Chelation Ion-Exchange Studies of Acrylamide and Furfural Copolymer Resin

Damini Surendra Shedmake[1], Jyotsna V. Khobragade[2*], W. B. Gurnule[3]

[1]Department of Chemistry, Janata Mahavidyalaya, Chadrapur, Email: damishedmake123@gmail.com
[2*]Department of Chemistry, Gurunanak College of Science, Ballarpur, Email: jdr2105@gmail.com
[3]Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur-440024, Maharashtra, India,
Email:wbgurnule@gmail.com

***Corresponding Author: -** Jyotsna V. Khobragade
[*]Department of Chemistry, Gurunanak College of Science, Ballarpur, Email: jdr2105@gmail.com

ABSTRACT

Acrylamide, 8-hydroxyquinoline, and furfural were condensed using an acid catalyst to make 8-HQAF copolymer resin. Various physicochemical techniques were used to characterise the produced copolymer. Numerous characterization techniques, including elemental analysis, UV–Visible, ^{1}H NMR, FTIR, XRD, and SEM were employed to evaluate the structure and properties of the copolymer resin. A measurement of the cation interchange capability was completed, 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 coefficient of distribution in EDTA medium at a range of different pH values.

Keywords: Copolymer, Morphology, Polycondensation, Resin, 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, characterisation, and thermal degradation of a terpolymer composed of 8-hydroxyquinoline, formaldehyde, and acrylamide.[6,]Ion-exchangers are frequently utilised in the purification of water and reduction of pollution.[7, 8] A few hydroxybenzoic acid formaldehyde and 4-hydroxyacetophenone-biuret-formaldehyde copolymers have been depicted and viewed as used as particle exchangers.[9, 10] Because of the presence of chelating and particle trade bunches in a similar polymer framework, the polymer tar under still up in the air to be a cation exchanger. The sap can consequently possibly be used to purge squander water when significant. This chelating and helpful polymer has a particle that can eliminate metal particles from waste solutions. Ion-exchange technology has recently been realistic to the detection and removal of heavy metal ions from waste water. With the help of formaldehyde, p-cresol, and oxamide, a copolymer resin was created. For the chelating ion-exchange characteristics of Ni(II), Cu(II), Pb(II), Co(II), Zn(II), Fe(II) and Cd(II) ions, the copolymer was examined. The selected metal ions were eliminated using the batch equilibrium approach. For Ni(II), Cu(II) and Fe(II) ions, the copolymer exhibited better metal ion uptake than for Zn(II), Pb(II), Cd(II) and Co(II), ions.[11]Other applications include the preconcentration of certain metal ions and the preconcentration of other metal ions. In an acid media, the polycondensation process was used to create the copolymer 8-HQAF from the monomers 8-Hydroxyqunoline, 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 ion exchange of the copolymer resin was performed using a batch equilibrium method. In order to analyse the structure of the copolymer as well as its properties, a number of different characterisation methods, such as UV–Visible, FTIR, elemental analysis, XRD, and SEM, were utilised.

EXPERIMENTAL

Material

8-Hydroxyquinoline acid, acrylamide and form aldehyde 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- furfural (8-HQAF) copolymer was synthesised by polycondensation of 8-Hydroxyquinoline, furfural and acrylamide with 2M HCl in the ratio 2:1:3an oil bath at a temperature of 123 ± 2 ^{0}C with occasional shaking for about 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 sometimes with warm 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 about 88% (Fig.1).

