Evaluation of the Influence of Different Electrolytes on the Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+} metal ions uptake Capacity, Rate and Distribution byCopolymers Derived from Salicylic Acid, and Thiosemicarbazide

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***Abstract*:The Present work deals with the study of influence of different electrolytes such as NaCl,$NaNO_3$, $NaClO_4$, Na_2SO_4 , on Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Pb^{2+} metal ions taken up by a given amount of copolymer also determined their rate distribution ratio of metal ions at different pH. The chelating ion-exchange study was carried out over a wide range of pH, shaking time and in medium of various ionic strengths. The condensation of of Salicylic acid and thiosemicarbazide with formaldehyde was carried out in the presence of 2M HCL as a catalyst at 126 ± 2 ^{0}C for 5 hrs. with molar proportion of reactants in order to synthesize the new copolymer. The copolymer (SATF-I) was characterized by FT-IR, UV-Visible ^{1}H-NMR Spectroscopy.**

***Keywords:*Electrolytes, Rate, Distribution, Metal Ions, Ion-exchange, Synthesis, Condensation, Copolymer.**

I.INTRODUCTION

Heavy metals such as Lead,Arsenic, Mercury, Cadmium, Chromium, Nickel, Zinc have hazardous effects in Damage to the foetal brain, skin manifestation, visceral cancers, vascular diseases, Kidney damage, renal disorder etc. Ion-exchange is one of the use techniques to remove heavy metal ions present in water. Copolymer resins prepared by condensation method plays a vital role and are found to be good cation exchanger having both ion-exchange group and chelating group in the same polymer matrix and the resin can be used selectively for the purpose of purification of waste water..

Ion-exchange has attained the status of a unit operation in chemical industries and has mostly replaced operations like distillation and other traditional methods of separations. Many methods such as electrodeposition, co-precipitation and solid-liquid extraction have been developed for pre-concentration and removal of metal ions [1-2].

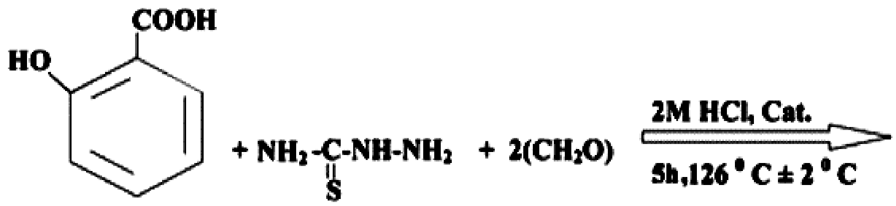
Electrolytes plays an important role in the field of electrochemistry and ion-exchange study. The strong and week electrolytes decides the conduction of electrons by the ions i.e deposition or uptake will more or less. Hence in this article, the study of evaluation of the Influence of different electrolytes on theCo $^{2+}$, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} ionsmetal ions uptake, rate and distribution by copolymers have been carried out. The copolymers was synthesized from Salicylic acid, thiosemicarbazide and formaldehyde (SATF-I). The metal ion uptake capacity of the copolymer resin was studied by using batch equilibrium method for Co $^{2+}$, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} ions in different electrolytes, pH range and time intervals are also examined and reported for the first time. Copolymer resin is characterized by elemental analysis, spectral studies (FTIR, ^{1}H NMR) [3].

II.EXPERIMENTAL

A. Synthesis of SATF-I

The condensation of the organic compounds Salicylic acid (0.1 mol) and thiosemicarbazide (0.1 mol) with formaldehyde (0.2 mol) in a molar ratio of 1:1:2 was carried out in the presence of 2 M 200 ml HCl as a catalyst at 126 ^{0} C ± 2 ^{0} C for 5h.in order to synthesize the new SATF-I copolymer. The methanol and hot water was used to washedthe separated copolymer.

It is then extracted with diethyl ether and then with petroleum ether to remove Salicylic acid – thiosemicarbazideformaldehyde copolymer which might be present along with SATF-I copolymer. The yellow color resinous product wasthen purified by dissolving in 10% aqueous sodium hydroxide solution, which was then filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel[4-7].



Salicylic Acid ThiosemicarbazideFormaldehyde

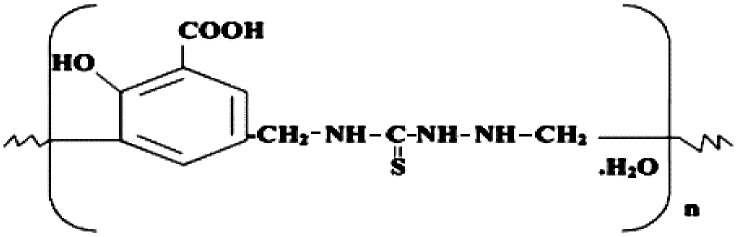


Fig. 1: Synthesis of SATF-I copolymer resin

B. Ion-exchange property:The ion-exchange property of the SATF-I copolymer resin was determined at three different variations given below.

