(REVIEW ARTICLE)

Removal of Heavy Metal Ions from Water Using Chelating Copolymer Resin-IV Derived from 2-Hydroxy, 4-Methoxybenzophenone, 1, 5-Diaminonaphthalene and Formaldehyde

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Abstract

The resin 2-H, 4-MBP-1,5-DANF-IV was synthesized by the condensation of 2-hydroxy, 4-methoxybenzophenone and 1, 5-diaminonaphthalene with formaldehyde in the presence of hydrochloric acid as a catalyst. The resin was characterized by elemental analysis, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and UV-Visible spectral studies. The chelation ion-exchange properties was studied for Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+} and Pb^{2+} ions employing a batch equilibrium method. It was used to study of the selectivity of metal-ion uptake involving the measurements of the distribution of a given metal ion between the copolymer sample and a solution containing the metal ion. The study was carried out over a wide pH range and in media of various ionic strength. The resin depicted a higher selectivity for Cu^{2+} and Ni^{2+} ion than for Co^{2+}, Zn^{2+} and Pb^{2+} ions.

Keywords: Copolymer; Ion-exchange properties; Batch equilibrium; Chelating; Concentration

1. Introduction

Many industries are responsible for polluting the with heavy metal ions contained in their waste water. The heavy metal ions present in waste water are one of the harmful pollutants of the environment as it accumulates in living tissues, causing many destructive effects. Effluents generated by industries such as non-ferrous metal works, aircrafts plating, petroleum refineries etc. generally have a complex composition which includes metals ions or complexes suspended, solids and other components. Many methods have been developed for the removal of metal ions such as co-precipitation, electro deposition and solvent extraction. However the removal of metal ions by chelating ion exchange resin using Batch equilibrium method has gained rapid acceptance because of its wide variety of high degree of selectivity, sorbent phases, enhanced hydrophilicity and high loading capacity [1].

Gurnule and coworker have synthesized the chelating ion-exchange resin from phallic acid - melamine - formaldehyde and characterized by FT-IR, ^{1}H-NMR and elemental analysis. Metal ion uptake capacity of the resin has been carried out by Batch equilibration method for different metal ions at different concentrations [2]. Separation of toxic metals ions from waste water using pyrogallol-biuret-formaldehyde copolymer resin has reported by Rahangdale et al. [3]. Gurnule et al. have studied the chelation ion exchange properties of copolymer resin synthesized from 1,5-diaminonaphthalene, 2,4-dihydroxypropiophenone and formaldehyde [4]. Comparative study of strong anion exchange poly (Styrene-co-EGDMA-co-VBC) and strong anion exchange hyper crosslinked poly (HEMA-co-EGDMA-co-VBC) was reported by N. Abdullah et al. [5]. The copolymer resin synthesized from salicylic acid and diaminobenzoic acid with formaldehyde and its chelating ion-exchange properties was studied by Masram et al. and the resin was found to be, selectivity for Fe^{+3}, Cu^{2+} and Ni^{2+} ion than for Zn^{2+}, Co^{2+} and Pb^{2+} ions [6]. Ravichander et al. have synthesized and studied the antimicrobial

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and ion-exchange properties of copolymer resin derived from substituted resorcinol, biuret and formaldehyde [7]. The copolymer resin was prepared by condensation of salicylic acid, semicarbazide and formaldehyde in presence of acid catalyst and studied its ion-exchange properties for Co (II), Zn (II), Cu (II), Ni (II), and Pb (II) ions by Nandekar et al. and the study was carried out at different shaking time, over a wide pH range, in the medium of different ionic strengths and reported that higher selectivity for Ni (II) and Cu (II) than for Co (II), Zn(II) and Pb (II) ions [8].

However, the literature survey have revealed that no copolymer has been synthesized using monomer of 1, 5-diaminonaphthalene, 2-hydroxy, 4-methoxybenzophenone, and formaldehyde. The present investigation deals with the synthesis, characterization and removal of heavy metal ions by using 2-H, 4-MBP-1,5-DANF-IV copolymer resin for Zn^{2+} ,Cu^{2+}, Co^{2+}, Ni^{2+}, and Pb^{2+} ions.

