SYNTHESIS, CHARACTERISATION AND APPLICATION OF PHENOL-FORMALDEHYDE RESIN BLENDED WITH SULPHONATED *PHYLLANTHUS EMBLICA*, LINN., CARBON

R.K.SEENIVASAN[*1], D.RAGAVAN[2], A.GIRIJA[3] and R. MUTHURAMALINGAM[4]

[*1]Department of Chemistry, Government Arts College, Melur, Madurai-625007, India

[2]Department of Chemistry, Raja Durai Singam Government Arts College, Sivagangai

[3]Department of Chemistry, Mohamed Sathak Engineering College Kilakarai

[4]Department of Chemistry, PTMTM College, Kamuthi

∗Author for corresponding -E-mail: rksvasan@rediffmail.com

Mobile: +919442879521

Fax: 0452-2415467

Abstract

Phenol – Formaldehyde Resin (PFR) is blended with Sulphonated *Phyllanthus emblica*, Linn., Carbon (SPEC) in various proportions by weight percentage (0-50%w/w). A few composite cation-exchangers were prepared by varying the amount of SPEC (a source of cheap and renewable plant material) in the blends from 10 to 50% *(w/w)*. Reaction conditions for the preparation of blends were optimised. IR spectra, TGA traces, and SEM photos were taken for the characterization of resins. Physico-chemical, properties of the composite resins have been determined. The composites are insoluble in various solvents and reagents and stable towards heat.   Cation exchange capacity (CEC) of the composite resins, decreased with the increasing percentage of SPEC in the blend. Thermodynamic equilibrium constants (lnK) are calculated for H^+ - Zn^{2+} exchanges on the resins having a different amount of SPEC. Thermodynamic parameters are also calculated and suitable explanations are given. The composites up to 20% *(w/w)* blending retains all the essential properties of the original PFR, since the *Phyllanthus emblica,* Linn., is the low cost, freely available plant material. Therefore, the composites could be used as low cost ion-exchangers, when SPEC partly replaces the original PFR up to 20% *(w/w)* blending without affecting the properties of PFR.

Keywords: Phenol – formaldehyde Resin – Sulphonated *Phyllanthus emblica;* Linn Carbon – Cation Exchange Capacity – Composite resin – low cost Ion Exchangers.

Council for Innovative Research

1. Introduction

Industrialised nations of the world are taking active measures to control the environmental pollution caused by chemicals. In the wastewater treatment, usually a decreasing level of pollutants is achieved rather than the selective removal and recovery. Ion exchange is an appropriate technique for the removal and recovery, as it is employed in the separation and concentration of ionic materials from liquids[1]. Ion-exchange process finds a valuable place in the treatment of metal wastes from plating and other industrial processes.

Many commercial ion exchangers originate from petroleum products and there is a continual increase in their cost. Hence, there is an urgent need to find out the new low cost ion exchange resins (IERs) and reduce its cost by blending it with sulphonated carbons prepared from plant materials. Such types of low cost ion exchangers can be prepared by blending cheaper and freely available plant materials containing phenolic groups. Ion-exchange process finds a valuable place in the treatment of metal wastes from plating and other industrial processes. Attempts have also been made to prepare cheaper cationic resins from waste materials and natural products. Earlier studies have shown that the cheaper composite ion-exchangers could be prepared by partially blending the macro porous phenol-formaldehyde sulphonic acid resin matrix by sulphonated charcoals prepared from coal[2], saw dust[3], spent coffee[4], cashew nut husk[5], wheat husk[6], turmeric plant[7], spent tea, gum tree bark[8], a*ccacia nilotica* [9] and *Egyptian bagasse pith* [10]. activated carbons obtained from agricultural wastes[11], *Terminalia chebula* Retz., Carbon[12] *Achyranthes aspera,*Linn., Carbon[13], *Eugenia jambolana,* Lam, Carbon[14], Heavy metals are also removed by bamboo activated carbon, natural clinptitolite, titanate nanoflowers and poly(Hydroxy ethyal methacrylate/Malemic acid) hydro gel[15-18]

The aims and objectives of the present work are to synthesise, characterise (by IR, TGA and SEM studies) the new composite ion exchangers of PhOH – HCHO type blended with sulphonated **Phyllanthus emblica**, Linn., carbon (SPEC) and to estimate the physico - chemical properties including cation exchange capacity (CEC) for some selective metal ions, to study the selectivity coefficients of H^+ - Zn^{2+} exchanges and to find out the optimum conditions for using cationic resins for the separation of Zn^{2+} from H^+ ions.

2. Experimental

2.1 Materials

The raw/plant material used was *Phyllanthus emblica,* linn. This plant material freely available in Tamil Nadu, India. Phenol and formaldehyde used were of Fischer reagents (India). LR grade of con. sulphuric acid (Sp.gr.= 1.82) was used. The plant material was locally collected, cleaned, dried and cut into small pieces of about 0.5cm length. The other chemicals / reagents used were of chemically pure grade (AnalaR) procured from SD fine chemicals, India.

2.2 Methods

Phyllanthus emblica, Linn., (500g) was carbonised and sulphonated by con. sulphuric acid, washed to remove excess free acid and dried at 70^0C for 12 h. It was labeled as SPEC.

Pure phenol – formaldehyde resin was prepared according to the literature method [3, 6 – 8]. It was then ground, washed with distilled water and finally with double distilled (DD) water to remove free acid, dried, sieved (210 – 300 μm) using Jayant Sieves (India) and preserved for characterisation [3,6-8,19]. It was labeled as PFR.

The composites were obtained as per the method reported in literature[3,6– 8]. The products with 10, 20, 30, 40 and 50% (*w/w*) of SPEC in the blend / composites, respectively were labeled as PE1, PE2, PE3, PE4 and PE5. A separate sample of SPEC was also subjected to the characterization, instrumental and physico - chemical studies.

