



CHELATION ION-EXCHANGE PROPERTIES OF 8-HYDROXY QUINOLINE-ACRYLAMIDE- FORMAL DEHYDE COPOLYMER RESIN

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Abstract

8-Hydroxyquinoline, acryl amide, and formaldehyde were condensed using an acid catalyst to make 8-HQAF copolymer resin. Various physicochemical techniques were used to characterize the produced copolymer. Numerous characterization techniques, including elemental analysis, FTIR, UV-Visible, NMR (¹H and ¹³C), XRD, and SEM, were employed to examine the structure and properties of the copolymer resin. In order to determine the heat stability of the copolymer resin and its kinetic parameter, the TGA method was utilized. For the purpose of determining the activation energy, Freeman-Carroll (FC) and the Sharp-Wentworth (SW) procedures were utilized. It was discovered that the decomposition reaction for the copolymer was of the first order, whereas for the composite, a higher order was produced. Based on the findings, the activation energy, frequency factor, and entropy change all point to the copolymer's impressive capacity for withstanding high temperatures. A measurement of the cation exchange capacity was performed, and the influence of pH and metal ion concentration on the capability of ion exchange was investigated. Using the batch equilibration approach, we also investigated the ratio of cation exchange and the distribution coefficient in EDTA medium at a range of different pH values.

Keywords: Copolymer, Morphology, Thermal degradation, Poly condensation, Resin, Activation energy, Chelation Resin, Batch Equilibration.

Introduction

The class of polymers known as copolymers is particularly unique and noteworthy due to the wide range of applications to which it can be put. The structure of these polymers can be crystalline, amorphous, or resinous in appearance [1-4]. In recent years, there has been a significant rise in the application of copolymers for the current generation; as a result, these molecules now hold a unique place in the study of polymer science [5]. Gupta and his colleagues have investigated the kinetics of thermal degradation for polymer 2-amino-6-nitrobenzothiazole, melamine, and formaldehyde. Michael et al. analysed the synthesis, characterization, and thermal degradation of a terpolymer composed of 8-hydroxyquinoline, formaldehyde, and acrylamide [6-7]. Rahangdale and his colleagues conducted research on the heat degradation of a polymer that was produced from 2,4-dihydroxyacetophenone, formaldehyde, and dithioxamide [8-9]. Oxidation of the 8-hydroxyquinolate was the starting point for the synthesis of poly(8-hydroxyquinoline), also known as PHQ. In addition to this, polymeric metal is of tremendous importance in a number of other subfields of chemistry. Several distinct techniques, such as ¹H NMR spectroscopy, FTIR spectroscopy, differential scanning calorimetry (DSC), thermal gravimetric (TG), and differential thermal gravimetric (DTG), have been utilized in its characterization. At a negatively charged electrode potential, the cathodic stripping voltammetric of the PHQ, which was carried out at the hanging mercury dropping electrode (HMDE), displays a weak

signal. The spectro analytical sensitivity of PHQ coordination polymers with an assortment of metal ions has been calculated. Potentiometric Studies of a Polymeric and Coordination Polymeric Form of 8-Hydroxyquinoline The spectrophotometric method was utilized in order to conduct study on the cation exchange characteristics. Studies were conducted on the immobilization of polymeric, monomeric, and polymeric chelate forms of the (8- Hydroxyquinoline) matrix when it was integrated in aluminium oxide. In addition to this, the immobilisation of polymeric, monomeric, and polymeric chelate forms of the (8- Hydroxyquinoline) matrix was converted into silica gel, and the results were examined [10- 12]. Application of Analytical Techniques, Obtaining a patent about Poly(8-Hydroxyquinoline) immobilized on some substance as risen for removal of metal ion is one of the many applications that can be used for previous studies conducted in a variety of fields.

Other applications include the preconcentration of certain metal ions and the preconcentration of other metal ions. Other applications include: In an acid media, the polycondensation process was used to create the copolymer 8-HQAF from the monomers 8-Hydroxyquinoline, acrylamide, and furfural in a molar ratio of 2:1:3. Several different physico-chemical methods were used in order to characterise the synthetic copolymer resin that was created. In this work, the thermogravimetric analysis of the copolymer resin was performed using a nonisothermal thermogravimetric analysis approach. This technique requires the sample to be subjected to a situation in which the temperature is continuously increased at a linear rate. A thermal investigation of the resins was carried out in order to ascertain the processes by which they decompose and their degrees of relative thermal stability. In order to analyse the structure of the copolymer as well as its properties, a number of different characterisation techniques, such as elemental analysis, FTIR, UV-Visible, XRD, and SEM, were utilised. In order to determine the heat stability of the copolymer resin and its kinetic parameter, the TGA method was utilised.

