INTERNATIONAL JOURNAL OF RESEARCHES IN BIOSCIENCES, AGRICULTURE AND TECHNOLOGY

SEPARATION OF TOXIC METALS IONS FROM WASTE WATER USING PYROGALLOL-BIURET-FORMALDEHYDE COPOLYMER RESIN

Sanjiokumar S. Rahangdale[1], Dinesh D. Kamdi[2], Jyotsna V. Khobragade[3] and Wasudeo B. Gurnule*[2]

[1]Department of Chemistry, Jagat Arts, Commerce and Indiraben Hariharbhai Patel Science College, Goregaon-441801, India

[2]Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara Square, Nagpur-440024, Maharashtra, India

[3]Department of Chemistry, Gurunank Science College, Ballarpur-442701, India

Email: wbgurnule@gmail.com

ABSTRACT:

The PBF copolymer resin was synthesized by the condensation of pyrogallol and biuret with formaldehyde in the presence of 2M HCl as a catalyst at 124 ± 2 °C for 5 h with molar proportion of reactants. The PBF copolymer resin has been characterized by UV-visible, IR and proton NMR spectral studies. The PBF copolymer proved to be a selective chelating ion-exchange polymer for certain metals. Chelating ion-exchange properties of this polymer were studied for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{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 Fe^{3+}, Cu^{2+}, Ni^{2+} than for 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 PBF copolymer resin increases with the increasing pH of the media.

Key words: - Synthesis, Condensation, Spectral studies, Ion-exchange property, Distribution ratio.

INTRODUCTION:

Ion exchange resin is a new type of adsorption and separation materials that can be used in the form of resins and fiber bundles (Lee C et.al. 2017). A large amount work has been carried out on the customized synthesis, characterization and applications of various inorganic and organic polymers. Particularly, research in the area of coordination polymers has witnessed an upsurge during the past few decades. The discovery of the Prussian blue in 1704 has marked the beginning of first man made coordination polymer. Coordination polymers comprises of addition of metal ions into the polymeric backbone leading to the formation of the polymer-metal complex with enhanced chemical, mechanical and optical properties which have myriads of applications (Colon YJ et. al. 2020, Liu J et. al. 2020, Yang XG et. Al. 2019, Liu JQ et. Al. 2020, Hu Y et. Al. 2019). A copolymer resin generally consist of three distinct monomers bonded in an end-to-end fashion and have applications in the area of porous and hybrid films (Phillip AW et. al. 2011), solar cells (Kang TE et. al. 2013), ferroelectric and electromechanical devices (Xu H et. al. 2001), in biological and medical fields (Fustin CA et. al. 2005). Notably, Ahamed and coworkers have synthesized the copolymer resin of Anthranilic acid, Salicylic acid and

Formaldehyde and studied their metal ion binding capacities and thermal degradation properties (Ahamed MAR et. al. 2010). Similarly, Bhatt and co-workers have reported the copolymer of p-hydroxybenzoic acid, Formaldehyde and Resorcinol and investigated their uptake against heavy metal ions (Bhatt RR et. al. 2012). The study pertaining to chelation of metal ion using an ion-exchange copolymer resin derived from Salicylic acid was reported by Shah *et* al. 2007. Resorcinol-Formaldehyde resin has been used as precursor in the extension of stober method of monodispersed polymer leading to the formation of four-coordinate covalently bonded silica-like frame works *via* polymerization (Liu J et. al. 2011).

Inspired from the above studies, we have also explored the synthesis, characterization and ion-exchange properties of copolymer derived from pyrogallol and biuret with formaldehyde. This paper has been described the development of a novel ion-exchanger resin for the desalination of waste water which is high in Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}ions as well as suspended solids in waste water. Some commercially available ion-exchange resins are given below in Table 1.

METHOD AND METHODOLOGY:

The entire chemicals used in the synthesis of various new copolymer resins were procured from the market and were chemically pure grade. Whenever required they were further purified by standard methods like thin layer chromatography, re-precipitation and crystallization which are generally used for the analytical purification purpose.