2.3 Characterisation of samples

2.3.1. Instrumental Studies

FT-IR spectral data of pure resin (PFR), 10% *(w/w)* composite and pure sulphonated *Phyllanthus emblica*, Linn., carbon (SPEC) were recorded with a JASCO FT-IR 460 plus FT-IR spectrometer by using KBr pellets. To establish the thermal degradation of the samples, TGA and DTA traces were obtained for phenol – formaldehyde resin (PFR) and 20% *(w/w)* composite resin by using TZSCH- Geratebau GmbH Thermal analysis. SEM photos of pure resin (PFR), the 20% *(w/w)* SPEC and the pure SPEC as model ion exchangers were obtained using Hitachi Scanning Electron Microscope (Model S-450) Japan.

2.3.2. Physico Chemical Characteristics

Samples were ground and sieved into a size of 210 – 300μm using Jayant sieves (India). This was used for further characterisation by using standard procedures [3,7,8,] to find out the values of absolute density, percentage of gravimetric swelling and percentage of attritional breaking. The solubility of these samples were tested by using various organic solvents and inorganic reagents.

The values of cation exchange capacity CEC were determined by using standard titration technique [20] as per the literature method [21]. The effect of initial concentration of metal ions, particle size, chemical and thermal stability of the resin on CEC were determined [22].

After the exchange of H^+ ion by the metal ions, the regeneration level of the composites loaded with metal ions were determined by using NaCl (brine) solution. The equilibrium constants (K_{eq}) of ion exchange reaction between metal ions (Zn^{2+}) and the PFR and its composites were obtained as per the literature method [23,24].

3. Results and Discussion

3.1. Preparation

The experimental and theoretical compositions of SPEC in the composites (PE1 – PE5) are in good agreement with each other (Table 1). The results are similar to those obtained by others [2 – 4]. This indicate that the preparative method adopted for the synthesis of PFR and its composites (PE1 – PE5) are more reliable and reproducible. 11.5ml of formaldehyde, 12.5ml of Con. Sulphuric acid and 11ml of phenol are found to be optimum. [7-11]

3.2. Instrumental Studies

FT-IR studies are used to confirm the ion exchangeable groups based on various stretching frequencies [25]. Figs.1a and b indicate the appearance of absorption bands at 1039 – 1059 cm^{-1} (S = 0 str.), 1114 – 1163 cm^{-1} (SO_2 sym str) and 575 – 603 cm^{-1} (C – S str.) in pure resin (PFR), composite resin with 10% SPEC and pure SPEC, which confirm the presence of sulphonic acid group .

The appearance of broad absorption band at 3291 – 3409 cm^{-1} (bonded –OH str.) indicates the presence of phenolic and sulphonic –OH group in the samples. The appearance of absorption band at 1615 – 1643 cm^{-1} (C-C str) confirms the presence of aromatic ring in PFR, composite resin with 10% (*w/w*) SPEC in PFR and pure SPEC. The absorption band at 1510 – 1470 cm^{-1} (-CH$_2$.def) concludes the presence of –CH$_2$ group in the samples. The weak absorption band at 902 – 920 cm^{-1} (-C-H def.) in the samples indicates that the phenols are tetra substituted.

Thermo gravimetric analysis (TGA) is used for rapidly assessing the thermal stability of various substances [26]. TGA traces shown in Figs.2a and b reveal that there is a very small loss in weight (6%) for both PFR and composite resin with 20% (*w/w*) SPEC up to 80^{0}C. This is due to the loss of moisture absorbed by the PFR resin and composite resin with 20% (*w/w*) SPEC. Upto 190^{0}C there, is approximately 20% weight loss in PFR and 16% loss in weight in composite resin with 20% (*w/w*) SPEC. Up to 350^{0}C, approximately 41% loss in weight in PFR and approximately 26% weight loss in composite resin with 20% (*w/w*) SPEC was observed. Similarly, up to 450^{0}C approximately 57% loss in weight in PFR and 48% weight loss in composite resin with 20% (*w/w*) SPEC was observed.

Two exothermic peaks were obtained in the DTA curve of PFR, one approximately at 80^{0}C and another one at 466^{0}C, respectively (Fig.2a). At 80^{0}C, the presence of a broad peak was observed, due to the dehydration process of resin (PFR). A peak at 466^{0}C, indicates, the chemical changes of pure resin, which reflect approximately 57% weight loss in PFR.

DTA curves of composite resin with 20% (*w/w*) SPEC (Fig.2b) show that, the same two exothermic peaks were obtained at 103^{0}C and at 526^{0}C, respectively. Again the first broad peak indicates the dehydration of composite resin with 20% (*w/w*) SPEC and second moderate sharp peak indicates the chemical changes of composite resin with 20% (*w/w*) SPEC, which reflect approximately 55% weight loss in composite resin with 20% (*w/w*) SPEC.

From Figs. 2a and b, it is concluded that, the limiting temperature for the safer use of PFR, and composite resin with 20% (*w/w*) SPEC as ion exchangers is 80^{0}C, since the resins degrade thermally after 80^{0}C.

SEM photos of PFR, (Fig.3a and b), composite resin with 20% (*w/w*) SPEC (Fig.3c and d) and pure SPEC (Fig.3e and f) with different the magnification by 60 and 1000 times respectively are given in Fig 3.

Scanning electron microscope (SEM) photos reveal that all these samples are macroporous in nature. The high macroporous charcoal obtained from *phyllanthus emblica*, Linn form the reservoir in which the phenol-formaldehyde sulphonic acid particles are deposited. Hence the pore diameter decreases in composite resin with 20% (*w/w*) SPEC (Fig.3c and d) as compared to pure SPEC. Therefore, composite resin with (20% (*w/w*) SPEC) having high mechanical stability and low attritional breaking (Table-2) compared to pure SPEC. At the same time, increasing the percentage amount of SPEC in PFR will decrease the stability of three-dimensional network in polymeric matrix. Hence, the mechanical stability, density, decreases from original pure resin (PFR) to pure SPEC.