Experimental

Material

8-Hydroxyquinoline acid, acrylamide and formaldehyde was possible to acquire from Central Scientific Company Nagpur. The solvents like HCl, Himedia was the source of the DMSO that was purchased. The entire assortment of chemicals is of the pure and analytical quality.

Synthesis of 8-HQAF Copolymer Resin

p-Hydroxyquinoline-acrylamide- formaldehyde (8-HQAF) copolymer was synthesised by polycondensation of 8- Hydroxyquinoline, formaldehyde and acrylamide with 2M HCl in the ratio 2:1:3 in an oil bath at a temperature of 123

5hrs. The copolymer obtained was black in color, rinsed with hot water until all of the chloride ions were removed from it. The process is repeated several times with hot water, it was then dried in a vacuum at a temperature above silica gel after being filtered. The dried, powdered and purified copolymer was further finely crushed. The yield of the copolymer was found to be about 88%.

The production of polymers from resources that can be replenished has captured the interest of a significant number of research workers [1]. There has been a significant amount of work reported from the laboratories on the synthesis, characterisation, structure, and thermal studies of a number of different polymers [2]. In order to examine the various kinetic characteristics associated with the copolymer, both the Freeman-Carroll and the Sharp- Wentworth methods have been utilised. In particular, the procedures for TGA research [3] are predicated on the assumptions of the Arrhenius equation, which state that the barriers posed by thermal energy and diffusion are deemed to be minimal. The chemicals that were utilised were either of the chemically pure or analytical reagent grade. The synthesis of 8-HQAF was carried out by condensing 8-hydroxyquinoline, formaldehyde and Acrylamide in a mole ratio of 2:3:1 in the presence of 2M HCl as a catalyst at a temperature of 130 degrees Celsius for eight hours. This process was detailed earlier in reference 12. In order to use it in all of the many experiments that were conducted for the ion-exchange study, the purified polymer had to be extremely finely ground so that it could fit

through a sieve with a mesh size of 300. A polymer sample that weighed 25 mg was first suspended in a solution that included 25 ml of an electrolyte whose concentration was known. This step was done with the intention of evaluating metal uptake even if the electrolyte concentrations that were present in the environment varied. Either 0.1 N HNO₃ or 0.1 N NaOH was used to bring the pH of the suspension up to the desired level so that it could be used. At a temperature of 25 degrees Celsius, the suspension was mixed for a total of twenty-four hours. Following the addition of 2 ml of a solution with a concentration of 0.1 M of the metal ion, the pH of this suspension was brought up to the desired level. The mixture was agitated once more at 25°C for twenty-four hours before it was filtered [6-7].

After that, the polymer was rinsed and put through a filter. When the filtrate and the washings were mixed together, for the purpose of determining how many metal ions were present, a titration was performed against a reference solution of ethylene diamine tetraacetic acid. In addition to the other experiments, a blank experiment was carried out in exactly the same way as the others, but the polymer sample was omitted from it. In addition, an estimate was made for the amount of metal ions present in the blank. The difference between the reading taken with a blank strip and the reading taken during the experiment provides a definition for the distribution ratio.

experiment was used to compute the quantity of metal ion that was absorbed by the polymer while it was in the presence of an electrolyte whose concentration was known.

The experiment was conducted multiple times in the presence of various electrolytes containing seven distinct types of metal ions, including.