1) Determination of metal uptake in the presence of different electrolytes and their different concentrations :

The 25 mg copolymer sample was suspended in 25 ml an electrolyte solution of known concentration. The pH of the suspension was maintain with 0.1 M HNO_3 or 0.1 M NaOH. The solution was stirred for 24 h at 30ºC. To this solution 2 ml of 0.1 M solution of the metal ion was added and pH was adjusted to the required value. The mixture was again stirred at 30ºC for 24 h. 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 at the same pH.The same titration has been carried out without polymer (blank reading). The uptake of amount of metal ion by copolymer was calculated from the difference between a blank experiment without copolymer and the reading in the actual experiments. The experiment was repeated in the presence of several electrolytes .The buffer used was Dil. HNO_3/Dil. NaOH, Aq. NH_3/NH_4CL, Hexamine, and Indicator used wasFast Sulphone Black-F, Mureoxide,Xylenol orange, Eriochrome Black-T.

The metal ion uptake can be determined as: *Metal ion uptake by copolymer = (X-Y) Z milimols / gm*

Where Z (ml) is the difference between actual experimental reading and blank reading; X (mg) is metal ion in 2 ml,(0.1 M metal nitrate solution) before uptake; and Y (mg) is metal ion in 2 ml (0.1 M metal nitrate solution) after uptake.By using this equation the uptake of various metal ions by resin can be calculated and expressed in terms ofmillimols per gram of the copolymer [8-10].

2) Estimation of rate of metal ion uptake as a function of time: A series of experiments were carried out, in order to estimate the time required to reach the state of equilibrium under the given experimental conditions, in which the metal ion taken up by the chelating resins was determined from time to time at 30ºC (in the presence of 25 ml of 1 M $NaNO_3$ solution).

Metal ion taken up at different times (%) = $\dfrac{Metal\,ion\,adsorbed}{Metal\,ion\,adsorbed\,at\,equilibrium}\times 100$

Percentage of metal ion adsorbed after 1 h = (100X) / Y

Where X is mg of metal ion adsorbed after 1 h and Y is mg of metal ion adsorbed after 25 h.[11-12].

3)Evaluation of the distribution of metal ions at different pH:

The distribution of each of the five metal ions i.e., $Co^{2+,}$ $Ni^{2+,}$ $Cu^{2+,}$ $Zn^{2+,}$ and $Pb^{2+,}$ ions between the polymer phase and the aqueous phase was determined at 30ºC and in the presence of 1 M $NaNO_3$ solution. In order to study the influence of of electrolyte on metal ion uptake capacity the experiments at different pH valueswere carried out as described above. The distribution ratio, D, is defined by the following relationship.

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

III. RESULTS AND DISCUSSION

A. FT-IR Spectra :

A broad band appeared in the region 2800-3200cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding . The sharp band displayed at 1600-1400 cm^{-1}may be due to the stretching vibrations of carbonyl group (C=O) of both as well as (C=S) moiety . The sharp band at 2800-3000 cm^{-1} may be assigned due to presence of -NH in thiosemicarbazide moiety. A strong sharp peak at1625-1500 cm^{-1} may be ascribed to aromatic skeletal ring . The bands obtained at 1400 – 1200 cm^{-1} suggest thepresence of methylene bridges in the polymer chain. The weak band appearing at 726 - 760 cm^{-1} is assigned to C –OH bond. 1,2,4,6 tetrasubstitution of aromatic ring is recognized from the bands appearing at 905, 1083, 1201, and 1292cm-1 respectively [3].