3.3. Physico Chemical Characteristics

3.3.1. Absolute Density

Absolute density values (Table 2) decrease from pure resin to the composite resin containing highest % (*w/w*) of SPEC and then finally to pure SPEC.

The density of composite resin in dry (dehydrated) and wet (hydrated) form depends upon the structure of resin, degree of cross linking and its ionic nature[27]. As expected the values of absolute density decrease with the increase in SPEC content (% *w/w*) in the composite. The value of high absolute density (in both dry and wet condition) indicates high degree of cross linking, and hence suitable for making columns for treating polar and non polar effluents liquids of high density. The values of absolute densities of the resins in the dehydrated states are higher than that of the hydrated state. Moreover, the values of absolute density in wet and dry states are close to each other, indicating that the pores of the sample may be macro porous in nature [28].

3.3.2. Gravimetric Swelling

The value of gravimetric swelling percentage (Table 2) decreases from PFR (85.56%) to SPEC (45.06%). The average % of gravimetric swelling of the resin decreased with increasing SPEC content in the composite. The values of gravimetric swelling percentage are found to be 89.03, 75.12 and 69.54 respectively, for 10, 20 and 30% (*w/w*) blending of SPEC with the parent resin, *viz.*, PFR. This indicates that up to 20% (*w/w*) SPEC could be mixed with the PFR without affecting its property. The rigidity of the resin matrix was proved from the swelling measurements. Therefore, the cationic resins with higher SPEC content showed lower swelling which revealed much lower rigid shape, and the rigidity decreased with the increase in % of SPEC content in the composite. It indicates that, pure resin and composites are rigid with non gel macro porous structure[19].

3.3.3. Attritional Breaking

Attritional breaking values (Table 2) increase with the increase in SPEC content in the resins, representing the stability of the resin, which decreases from pure resin to SPEC. Therefore, the mechanical stability is good upto 20% *(w/w)* substitution of SPEC with pure resin. This observation indicates that, the capillaries of the resin may occupy by the sulphonated carbon (SPEC) particles [6-8].

3.3.5. Solubility of IERs

The chemical stability of the samples in terms of its solubility in various solvents and reagents was determined. It reveals that PFR, composites and SPEC are practically insoluble in almost all the solvents and reagents. Therefore, these samples could be used as ion exchangers for treating non-aqueous effluents. However, the samples were found to be partially soluble in 20% (*w/v*) NaOH solution, which indicate the presence of phenolic groups. Hence, these ion exchange materials cannot be used for the treatment of industrial effluents having high alkalinity. The insolubility of the samples even in the trichloroacetic acid expresses the rigidity *i.e.,* having high degree of cross-linking in them.

3.4. Cation Exchange Capacity

CEC data are given in Table 3, which indicate that, the CEC values decrease (for 0.1M solution of metal ions) CEC range, in $m.mol.g^{-1}$ for 0- 100% SPEC:- 0.822 – 0.109 for Na^+ ion; 1.624 – 0.650 for Fe^{2+} ion; 1.835 – 0.920 for Cu^{2+} ion; 1.644 – 0.536 for Ca^{2+} ion; 1.816 -0.672 for Mg^{2+} ion; 1.779 – 0.601 for Zn^{2+} ion and 1.840 – 0.768 for Pb^{2+} ion when the %*(w/w)* content of SPEC in PFR increases 0 - 100.

The relative value of CEC of individual metal ion depends upon its atomic radius or atomic number [29]. At the same time, the CEC also depends upon the anionic part of the metal salt. *i.e.,* inter ionic forces of attraction between anions and cations, which plays a vital role in cation exchange capacity of a particular metal salt solution [23, 24].

From the CEC data given in Table 3, the cation exchange capacity of the samples was found to decrease in the following order.

$$Pb^{2+} > Mg^{2+} > Zn^{2+} > Ca^{2+} > Cu^{2+} > Fe^{2+} > Na^+$$
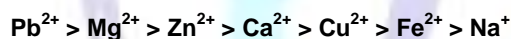
3.4.1. Selectivity of metal ions

The selectivity order of metal ions *i.e.*, orders of CEC values also depends upon the ionic potential and the hydrated atomic radius of the metal ions in solution [24]. The order of exchange affinities of various metal ions is not unique for all the ion exchange systems. Only under dilute conditions, Hofmeister or lyotropic series [27] is applicable. But, under high concentration the order is different [27]. It is equally important to note that the relative behaviour of these ions for other ionic phenomena is different from the affinity order under the same experimental conditions [30]. The observed order in the present study is different from that of the Hofmeister or lyotropic series [27]. This may be due to the concentration of the influent metal ion solutions, which is relatively high and also due to the selectivity of the metal ions.

Also, the CEC data given in the Fig.4, conclude that, the composite up to 20% *(w/w)* mixing of SPEC with PFR retains 78.75 –92.45% of CEC for all metal ions. Hence, 20% (*w/w*) blending of SPEC in PFR will reduce the cost of original resin. It is observed that there is a continuous decrease in cation exchange capacity (CEC), as the percentage of SPEC content in the composite increases. Hence, any chemical method requiring ion exchangers of low value of CEC, 20% (*w/w*) blended SPEC –PFR resin could be used. SPEC can be inexpensively prepared from the corresponding plant materials, which is freely available in plenty, in this study area *viz.,* Tamil Nadu, India.

The percentage values of CEC for exchange of H^+ ions with Na^+, Fe^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+} and Pb^{2+} ions in 0.1M solution are about 60-65% for PE1 – PE5 compared to pure commercial (SD's) resin (100%). This indicates that the composites can partially replace commercial IERs in making the ion exchangers for industrial applications.

3.4.2. Effect of Initial Concentration of Ca^{2+} ion on CEC

The values of cation exchange capacity (CEC) increase with the increase in the concentration of Ca^{2+} ions. The equilibrium load of Ca^{2+} ions in unit mass of resin linearly increases with the increase in the initial concentration of Ca^{2+} ions in solution from 0.025M to 0.15M [31]. Linear plots were obtained (not shown) between these values. The values of slope, intercept and correlation co-efficient are given in Table 4. Beyond 0.15M, there is a levelling effect of the value of CEC (*i.e.,* a constant CEC value) is noticed for the metal ions at high concentrations above 0.15M. Hence, up to 0.15M

concentration of solution of metal ions, the composite resins could be applied, since they act as good ion-exchangers in the concentration range.