In order to ascertain the amount of time required to attain the state of equilibrium under the experimental conditions that were specified, a series of experiments of the kind described above were carried out. During these experiments, the amount of metal ion uptake by the chelating resins was estimated at various time intervals at a temperature of 25 degrees Celsius (in presence of 25 ml of 1M NaNO₃ solution). Within twenty-four hours, the state of equilibrium was achieved under the conditions that were presented. The ratio of the number of metal ions that are taken up after a specific period of time to the amount that would be present in equilibrium (Table 3 and 4). At a temperature of 25 degrees Celsius, a metal/1M NaNO₃ solution was used to measure how each of the seven metal ions was distributed between the aqueous phase and the polymer phase. The studies were conducted in the same manner as stated above, but at a variety of pH levels. The following equation provides a definition for the distribution ratio referred to as D:

Weight (in mg) of metal ion taken up by 1 g of terpolymer

$$D = \frac{\text{Weight (in mg) of metal ion taken up by 1 g of terpolymer}}{\text{Weight (in mg) of metal ions present in 1 ml of solution}}$$

Results and discussion

Tables I and 2 the results of the investigation on the batch equilibrium will be presented that was conducted with the terpolymer sample 8-HQAF. These findings may be found below. In order to determine the selectivity of the 8-HQAF terpolymer for the desired metal ions, a number of factors, including the manner in which electrolytes influence metal ion selectivity, the absorption rate, and the

distribution ratio between the terpolymer and the solution containing the metal ions, were all investigated. This was done so that the selectivity of the 8-HQAF terpolymer could be determined.

Elemental analysis:

The estimated and experimental result for carbon (74%), hydrogen (4.78%), nitrogen (4.33%), and oxygen (20.06%), which are all in good alignment with one another, was used

to determine the percentage of elements present analysis support the copolymer predicted

Table 1 Elemental analysis and empirical formula of copolymer resin.

Copolymer resin	% of C Observed (Cal.)	% of H Observed (Cal.)	% of O Observed (Cal.)	% of N Observed (Cal.)	Emperical formula	Emperical formula weight
8- HQAF	73.90% (74%)	5.76 (4.78%)	18.98% (20.06%)	4.01% (4.33%)	C ₃₆ H ₁₈ O ₇ N ₂	339

in the copolymer. The benefits of elemental structure C₃₆H₁₈O₇N₂. [14-16]

UV-visible spectra:

While the less intense band may be caused by $\pi \rightarrow \pi^*$ the appearance of the more intense band can be explained by $n \rightarrow \pi^*$ electronic transition. The additional shift of absorption from the basic value (240 nm and

310 nm, respectively) to the longer wavelength area may be caused by conjugation action and the presence of phenolic hydroxyl group, which is responsible for the hyperchromic effect, or max higher value.

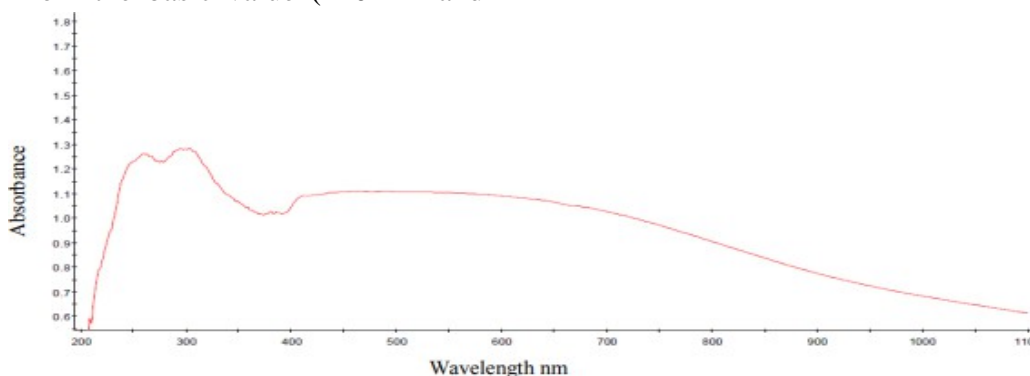


Figure 1. U V spectra of co-polymer 8-HQAF

FT-IR spectral analysis

In fig. 2, the FTIR spectrum of 8-HQAF was used to analyse the structure of the synthesised resin. The amine group of the Ar-NH group and -OH group combined in the copolymer is responsible for the broad peak that was observed in the vicinity of 3423.12 cm⁻¹. Aromatic ring stretching modes are responsible for a peak that appeared at 2755 cm⁻¹. The presence of the CH₂ bond in the copolymer is what caused a peak to arise in the region of 2825 cm⁻¹. The -NH bridge from the

copolymer was what created the distinct adsorption band at 3258.21. A band at 2927 suggests that the copolymer underwent CH₂ stretching. [17,18]