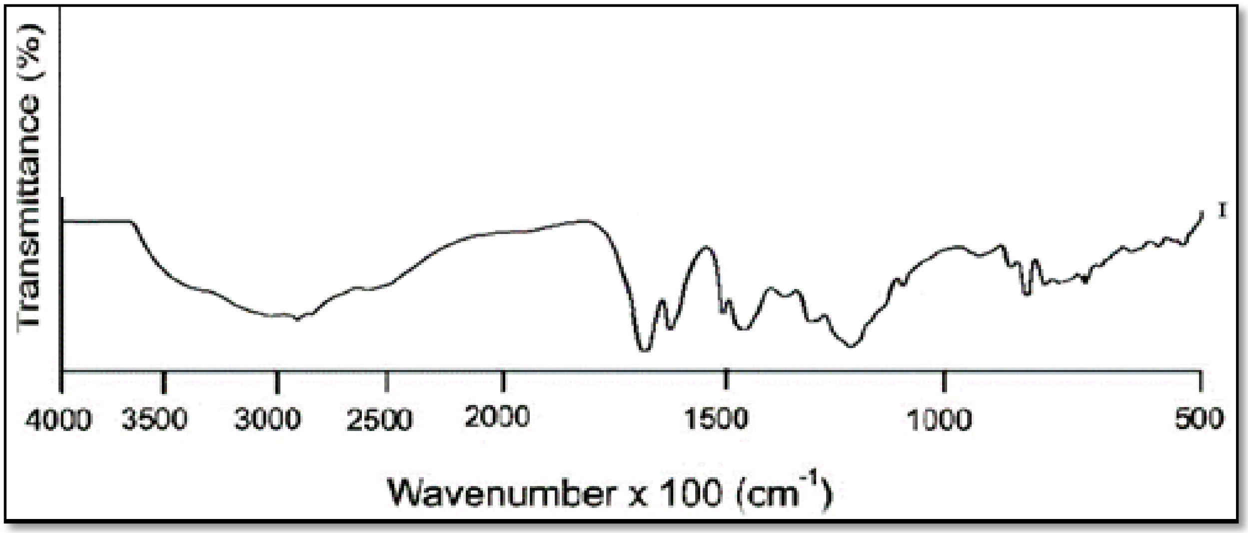


Fig.2: Infra-Red Spectroscopy of SATF-I copolymer Resin

B.NMR Spectra:

The NMR spectra of SATF-I copolymer resins show a weak multiple signal (unsymmetrical pattern) in the region 6.5 to 7.0 (δ) ppm which is due aromatic protons. A medium singlet peak appeared at 3.5 – 4.0 (δ) ppm may be assigned to methyl protons of Ar-CH2-NH group. Intense signal appeared in the region 2 – 3 (δ) ppm may be due to Ar–CH2-NH .Triplet signal appeared in the region 3.42 – 4.84 (δ) ppm can be assigned to amido proton of –CH2-NH-CO-linkage[3].

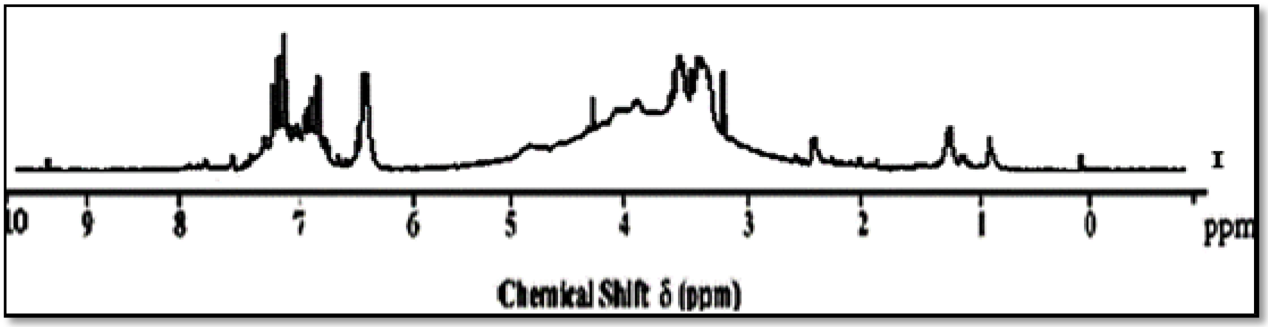


Fig.3: NMR Spectroscopy of SATF-I copolymer Resin

C. Determination of Metal Uptake in the Presence of Various Electrolyte :

The evaluation of influence of chloride, nitrate, chlorate and sulphate at various concentrations on the equilibrium of metal – resin interaction have been examined and tabulated in Table.I and in Fig.4-8. The amount of metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Pb^{2+} taken up by copolymer in the presence of nitrate and per chlorate ions, the uptake of ions increases with increasing concentrations of the electrolyte [8-10].

The uptake of Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Pb^{2+} ions decreases with increasing concentration of the chloride and sulphate electrolytes. This may be due to the chloride and sulphates ion forming strong chelates with metal ions, while the other anions i.e nitrate and perchlorate form weak chelates[11-12]. The position of the metal chelate equilibrium is less influenced in the presence of nitrate and perchlorate and ions than that of chloride and sulphates ion.