3.4.3. Effect of Stability of IERs on CEC

The effect of different reagents on the values of CEC for various cationic resins is shown in Table 5. On treatment with 0.2M NaOH, 1.0 – 2.2% reduction in CEC value was noted. Upon treatment of the resins with organic solvent like benzene, the loss in CEC was noted to be 1.0 - 3.0%. The decrease in CEC value on treatment with boiling water was 0.4 – 1.5%, for composites with different amounts of SPEC in the resin. When the resins were heated for 10 h at 100^0 C the value of CEC decreased (8 – 18%) compared to the resins, which were not heated. All these observations reveal that the composites have good thermal and chemical stability.

CEC data given in Table 6, described that the particle size of $<210\ \mu m$ are fine, 300 - 500μm and $> 500\mu m$ are coarse as to cause very low cation exchange capacity (CEC) compared to 210 - 300μm particle size. Hence, in order to have the effective CEC, the bed size and particle size of IER should be maintained and the recommended particle size of IER is 210 - 300μm for preparing columns for in ion exchange studies.

3.4.4. Regeneration of IERs

The regeneration data obtained with forty ml of 0.2M brine (NaCl), effectively regenerates all the composite resins and SPEC. Forty ml of 0.25M brine solution effectively act as a regenerating agent for original PFR (Fig.5). Most of the commercial IERs are in Na$^+$ form and hence 40ml of 0.2M NaCl was used as a regenerant for every 2g of the resin.

3.5. Equilibrium Constant and Thermodynamic Parameters

The thermodynamic equilibrium constants (lnK) are given in Table 7 for the removal of Zn^{2+} ions using PFR and composites (R-SO$_3^-$ H$^+$). It has been found that the equilibrium constant for the ion exchange reaction increased with the increase in temperature and decreased with the increase in the content of SPEC (% w/w) in the resin. The standard values of thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) were computed and listed in Table 8. The thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) increase from 100% pure SPEC to different composite resins and PFR. ΔG^0 values ranges from – 453 to -1033 J mol^{-1}, which indicate that the ion exchange reaction was spontaneous. This is attributed due to the negative values of Gibbs free energy. The stability of the system increased when Zn^{2+} ions bound with IERs. The ΔH^0 values range from 1577 - 9462 J.mol^{-1}, which implied that the ion exchange reaction between the IERs and aqueous solution of Zn^{2+} was endothermic. Similarly, it was found that the ΔS^0 values range from 6.70 - 34.64 J mol^{-1} K^{-1}, which indicates the increased randomness or disorderliness from 100% SPEC to composite with decreasing % (w/w) of SPEC and finally PFR. This may be due to higher amount of Zn^{2+} ions entering into the resin and therefore causing much more amount of H$^+$ ions released into the solution. Hence, the increased amount of H$^+$ ions in solution reflects the randomness or disorderliness $i.e.$, ΔS^0 values decrease from PFR to composite with higher content of SPEC and finally to pure SPEC. Hence, PFR has higher CEC values and therefore has higher positive ΔS^0 value. The results are consistent with the earlier report [10].

4. Conclusion

It is concluded from the present study that PFR sample could be blended up to 20% (w/w) of SPEC, without affecting its spectral, thermal, and textural and physic chemical properties. The IERs are characterised by its spectral, thermal and SEM data and its physico chemical properties. The effect of particle size and the effect of initial concentration of Ca^{2+} ions on CEC, its regeneration level by using NaCl, and the CEC values of various metal ions, reveal that the resin substituted with 20% (w/w) SPEC was very close to the original PFR resin. Equilibrium constant for the removal of Zn^{2+} ion and thermodynamic parameters reveal that the process is spontaneous, endothermic and occur with randomness. Hence, blending of PFR with SPEC will definitely lower the cost of IER.

Table 1. Amount of reagents used and yields of PFR and its composites prepared from Sulphonated *Phyllanthus emblica,* Linn., Carbon (SPEC)

Sample	% of SPEC in PFR Theoretical	Amount of Reagents used				Yield 'g'	% of SPEC in PFR Experimental
		Phenol (mL)	Formaldehyde (mL)	Con.H$_2$SO$_4$ (mL)	SPEC		
PFR	0	10.0	11.5	12.5	0.000	17.000	0.00
PE1	10	10.0	11.5	12.5	1.889	18.836	10.03
PE2	20	10.0	11.5	12.5	4.250	21.280	19.97
PE3	30	10.0	11.5	12.5	7.286	24.630	29.58
PE4	40	10.0	11.5	12.5	11.333	28.260	40.10
PE5	50	10.0	11.5	12.5	17.000	34.280	49.59
SPEC	100	--	--	--	--	--	100

Table. 2. Physico - chemical properties of PFR and its Composites prepared from Sulphonated *Phyllanthus emblica,* Linn., Carbon (SPEC)

Sample	% of SPEC in PFR	Density (g mL^{-1})		% of Gravimetric swelling	% of attritional breaking
		Wet	Dry		
PFR	0	2.011	2.066	85.56	8.00
PE1	10	1.694	1.384	78.11	12.00
PE2	20	1.483	1.379	72.66	13.23
PE3	30	1.376	1.302	68.23	20.79
PE4	40	1.343	1.298	57.45	22.00
PE5	50	1.303	1.205	52.99	24.00
SPEC	100	1.044	1.037	38.67	34.00

Table. 3. Cation exchange capacity of H$^+$ form of the IERs prepared from SPEC for various metal ions

Sample	% of SPEC in PFR	Cation exchange capacity(m.mol g^{-1}) (0.1M effluent)						
		Na$^+$	Fe^{2+}	Cu^{2+}	Ca^{2+}	Mg^{2+}	Zn^{2+}	Pb^{2+}
PFR	0	0.822	1.624	1.835	1.644	1.816	1.779	1.840
PE1	10	0.803	1.533	1.548	1.567	1.722	1.674	1.716
PE2	20	0.760	1.325	1.445	1.458	1.559	1.511	1.583
PE3	30	0.722	1.150	1.395	1.375	1.410	1.470	1.494
PE4	40	0.711	1.040	1.337	1.243	1.349	1.373	1.445
PE5	50	0.668	1.020	1.264	1.090	1.273	1.279	1.324
SPEC	100	0.109	0.650	0.920	0.536	0.672	0.601	0.768

Table 4. Correlation analysis on the effect of initial concentration of Ca^{2+} ion on CEC of PFR, Composites and SPEC at 30^{0}C.