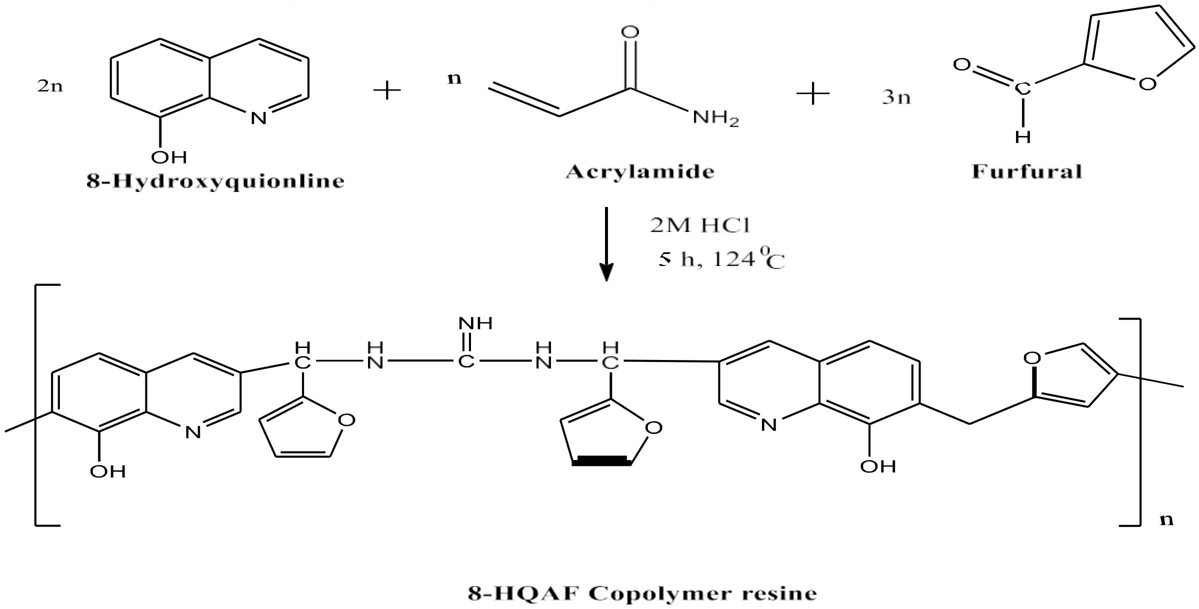

Fig.-1: Synthesis of 8-HQAF Copolymer Resin

RESULTS AND DISCUSSION

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 as shown inTable-1, was used to determine the percentage of elements present in the copolymer. The benefits of elemental analysis support the copolymer's predicted structure $C_{36}H_{18}O_7N_2$.[12]

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.)	Empirical formula	Empirical formula weight
8-HQAF	73.90% (74%)	5.76 % (4.78 %)	18.98 % (20.06 %)	4.01 % (4.33 %)	$C_{36}H_{18}O_7N_2$	339

UV-visible spectra

The less intense band can be as a result of $\pi \rightarrow \pi^*$ presence of the extra extreme band may be defined by way of $n \rightarrow \pi^*$ transition. The extra shift of absorption from the basic price (230 nm and 320 nm, respectively) to the longer wavelength location may be as a result of conjugation motion and the presence of phenolic hydroxyl institution, which is answerable for the hyperchromic effect or greater value (Fig.2).[13]

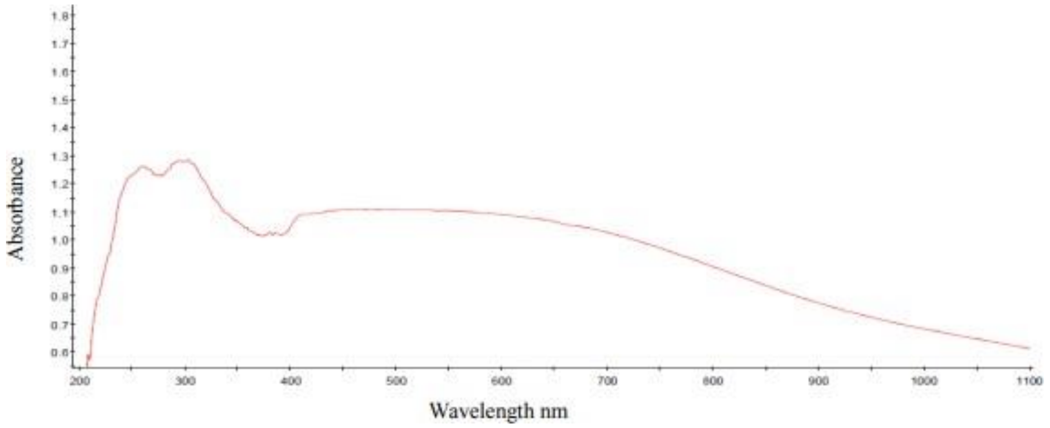

Fig.-2: UV-Visible Spectra of 8-HQAF Copolymer Resin

FT-IR spectral analysis

In Fig.3, 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 accountable 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 $-CH_2$ 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 CH_2 stretching.[14, 15]

