

Chelation Ion Exchange Studies of Copolymer Resin from o-Toluidine, Biuret and Formaldehyde

Sanjiokumar S. Rahangdale¹ Murlidhar K. Rahangdale² and Wasudeo B. Gurnule³

¹Department Of Chemistry, Jagat Arts, Commerce And Indirabenharibhai Patel Science College, Goregaon-441801, India

²Department Of Chemistry, Nagarjuna Institute Of Engineering, Technology & Management, Nagpur-440001, India

³Department Of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara Square, Nagpur-440024, Maharashtra, India

Email: rahangdalessr@gmail.com

Abstract

The TBF copolymer resin was synthesized by the condensation of o-Toluidine and biuret with formaldehyde in the presence of 2M HCl as a catalyst at 120 ± 2 °C for 5 h with molar proportion of reactants. The TBF copolymer proved to be a selective chelating ion-exchange polymer for certain metals. Chelating ion-exchange properties of this polymer were studied for Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , and Pb^{2+} ions. A batch equilibrium method has been employed in the 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 strengths. The polymer showed higher selectivity for Cu^{2+} , Ni^{2+} than for Co^{2+} , Zn^{2+} , and Pb^{2+} ions. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken by TBF copolymer resin increases with the increasing pH of the media.

Keywords: Synthesis, Condensation, Ion-exchange property, Distribution ratio.

Introduction

A resin is said to be ampholytic ion-exchanger resin if it contains both cation and anion as exchangeable ion. Some ion-exchanger resins have chelating properties making them highly selective towards certain metal ions. Studies of chelation ion-exchange properties of copolymer resin derived from 1,5-diaminonaphthalene, 2,4-dihydroxy-propionophenone and formaldehyde (Das NC et al, 2022). Gharbi et al. (Gharbi S. 2014) have synthesized the chelating ion exchange resin by the condensation of 8-hydroxyquinoline with pyrogallol using formaldehyde as a cross linking agent at 120°C in DMF in the presence of HCl acid as catalyst. The cation exchange capacity was measured and the effect of pH and metal ion concentration on the ability of the ion-exchange were studied. The ratio of cation exchange reaction and the distribution coefficient in tartaric acid medium at different pH were also studied using the method of batch equilibrium. Rahangdale studied separation of toxic metals ions from waste water using pyrogallol-biuret-formaldehyde copolymer resin (Sanjiokumar S. Rahangdale et al 2020). A batch equilibrium method was employed in the study of the selectivity of metal ion uptake. The study was carried out over a wide pH range and in media of various ionic strengths. The polymer showed higher selectivity for Fe^{3+} , Cu^{2+} ions than for Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} ions. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken by resin is increases with the increase of PH of the medium. The metal uptake properties of chelating azo polymeric resin were studied (Keerthiga et al. 2015). Synthesis and chelate ion exchange properties of copolymer resin: 8-hydroxyquinoline-5 sulphonic acid-catechol-formaldehyde (Mandavgade SK et.al. 2022). The chelating properties of synthesized resin such as total ion-exchange capacity, effect of pH, concentration and time for different metal ions Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) were also studied by employing batch equilibrium method. A new chelating copolymer resin (o-AABF) was synthesized through copolymerization of o-amino acetophenone, biuret and formaldehyde in acidic medium (HCl) by condensation reaction. Selectivity and binding capacity of copolymer resin studied by batch equilibrium method towards Ni^{2+} , Co^{2+} , Cd^{2+} , Zn^{2+} and Cr^{3+} in different pH and treatment time (Rashid and Coworker, 2017). A novel hexylthioglycolate ion-exchange resin from poly (ethyl acrylate - acrylonitrile - divinyl benzene) beads were prepared and adsorption capacities of this resin for Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hr(II), and Pb(II) at different pH was studied. (Dwivedi and coworker, 2014).

Synthesis of o-Toluidine–Biuret–Formaldehyde (o-TBF) Copolymer Resin.