Sample	Correlation Co-efficient	Slope	Intercept
PFR	0.988	0.700	0.0125
PE1	0.992	0.346	0.0226
PE2	0.983	0.331	0.0204
PE3	0.985	0.310	0.0197
PE4	0.994	0.282	0.0181
PE5	0.978	0.280	0.0160
SPEC	0.975	0.167	0.0107

Table 5. Chemical and Thermal effect on CEC of PFR and its composites obtained from Sulphonated *Phyllanthus emblica,* Linn. Carbon (SPEC) for exchange with 0.1M Mg^{2+} ions at 30^{0}C

Reagents	Cation Exchange Capacity m.mol. g^{-1}					
	PFR	PE1	PE2	PE3	PE4	PE5
Original Capacity	1.816	1.722	1.559	1.410	1.349	1.273
0.2M NaOH boiled for 1 h	1.798	1.685	1.533	1.380	1.325	1.265
Benzene boiled for 1h	1.762	1.693	1.538	1.376	1.329	1.260
Boiling water for 1h	1.800	1.713	1.540	1.389	1.333	1.268
Thermal treatment in hot air-oven at 100^{0}C for 12h.	1.671	1.515	1.356	1.198	1.147	1.044

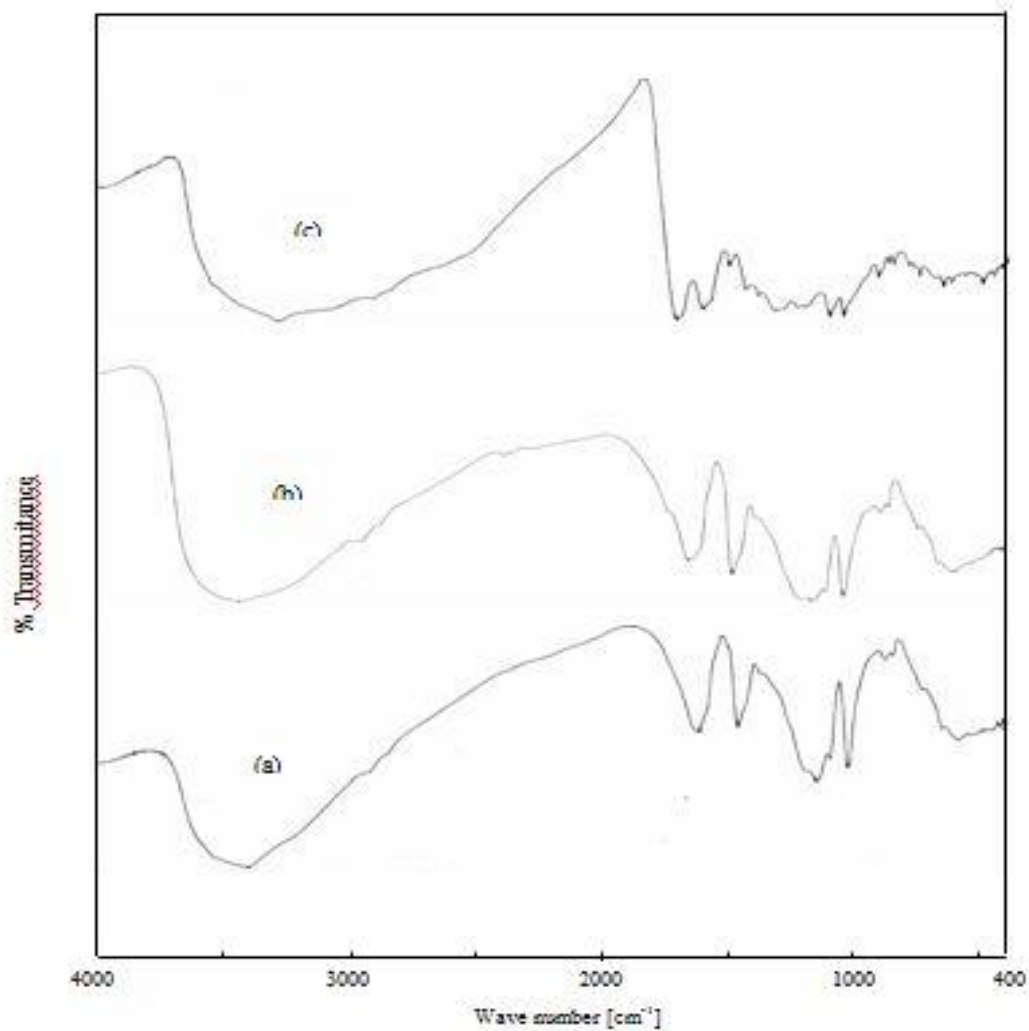**Table 6.Effect of particle size on CEC of PFR and composite obtained blending PFR with 20% (*w/w*) of SPEC**

Sample	Particle Size Micron	Cation exchange Capacity (m.mol g^{-1})			
		Na$^+$	Mg^{2+}	Ca^{2+}	Zn^{2+}
PFR	< 210	0.785	1.409	1.047	1.325
	210 – 300	0.822	1.816	1.644	1.779
	300 – 500	0.793	1.475	1.562	1.680
	> 500	0.780	1.350	1.432	1.651
PE2	< 200	0.702	1.156	0.988	1.043
	210 – 300	0.760	1.559	1.458	1.511
	300 – 500	0.754	1.119	1.668	1.292
	> 500	0.702	1.090	1.105	1.283