2. Material and Methods

All the chemicals were AR or chemically pure grade. The 1, 5-diaminonaphthalene, 2-hydroxy, 4-methoxybenzophenone, formaldehyde, DMF, DMSO,THF, acetone and dimethylether were purchased from Merck, India.

2.1. Synthesis of 2-H, 4-MBP-1,5-DANF-IV copolymer

The 2-H, 4-MBP-1,5-DANF-IV copolymer resin was synthesized by condensation polymerization of 2-hydroxy, 4-methoxybenzophenone, and 1, 5-diaminonaphthalene with formaldehyde in the presence of 2M hydrochloric acid as catalyst in 4:2:7 molar proportion of reactants at 126 ± 2 ^0C in an oil bath for about 5hrs. The solid product obtained was immediately removed and washed several times with hot water. The product obtained was extracted with diethyl ether to remove 2-hydroxy, 4-methoxybenzophenone formaldehyde copolymer which might be present along with 2-H, 4-MBP-1, 5-DANF-IV copolymer. The dried resin was further purified by dissolving in 8% NaOH and regenerated 1:1 (v/v) HCl/water with stirring. The sample was dried, powdered and kept in a vacuum desicator. The yield of the resin was found to be 81%. The reaction sequence of the synthesis has been shown in Figure-1.
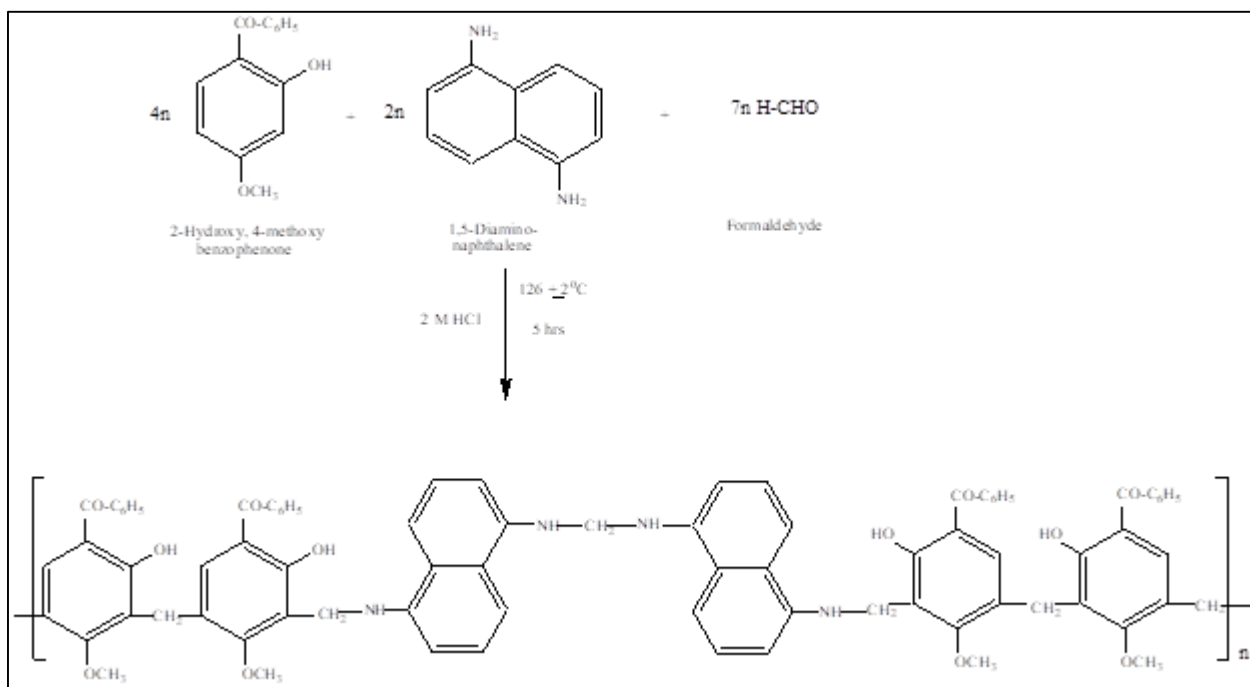
Figure 1 Synthesis of 2-H, 4-MBP-1,5-DANF-IV copolymer resin

2.2. Physico-chemical and analytical studies

The newly synthesized copolymer resin has been subject to micro analysis of C, H and N on Elemental Vario EL III Carlo Erba 1108. Infrared spectra has been scanned in the range of 4000-500 cm^{-1} in KBr pellets in najol mull on Perkin-Elmer-Spectrum RX-I, FT-IR Spectrophotometer. The ^{1}H-NMR spectrum of copolymer has been scanned on Bruker Advance -II 400 MHz NMR spectrophotometer using DMSO-d_6 as a solvent. All the spectral and analytical studies for the copolymer resin has been carried out at STIC, Cochin University, Cochin, India.