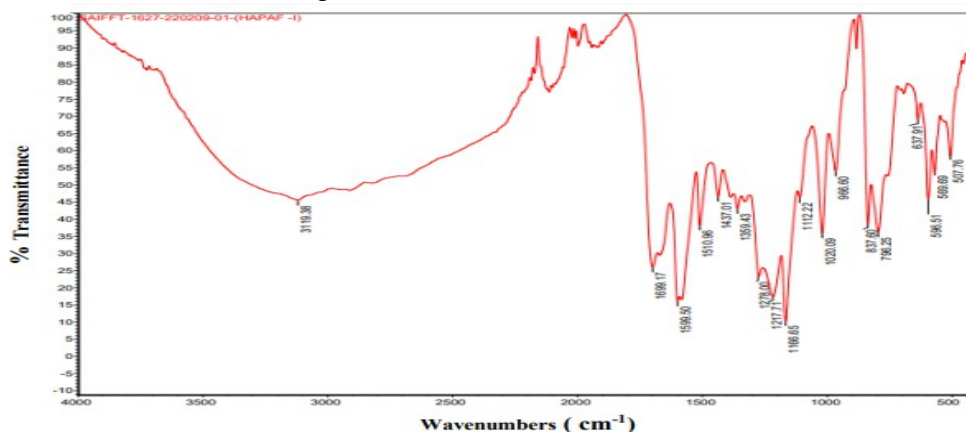


Figure 2. FTIR spectra of copolymer 8-HQAF

¹H NMR Spectroscopy:

NMR spectroscopy for ¹H Figure 3 displays the proton nuclear magnetic resonance spectrum. The methylene proton that caused the signal at 2.3 ppm may have been attributed to Ar-CH₂-N.

analysed using scanning electron micrographs, the results of which are shown in Figures 2 and 3, respectively. The photograph taken with an optical camera of the synthetic resin revealed that it has a brown appearance. The crystalline-amorphous structure is modelled after a fringed

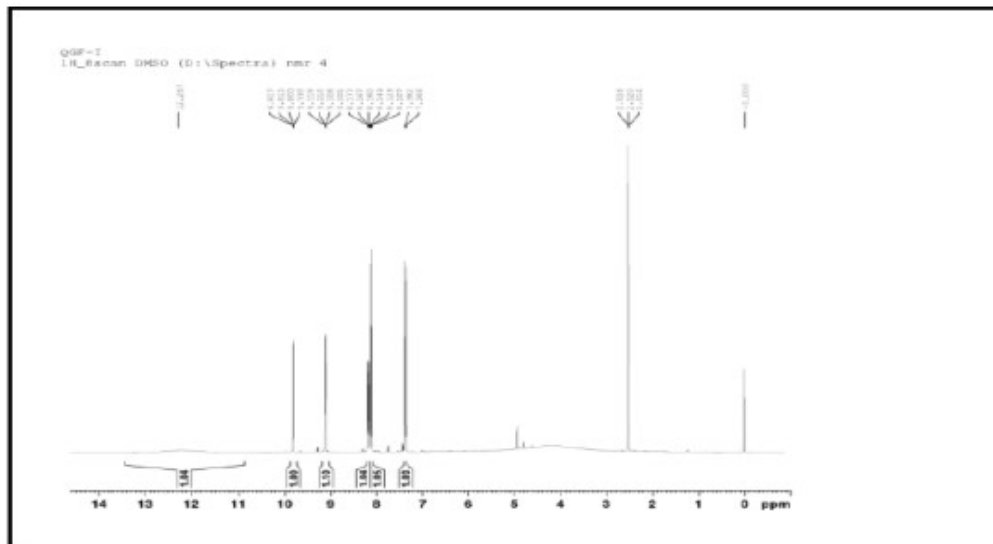


Figure 3. ¹H NMR spectra of copolymer 8-HQAF

The aromatic ring proton in the local range of 6.2-7.9 (ppm) can be assigned. At 9.2(δ) ppm, a Phenolic hydroxyl group exhibits a strong signal. The lack of power at 6.97(δ) ppm may be the result of -NH bridging protons.