Table 7. Thermodynamic equilibrium constant (in terms of ln K) for H$^+$ / Zn^{2+} Exchange of PFR, Composites and SPEC

Samples	% of SPEC in PFR	ln K			
		30^{0}C	40^{0}C	50^{0}C	60^{0}C
PFR	0	0.41	0.53	0.62	0.74
PE1	10	0.39	0.49	0.60	0.66
PE2	20	0.35	0.43	0.49	0.54
PE3	30	0.28	0.34	0.40	0.48
PE4	40	0.26	0.31	0.36	0.41
PE5	50	0.23	0.27	0.32	0.36
SPEC	100	0.18	0.20	0.23	0.26

Table 8. Standard Gibbs free energy, enthalpy and entropy of H$^+$/Zn^{2+} ion exchanges on various IERs at 30^{0}C.

Sample	$-\Delta G^0$ (J mol^{-1})	ΔH^0 (J mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
PFR	1033	9462	34.64
PE1	982	7888	29.27
PE2	882	6310	23.74
PE3	705	4731	17.94
PE4	655	3943	15.17
PE5	579	3154	12.32
SPEC	453	1577	6.70

Fig.1   FT-IR Spectra of (a) PFR, (b) composite resin with 10 % (w/w) SPEC and (c) Pure SPEC (100%)
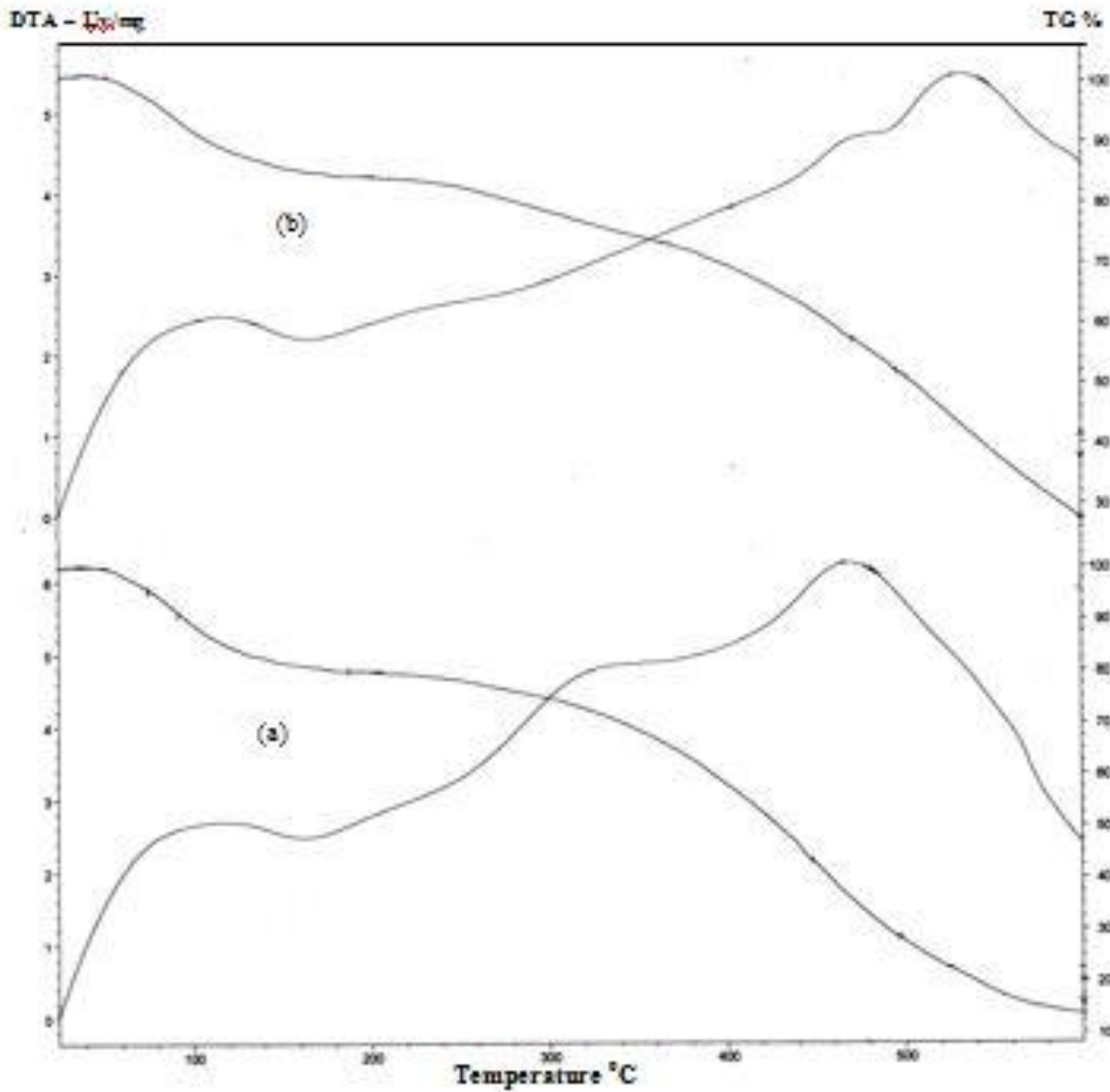
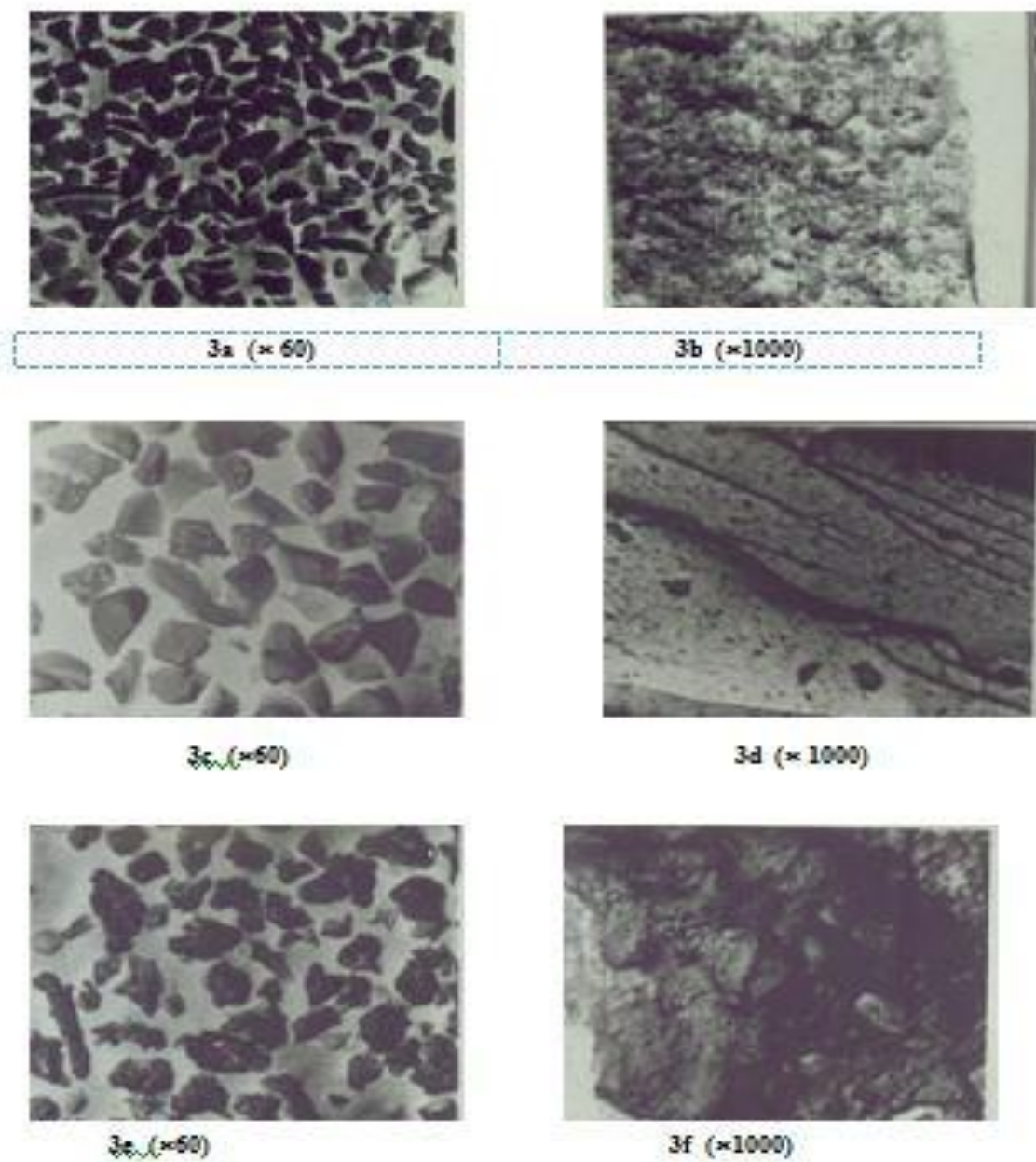**Fig2.   Thermal studies of (a) PFR and (b) composite resin with 20% (*w/w*) of SPEC**