Synthesis of PBF-IV Copolymer Resin

The new copolymer resin PBF-IV was synthesized by condensing pyrogallol(0.4mol) and biuret (0.1mol) with formaldehyde (0.6mol) in the mol ratio of 4:1:6 in the presence of 2M

200 ml HCl as a catalyst at $120^0C \pm 2^0C$ for 5 hrs, in an oil bath with occasional shaking, to ensure thorough mixing. The separated copolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove pyrogallol-biuret copolymer which might be present along with PBF-IV copolymer. The brown colour resinous product was immediately removed from the flask as soon as the reaction period was over and then purified. The reaction and the suggested structure of PBF-IV is shown in fig.1

The copolymer was purified by dissolving in 10% aqueous sodium hydroxide solution, filtered and re-precipitated 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 of PBF-IV thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuumdesiccator over silica gel.

Characterization of the Copolymer

Electron absorption spectrum of copolymer resin in DMSO (spectroscopic grade) was recorded on shimadzu double beam spectrophotometer in the range of 200 to 850 nm, Infra-red spectra of PBF-IV copolymer resin was recorded on Perkin-Elmer-983 spectrophotometer in KBr pallets in the wave number region of 4000-400 cm-1, Nuclear Magnetic Resonance (NMR) spectra of newly synthesized copolymer resin has been scanned on Bruker Advanced 400 NMR spectrometer using DMSO-d6 at sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh. SEM has been scanned by FEI-Philips XL-30 electron microscope.

Ion-exchange properties

The ion-exchange property of PBF-IV 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 $0.1M$ HNO_3 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 $1M$ $NaNO_3$ 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 $0.1M$ HNO_3 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 25^0C (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

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

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 Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}ions.

Evaluation of the distribution of metal ions at different pH

The distribution of each one of the five metal ions, i.e. Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Pb^{2+} between the copolymer phase and the aqueous phase was estimated at 25⁰C and in the presence of a 1M $NaNO_3$ 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.

Metal ion adsorbed (uptake) by the resin

$$= \frac{ZX}{Y} \frac{2}{0.025} = \left(\frac{ZX}{Y}\right)80$$

RESULTS AND DISCUSSION

The newly synthesized purified PBF-IV copolymer resin was found to be reddish brown in colour. The copolymer is soluble in solvents such as DMF, DMSO and is insoluble in almost all other organic solvents.

Electronic Spectra

The UV–visible spectra (Fig. 2) of the PBF-IV copolymer sample in pure DMSO was recorded in the region 200-850 nm at a scanning rate of 100 nm min-1 and a chart speed of 5 cm min-1. The PBF-IV copolymer sample displayed two characteristic broad bands at 240-260 nm and 310-330 nm. Both of these bands seem to be merged with each other because of their very broad nature. These observed position for the absorption bands indicate the presence of a carbonyl (C=O; ketonic) group having a carbon–oxygen double which is in conjugation with -NH group. The former band (more intense) can be accounted for by n→π* transition while the latter band (less intense) may be due to a π→π* transition (Roy PK et. al. 2004). The bathochromic shift (shift towards longer wave length) from the basic values of the >C=O group viz. 320 and 240 nm, respectively may be due to the combined effect of conjugation of >C=O and NH groups and phenolic hydroxyl group (auxochrome) and quinolinering (Patel H. J. et. al. 2008).

Infrared Spectra

Infrared spectra of PBF-IV copolymer resin is shown in Fig.3 and IR spectral data are tabulated in Table 3. Very broad band appeared in the region 3506cm-1 may be assigned to the stretching vibration of phenolic –OH groups exhibiting intermolecular hydrogen bonding between -OH and >C=O and NH group of amide (Selema Helena et. al. 1997). The bands obtained at 1385 cm-1 suggest the presence of methylene (-CH2-) bridges. A sharp strong peak at 1552 cm-1 may be ascribed to aromatic skeletal ring breathing modes. The 1,2,3,5 tetra substitution of aromatic benzene ring can be recognized from sharp and medium/weak absorption bands appeared at 957, 1072 and 1141cm-1 respectively. The presence of C-H stretching of aromatic ring may be assigned as a sharp and strong band at 3110 cm-1 which seems to be merged with very broad band of phenolic hydroxy group.