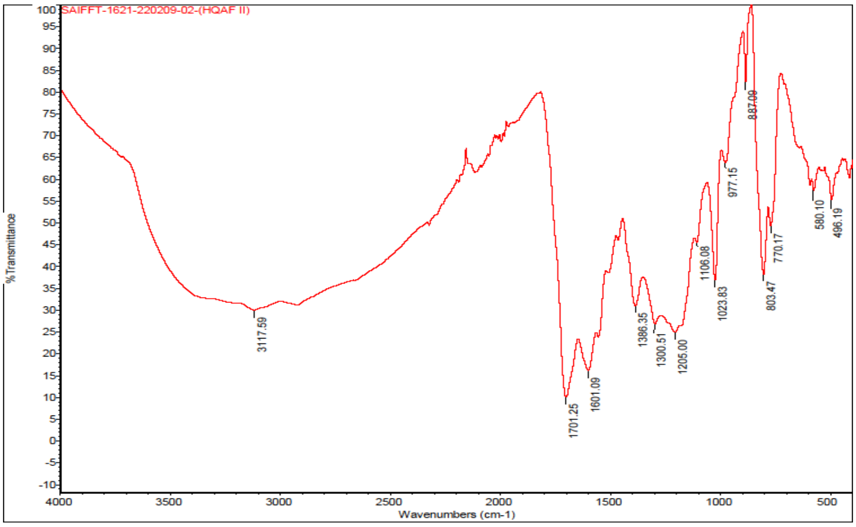

Fig.-3: FT-IR Spectra of 8-HQAF Copolymer Resin

^{1}H NMR Spectroscopy

NMR spectroscopy for ^{1}H Fig.4 displays the proton nuclear magnetic resonance spectrum. The methylene proton that caused the signal at 2.3 (δ) ppm might be attributed to $Ar-CH_2-N$. The aromatic ring proton in the local range of 6.2-7.9 (ppm) can be assigned.[16] At 9.2(δ)ppm, a Phenolic hydroxyl group exhibits a strong signal. The lack of power at 6. 86 (δ) ppm may be the result of -NH bridging protons[17].

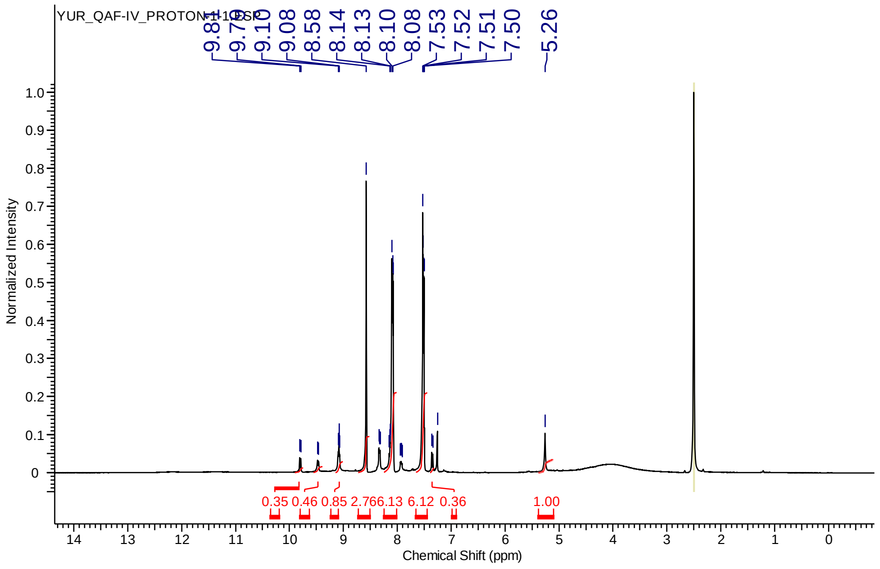

Fig.-4: ^{1}H NMR Spectra of 8-HQAF Copolymer Resin

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.5. The resin's morphology shows spherules and a fringed model.The spherules have a smooth, complicated polycrystalline floor. This demonstrates that the copolymer resin is evidently crystalline. A fringes model of the amorphous-crystalline structure is likewise displayed. The degree of crystallinity is decided by using how acidic the monomer is. The copolymer famous additional amorphous characteristics, which includes a closed-packed floor with deep pits and the reactivity of energetic websites concealed within the copolymer matrix. There is evidence of a small quantity of holes and cracks, which may be the end result of air voids which can be beneficial for ion alternate research.[18]The morphology of the insert resin pattern turned into analysed using scanning electron micrographs, the effects of which might be proven in Fig.5.