2.3. Ion-exchange properties

The batch equilibrium method has been used to determine the ion exchange properties of 2-H, 4-MBP-1,5-DANF-IV copolymer resin. The influence of various electrolytes at different concentration and pH, the rate of metal ion uptake and distribution of metal ion between the solution and copolymer phase has been studied.

2.4. Determination of metal ion uptake in the presence of electrolytes of different concentrations

The copolymer sample (25 mg) was suspended in $NaNO_3$ electrolyte solution (25 ml) of known concentration. The pH of the solution was adjusted by using either 0.1 N NaOH or 0.1 N HCl. The suspension was stirred at 25 ^{0}C for a24 hrs. The 0.1M solution of the metal ion (2 ml) was added to this suspension and the required pH was adjusted. Again the mixture was stirred for 24 hrs at 25 ^{0}C and then filtered. The solid was washed and the filtrate and washings were combined and titrated against standard EDTA to determine the metal ion content. The amount of metal ion uptake of resin was calculated from the difference between the reading in actual experiments and a blank experiment without polymer. Same experiment was repeated in the presence of electrolytes such as NaCl, Na_2SO_4 and $NaClO_4$ at different concentrations [9].

2.5. Evaluation of the rate of metal ion uptake

In order to determine the time required to reach the state of equilibrium under given experimental conditions, a series of experiments of the type described above were carried out in which the metal ion uptake by chelating resins was evaluated from time to time in the presence of 1M $NaNO_3$ (25 ml) solution at 25 ^{0}C. Under given conditions it was assumed that the state of equilibrium was established within 24 hrs. Rate of metal ions uptake is expressed as percentage amount of metal ions taken up after a certain time related to that at the state of equilibrium [10].

2.6. Evaluation of the distribution of metal ions at different pH

The distribution of each one of the five metal ions Cu(II), Co(II), Ni(II), Zn(II) and Pb(II) between the aqueous phase and copolymer phase was estimated at 25 ^{0}C in the presence of a solution of 1M, $NaNO_3$ solution. The experiments were carried out as described earlier at different pH. The Distribution ratio (D) was calculated with the following relationship

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

# 3. Results and Discussion

3.1. Elemental analysis

The 2-H, 4-MBP-1,5-DANF-IV copolymer resin was found to be brown in color. The resin is soluble DMF, DMSO and THF but insoluble in almost all other inorganic and organic solvents. The copolymer was then analyzed for carbon, hydrogen and nitrogen content and found to be good agreement with calculated value. The empirical formula and empirical formula weight, which is shown in the Table-1.

Table 1 Elemental analysis and empirical formula of copolymer resin

| Copolymer resins	% of 'C' observed calculated	% of 'H' observed calculated	% of 'N' observed calculated	Empirical formula of repeat unit	Empirical formula of repeat unit
2-H, 4-MBP-1,5-DANF-IV	75.89 75.69	5.13 5.23	3.46 4.30	$C_{82}H_{68}N_4O_{12}$	1300

