more selectively than any other metal ions under study. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be Fe (III) > Cu (II) > Ni (II) > Zn (II) > Co (II) > Pb (II) > Cd (II). Thus 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 [18]. For example, the result suggest the optimum pH 6.0, for the separation of Co(II) and Ni (II) with distribution ratio 'D' at 445.4 and 914.1 respectively using the p-COF-II terpolymer resin as ion-exchanger. Similarly, for the separation of Cu (II) and Fe (III) the optimum pH is 3, at which the distribution ratio 'D' for Cu (II) is 68.6 and that for Fe (III) are 368.2. The lowering in the distribution of Fe (III) was found to be small and, hence, efficient separation could be achieved [19, 20, 21].

Ion exchange properties of various resins can be studied by comparing their ion exchange capacity. The ion exchange capacity (IEC) is a fundamental and important quantity for the characterization of any ion exchange material. It is defined as the amount of ion that undergoes ion exchange in a definite amount of material, under specified experimental conditions. However, there may be complication in the determination of the capacity [21]. The ion exchange capacity of p-COF-II terpolymer has been calculated, which was found to be 3.98 mmol.g⁻¹ which indicates that p-COF-II terpolymer resin is better ion exchanger than phenolic and some polystyrene commercial ion exchangers.

Some commercially available ion-exchange resins are given below:

Trade Name	Functional Group	Polymer Matrix	Ion-exchange Capacity (mmol.g ⁻¹)
Amberlite IR-120	-C ₆ H ₄ SO ₃ H	Polystyrene	5.0-5.2
Duolite C-3	-CH ₂ SO ₃ H	Phenolic	2.8-3.0
Amberlite IRC-50	-COOH	Methacrylic	9.5
Duolite ES-63	-OP(O)(OH) ₂	Polystyrene	6.6
Zeocarb-226	-COOH	Acrylic	10.00
Dowex-1	-N(CH ₃) ₃ Cl	Polystyrene	3.5
Amberlite IRA-45	-NR ₂ , -NHR, -NH ₂	Polystyrene	5.6
Dowex-3	-NR ₃ , -NHR, -NH ₂	Polystyrene	5.8
Allassion A WB-3	-NR ₂ , -N ⁺ R ₃	Epoxy-Amine	8.2

For the strongly acidic cation exchange resin such as cross linked polystyrene sulphonic acid resins, the ion exchange capacity is virtually independent of the pH of the solutions. For weak acid cation exchangers, such as those containing carboxylate group, ionizations, occurs only in alkaline solution. Similarly weakly basic cation exchanger does not work above pH-9.

CONCLUSION

1. The plots of log σ vs $1/T$ is found to be linear in the temperature range under study, which indicate that the Wilson's exponential law $\sigma = \sigma_0 \exp(-\Delta E/KT)$ is obeyed.
2. Electrical conductivity of each of this terpolymer resin increases with increase in temperature. Hence, this terpolymer may be ranked as semiconductor.
3. A terpolymer p-COF-II based on the condensation reaction of p-Cresol and oxamide with formaldehyde in the presence of acid catalyst was prepared and is found to be a selective chelating ion-exchange terpolymer resin for certain metals. The terpolymer resin showed a higher selectivity for Fe³⁺, Cu²⁺ and Ni²⁺ ions than for Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ ions.
4. The uptake of some metal ions by the resin was carried out by the batch equilibrium technique. The uptake capacities of metal ions by the terpolymer resin were pH dependent. From the results of distribution coefficients, it can be observed that Cu (II) has higher value of distribution ratio. Due to considerable difference in the uptake capacities at different pH and media of electrolyte, the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to use for separation of particular metal ions from their admixture.

Contribution of the results to the development of an important area of research

Because of the remarkable properties and the lower cost of manufacturing p-COF-II terpolymer resin can have major potential application in various sectors.

The p-COF-II has semiconducting nature and when the voltage is passed through the thin film of this terpolymer resin then it emits light, this remarkable property of this resin make it an

attractive alternative to form a wide range of semiconducting electronic devices, such as transistors, light emitting diodes, solar cells etc.

The ion-exchange capacity of p-COF-II terpolymer resin is 3.98 meq/gm which indicate that this resin in better ion-exchanger then some polystyrene and phenolic commercial ion-exchanger. This remarkable high ion-exchange capacity would like to point out several important applications, such as in the treatment of water for drinking and waste water treatment. The p-COF terpolymer resin can soften the water deionize it and even be used in desalination. The p-COF resin can also be used in recovery of valuable metals at industrial level from waste solutions.

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