The photographs 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 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.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.[19]

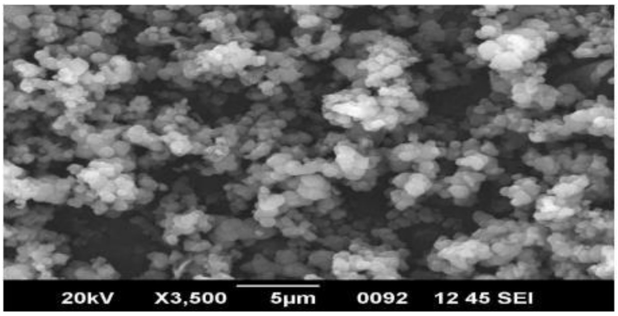

Fig.-5: SEM images of 8-HQAF Copolymer Resin

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 XRD of 8-HQAF Copolymer (Fig.6). 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 = 120, 140, 180, 210, 260, 280, 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.

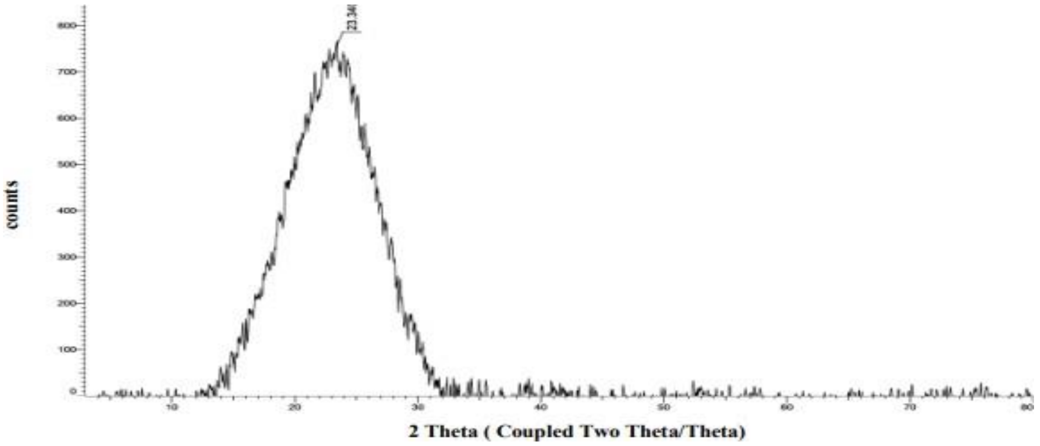

Fig.-6: XRD Spectra of 8-HQAF Copolymer Resin

Ion Exchange Study

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. 0.1 N HNO_3 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 m1 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. 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 diaminetetraacetic acid[20-25].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 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. Various electrolytes containing seven different types of metal ions, including Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} were used in the experiment multiple times. A series of experiments of the kind described above were conducted in order to determine the length of time needed to reach the state of equilibrium under the prescribed experimental conditions. These studies involved measuring the quantity of metal ion uptake by the chelating resins across a range of time periods at a temperature of 25 degrees Celsius (in the presence of a 25 m1 solution of l M NaN03). 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 $NaN0_3$ solution was used to measure how each of the seven metal ions was distributed between and 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:

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

Tables 2 and 3 the results of the investigation on the batch equilibrium will be presented that was conducted with the copolymer sample 8-HQAF. These findings may be found below. In order to determine the choosiness of the 8-HQAF copolymer for the desired metal ions, a number of factors, including the manner in which electrolytes influence metal ion selectivity, the absorption rate, and the ratio of distribution among the copolymer 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.

Effect of electrolytes on metal uptake

According to the information that is displayed in Table 2, the number of metal ions that are absorbed from a specific amount of copolymer 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 copolymers. In addition to this, the uptake of ions such as Co^{2+}, Zn^{2+} ,Cd^{2+}, Pb^{2+} when the concentration of ions such as chloride, nitrate, perchlorate, and sulphate falls[18, 19]. This is something that may be defined using the stability constants of the diverse complexes which Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} ,Cd^{2+}, Pb^{2+} ions form with those anions[23]. SO_4^{2-} is anticipated to shape sturdy complexes with Fe3+, Ni2 and Cu^{2+}, ions, while ClO_4^-, NO_3^- and are anticipated to form vulnerable complexes and, therefore, cannot have an effect on the position of the Fe^{3+}, Cu^{2+}, Ni^{2+} chelates equilibrium as a lot as SO_4^{2-}. ClO_4^-, NO_3^- and CT would possibly form alternatively strong chelates with Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and consequently, is probably predicted to have an impact at the equilibrium position of the Co^{2+}, Zn^{2+}, $Cd^{2+}$and Pb^{2+} chelates.[26-30] Other researchers on this discipline have also observed a sample of this nature.