3.2. Infrared spectra

Infrared spectra of 2-H, 4-MBP-1, 5-DANF-IV copolymer resin is presented in Figure 2. A strong band which is appeared at 3390 cm^{-1} may be due to the stretching vibration of the phenolic hydroxyl group. A sharp and strong band at 1602 cm^{-1} may be assigned to the stretching vibration of >C=O group. The strong band observed at 2938 cm^{-1} may be on account of the stretching vibrations of –NH group. The strong band observed at 1107 cm^{-1} region may be due to the Ph-O-CH$_3$ ether linkage. The weak band appeared at 1345 cm^{-1} is attributed to –CH$_2$ methylene bridge [11-13].
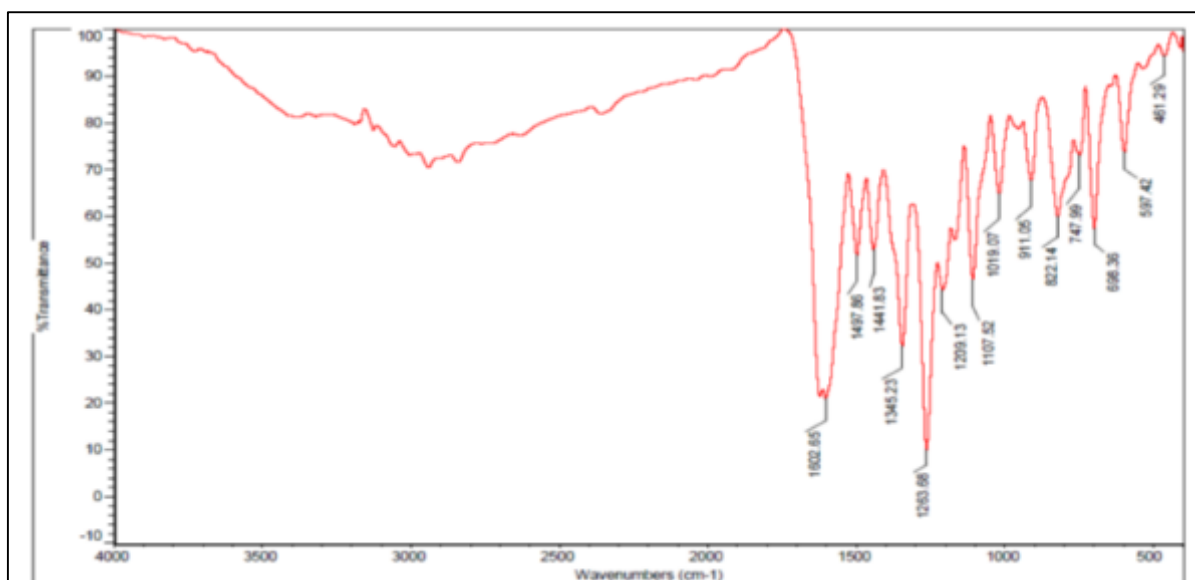
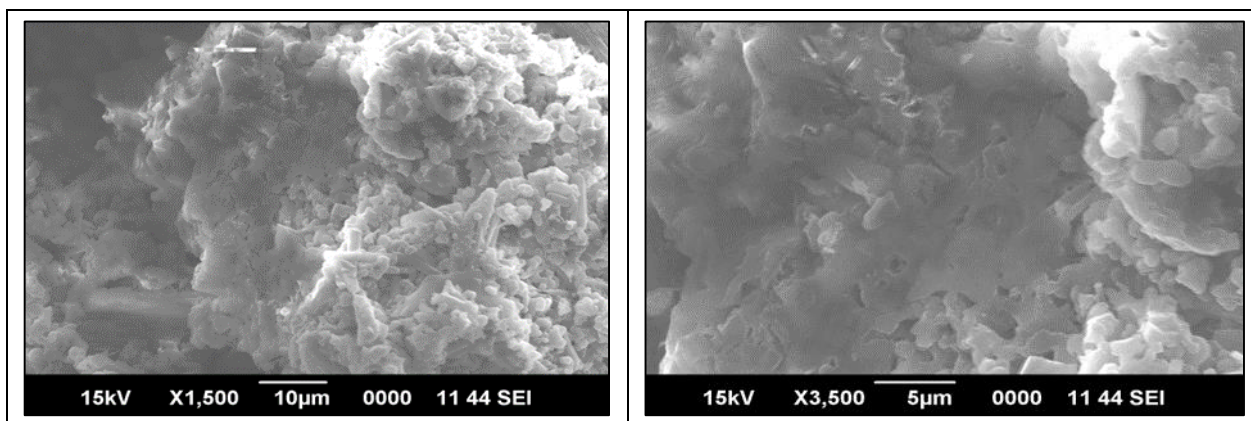**Figure 2** FT-IR spectra of 2-H, 4-MBP-1,5-DANF-IV copolymer resin