NMR spectra

The NMR spectrum of the copolymer was scanned in DMSO-d6. The spectrum is given in Fig.4. The spectral data are given in Table 4. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature (Kapadia M. et. al. 2008). The medium singlet at 2.53-2.59 (δ) ppm may be due to the methylene proton of Ar-CH2 bridge. The singlet obtained in the region of 8.97 (δ) ppm may be

due to the methylene proton of Ar-CH_2-N moiety. The signals in the region 7.45 (δ) ppm are attributed to protons and –NH bridge. The weak multiplate signal (unsymmetrical pattern) in the region of 6.54-6.75 (δ) ppm may be attributed to aromatic proton (Ar-H). The signal in the range of 7.33 to 7.76 (δ) ppm may be due to phenolic hydroxyl protons. The position of the signal of phenolic hydroxyl proton is slightly shifted to downfield, indicating clearly the intramolecular hydrogen bonding of -OH group (Masram D. T. et. al. 2014).

Scanning Electron Microscopy (SEM)

Figure 5 shows the scanning electron microscopy (SEM) micrographs of the pure PBF-IV copolymer sample at 1500X and 3000X magnification (Singru R. N. et. al. 2010). The morphology of resin exhibits growth of crystals from polymers solution corresponding to the most prominent organisation in polymers on a large scale such as in size of few mille metre sspherulites. The morphology of resin shows a fringed micelle model of the crystalline-amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. The micrograph of pure sample shows the presence of crystalline-amorphous layered morphology which is the characteristic of polymer. The monomers have crystalline structure but during condensation polymerization of some crystalline structure lost into amorphous nature.

On the basis of the nature and reactive position of the monomers, elemental analysis UV-visible, IR, NMR spectral studies and taking into consideration the linear structure of other phenol formaldehyde and the linear branched nature of urea-formaldehyde polymers, the most probable structure has been proposed for PBHF-IV copolymer resin, has been shown in Fig. 1.The morphology of the resin shows the transition between crystalline and amorphous

nature, when compare to the other resin, the PBF-IV copolymer resin is more amorphous in nature, hence, higher metal ion exchange capacity.

Ion-exchange properties

Batch equilibrium technique developed by Gregor et al and De Geiso et al were used to study ion exchange properties of PBF-IV copolymer resin. The results of the batch equilibrium study carried out with the copolymer PBF-IV. Seven metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} in the form of aqueous metal nitrate solution were used. The experiments were repeated for six times and the mean standard deviations were calculated at different concentrations, shaking times and pH of the solutions and have been found to be as follows.

At different concentrations:

Metal ions	Fe^{3+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
Standard Mean deviation	0.47	0.74	0.97	0.39	0.71	0.67	0.89

At different shaking times :

Metal ions	Fe^{3+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
Standard Mean deviation	17.24	17.28	18.46	19.48	19.39	27.01	24.99

At different pH of the solutions :

Metal ions	Fe^{3+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
Standard Mean deviation	453.96	422.54	213.45	157.01	63.94	78.64	93.21

The strength of ion exchange capacities of various resins can be studied by comparing their ion exchange capacities. The ion exchange

capacity (IEC) is a fundamental and important quantity for the characterization of any ion exchange material. It is defined as the amount of ion that undergoes exchange in a definite amount of material, under specified experimental conditions. The ion exchange capacity of PBF-IV copolymer has been calculated, which was found to be 4.3 mmol g^{-1} which indicates that PBF-IV copolymer resin is better ion exchanger than commercial phenolic and some polystyrene commercial ion exchangers.

CONCLUSION

A copolymer PBF-IV based on the condensation reaction of pyrogallol and biuret with formaldehyde in the presence of acid catalyst was prepared. PBF-IV is a selective chelating ion-exchange copolymer resin for certain metals. The copolymer resin showed a higher selectivity for Fe^{3+},Cu^{2+} and Ni^{2+}ions than for Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} 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.

Acknowledgement

REFERENCES:

Ahamed MAR, Azarudeen RS, Karunakaran M, Burkanudeen AR (2010). Synthesis, characterization, metal ion binding capacities and applications of a terpolymer resin of anthranilic acid/ salicylic acid/ formaldehyde. Iran. Polym. J. 19, 635-646.

Boto BA, Pawlowski L (1987). Waste Water Treatment by Ion Exchange, Chapman & Hall, NewYork.

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 sorptiondynamics. Malays. J. Anal. Sci. 16, 117-133.

Colon YJ., Furukawa S., (2020). Understanding the role of linker flexibility in soft porous coordination polymers. Mol. Syst. Des. Eng. 5, 284-293.