Fig.3   SEM photos are PFR (a and b), composite resin with 20% (*w/w*) SPEC (c and d) and pure 100% SPEC (e and f)
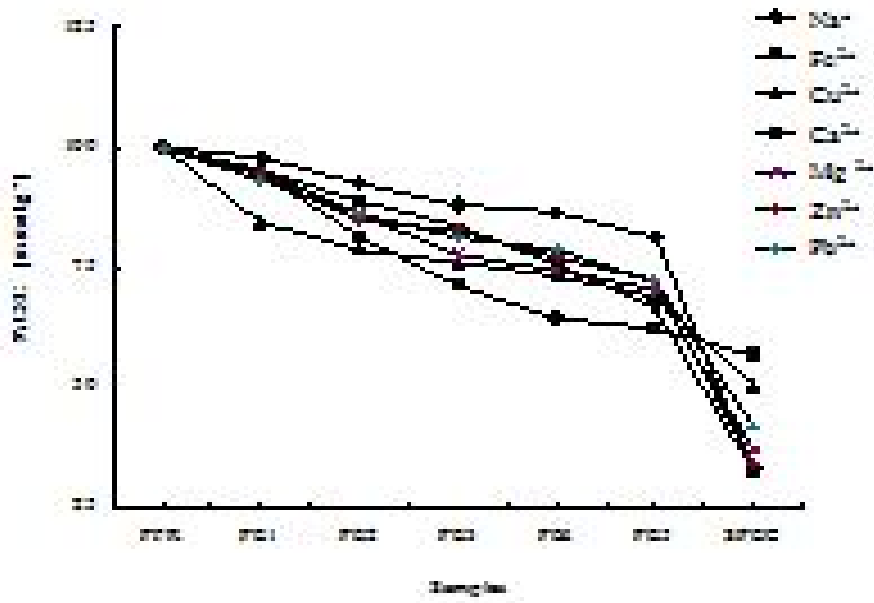
Fig.4 Cation Exchange Capacities of H⁺ form of PFR, Composites and SPEC for Selective metal ions
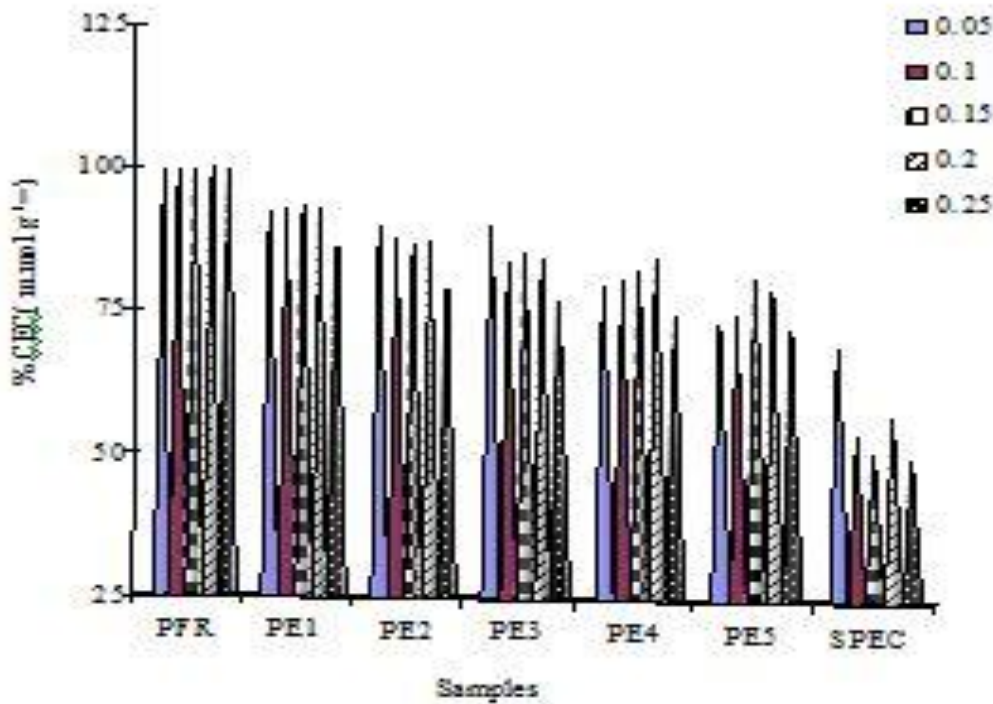