3.3. ^{1}H-NMR spectra

The ^{1}H-NMR spectra of 2-H, 4-MBP-1,5-DANF-IV copolymer is shown in Figure 3. The weak multiplet signal (unsymmetrical pattern) in the region at δ 7.6 ppm, which indicates the proton of aromatic ring (Ar-H). The weak signal observed in the region δ 7.2 ppm which is due to phenolic –OH proton in intramolecular hydrogen bonding (Ar-OH). The appearance of singlet at δ 3.5 ppm reveals the presence of Ar-O-CH$_3$ proton. The methylenic proton of Ar-CH$_2$-N linkage may be due to signal which appears in the region δ 3.8 ppm. The presence of triplet signal in the region δ 6.7 ppm indicates the proton of –NH bridge [14-16].
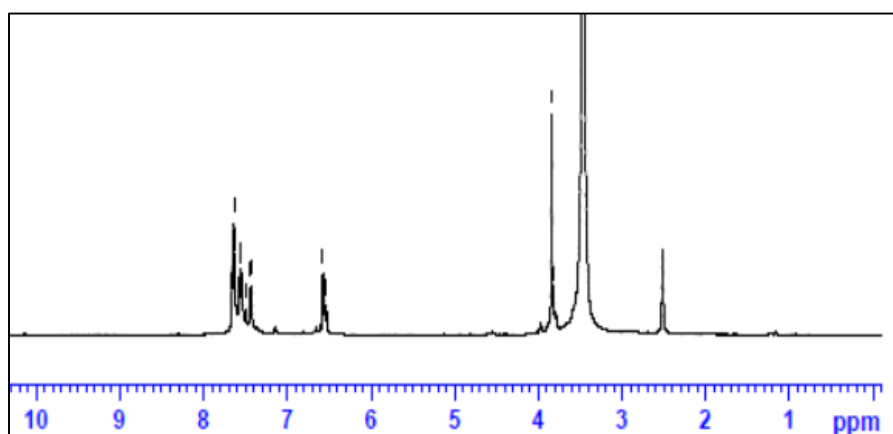
Figure 3 H^1-NMR-spectra of 2-H, 4-MBP-1,5-DANF-IV copolymer resin

3.4. Scanning electron microscopy

The surface analysis has been found great use in understanding the surface feature of the materials. The morphology of the resin was studied by scanning electron micrograph at different magnification which is shown in Figure-4. It gives information of defects in structure and surface topography. The morphology of resins indicates spherulites and fringed model. The spherules are complex polycrystalline formation having as smooth as good surface. This reveals the crystalline nature of copolymer sample 2-H, 4-MBP-1,5-DANF-IV. It also indicates the fringes model of amorphous crystalline structure. But the photograph shows fringed and scatted nature having shallow pits indicates transition between amorphous and crystalline. Due to amorphous nature, resin shows higher metal ion exchange capacity [17, 18].

Figure 4 SEM micrograph of 2-H, 4-MBP-1,5-DANF-IV copolymer resin

3.5. Determination of metal uptake in the presence of various electrolytes and different concentrations

The effect of ClO_4^{-1}, Cl^{-1}, NO_3^{-1} and SO_4^{-2} at various concentrations on the equilibrium of metal-copolymer interaction has been examined. The amount of metal ions taken up by a given amount of copolymer sample depends on the nature and concentrations of the electrolyte present in the solution which is presented in Table-2. I

Table2 Evaluation of the effect of different electrolytes on the uptake[a] of several metal ions by 2-H, 4-MBP-1,5-DANF-IV copolymer

Metal ion	pH	Conc.	Weight of metal ion (in mg.) taken up in the presence of			
			NaClO$_4$	NaCl	NaNO$_3$	Na$_2$SO$_4$
Cu^{2+}	4.5	0.01	2.50	2.31	2.15	4.17
		0.05	3.16	2.89	2.49	3.56
		0.10	3.85	3.50	2.95	2.99
		0.50	3.98	3.38	3.42	2.24
		1.00	4.16	4.19	4.17	1.07
Ni^{2+}	4.5	0.01	1.82	1.33	1.72	3.53
		0.05	1.99	1.58	1.99	3.09
		0.10	2.39	2.64	2.39	2.91
		0.50	3.17	2.59	2.68	1.89
		1.00	3.99	3.09	3.09	1.03
Co^{2+}	5.0	0.01	1.82	1.94	1.99	2.04
		0.05	1.74	1.72	1.83	1.85
		0.10	1.45	1.48	1.58	1.72
		0.50	1.17	1.08	1.15	1.19
		1.00	0.74	0.64	0.98	0.72
Zn^{2+}	5.0	0.01	1.83	1.66	2.22	2.12
		0.05	1.71	1.64	2.14	1.88
		0.10	1.33	1.52	1.23	1.44
		0.50	1.27	1.17	1.00	0.91
		1.00	0.98	0.80	0.88	0.67