Fustin CA, Abetz V, Gohy JF (2005). Triblockterpolymer micelles: A personal outlook. Eur. Phys. J.E. 16, 291-302.

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.

Hu Y, T. Lv, T, Ma Y, Xu J, Zhang Y, Hou Y, Huang Z, Ding Y (2019). Nanoscale coordination polymers for synergistic NO and chemodynamic therapy of liver cancer. Nano Lett. 19, 2731-2738.

Kang TE, Cho HH, Kim HJ, Lee W, Kang H, Kim JB (2013). Importance of optimal composition in random terpolymer-based polymer solar cells. Macromol. 46, 6806-6813.

Katkamwar S. S., Ahamed M. and Gurnule W. B. (2012). Studies of chelation ion-exchange properties of copolymer resins derived from p-cresol, dithiooxamide and formaldehyde. J. Environ. Res. Develop., 7(1A), 330-337.

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.

Lee C, Alvarez PJJ, Nam A, Park S, Do T., Choi U., Lee S., (2017). Arsenic (V) removal using an amine doped acrylic ion exchange fiber: kinetics, equilibrium, and regeneration studies. Journal of hazardous materials. 325,223-229.

Liu J, Xia S, Que Q, Suo H, Liu J, Shen X, Cheng F (2020). Naphthalimide containi9ng coordination polymer with mechanoresponsive luminescence and excellent metal ion sensing properties. Dalton Trans. https://doi.org/10.1039/C9DT04928B. Liu JQ, Luo ZD, Pan Y, Singh AK, Trivedi M, Kumar A (2020). Recent developments in luminescent coordination polymers: Designing strategies, sensing application and theoretical evidences. Coord. Chem. Rev. 406, 213145.

Liu J, Qiao SZ, Liu H, Chen J, Orpe A, Zhao D, Lu GQ (2011). Extension of the stober method to the preparation of monodisperse resorcinol- formaldehyde resin polymer and carbon spheres. AngewandteChemie 123 (26), 6069-6073.

Mane VD, Wahane NJ, Gurnule WB (2009). 8-hydroxyquinoline-5-sulphonic acid-thiourea- formaldehyde copolymer resins and their ion-exchange properties. J ApplPolymSci, 111, 3039.

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.

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.

Phillip AW, Dorin MR, Werner J, Hoek VME, Wiesner U, Elimelech M. (2011). Enhanced performance of terpolymer resin derived from resorcinol. Nano. Lett. 11, 2892-2900.

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 FunctPolym, 55, 255-265.

Roy PK, Rawat AS, Choudhary V, Rai PK (2004). Synthesis and analytical application of a chelating resin based on a cross linked styrene/ maleic acid copolymer for the extraction of trace-metal ions. J.ApplPolymSci, 94,1771-1779.

Selma Helena De Almeida, Yoshio Kawano (1997). Ultraviolet-visible spectra of nafion membrane.Europ. Polym. J., 33(8), 1307-1311.

ShahBA, ShahAV, 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.

Singru RN, Zade AB, Gurnule WB (2010). Chelating ion-exchange properties of copolymer resins derived from p-cresol, oxamide and formaldehyde.J App PolymSci, 116, 3356-3366.

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.

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.

Xu H, Cheng ZY, Dana Olsan, Mai T, Zhang QM (2001). Ferroelectric and electrochemical properties of poly (vinylidene-fluoride-trifluoroethylene-chlorotrifluoroethylene) terpolymer. Appl. Phys. Lett. 78, 2360.

Yang XG, Zhai ZM, Lu XM, Zhao Y, Chang XH (2019). Room temperature phosphorescence of Mn (II) and Zn (II) coordination polymers for photoelectron response applications. Dalton Trans. 48, 10785-10789.

Table 1. Commercial ion-exchange resins with trade name.