The four different types of o-TBF copolymer resins have been successfully synthesized and abbreviated as given in Table 1.

Synthesis of o-TBF-I copolymer resin

The new copolymer resin o-TBF-I was synthesized by condensing o-Toluidine (1.07 g, 0.1 mol) and biuret (1.03 g, 0.1 mol) and formaldehyde (7.50 ml, 0.2 mol) in molar ratio of 1:1:2 in the presence of 2M (200 ml) HCl as a catalyst at $122^\circ\text{C} \pm 2^\circ\text{C}$ for 5 hrs in the round bottom flask attached with water condenser and was heated in an oil bath with occasional shaking to ensure thorough mixing. The temperature of oil bath was controlled by dimmer state (Sanjiokumar et al, 2019, 2020, 2021). The resinous cream product obtained was removed

immediately as soon as the condensation reaction was over. The reaction is shown as follows in Fig. 1. The novel copolymer/activated charcoal composite was prepared by o-TBF copolymer and activated charcoal in 1:2 ratio. The copolymer was dissolved in 25 ml of DMSO and the activated charcoal was added into it and the mixture was subjected to ultrasonification for 3 hrs with constant stirring for 24 hrs at room temperature. After the specific time, the obtained composite was separated, filtered and dried at 70°C for 24 hrs (Santosh P. et.al. 2020).

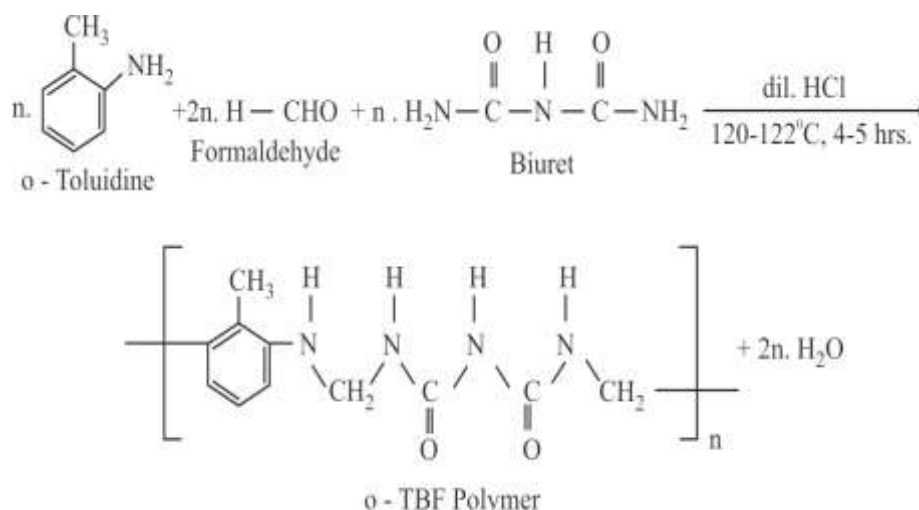


Fig. 1 : Reaction and Suggested Structure of o-TBF Copolymer Resin

Purification of Resins

The separated copolymer resin was washed with hot water and methanol to remove unreacted starting materials and monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 4-hydroxybenzoic acid-formaldehyde copolymer which might be present along with o-TBF copolymer. The product so obtained was further purified by reprecipitation technique. For this purpose the copolymer resin was dissolved in 10% aqueous sodium hydroxide solution, stirred well, filtered, and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v concentrated hydrochloric acid/distilled water) with constant and rapid stirring to avoid lump formation. The process of re-precipitation was repeated twice. The copolymer sample o-TBF-I thus obtained was filtered and washed several times with hot water, dried in air, powdered and kept in vacuum desiccators over silica gel. The yield of the copolymer resin was found to be 81%. Similarly other copolymer resins o-TBF-II, o-TBF-III and o-TBF-IV were synthesized by varying the molar ratios of the starting materials viz. (2:1:3), (3:1:5) and (4:2:7), respectively with little variation of experimental conditions. The samples, yields and reaction details are tabulated in Table 1.