		0.01	1.33	1.93	2.19	1.99
		0.05	1.24	1.72	1.89	1.84
Pb^{2+}	6.0	0.10	1.03	1.39	1.61	1.62
		0.50	0.94	1.16	1.19	1.08
		1.00	0.78	0.84	0.78	0.94

[a]$[M(NO_3)_2]$ = 0.1 mol/l; Volume = 2 ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time: 24 h : Room temperature.

In the presence of ClO_4^{-1} and Cl^{-1} ions the uptake of Ni(II) and Cu(II) ions increases with increasing concentration of electrolytes, where as the uptake of Co(II), Zn(II), and Pb(II) ions decreases with increasing both electrolytes concentration. But in the presence of NO_3^{-1} ions, the uptake of Ni(II) and Cu(II) ions increases with increasing concentration of the electrolyte where as the uptake of Zn(II), Co(II), and Pb(II) ions decreases with increasing concentration of $NaNO_3$ electrolyte. However, in the presence of SO_4^{2-} ions, the uptake of Cu(II), Co(II), Ni(II), Zn(II), and Pb(II) ions decreases with increasing Na_2SO_4 electrolyte concentration. This is on account of perchlorate, chloride and nitrate ions forms weak complexes with Cu (II) and Ni(II) ion while sulphate ion forms strong complexes with Cu(II) and Ni(II). But perchlorate, chloride and nitrate ions forms strong complexes with Co(II), Zn(II) and Pb(II) [19, 20].

3.6. Rate of metal ion uptake as a function of time

To estimate the time required to attain the equilibrium, the rates of metal ion uptake by 2-H, 4-MBP-1,5-DANF-IV resin were measured for Ni(II), Co(II), Cu(II), Pb(II) and Zn(II) ions. The dependence of the rate of metal-ion uptake on the nature of the metal ions which is presented in Table-3. These results shows that the time taken for the uptake of the different metal ion depended on the nature of the metal ions under the given conditions. The experimental data, shows that to attain the equilibrium Cu(II), Ni(II), Zn(II) and Co(II) ions required about 5 hrs, where as Pb(II) ions required almost 6 hrs. The experimental results indicates that the rate of metal-ion uptake of Ni(II), Co(II), Cu(II), Zn(II) is more than Pb(II). This trends is due to Ni(II), Co(II), Cu(II), Zn(II) have nearly equal ionic size but Pb(II) has relatively large ionic size [21].

Table3 Comparison of the rates of metal (M) ion uptake[a] by 2-H, 4-MBP-1,5-DANF-IVcopolymer

Metal ion	pH	% of metal ion uptake[b] at different time (hrs.)					
		1	2	3	4	5	6
Cu^{2+}	4.5	63.4	71.3	78.5	85.2	96.5	----
Ni^{2+}	4.5	71.2	76.2	80.4	88.1	95.1	----
Co^{2+}	5	55.6	67.3	71.1	79.7	96.3	----
Zn^{2+}	5	56.3	61.3	71.5	88.5	96.4	----
Pb^{2+}	6	39.2	58.4	69.3	80.3	88.2	97.2

[a]$[M(NO_3)_2]$= 0.1 mol/l; volume : 2ml; $NaNO_3$ = 1.0 mol/l; volume: 25ml, Room temperature;
[b]Metal ion uptake = (Amount of metal ion absorbed x 100) / amount of metal ion absorbed atequilibrium.