Table-2: Effect of electrolytes on metal uptake

Metal Ions	pH	Conc.	$NaClO_4$	NaCl	$NaNO_3$	Na_2SO_4
Fe^{3+}	2.75	0.01	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
Cu^{2+}	4.5	0.01	2.28	2.56	2.76	3.53
		0.05	2.74	2.52	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
Ni^{2+}	4.5	0.01	1.34	0.94	0.76	3.21
		0.05	1.45	1.21	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
Co^{2+}	5.0	0.01	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	1.52	1.19
		1.00	0.42	0.62	0.76	0.83
Zn^{2+}	5.0	0.01	2.39	2.89	2.31	1.56

		0.05	2.01	1.54	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	0.32	0.25
Cd^{2+}	5.0	0.01	2.12	1.88	2.71	1.96
		0.05	1.81	1.44	2.06	1.49
		0.10	1.35	1.17	1.14	1.19
		0.50	0.82	0.93	0.74	0.58
		1.00	0.69	0.44	1.70	0.36
Pb^{2+}		0.01	1.38	1.65	1.56	2.71
		0.05	0.81	1.52	1.11	1.54
		0.10	0.69	1.46	0.75	1.38
		0.50	0.58	0.86	0.28	1.24
		1.00	0.50	0.72	0.28	0.81

$$M^{n+0.36}(NO3)n = 0.1\,\frac{mol}{l}; Volume\ of\ electrolyte\ solution: 25\ ml; volume\ of\ metal\ ion\ solution = 2ml; weight\ of\ resin = 25mg;\ time = 24h;\ room\ temperature$$

Rate of metal uptake

It has been demonstrated that the type of metal has an influence on the rate of metal ion uptake, which is broken down in Table 3. 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 essential for the uptake of various metallic ions at a selected degree is contingent on the character of the metal ion as well as the conditions which might be now in place. It has been found that Fe^{3+} ions require about 4 hours for the status quo of equilibrium, whereas Cu^{2+}, Ni^{2+} ions require about 6 hours for Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}ions require nearly 7 hours for equilibrium. Thus, the price of metallic ion uptake conforms to the series Fe^{3+}> $Cu^{2\ +}$,Ni^{2+}> Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}. This form of tendency turned into previously noted by using different earlier researchers (Fig.-7).[31-39]

Table-3: Percentage of metal ion uptake at time

Metal ions	pH	Percentage of the amount of metal ion[a] taken up[b] at different time (hrs)						
		0.5	**1**	**2**	**3**	**4**	**5**	**6**
Fe3+	2.75	54	77	89	96	99	-	-
Cu^{2+}	4.5	40	53	66	73	80	89	108
Ni^{2+}	4.5	42	48	54	63	73	87	99
Co^{2+}	5.0	25	36	50	57	70	79	89
Zn^{2+}	5.0	28	41	50	66	66	79	90
Cd	5.0	32	32	48	64	76	88	91
Pb^{2+}	6.0	21	21	24	28	37	67	87

$M^{n+}(NO3)n = 0.1\frac{mol}{l}; Volume: 2ml; NaNo3 = 1\frac{mol}{l}; volume = 25ml; room\ temperature$ Metal ion uptake = Amount of metal ion absorbed x 100 / Amount of mrtal ion absorbed at equilibrium

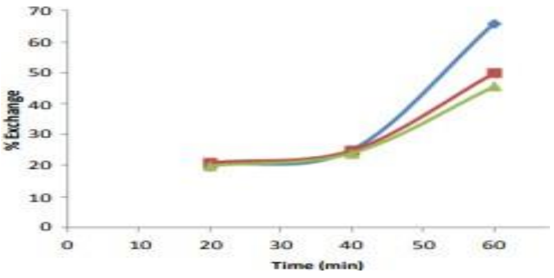

Fig.-7: Rate of metal ion uptake 8-HQAF copolymer resin

Distribution ratios 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 up to a particular pH value for each individual metal ion. The findings also suggest that the copolymer takes up theFe^{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 19 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.[24] This may be due to the fact that the metal complexes have low stability constants, which hints that the ligand stabilisation energy of these complexes is on the lower end of the spectrum. This could be explained by the metal complexes' low ligand stabilisation energy or low stability constants of the complexes themselves as a whole (Fig.-8).