Table 1 Synthesis and Physical Data of o-TBF Copolymer Resins

Copolymer Resin Abbreviation	Reactans			Molar ratio	Catalyst 2M/ HCl (ml)	Reflux Temp. (K)	Time (hr)	Yield (%)	Melting point (K)
	o-Toluidine o-T (mol)	Biuret B (mol)	Formaldehyde F (mol)						
o-TBF-I	0.1	0.1	0.2	1:1:2	200	395	5	69	434
o-TBF-II	0.2	0.1	0.3	2:1:3	200	395	5	79	423
o-TBF-III	0.3	0.1	0.5	3:1:5	200	395	5	86	429
o-TBF-IV	0.4	0.2	0.7	4:1:6	200	395	5	78	442

Ion-exchange properties

The ion-exchange property of TBF-copolymer resin was determined by the batch equilibrium method (Mane VD et. al. 2009, Tarase M. V. et. al. 2008, Gupta RH et. al. 2008, Suzuki E. 2002).

Determination of metal uptake in the presence of various electrolytes and different concentration

The copolymer sample (25 mg) was suspended in an electrolyte solution (25 ml) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1M HNO₃ or 0.1M NaOH. The suspension was stirred for 24 hrs at 30°C. To this suspension 2 ml of 0.1M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 30°C for 24 hrs. The polymer was then filtered off and washed

with distilled water. The filtrate and the washing were collected and then the amount of metal ion was estimated by titrating against standard EDTA (ethylene diamine tetra-acetic acid) at the same pH (experimental reading). The same titration has been carried out without polymer (blank reading). The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments. The experiment was repeated in the presence of several electrolytes (Rahangdale PK et. al. 2003). Metal ion, its pH range, buffer used, indicator used and colour change are given in Table 1. The metal ion uptake can be determined as, Metal ion adsorbed (uptake) by resin = (X-Y) Z millimols / gm.

Where,

'Z' ml is the difference between actual experimental reading and blank reading.

'X' mg is metal ion in the 2ml 0.1M metal nitrate solution before uptake.

'Y' mg is metal ion in the 2ml 0.1M metal nitrate solution after uptake.

By using this equation the uptake of various metal ions by resin can be calculated and expressed in terms of millimols per gram of the copolymer.

Estimation of rate of metal ion uptake as function of time

The time required for attaining the state of equilibrium under the given pH was evaluated by a series of experiment carried out to determine the amount of metal ion adsorbed by the copolymer at specific time intervals. The copolymer sample (25mg) was mechanically stirred with 25ml of 1M NaNO₃ to allow the copolymer to swell at room temperature. Metal ion solution (0.1M, 2ml) was added to this and pH of the content was adjusted to the required value by addition of either 0.1M HNO₃ or 0.1M NaOH. After the specific time interval, the particular suspension was filtered and washed with the distilled water. The filtrate was collected and the unabsorbed metal was estimated by titration with standard EDTA solution using appropriate indicator. Under the experimental condition it is observed that, the state of equilibrium is established within 24 h at 25°C (Boto BA, 1987). The rate of metal ion uptake is expressed as the percentage of the amount of metal ion taken up after a specific time related to that in the state of equilibrium. The percent amount of metal ions taken up at different time is defined as

$$\text{Percentage of metal ion uptake at different time} = \frac{\text{Amount of metal ion adsorbed at different time}}{\text{Amount of metal ion adsorbed at equilibrium}} \times 100$$

Using this expression, the amount of metal adsorbed by polymer after specific time intervals was calculated and expressed in terms of percentage metal ion adsorbed. This experiment was performed using 0.1M metal nitrate solution of Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, and Pb²⁺ ions.

Evaluation of the distribution of metal ions at different pH

The distribution of each one of the five metal ions, i.e. Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺ and Pb²⁺ between the copolymer phase and the aqueous phase was estimated at 25°C and in the presence of a 1M NaNO₃ solution. The experiments were carried out as described above at different pH values. The distribution ratio (D) was defined by the following relationship (Boto BA, 1987).