The amount of uptake of Co^{2+}, Zn^{2+} and Pb^{2+} ions by the copolymer under the influence of nitrate is higher than that of the other metal ions. This may be due to the Co^{2+}, Zn^{2+} and Pb^{2+} ions form weak chelates with the anions of the nitrate electrolytes [13-15].The amount of uptake of Ni^{2+} and Pb^{2+} ions by the copolymer under the influence of chloride is higher than that of the other metal ions. This may be due to the Ni^{2+} and Pb^{2+} ions form weak chelates with the anions of the chloride electrolytes. The amount of uptake of Co^{2+}, Zn^{2+} and Pb^{2+} ions by the copolymer under the influence of perchlorate is higher than that of the other metal ions. This may be due to the Co^{2+}, Zn^{2+} and Pb^{2+} ions form weak chelates with the anions of the perchlorate electrolytes. The amount of uptake of $Cu^{2+,}$ $Ni^{2+,}$ Co^{2+}, Zn^{2+} and Pb^{2+} ions by the copolymer under the influence of sulphate is lower for all the metal ions. This may be due to the $Cu^{2+,}$ $Ni^{2+,}$ Co^{2+}, Zn^{2+} and Pb^{2+} ions form strong chelates with the anions of the sulphate electrolytes.In addition, the copolymer has more porosity in its structure they can accommodate metal ions of specific size, easily into its cavities and acts as a better cation-exchanger [16-18].

TABLE I

EVALUATION OF THE INFLUENCE OF DIFFERENT ELECTROLYTES ON THE UPTAKE OF METAL IONS

Metal Ion	Electrolyte Concentration (mole/lit)	Weight of metal ion (mg)taken up in presence of			
		$NaNO_3$	NaCl	$NaClO_4$	Na_2SO_4
Cu^{2+}	0.01	0.25	0.59	0.04	0.59
	0.05	0.29	0.38	0.08	0.53
	0.10	0.19	0.72	0.13	0.42
	0.50	0.22	0.33	0.16	0.33
	1.00	0.29	0.42	0.25	0.14
NI^{2+}	0.01	0.31	0.43	0.04	0.53
	0.05	0.43	0.43	0.06	0.45
	0.10	0.46	0.51	0.1	0.34
	0.50	0.55	0.47	0.17	0.26
	1.00	0.57	0.59	0.22	0.16
Co^{2+}	0.01	0.24	0.35	0.11	0.66
	0.05	0.28	0.31	0.15	0.61
	0.10	0.43	0.31	0.27	0.49
	0.50	0.55	0.31	0.43	0.42
	1.00	0.67	0.20	0.62	0.31
Zn^{2+}	0.01	0.09	0.70	0.07	0.64
	0.05	0.13	0.74	0.12	0.60
	0.10	0.26	0.65	0.20	0.49
	0.50	0.48	0.65	0.46	0.38
	1.00	0.70	0.65	0.54	0.19
Pb^{2+}	0.01	0.41	1.11	0.17	2.18
	0.05	0.69	0.83	0.41	2.00
	0.10	1.11	1.38	0.80	1.57
	0.50	1.80	1.24	1.57	1.08
	1.00	2.07	1.66	1.84	0.62

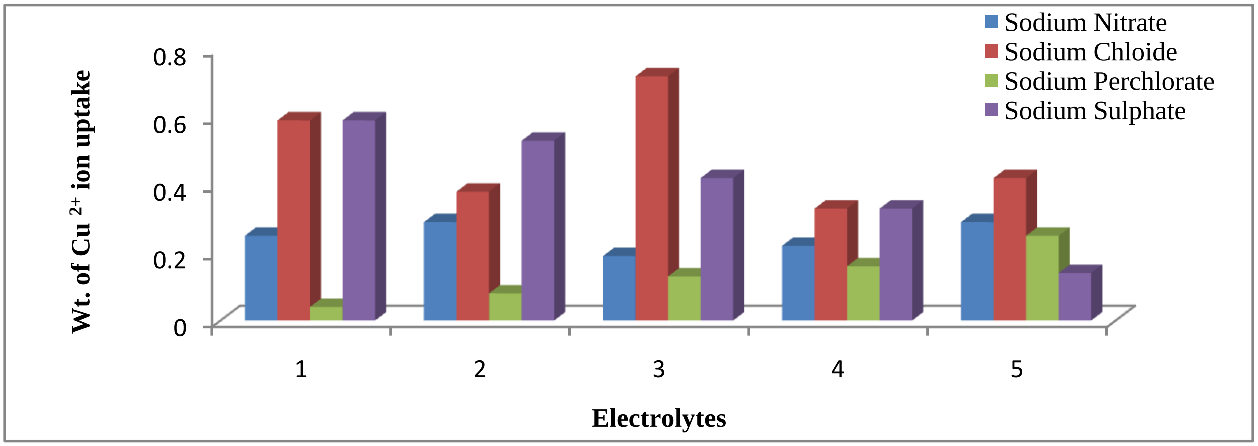


Fig-4: Weight of Cu^{2+}ions uptake by SATF-I under the influence of electrolytes