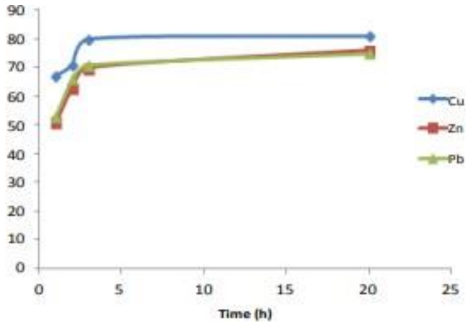

Fig.-8: Distribution ratios of metal ions at different pH8-HQAF copolymer resin

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+}.[25] 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 (Fig.-9).

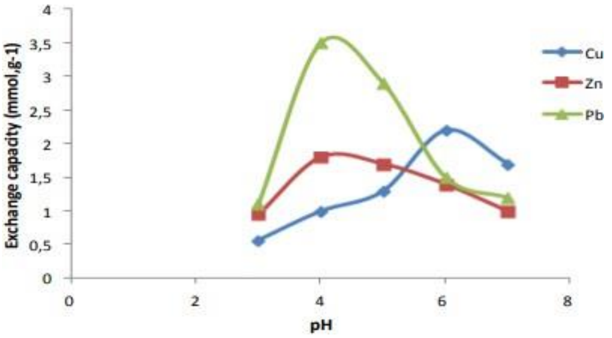

Fig.-9. Effect of PH on cation exchange capacity

CONCLUSIONS

The condensation reaction of 2-amino-6-nitro-benzothiazole and acrylamide with furfural in the presence of an acid catalyst was used to create the polymer 8-HQAF-II. The 8-HQAF-II copolymer resin is a particular metal-specific selective chelating cation exchange polymer resin. The polymer resin's ability to absorb metal ions was pH-dependent.The 8-HQAF-II resin's stability and reusability for the removal of metal ions were also rather good. As a result of the findings, it is possible that the synthesised copolymer resin would function as a highly effective and promising cation exchanger to remove poisonous and damaging metal ions from contaminated water bodies and industrial effluents.

ACKNOWLEDGMENT

Creators convey earnest gratitude to the Principal Kamla Nehru Mahavidyalaya Nagpur, India for their help and for giving fundamental research centre and also to the Director, SAIF STIC Cochin, Indian Institute Technology, Mumbai for spectral examinations.

REFERENCES

1. R. El-shazly, R. Kamal, A. Nassar, N. Ahmed and G. Sayed,*Applied Petrochemical Research*,**10**, 115 (2020).
2. T.Sasikala, K.Greeshma, P.Gnana, S.Muthulingam and C.Nandhakumar. GSC *Advanced Research and Reviews*, **05**, 19 (2020).
3. W.B. Gurnule, Y.U. Rathod and A.D. Belsare,*Materials Today Proceedings*, **29(4)**, 1044 (2020).
4. R.N.Singru, W.B.Gurnule, V.A.Khati, A.B. Zade and J.R.Dontulwar, *Desalination*., **263,**200-210 (2010).
5 P. M. Gupta, Y. U. Rathod, V. U. Pandit, R. H. Gupta and W. B. Gurnule,*Materials Today: Proceedings*, **53**, 101 (2022).
6. P. E.P. Michael, J.M. Barbe, H.D. Juneja, and L. J. Paliwal, *European Polymer Journal* **43**, 12 4995 (2007)
7. R.S. Azarudeen, M.A. RiswanAhamed, R.Subha and A.R. Burkanudeen, *Journal of Chem.Tech. Biotech.*, **90,** 2170(2015).
8. R.S. Azarudeen, M.A. RiswanAhamed, M. Thirumarimurugan and N. Prabu, *Polym. Adv. Tech*., **27**,235 (2016).
9. P.K. Rahangdale, W.B. Gurnule, L.J. Paliwal and R.B. Kharat, *Reactive Functional Polymer*, **55**, 265(2003).
10. V.D. Mane, N.J. Wahane and W.B. Gurnule, *Journal of Applied Polymer Science*, **111**, 3039(2009)