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

If we consider

'Z' is the difference between actual experiment reading and blank reading,

'X' gm is the amount of metal ion in 2ml 0.1M metal nitrate solution,

'Y' gm of metal ion in 2ml of metal nitrate solution after uptake.

$$\text{Metal ion adsorbed (uptake) by the resin} = \frac{ZX}{Y} \frac{2}{0.025} = \left(\frac{ZX}{Y} \right) 80$$

Table 2. Data of experimental procedure for direct EDTA titration

Metal Ion	pH range	Buffer used	Indicator used	Colour change
Fe(III) Cu(II)	2-3 9-10	Dil.HNO ₃ /dil.NaOH Dil.HNO ₃ /dil.NaOH	Variamine blue Fast sulphone black-F	Blue to Yellow Purple to green
Ni(II)	7-10	Aq.NH ₃ /NH ₄ Cl	Mureoxide	Yellow to violet
Co(II)	6	Hexamine	Xylenol orange	Red to yellow
Zn(II) Cd(II)	10 5	Aq.NH ₃ /NH ₄ Cl Hexamine	Eriochromeblack-T Xylenol orange	Wine red to blue Red-Yellow
Pb(II)	6	Hexamine	Xylenol orange	Red to yellow

Result And Discussion

o-Toluidine-Biuret -Formaldehyde (o-TBF) Copolymer Resins

The experimental result of the batch equilibrium study carried out for all the four o-TBF copolymer resins are given in the Table 3 to 5. From this study, the following generalization was made.

(a) Effect of Electrolytes on Metal Ion Uptake

The amount of metal ions taken up from a given amount of o-TBF copolymers and its composite depends on the nature and concentration of the electrolyte present in the solution. In presence of perchlorate, chloride and nitrate ions, the uptake of Cu^{2+} and Ni^{2+} ions increases with increasing concentration of the electrolytes, whereas in presence of sulphate ions, the amount of the above mentioned ions taken up by the copolymers decreases with increasing concentration of the electrolytes (Shah BA, 2007). Moreover, the amount of Co^{2+} , Zn^{2+} and Pb^{2+} ions taken up by the copolymer samples decreases with increasing concentration of the chloride, nitrate, perchlorate and sulphate ions (Masram DT, 2014). This may be explained in terms of the stability constants of the complexes which Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} ions form with these anions. SO_4^{2-} might form rather strong complexes with Ni^{2+} and Cu^{2+} ions, while ClO_4^- , NO_3^- and Cl^- might form weak complexes and, therefore, might not be expected to influence the position of the Ni^{2+} and Cu^{2+} chelates equilibrium as much as SO_4^{2-} . Sulphate, perchlorate, nitrate and chloride might form rather strong chelates with Co^{2+} , Zn^{2+} and Pb^{2+} and therefore might be expected to influence the position of the Co^{2+} , Zn^{2+} and Pb^{2+} chelates equilibrium. This type of trend has been observed by other earlier workers in the field (Katkamwar SS. 2012, Bhatt RR et al, 2012). The metal ion capacity of copolymer/activated charcoal composite is also found to be higher. The copolymer and composite was found to possess higher metal ion uptake for Co^{2+} and Cd^{2+} than the other selective metal ions.

(b) Evaluation of the Rates of Metal Ion Uptake

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried out while operating as close to equilibrium conditions as possible. The data of metal ion uptake at various shaking time intervals. These results indicate that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ion under given conditions. It is found that Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} ions require about 5h for the establishment of the equilibrium where as Pb^{2+} ions required almost 6h for equilibrium. Thus, the rate of metal ion uptake follows the order Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} > Pb^{2+} for all the copolymers and its composite. The trend is good agreement with earlier workers (Singru RN, 2010). The metal ion capacity of copolymer/activated charcoal composite is also found to be higher. The copolymer and composite was found to possess higher metal ion uptake for Co^{2+} and Cd^{2+} than the other selective metal ions.