SEM morphological details

SEM images taken at various magnifications were used to examine the morphology of the produced 8-HQAF copolymer and are shown in Fig. 4. The resin's morphology shows spherules and a fringed model. The spherules have a smooth, complicated polycrystalline surface. This demonstrates that the copolymer resin is naturally crystalline. A fringes model of the amorphous-crystalline structure is also displayed. The degree of crystallinity is determined by how acidic the monomer is. The copolymer exhibits additional amorphous characteristics, including a closed-packed surface with deep pits and the reactivity of active sites concealed inside the copolymer matrix. There is evidence of a small number of holes and cracks, which may be the result of air voids that are helpful for ion exchange research. [20]

The morphology of the insert resin sample was

structure that may be seen in the morphology of the resin. The fringes illustrate the transition stage between the crystalline and amorphous phases of the material. [20-24]. When compared to anthranilic acid-formaldehyde-resorcinol resin and 8-hydroxyquinoline-formaldehyde-pyrogallol resin, which were both described earlier, the resin displays a more amorphous nature with a closed packed surface that has deep pits[25]. It has been discovered that surface analysis can be helpful in better comprehending the surface characteristics of the material. The shape of the resin components crystal formation from polymer solutions corresponds to the largest organisation on a large scale in polymers, for example, in the size of spherulites that are only a few millimetres in diameter.

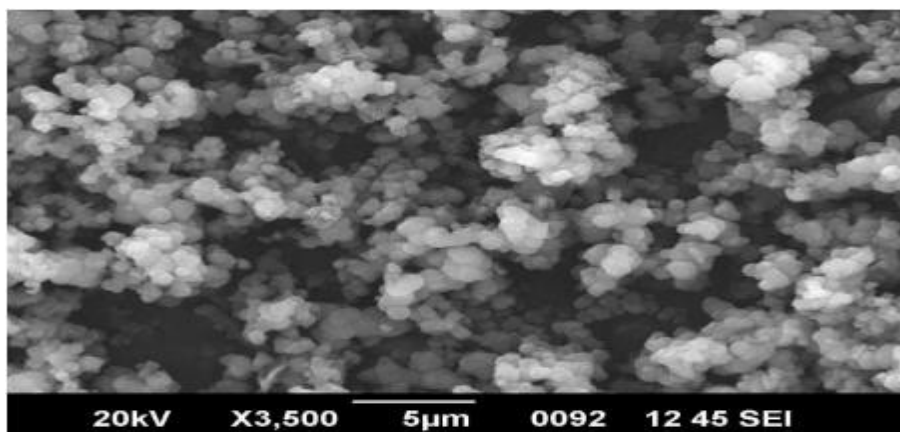


Figure 4. SEM of 8-HQAF Copolymer

X-RAY Diffraction

The degree of crystallinity, the orientation of the crystals, and the size of the lattice are the three most important aspects of investigating the crystal structure. Herman, Karst, and Flaschner developed a quantitative method for determination of the degree of the crystallinity, which can be defined as the relative proportion of crystalline domain in the crystalline-amorphous composite structure.

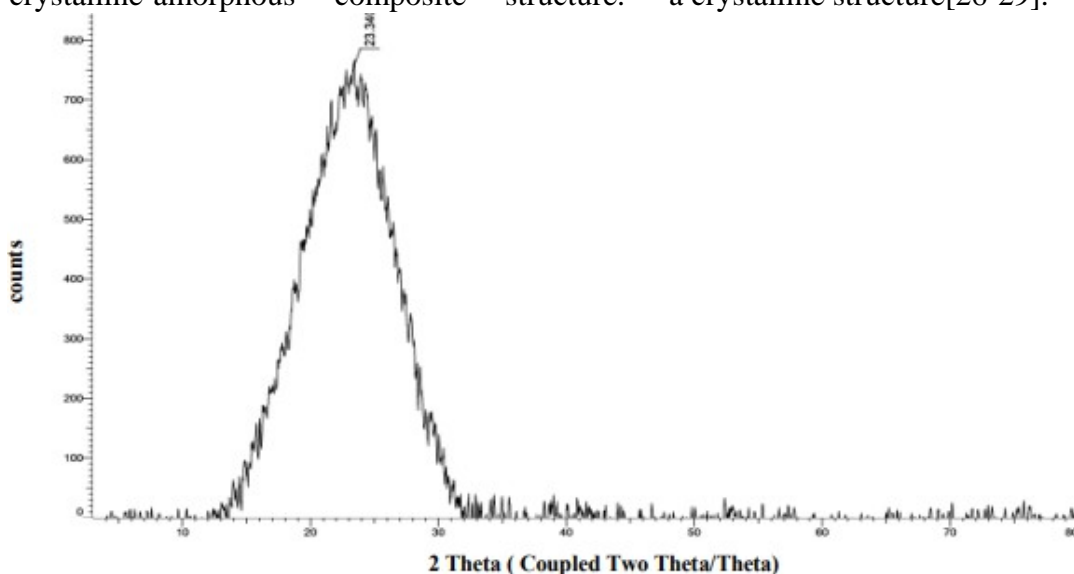


Figure 5. XRD spectra of 8-HQAF

Preparation of solid coordination of Some Polymeric Materials with Some Metal Ions