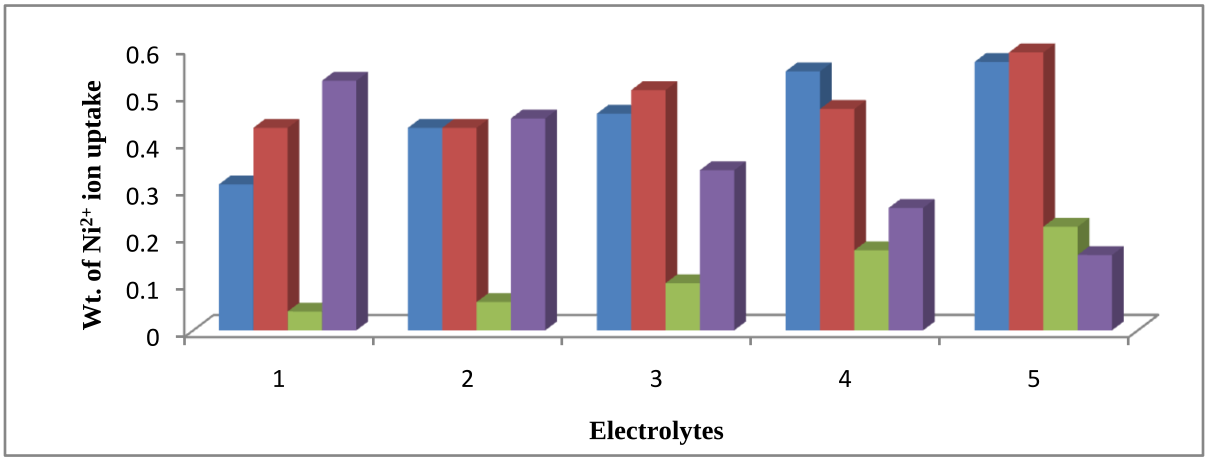


Fig-5 : Weight of Ni^{2+} ions uptake by SATF-I under the influence of electrolytes

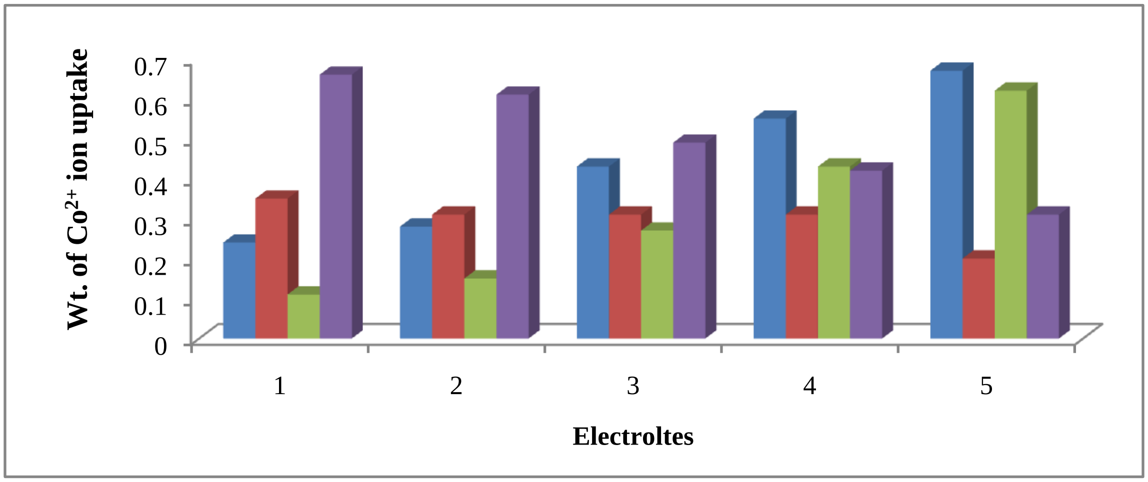


Fig.-6: Weight of Co^{2+} ions uptake by SATF-I under the influence of electrolytes