(c) Distribution Ratio of Metal Ions at Different pH

The results of effect of pH on the amount of metal ion distributed between two phases can be explained by the result. The data on the distribution ratio as a function of pH indicates that the distribution of each metal between the polymers phases and aqueous phase increase with increasing pH of the medium. The results indicate that the relative amount of metal ion adsorbed by the copolymer resin and its composite increase with increasing pH of the medium. The study was carried out upto definite pH value for the particular metal ion to prevent hydrolysis of the metal ions at higher pH. Cu^{2+} and Ni^{2+} have highest distribution ratio at pH 2.5 to 6, therefore these ions can be taken up more selectively between the ranges of pH 2.5-6. The other three ions Co^{2+} , Zn^{2+} and Pb^{2+} have lower distribution ratio over pH range of 2.5 to 6. The different distribution ratio obtained for different metal ions may be due to the difference in stability of the complex formation during adsorption. The high distribution ratio may be due to higher stability constant of metal ligand complexes and vice versa. Cu^{2+} and Ni^{2+} may form more stable complex, indicate that these ions adsorbed more selectively to the higher extent, rather than Co^{2+} , Zn^{2+} and Pb^{2+} which may form rather weak complexes with ligand during the course of time, therefore these ions adsorb to a least extent over an entire pH range study (Patel HJ et al 2008). The metal ion capacity of copolymer/activated charcoal composite is also found to be higher. The copolymer and composite was found to possess higher metal ion uptake for Co^{2+} and Cd^{2+} than the other selective metal ions. But, when the pH increases, the concentration of H^+ decreases which leads to the higher mobility of heavy metal ions for the higher uptake by the synthesized adsorbents. In the present study the observed order of distribution ratios of divalent ions measured in the range of pH 2.5 to 6 is found to be $\text{Cu (II)} > \text{Ni (II)} > \text{Co (II)} > \text{Zn (II)} > \text{Pb (II)}$. The results are in good agreement with earlier co-workers (Kapadia M et al 2008). Hence, the results of this type of study are helpful in selecting the optima pH for a selective uptake of a metal ion from a mixture of different ion.

Table 3 Effect of metal ion uptake by composite

Metal	Concentration Of electrolytes (mol L ⁻¹)	Metal ion uptake in the presence of electrolytes(m.mol/g)		
		NaCl	NaNO ₃	NaClO ₄
Cu ²⁺	0.1	1.63	1.61	1.64
	0.5	1.61	2.384	2.15
	1.0	2.8	2.195	2.13
Ni ²⁺	0.1	0.7468	1.453	0.481
	0.5	1.11	1.674	0.746
	1.0	1.274	1.816	0.82
Co ²⁺	0.1	1.09	0.847	0.56
	0.5	1.08	1.09	0.641
	1.0	1.186	1.60	0.753
Zn ²⁺	0.1	0.421	0.469	0.631
	0.5	0.56	0.748	0.712
	1.0	0.56	1.089	0.86
Pb ²⁺	0.1	0.319	0.397	0.584
	0.5	0.489	0.632	0.691
	1.0	0.593	0.898	0.734

Table 4 Rate of metal ion uptake by composite

Metalion	Equilibrium attainment (%)						
	Time (h)						
	1	2	3	4	5	6	7
Cu ²⁺	31	55	79	99	-	-	-
Ni ²⁺	10	25	38	52	63	81	79
Co ²⁺	12	27	35	56	65	81	84
Zn ²⁺	14	19	29	31	45	51	78
Pb ²⁺	4	5	9	14	33	42	61

Table 5 Metal ion uptake at different pH by composite

Metalion	Metal ion uptake (m.mol/g)					
	pH of the medium					
	1.5	2	3	4	5	6
Cu ²⁺	0.59	1.11	1.13	1.45	1.85	2.51
Ni ²⁺	0.49	0.93	0.98	1.11	1.45	2.98
Co ²⁺	0.27	0.48	0.75	0.87	1.11	1.71
Zn ²⁺	0.22	2.29	0.14	0.50	0.79	1.31
Pb ²⁺	0.13	0.25	0.32	0.40	0.68	1.10