The study of metal-containing polymers is crucial to the scientific community because these systems have an advantage in a wide range of chemical processes over non-polymeric- metal salts. Polymeric metal, and even greater over, are of enormous significance in a variety of areas of chemistry, such as mining separations, catalytic reactions,

Figure 4. SEM of 8-HQAF Copolymer The Ruland and Vonk method was used in the investigation that was described above for the purpose of determining the degree of crystallinity value. All of the steep peaks around the coordinates $2\theta = 120, 140, 180, 210, 260, 280, \text{ and } 300$ suggest that the polymeric material has a highly crystalline character. Following examination of the data, it has been determined that the synthetic polymer has a crystalline structure [26-29].

medicine, biochemistry, environmental chemistry, and so on. This is because polymeric metals are even greater over.

For instance, it was discovered that molecular chelates with Rh(III) were effective hydrogenation catalysts for olefins and some acid derivatives. Antibacterial activity was discovered in polymers containing

triethylenetetramine side chains and/or thio-groups that were complexed with metals. The polymers were tested on Escherichia coli and staphylococcus aureus. Instead, the interactions of metal ions with immobilised organic polymer might result in the formation of numerous different complexes on the solid surface

electrodes. However, due to the fact that the connected ligands have decreased mobility, the complexes that are generated at the solid-solution interface are subject to a few restrictions.

By the use of a bidentate 8-quinolinol in which pair of 8-hydroxyquinolines A linear aliphatic bridge connects the end groups of the molecule, Thomsen et al. have discovered a potentially useful method for increasing the capacity of 8-quinolinol compounds to bind chelating agents in preparation for the production of coordination polymers. This method involves the utilisation of an 8-quinolinol compound with two 8-hydroxyquinolines end groups. The method for determining Mw as well as the diameters of polymer coils is well stated in terms of how light scattering works. Polymer chelates are widely utilised for this purpose because they give a one-of-a-kind structural environment for complexation, and are simultaneously functionalized by a large number of ligands. The complexation of a ligand like this one is governed by a number of distinct parameters, factors such as the make-up of the polymer backbone and the characteristics of the complexing medium are taken into consideration. In accordance with the following approach, the preparation of solid coordination polymers was carried out[30-34]. The elemental analysis of the PHQ-Cu (II) matrix in conjunction with the suggested formulas that are given various stoichiometries

about the amounts of water. The chemical equation of the polymer complex agrees with these findings, which are compatible with it, which states that PHQ interacts with one core metal ion at four coordination sites, and two water molecules are required for each Cu(II).

Effect of electrolytes on metal uptake

According to the information that is presented in Table 3, the number of metal ions that are absorbed from a specific amount of polymer is determined by the kind of electrolyte that is present in the solution as well as its concentration. The absorption of Fe^{3+} , Cu^{2+} , Ni^{2+} ions increases as the electrolyte concentration rises in the presence of chloride, perchlorate, and nitrate ions. On the other hand, in an environment where sulphate ions are present. When there is a rise in the concentration of electrolytes, there is a corresponding drop in the amount of the ions discussed before that are absorbed by the terpolymers. In addition to this, the uptake of ions such as Co^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} rises when the concentration of ions such as chloride, nitrate, perchlorate, and sulphate falls[35-40]

This is something that may be described using the stability constants of the various complexes which Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} ions form with these anions[41]. SO_4^{2-} is expected to form strong complexes with Fe^{3+} , Ni^{2+} and Cu^{2+} ions, while ClO_4 , NO_3 and are anticipated to form weak complexes and, consequently, cannot affect the position of the Fe^{3+} , Cu^{2+} , Ni^{2+} chelates equilibrium as much as SO_4 , ClO_4 , NO_3 and CT might form the strong chelates with Co^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and, therefore, might be expected to influence the position of the Co^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} chelates equilibrium. This type of trend has also been observed by other investigators in this field