Trade Name	Functional Group	Polymer Matrix	Ion-exchange Capacity (milimol g^{-1})
Amberlite IR-120	$-C_6H_5-SO_3H$	Polystyrene	5.0 – 5.2
Duolite C-3	$-CH_2\ SO_3H$	Phenolic	2.8 – 3.0
Amberlite IRC-50	-COOH	Methacrylic	9.5
Duolite ES-63	$-OP(O)(OH)_2$	Polystyrene	6.6
Zeocarb -226	-COOH	Acrylic	10.0
Dowex-1	$-N(CH_3)_3Cl^-$	Polystyrene	3.5
Amberlite IRA-45	$-NR_2, -NHR, -NH_2$	Polystyrene	5.6
Allassion A WB-3	$-NR_2, -NR_3$	Epoxy-Amine	8.2

Table 2. Data of experimental procedure for direct EDTA titration

| Metal Ion	pH range	Buffer used	Indicator used	Colour change
Fe(III)	2-3	Dil.HNO3/dil.NaOH	Variamine blue	Blue to Yellow
Cu(II)	9-10	Dil.HNO$_3$/dil.NaOH	Fast sulphone black-F	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)	10	Aq.NH$_3$/NH$_4$Cl	Eriochromeblack-T	Wine red to blue
Cd(II)	5	Hexamine	Xylenol orange	Red-Yellow
Pb(II)	6	Hexamine	Xylenol orange	Red to yellow

Table 3. IR Frequencies of PBF-IV copolymer resin

Observed band frequencies (cm⁻¹) of PBF-IV	Assignment	Expected band frequencies (cm⁻¹)
3400b	-OH phenolic intermolecular hydrogen bonding	3750-3200
2926.4(b,st)	>NH stretching (Amide/Imides)	3400-3100
2345.7(sh,st)	Aryl C-H stretching	3200-3000
1500.8(sh)	-C=C-streching (aromatic vibration	1600-1500
1464.1(sh,st)	-NH bending of secondary amide	1570-1450
1373.5(sh,st)	-CH₂- bridge	1390-1370
1221.1(m)	-CH₂- plane bending	1300-1220
814.1(sh)	Tetrasubtituted aromatic ring	830
970.3(m) 1041.7(m) 1113.1(m)	2,5,6,8 substitution in aromatic ring	950 1058 1125