Conclusion

A copolymer TBF based on the condensation reaction of pyrogallol and biuret with formaldehyde in the presence of acid catalyst was prepared. TBF is a selective chelating ion-exchange copolymer resin for certain metals. The copolymer resin showed a higher selectivity for Cu²⁺ and Ni²⁺ ions than for Co²⁺, Zn²⁺, and Pb²⁺ ions. The uptake of some metal ions by the

resin was carried out by the batch equilibrium technique. The uptake capacities of metal ions by the copolymer resin were pH dependent. From the results of distribution coefficients, it can be observed that Cu (II) has higher value of distribution ratio. Due to considerable difference in the uptake capacities at different pH and media of electrolyte, the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to use for separation of particular metal ions from their mixture.

Acknowledgment:

The authors express their gratitude to the Principal, Kamla Nehru Mahavidyalaya, Nagpur and Principal, Jagat College, Goregaon for providing laboratory facility.

References

1. Bhatt RR, Shah AB, Shah VA (2012). Uptake of heavy metal ions by chelating ion-exchange resin derived from p-hydroxybenzoic acid-formaldehyde-resorcinol: Synthesis, characterization and sorption dynamics. *Malays. J. Anal. Sci.* 16, 117-133.
2. Boto BA, Pawlowski L (1987). *Waste Water Treatment by Ion Exchange*, Chapman & Hall, New York.
3. Das NC., Rathod YU., Pandit VU., Gurnule WB. (2022) Studies of chelation ion-exchange properties of copolymer resin derived from 1,5-diaminonaphthalene, 2,4-dihydroxypropiofenone and formaldehyde. *Material Today Proceeding*, 53(1) 80-85.
4. Dwivedi P.R. and Verma J. K.(2014), *International Journal of Chemical and Environmental Engineering*, 5(1), 73- 81.
5. Gharbi S., Khiari J. and Jamoussi B (2014)., *American Chemical Sciences, Journal*, 4(6), 874-889,.
6. Gupta RH, Zade AB, Gurnule WB (2008). Resin IV: Synthesis and characterization of terpolymers derived from 2-hydroxyacetophenone, melamine and formaldehyde. *J. Appl. Polym*, 109 (5), 3315-3320.
7. Katkamwar S. S., Ahamed M. and Gurnule W. B. (2012). Studies of chelation ion-exchange properties of copolymer resins derived from p-cresol, dithioamide and formaldehyde. *J. Environ. Res. Develop.*, 7(1A), 330-337.
8. Kapadia M, Patel M, Joshi J (2008). Synthesis of phenolic resin and its polychelates with 4F-block elements: Thermal and adsorption studies. *Iran. Polym. J.*, 17(10), 767-779.
9. Keerthiga R., Vijayalaxmi S. and Kaliyappam T.(2015), *International Journal of Chem Tech Research*, 7(7), 2886-2893.
10. Mandavgade SK, Gurnule WB (2022). Synthesis and chelate ion exchange properties of copolymer resin: 8-hydroxyquinoline-5 sulphonic acid-catechol-formaldehyde. *Material Today Proceeding*, 60(4) DOI. 10.1016/j.matpr.2021.12.494.
11. Mane VD, Wahane NJ, Gurnule WB (2009). 8-hydroxyquinoline-5-sulphonic acid- thiourea-formaldehyde copolymer resins and their ion-exchange properties. *J Appl Polym Sci*, 111, 3039.
12. Masram D. T., Kariya K. P. and Bhave N. S. (2014). Synthesis of resin-VI: salicylic acid and formaldehyde resin and its ion-exchange properties. *Der PharmaChemica*, 6(3), 292-299.
13. Patel H. J., Patel M. G., Patel K. J., Patel K. H.(2008). Synthesis, characterization, thermal studies, and antimicrobial screening of poly (acrylate)s bearing 4-methyl coumarin side groups. *Iran. Polym. J.*, 17(8), 635-644.
14. Rasid A. K. and Omran K.A.(2017), *Asian Journal of Chemistry*, 29(1), 2419-2424.
15. Rahangdale PK, Gurnule WB, Paliwal LJ, Kharat RB (2003). Synthesis, characterization, and thermal degradation studies of copolymer resin derived from p-cresol, melamine, and formaldehyde. *React Funct Polym*, 55, 255-265.
16. Singru RN, Zade AB, Gurnule WB (2010). Chelating ion-exchange properties of copolymer resins derived from p-cresol, oxamide and formaldehyde. *J App Polym Sci*, 116, 3356-3366.
17. Shah BA, Shah AV, Bhandari NB, Bhatt RR (2007.) Studies of chelation ion-exchange properties of copolymer resin derived from salicylic acid and its analytical applications. *Iran. Polym. J.* 16,173-184.
18. Sanjiokumar S. Rahangdale, Narayan C. Das, Kiran Vajpai, Wasudeo B. Gurnule, (2019)
19. Synthesis, Characterization And Thermal Degradation Studies Of Copolymer Derived From 2,4-Dihydroxy Propiophenone And 4-Pyridylamine . *International Journal of Recent Scientific Research*, 10 (4A) 31772-31778.
20. Sanjiokumar S. Rahangdale, Nisha Tiwari, Manish Tiwari, Wasudeo B. Gurnule (2020). Antimicrobial Screening of Polymeric Resin Derived From 2, 2'-Dihydroxybiphenyl, Bouret and Formaldehyde, *Alochana Chakra*. IX (V), 74-84.
21. Sanjiokumar S. Rahangdale, Narayan C. Das, Kiran S. Vajpai And Wasudeo B. Gurnule(2020), Synthesis, Characterization And Thermal Degradation Study Of Copolymer Resin-Ii: Resulting From 2-Hydroxy, 4-Methoxybenzophenone, 1, 5-Diaminonaphthalene And Formaldehyde. *IJRBAT*, VIII (1) 194-204.
22. Sanjiokumar S. Rahangdale, Dinesh D. Kamdi, Jyotsna V. Khobragade And Wasudeo B. Gurnule (2020), Separation Of Toxic Metals Ions From Waste Water Using Pyrogallol-Biuret-Formaldehyde Copolymer Resin. *IJRBAT*, VIII (3) 259-268.