Fig.5 Regeneration level for PFR, its Composites and SPEC by using NaCl after exchange with Mg²⁺ ions

REFERENCE

1. Bolto. B.A and Pawlowsk L., Waste Water Treatment by Ion-exchange, Oxford & IBH Publ. Co., New Delhi, 1987.

2. Sharma N.L.N., Joseph Mary and Padma Vasudevan. *Res.Ind.*, **21,** (1976) 173

3. Padma Vasudevan and Sarma. N.L.N. *J.Appl. Poly.Sci.*, **23,** (1979) 1443

4. Mohan Rao. G.J., and Pillai, S.C. *J. Indian Inst .Sci.*, **36A,** (1954) 70

5. Shahha and Batna. S.L. *J. Appl. Chem.* Lond., **8,** (1953) 335

6. Dheiveesan. T., and Krishnamoorthy. S. *J. Indian Chem.Soc.*,**65,** (1988) 731

7. Kathiresapandian. D., and Krishnamoorthy. S. *Indian. J. Technol.*,**29,** (1991) 487

8. Mariamichel. A., and Krishnamoorthy. S. *Asian J. Chem.*, **9(1),** (1997) 136

9. Kannan .N., Seenivasan R.K., and Mayilmurugan. R. *Indian J. Chem. Technol.*, **10,** (2003) 623

10. Metwally M.S., Metwally. N.E and Samy. T.M. *J. Appl. Poly. Sci.*, **52,** (1994) 61

11. Kannan. N. Murugavel. S., Seenivasan R.K., and Rengasamy. G. *Indian J. Env. Prot.*, **23 (12**), (2003), pp. 1367 – 1376

12. Kannan. N.and Seenivasan. R.K. *J. Appl. Poly. Sci.* **101**,4104

13. Kannan. N.and Seenivasan .R.K. *J. Ion Exch.,***16**, 164 (2005)

14. Kannan.N.and Seenivasan .R.K. *Desalivation.,***216**, 77 (2006)

15. Fong Lo. S, Wang. S.Y, Tsai. M.J and.Lin. L.D, *Chemical Engg. Res. and Design,* **90(9)**,1397,(2012).

16. Jovanovic. M, Rajic. N and Obradovic. B. *J. Haz.Mat.*, **233**,57,(2012).

17. Huang J., Cao Y., Liu Z. and.Deng Z, Chem.Engg. J., **80(15)**,75,(2012).

18. Wu. N and Zale, *Chem.Engg., J.* **215**,894,(2013).

19. Natarajan. M and Krishnamoorthy. S. *Res. Ind.*, **38,** (1993) 278

20. Bassett. G.H, Jeffery.J, Mendham. J and Denney. R.C, Vogel's Text Book of Quantitative Chemical Analysis, 5th Edn. Longman Group Ltd., London, 1989.

21 Ramachandran. S and. Krishnamoorthy.S, *Indian J. Technol.***, 22,** (1984) 355

22 Chandrasekaran. M.B and Krishnamoorthy. S, *J. Indian Chem. Soc.*, **64,** (1987)134

23 Son.W.K, Kim. S.H and Park. S.G, *Bull.Korean Chem..Soc.*, 22 (1), (2001) 53

24 Dimov. D.K, Petrova.E.B, Panayotov. I.M and Tsvetanov. Ch.B, *Macromolecules*, **21,** (1990) 2733

25 Zagorodni.A.A, Kotova.D.L and. Selemenev.V.F, *Reac. Func. Poly.*, **53,** (2002) 157.

26 Anderson.H.C, *SPETrans.*, **1,** (1962) 202.

27 Kunin.R, *Ion Exchange Resin*, Wiley, Newyork and London, 2nd Edition, (1958)

28 Mariamichel. A, Krishnamoorthy .S., J.Sci.Ind.Res. **56** (1997) 680.

29 Mattson.S, *Ann. Agric. Coll.*, Sweden, **10,** (1942) 56

30 Bonner.O,. Easterling.G, Weit.D and Holland.V, *J.Am.Chem.Soc.*, **77,** (1955) 242

31 Kim.Y.K and Lee.K.J, *J.Nucl. Sci. Tech.*, **38** (9), (2001) 785

.