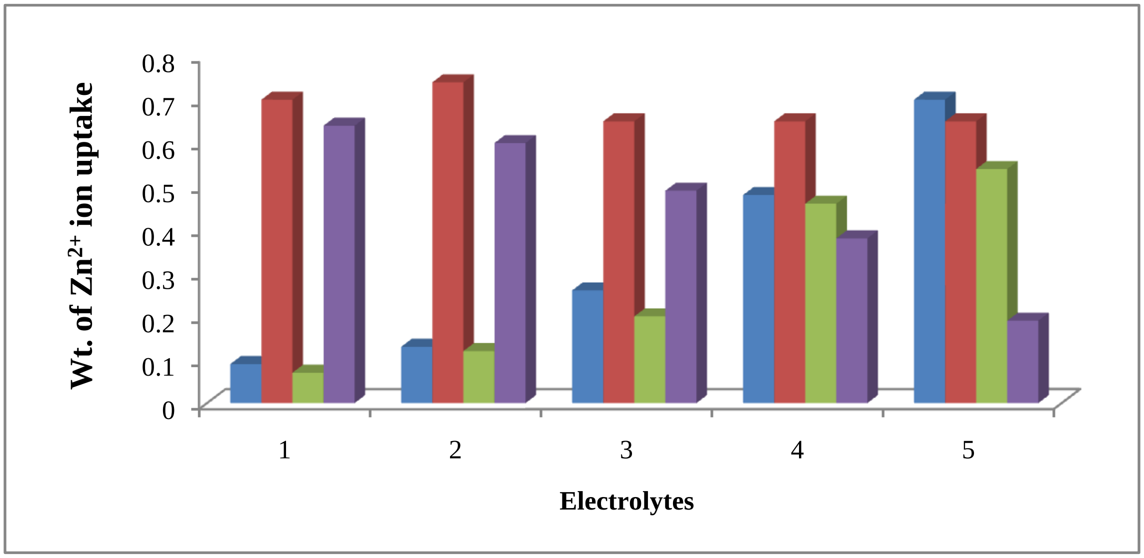


Fig.-7: Weight of Zn^{2+} ions uptake by SATF-I under the influence of electrolytes

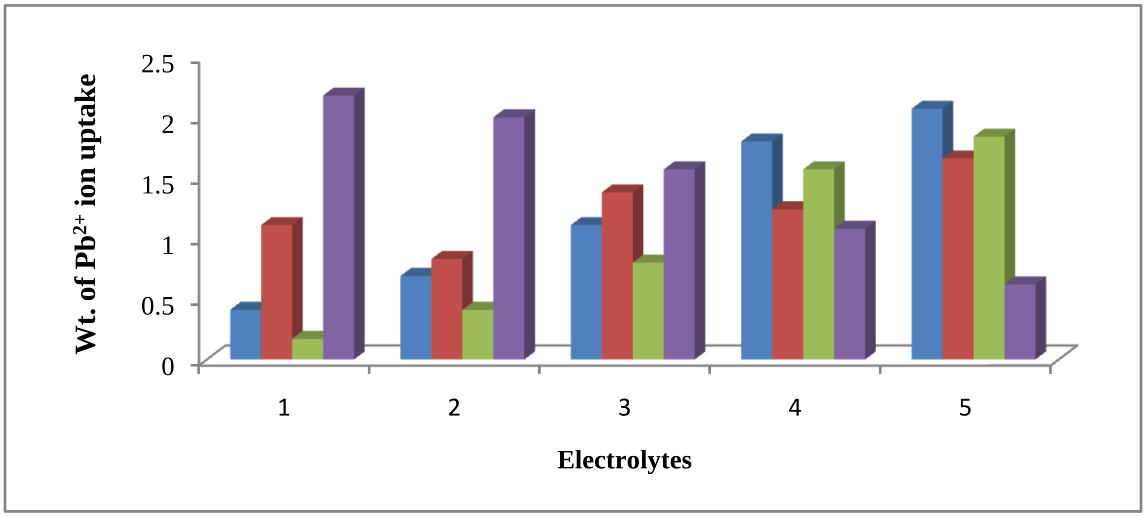


Fig.-8: Weight of Pb^{2+} ions uptake by SATF-I under the influence of electrolytes

D. Evaluation of the Rate of Metal-IonUptake **:**

To estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments were carried out, in which the metal ion taken up by the copolymer resin was estimated from the timeto room temperature (300 K) in the presence of 25 ml of a solution of $NaNO_3$. It was assumed that under the given conditions, the state of equilibrium was established within 24 h. The rate of metal-ion uptake was expressed as the percentage of the amount of metal ion taken up after a certain time related to that in the state of equilibrium [8-10].

The rates of ion absorption by SATF-I copolymer resin samples were measured for Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Pb^{2+} ions to determine the time required to reach the equilibrium.