23. Santosh P. Chakole, S. S. Rahangdale, Ketki S. Misar, Kiran S. Vajpai, W. B. Gurnule (2020), Synthesis and Characterization of Copolymer Resin Derived from 2, 2'-Dihydroxybiphenyl, Ethylenediamine and Formaldehyde, *Alochana Chakra*. IX (V), 666-673.
24. S. S. Rahangdale, S. P. Chakole, K. S. Vajpai and W. B. Gurnule (2021), Synthesis, Characterization And Photoluminescent Studies Of Organic Copolymer Derived From 2, 2'-Dihydroxybiphenyl And Propylenediamine. *JETIR*, 8(9) 174-180.
25. Sanjiokumar S. Rahangdale, Santosh P. Chakole, Jyotsna V. Khobragade, And W. B. Gurnule (2021), Thermal Degradation Studies of 2,2'-Dihydroxybiphenyl-Ethylenediamine-Formaldehyde Copolymer. *RJPBCS*, 12(6) 1-12.
26. Suzuki E (2002). High resolution scanning electron microscopy of immunogold labelled cells by the use of thin plasma coating osmium. *J Microscopy*, 208, 153-157.
27. Tarase MV, Zade AB, Gurnule WB (2008). Synthesis, characterization, and ion-exchange properties of terpolymer resins derived from 2, 4-dihydroxypropiophenone, biuret, and formaldehyde. *J ApplPolymSci*, 108, 738-746.