sh=sharp; b=broad; st= strong; m= medium; w=weak

Table 4. ¹H NMR Spectral Data of PBF-IV copolymer resin

| Observed Chemical Shift (δ) ppm of PBF-IV	Nature of proton assigned	Expected chemical shift (δ) ppm
4.46	Methylene proton of Ar-CH₂-N moiety	3.00 to 3.5
4.71	Proton of – NH bridge	5.00 to 8.00
7.61	Aromatic proton (Ar-H)	6.2 to 8.5
8.87	Proton of phenolic – OH involved intramolecular hydrogen bonding	8.00 to 10.00
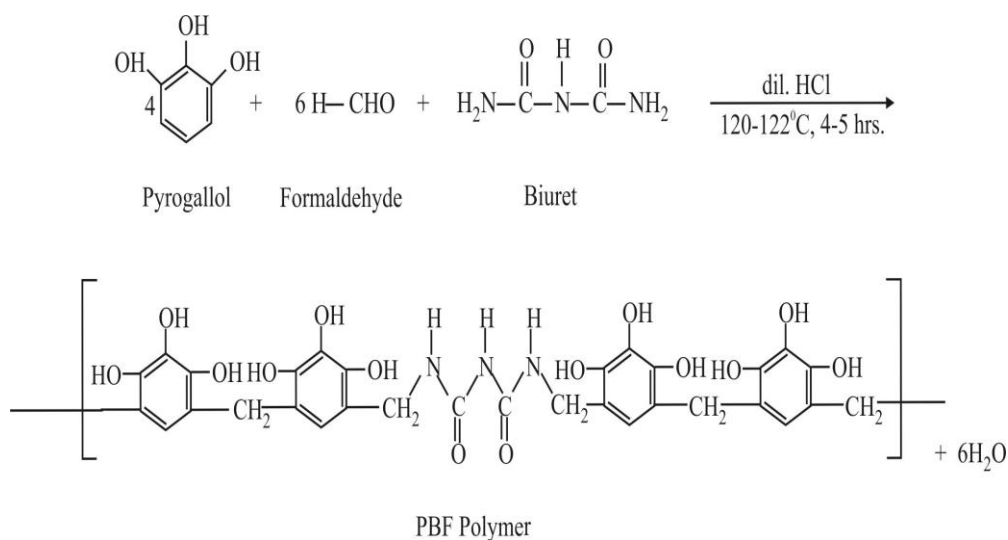
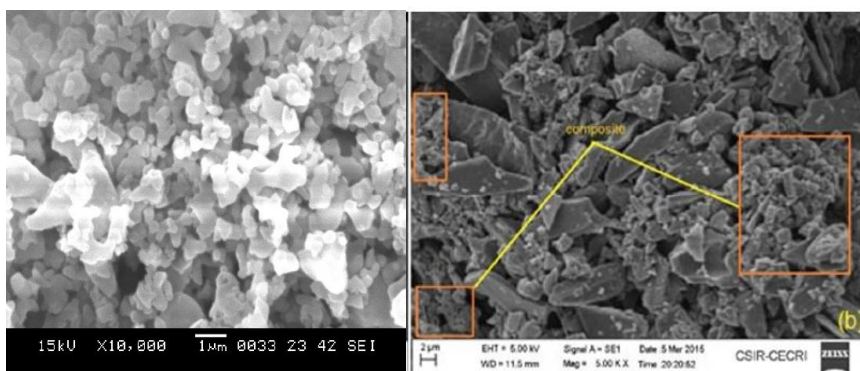**Fig.1 :Reaction and structure of representative PBF-IV copolymer resin**
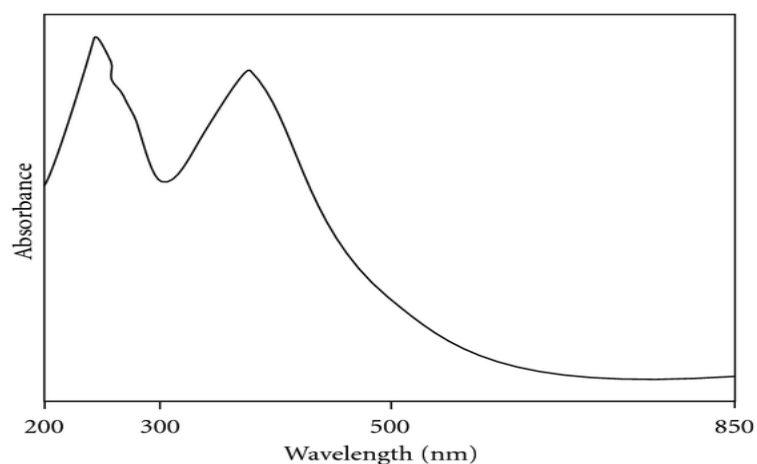
Fig. 2. Electronic Spectra of PBF-IV copolymer resin
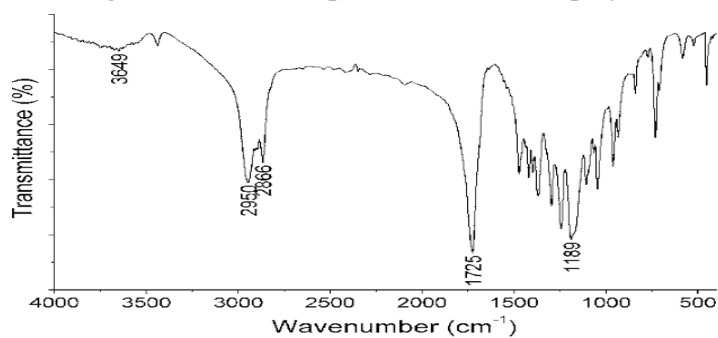
Fig.3. Infrared spectra of PBF-IV copolymer resin
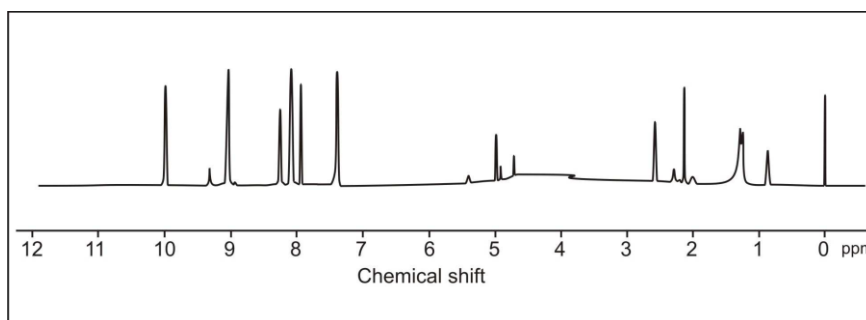
Fig.4. Nuclear magnetic resonance spectra of PBF-IV copolymer resin

Fig.5. SEM of PBF-IVcopolymer resin