3.7. Distribution ratios of metal ions at different pH

The effect of pH on the distributed of amount of metal ions between two phases is depicted in the Table-4. The distribution ratio shows that the comparative amount of metal ions uptake by the copolymer 2-H, 4-MBP-1,5-DANF-IV increases with increasing pH of the medium. The study was carried out up to a definite pH value for the particular metal ion, to prevent hydrolysis of the metal ions at higher pH. However, the increase magnitude is different for unlike metal cations. The distribution of metal ions Cu(II) and Ni(II) is selectively more comparatively than any other metal ions under investigation. The order of distribution ratio of metal ions is found to be Cu(II) > Ni(II) > Co(II) > Zn(II) > Pb(II). The results of the study are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different metal ions [22].

Table 4 Distribution Ratio 'D'[a] of different metal ions[b] as a function of different pH of 2-H, 4-MBP-1,5-DANF-IV copolymer resin

Metal ions	Distribution ratios of different metal ions at different pH							
	1.5	2.0	2.5	3.0	3.5	4	5	6
Cu^{2+}	-	-	91.6	97.3	148.5	262.3	516.3	1177.8
Ni^{2+}	-	-	77.2	94.1	111.2	240.2	488.1	881.1
Co^{2+}	-	-	50.3	75.1	100.1	182.4	244.2	339.1
Zn^{2+}	-	-	50.1	68.5	83.3	96.2	144.1	311.4
Pb^{2+}	-	-	58.6	72.4	95.4	113.1	162.0	266.3

[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] $[M(NO_3)_2]$ = 0.1 mol/l; volume : 2ml; $NaNO_3$ = 1.0 mol/l; volume: 25ml, time 24h (equilibrium state) at Room temperature.

4. Conclusion

The copolymer 2-H, 4-MBP-1,5-DANF-IV was prepared from 2-hydroxy, 4-methoxy benzophenone and 1, 5-diaminonaphthalene with formaldehyde in the presence of 2M, HCL acid by condensation technique. The structure of the resin has been confirmed by physico-chemical and spectral studies. The 2-H, 4-MBP-1,5-DANF-IV is a selective chelating ion-exchange copolymer for removal of heavy metal ions Ni(II), Co(II), Cu(II), Pb(II) and Zn(II) from water. Copolymer shows a higher selectivity for removal of Ni^{2+} and Cu^{2+} ion than for Co^{2+}, Zn^{2+} and Pb^{2+} ions. It can be concluded that the resins are very efficient for uptake of various heavy metals ions like copper, nickel and iron etc. So by the help of the resin the heavy metal ions Ni(II), Co(II), Cu(II), Pb(II) and Zn(II) can be separated from water.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

References

[1] P. K. P. Gaitry Chopra, Synthesis, characterization and metal ion binding capacities of resin derived fom p-nitrophenol, hexamine and formaldehyde, International Interdisciplinary Research Journal, 2014, 4(3), 242- 250.

[2] W. B. Gurnule and J. V. Khobragade, Removal of heavy metals using ion-binding copolymer involving pthallic acid with formaldehyde by batch equilibrium technique, I J R B A T, 2017, 5(2), 1-9 .

[3] S. S. Rahangdale, Dinesh D. Kamdi, Jyotsna V. Khobragade and Wasudeo B. Gurnule, Separation of toxic metals ions from waste water using pyrogallol – biuret - formaldehyde copolymer resin, International Journal of Researches in Biosciences, Agriculture and Technology, 2020, 8(3), 259-268.

[4] W. B. Gurnule, Y. U. Rathod, V. U. Pandit, N. C. Das, Chelation ion exchange properties of copolymer resin synthesized from 1,5-diaminonaphthalene, 2,4-dihydroxypropiophenone and formaldehyde, Materials Today: Procedings, 2022, 53, 80-85.

[5] N. Abdullah, M. Z. Yahya andR. Mahmod, Comparative study of strong anion exchange poly (Styrene-co- EGDMA-co-VBC) and strong anion exchange hypercrosslinked poly (HEMA-co-EGDMA-co-VBC), Chemical Engineering Research Bulletin, 2017, 19, 96-101.

[6] Dhanraj. T. Masram, Kiran. P. Kariya and Narayan. S. Bhave, Synthesis of resin-VI: Salicylic acid, diamino-benzoic acid and formaldehyde and its ion-exchange properties, Der Pharma Chemica, 2014, 6(3), 292- 299.