11. R.N. Singru, W.B. Gurnule, V.A. Khati, A.B. Zade and J.R. Dontulwar, *Desalination*, **263**,200 (2010).
12.A.R. Burkanudeen, R.S. Azarudeem, M.A. RiswanAhamed and W.B. Gurnule, *Polymer Bulletin*,**67**, 1553(2011).
13. R.S. Azarudeen, M.A. RiswanAhamed, M. Thirumarimurugan and N. Prabu, *Polymer Advanced Technology*, **27**, 235 (2016).
14. R. Mohurle and W. B. Gurnule, *International Journal in Physical and Applied Science* **5**, 33 (2018).
15.R. S. Azarudeen, M. A. R Ahamed, A.R. Burkanudeen, *Desalination*, **268**, 90 (2011).
16. N. C. Das, Y. U. Rathod, V. U. Pandit and W.B. Gurnule, *Materials Today Proceedings*, **53**, 80 (2022)
17.V. R. Bisen and W. B. Gurnule, *International Journal Current Engineering Science Research*, **6,** 1309 (2019).
18. Y.U. Rathod, S.B. Zanje and W.B. Gurnule, *Journal of Physics: Conference Series*.**1913**, 1 (2021).
19. Y.U. Rathod, V.U. Pandit, D.S. Bhagat, W.B. Gurnule, *Materials Today Proceedings*, **53**, 123 (2022).
20. P.A. Mishra, Y.U. Rathod, V.U. Pandit, W.B. Gurnule, *Materials Today Proceedings*, **53**, 86 (2022).
22. R. S. Azarudeen, R. Subha, D. Jeyakumar and A. R.Burkanudeen, *Separation. Purification Technology*, **116**, 366 (2013).
23. W. B. Gurnule and S. S. Katkamwar, *Journal of Current Engineering and Scientific Research*, **6(1)**, 1286-1296, (2019).
24.D.B. Patle and W.B. Gurnule, *Arabian Journal of Chemistry*, **9**,S648(2016).
25. J. V. Khobragade and W. B. Gurnule, ,*Int. J. Res. Biosci., Agri. & Tech.***V(2),** 486-491, (2017).
26. D. B. Patle and W. B. Gurnule, , *Arabian J,. Chem.*, **9**, S648-S658, (2016).
27. W. B. Gurnule, J. V. Khobragade and M.Ahamed, *J. Chem, Pharm. Res.*, **6(8),** 364-374, (2014,).
28. S.S. Rahangdale**,** W. B. Gurnule, ,*Desalination and Water Treatment*, **52**, 1-10 (2014).
29. W. B. Gurnule, *International Journal of Researches in Biosciences, Agriculture & Technology***, 1(2),** 376 (2014).
30. W. B. Gurnule, C. S. Makde and M.Ahamed, *J. Environ. Res. Develop*., **7(3),** 1183-1192, (2013).
31. J. V. Khobragade and W. B. Gurnule, *Journal of Science Information*, **6**, 48-51, (2013)
32. W. B. Gurnule**,** C. S. Makde and M.Ahamed, *J. Environ. Res. Develop*., **7(2),** 622-632, (2012**)**.
33. C. S. Makde**,**W. B. Gurnule and M.Ahamed, *Journal of Biological & Physical Sciences***1(IV**), 59-66, (2012).
34. W. B. Gurnuleand S. S. Katkamwar, *Rasayan Journal of Chemistry*, **5(3),** 365-375, (2012).
35. W. B. Gurnule,*International Journal of Environment and Resource***, 1(1),** 16-25, **(**2012).
36. W. B. Gurnule and S. S. Katkamwar,*J. Chem. Pharma. Res***.4(4),** 2193-2203 (2012).
37. S. S. Dhoteand W. B. Gurnule, *J. Der PharmaChemica***, 4(2),** 791-799 (2012).
38. D. B. Patle, W. B. Gurnule, and A. B. Zade, *Der PharmaChem J.* 3 (3), 341 (2011).
39. S. S. KatkamwarandW. B. Gurnule**,***Journal of Applied Polymer Science*, **123,** 1421, (2011).