Table:2 Evaluation of effect of different electrolyte on uptake of several metal ions
Weight in meq x 10 of the metal ion uptake in the presence of

Metal ions	Electrolyte(mol/l)	pH	NaClO4	NaCL	NaN ₃	Na ₂ SO ₄
<i>Fe</i> ³⁺	0.01	2.75	1.38	0.68	1.74	2.52
	0.05		2.30	1.06	2.16	1.60
	0.10		2.56	1.90	2.54	1.50
	0.50		2.88	2.36	2.71	1.06
	1.00		3.01	3.10	3.22	0.62
<i>Cu</i> ²⁺	0.01	4.5	2.28	2.56	2.76	3.53
	0.05		2.27	2.51	3.54	2.82
	0.10		3.12	3.01	3.59	2.02
	0.50		3.62	3.58	3.75	1.01
	1.00		4.88	3.92	4.07	0.31
<i>Ni</i> ²⁺	0.01	4.5	1.34	0.94	0.76	3.21
	0.05		1.45	3.21	0.76	1.82
	0.10		1.61	1.51	1.68	1.68
	0.50		1.68	1.76	1.87	1.55
	1.00		2.11	3.03	2.56	0.80
<i>Co</i> ²⁺	0.01	5.0	2.32	2.52	2.12	2.36
	0.05		2.05	1.85	1.73	1.93
	0.10		1.60	1.66	1.62	1.44
	0.50		0.94	0.87	1.58	1.19
	1.00		0.42	0.62	0.76	0.82
<i>Zn</i> ²⁺	0.01	5.0	2.39	2.89	2.32	1.57
	0.05		2.01	1.64	1.92	1.28
	0.10		1.52	0.89	0.86	1.09
	0.50		0.76	0.54	0.48	0.63
	1.00		0.62	0.34	0.33	0.26
<i>Cd</i> ²⁺	0.01	5.0	2.12	1.88	2.71	1.96
	0.05		1.81	1.41	2.06	1.49
	0.10		1.35	1.17	1.14	1.19
	0.50		0.82	0.93	0.75	0.59
	1.00		0.69	0.44	0.50	0.37
<i>Pb</i> ²⁺	0.01	6.0	1.38	1.65	1.70	2.71
	0.05		0.81	1.52	1.56	1.54
	0.10		0.69	1.46	1.11	1.38
	0.50		0.58	0.86	0.75	1.24
	1.00		0.36	0.72	0.28	0.81

$M^{n+}(NO_3)_m$; $n=0.1^m$;

volume of electrolyte solution: 25ml;

volume of metal ion solution=2ml;

weight of resin=25mg

time=24h; room temperature

Rate of metal up take

It has been demonstrated that the type of metal has an influence on the rate of metall ion uptake, which is broken down in Table 4. The rate is defined as the rate at which when an aqueous solution is brought into contact with a certain polymer, the concentration of metal ions in the solution shifts. According to the findings, the amount of time necessary for the uptake of various metal ions at a specific stage is contingent on the nature of the metal ion as well as the conditions that are now in place. It has been discovered that Fe^{3+} ions require approximately 4 hours for the establishment of equilibrium, whereas Cu^{2+} , Ni^{2+} ions require approximately 6 hours for Co^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} ions require almost 7 hours for equilibrium. Thus, the rate of metal ion uptake conforms to the sequence $Fe^{3+} > Cu^{2+}, Ni^{2+} > Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}$. This type of tendency was previously noted by other earlier researchers.

Table:3 Comparison of rate of metal ion up take
Percentage of metal ion uptake at time

Metal Ion	pH	0.5	1	2	3	4	5	6	7
Fe^{3+}	2.75	54	77	89	96	99	-	-	-
Cu^{2+}	4.5	40	53	66	73	80	89	100	-
Ni^{2+}	4.5	42	48	54	63	73	87	99	-
Co^{2+}	5.0	25	36	50	57	70	79	89	100
Zn^{2+}	5.0	28	41	50	60	66	79	90	99
Cd^{2+}	5.0	21	32	48	64	76	88	91	97
Pb^{2+}	6.0	11	21	24	28	37	67	87	98