The term refers to the change with time when they were in contact with the copolymer sample the experiment results, which are shown in Table 3 and Fig.8. A careful examination of the experimental data, which are shown in Table 3. shows that Pb^{2+}, Co^{2+} ions required almost 1 h for equilibrium, Zn^{2+} required 2 h, Cu^{2+}, Ni^{2+}, required 5h and 6h respectively. The experimental results revealed that the rate of metal-ion uptake followed the order of $Co^{2+} > Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$[11-12]

TABLE.III: PERCENTAGE OF THE AMOUNT OF METAL ION TAKEN UP AT DIFFERENT TIMES

Time (Hrs)	**Percentage of the amount of metal ion taken up at different times**				
	Cu^{2+}	**NI^{2+}**	**Co^{2+}**	**Zn^{2+}**	**Pb^{2+}**
1	3	5	34	28	29
2	6	9	40	36	42
3	12.5	18	65	45	58
4	20	27	70	51	77.5
5	37.5	36.5	85	65	81
6	55	40.5	90	70	86

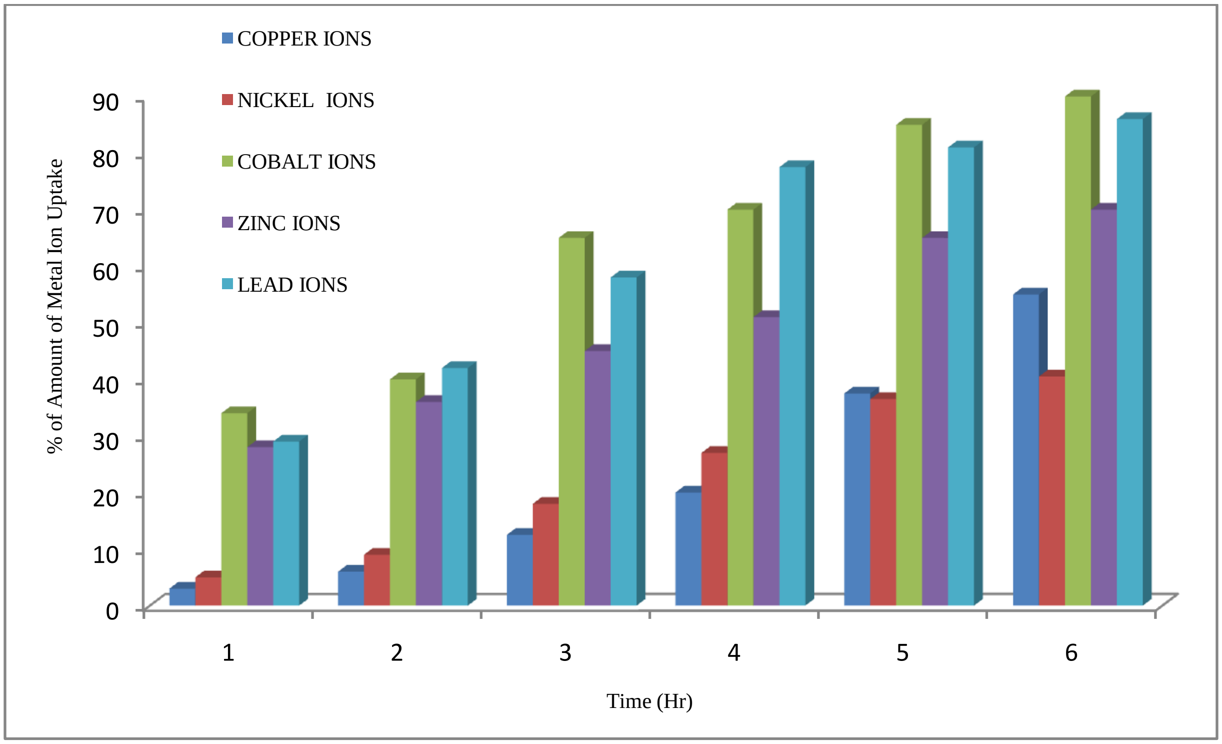


Fig-8: Percentage of amount of metal ions taken up at different times

E.Evaluation of the Distribution of Metal Ions at Different pH :

The distribution of each one of the five metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Pb^{2+}between the polymer phase and aqueous phase was estimated at 300 K and in the presence of a solution of $NaNO_3$.The study was restricted up to a maximum pH of 6.5, due to the hydrolysis of metal ion at higher pH. The amount of the metal ion which remained in the aqueous phase was estimated. If the original metal ion concentration is known, the metal ion adsorbed by the resin can be calculated. The effect of pH on the amount of metal ion distributed between the two phases is given in Table 4 and shown in Fig.9 which reveals that the amount of uptake of metal ions by the resin at equilibrium increases with increasing pH. It is assumed that the equilibrium state is attained at 25 ºC under the given conditions in 24 h.[[13-15]

The SATF-I copolymer resin takes up Co^{2+} and Pb^{2+} ions more selectively than the other ions under study at all pH values. Among the other ions taken up for the study, Zn^{2+} shows selective uptake under moderate pH values. Further, Cu^{2+} and Ni^{2+} ions have lower distribution over the pH range from 2.5 to 6.5. This can be explained as the weak stabilization energy of the metal chelates formed from these ions [16-18].