[7] M. Ravichander, G. A. Reddy, V. Malathi, J. Pochampalli and R. Thampu, Synthesis, antimicrobial and ion exchange studies of some terpolymer resins derived from substituted resorcinol, biuret and formaldehyde, Journal of Chemical and Pharmaceutical Research, 2015, 7(9), 868-871.

[8] Kamlakar Nandekar, Shailesh Mandavgade and W. B. Gurnule, Studies of chelation ion exchange properties of novel copolymer resin derived from salicylic acid and semicarbazide, Journal of Information Knowledge and Research in Humanities and Social, 2016,1(4), 177-188.

[9] Wasudeo B. Gurnule, J. V. Khobragade and Mudrika Ahamed, Synthesis, characterization and chelation ion-exchange properties of copolymer resin, Der Pharma Letters, 2014, 6(6), 297-303.

[10] S. P. Dhote, W. B. Gurnule and A. B. Zade, Metal ion binding properties of a terpolymer resin, IOSR, Journal of Applied Chemistry, ISSN: 2278-5736, 2014, 35-39.

[11] N. C. Das and W. B. Gurnule, Electrical conductivity study of novel organic copolymer resin synthesized from 2-hydroxy, 4-methoxybenzophenone, 1,5-diaminonaphthalene and formaldehyde, International Journal of Advance Research in Science, Communication and Technology, 2024, 4(1), 520-525,

[12] N. C. Das and W. B. Gurnule, Electrical conductivity of newly synthesized copolymer resin 2,4-dihydroxypropiophenone, 1,5-diaminonaphthalene and formaldehyde, International Journal of Advance Research in Sciene, Communication and Technology, 2023, 3(2), 345-351.

[13] W. B. Gurnule and N. C. Das, Synthesis, characterization and thermal degradation study of copolymer resin, Materials Today: Procedings, 2020, 29, 1071-1076.

[14] S. S. Katkamwar, M. Ahmed and W. B. Gurnule, Studies of chelation ion-exchange, properties of copolymer resin derived from p-cresol, dithiooxamide and formaldehyde, Journal of Environmental Research and Development, 2012, 1(7), 330-337.

[15] Manjiri Nagmote, Jeevan Dontulwar and Rajesh Singru, Electrical conductivity study of resin synthesized from 1-naphthol-4-sulphonoc acid, hexamethylene diamine and formaldehyde, Der Pharma Chemica, 2014, 6(6), 427-434.

[16] W. B. Gurnule, and N. C. Das, Kinetic study of non-isothermal decomposition of Copolymer resin derived from 2,4-dihydroxypropiophenone, 1,5-diaminonaphthalene and formaldehyde , Materials Today: Procedings, 2019, 15, 611-619.

[17] Jeevan Dontulwar, Synthesis and characterization of high performance polymer resin,1-N-4-SAHDF-1, International Journal of Pharmaceutical Science Review and Research, 2016, 39(1), 260-264.

[18] M. M. Yeole, Seema Shrivastava and W. B. Gurnule, Synthesis and characterization of copolymer resin derived from 4-methyl acetophenone, phenyl hydrazine and formaldehyde, Der Pharma Chemica, 2015,7(5), 124-129.

[19] W. B. Gurnule, and Sonali S. Dhote, Synthesis, characterization and chelating ion-exchange, properties of copolymer resin derived from 2,4-dihydroxybenzoic acid, ethylenediamine and formaldehyde, Der Pharma Chemica, 2012, 4(2), 791-799.

[20] W. B. Gurnule and D. B. Patle, Preparation, characterization and chelating ion-exchange, properties of copolymer resin derived from o-aminophenol, urea and formaldehyde, Elixir Appl. Chem., 2012, 50, 10338-10345.

[21] Rajesh N. Singru, Application of copolymer, 8-hydroxyquinoline,5-sulphonic acid-oxamide-formaldehyde resin-IV in water purification, Analytical and Bioanalytical Electrochemistry, 2011, 3(6), 601-613.

[22] Sanjiokumar S. Rahangdale, Anil B. Zade and Wasudeo B. Gurnule, Chelation ion exchange properties of 2,4-dihydroxyacetophenone terpolymer resin, E-Journal of Chemistry, 2009, 6(3), 835-843.