$M^{n+}(NO_3)_n = 0.1 \text{ mol/l}$; Volume: 2ml; $NaNO_3 = 1 \text{ mol/l}$; volume = 25ml; room temperature

Metal ion uptake = Amount of metal ion absorbed x 100 / Amount of metal ion absorbed at equilibrium

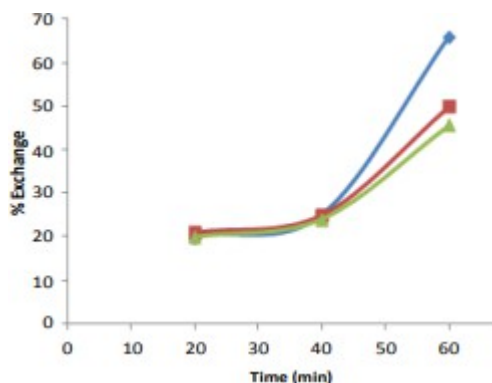


Figure 6. Rate of metal ion uptake at different time

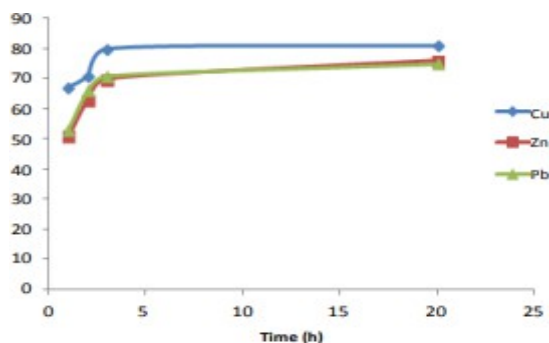
Distribution ratio of metal ions at different pH

The influence that pH has on the quantity of metal ions in its whole that are split up between the two phases was investigated. According to the findings, the proportional quantity of metal ions that are taken up by the terpolymers will increase as the pH of the media is increased. In order to prevent the hydrolysis of the metal ions at higher pH values, the investigation was carried out at a particular pH value for

each individual metal ion. The findings also suggest that the terpolymer takes up the Fe^{3+} ion in a more selective manner than it does any of the other metal ions that were investigated. There is a possibility that steric hindrance is to blame for the reduced distribution ratio of Fe^{3+} . Ni^{2+} and Cu^{2+} ions are among those that are taken up by the terpolymer in a more selective manner compared to the other metal ions. Over the pH range of 4-6, the distribution ratio D for the other four metal ions, namely

$Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}$ is rather low. This may be due to the fact that the metal complexes have low stability constants, which hints that the

This could be explained by the metal complexes' low ligand stabilization energy or low stability constants of the complexes themselves as a



ligand stabilisation energy of these whole. [42-45].
complexes on the lower end of the spectrum.

Figure 7. Distribution ratio of metal ions at different pH

Therefore, The following was found to be the order of selectivity of the terpolymer towards metal ions:

$Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$. As a result, the findings of this kind of investigation

are useful in determining the pH that is optimal for the selective uptake of a particular metal ion from a mixture containing a variety of different metal ions. [46-49]

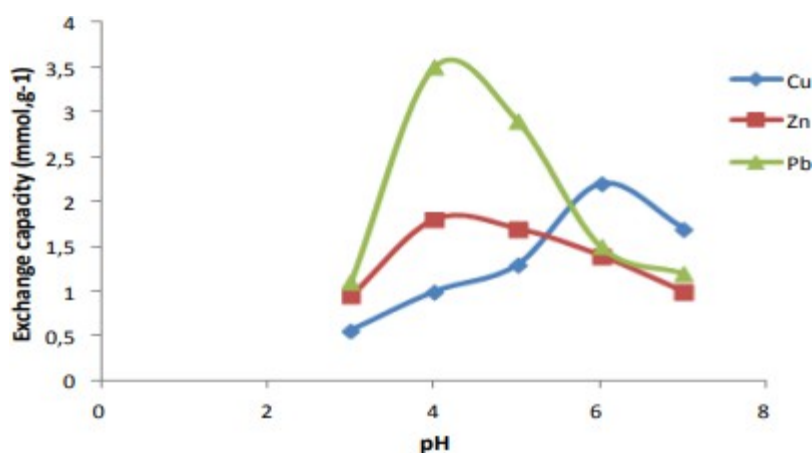


Figure 8. Effect of pH on cation exchange capacity

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