TABLE.IV
DISTRIBUTION RATIO OF THE METAL ION

pH	**Distribution ratio of the metal ion**				
	Cu^{2+}	**NI^{2+}**	**Co^{2+}**	**Zn^{2+}**	**Pb^{2+}**
2.5	20.85	12.5	34.34	59.25	45.79
3	38.09	20.42	44.44	110.8	59.25
3.5	47.86	31.25	54.54	188.8	104.3
4	59.2	39.13	200	188.8	165.0
5	72.7	39.28	958.9	355.5	466.6
6	113.1	54.16	674.0	391.5	800
6.5	139	141.3	1145.	466.6	1886

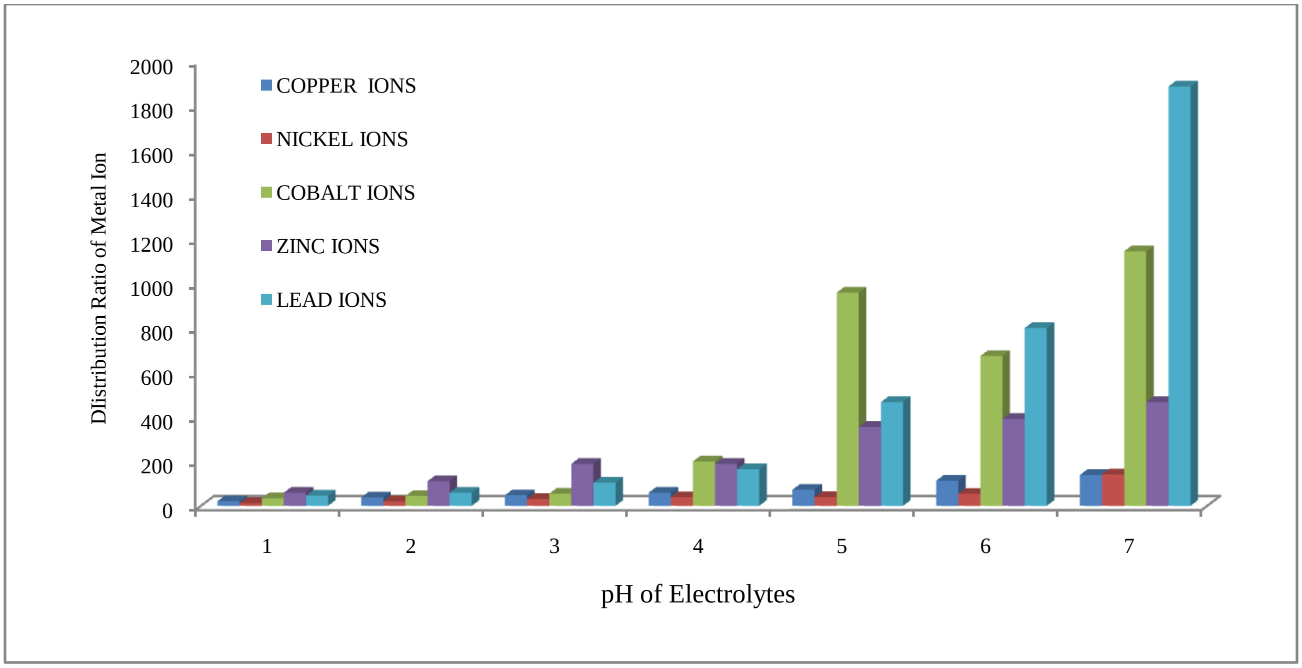


Fig.10: Distribution ratio of metal ions taken up at differentpH

Conclusion:

- A Copolymer SATF-I based on the condensation reaction of Salicylic acid and thiosemicarbazide with formaldehyde in the presence of acid catalyst was prepared.
- Copolymer SATF-I shows Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Pb^{2+} metal ions uptake capacity under the influence of different electrolytes such as NaCl,$NaNO_3$,$NaClO_4$, Na_2SO_4.
- In the presence of nitrate and per chlorate ions, the uptake of Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Pb^{2+} ions by SATF-I isincreases with increasing concentrations of the electrolyte. Where as the uptake of Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Pb^{2+} ions decreases with increasing concentration of the chloride and sulphate electrolytes.
- On the basis of the stability constants of the complexes formed, it has been conclude that, the chloride and sulphates ion forming strong chelates with metal ions, while the other anions i.e nitrate and perchlorate form weak chelates.
- The SATF-I resin is a selective chelating cation exchange polymer resin for certain metals.
- The rate of metal-ion uptake followed the order of $Co^{2+} > Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$
- The uptake capacities of metal ions by the polymer resin were pH dependent.

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