



Synthesis, characterization and applications of phenol-formaldehyde cationic matrices blended with sulphonated *Citrus aurantifolia*(L.) carbon

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ABSTRACT

Phenol-Formaldehyde resin (PFR) is used as a cross linking agent in blending of Sulphonated *Citrus aurantifolia* Carbon (SCAC). The ion exchangers were prepared by varying the amount of SCAC from 0 to 100% (w/w). The prepared materials (PFR, composites and SCAC) were characterised by FT-IR spectra, SEM and thermal (TGA) studies. The low cost ion exchangers (IERs) is used for the removal of some selective metal ions such as Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Mg^{2+} , Zn^{2+} and Pb^{2+} . The composites are stable in water, organic solvents, and mineral acid like 1M HCl and also in thermal treatment but soluble in some extent in 20% of (w/w) NaOH solution. The rational thermodynamic equilibrium constants ($\ln K_c$) are calculated for $\text{Mg}^{2+} - \text{H}^+$ and $\text{Zn}^{2+} - \text{H}^+$ ion exchanges with the composite resins having up to 20% (w/w) blending of PFR with SCAC. The cation exchange capacity (CEC) of the composite was found to decrease with the increasing the % of SCAC in PFR matrix. It was observed that the composites up to 20% (w/w) blending of PFR with SCAC retain all the properties of original PFR. Therefore, the blended composites should be used as low cost ion exchangers when SCAC partially replaces the original PFR up to 20% (w/w) blending without affecting the physico-chemical, thermal, spectral properties and CEC values of PFR.

Keywords: Phenol-formaldehyde resin, Sulphonated *Citrus aurantifolia* carbon, Cation exchange capacity, Composite resin, low cost ion-exchangers.

INTRODUCTION

The world is taking about dynamic processes to control the environmental pollution caused by chemicals. In industrial wastewater treatments, the cation exchange is a suitable technique for the removal and recovery of heavy metal ions, as it is employed in the separation and concentration of ionic materials from liquids [1]. Since the current commercial ion-exchangers owe their origin to Petroleum products and there is a continual increase in their cost. Hence, there is a crucial need to find out the new low-cost Ion-Exchange Resins (IERs) and reduce the cost of IERs by blending it with Sulphonated Carbons (SCs) prepared from plant materials. Activated carbon is generally used for the removal of various pollutants from wastewater. However, the regeneration of the activated carbon is the main problem [2]. Therefore, it is urgent to develop an adsorbent of better regeneration capacity for the separation and removal of heavy metal ions from the aqueous solution and wastewater.

Now a day's alkali-catalysed phenol-formaldehyde resins are used as composites or coating materials because of their excellent thermal stability, dielectric properties, and mechanical and flexural strength [3-5]. The wide use of PFR has promoted extensive research aimed to improve their final properties according to use. The phenolic resin is prepared by the reaction of phenol or substituted phenol with an aldehyde such as formaldehyde, in the presence of an acidic or basic catalyst. Phenolic resins are used as adhesives for binding wood-particleboards, fibre boards, plywood, nonwoven textiles and insulation materials, coatings, adhesives for papers and moulding compounds and water-based paints, as well as the manufacture of high-tech high-temperature resistant ion exchange resin with SC

obtained from cheaper and freely available plant material containing Phenolic groups in it. Ion exchange may be defined as the reversible interchange of ions between a solid phase (resin) and a liquid phase.

In earlier studies Phenol-Formaldehyde Resins (PFR) have been altered with Sulphonated Carbon prepared from natural products like Coal[6], Saw dust[7], Spent coffee[8], Turmeric plant[9], Egyptian bagasse pith[10], Spent tea, gum tree bark[11], *Accacia nilotica*[12] and *Achyranthes aspera* Linn., Carbon[13]. The present study deals with the preparation of new composites ion exchangers of phenol-formaldehyde resin blended with sulphonated *Citrus aurantifolia* carbon and to characterization and estimation the cation exchange capacity (CEC) or ion exchange capacity of some selective metal ions. The effect of particle size is also found the chemically and thermal nature of IERs.

EXPERIMENTAL SECTION

Phenol and formaldehyde were used of AR grade (Fischer reagents, India). AR grade of concentrated sulphuric acid (Sp.gr. =1.82) was used. The Peel of *Citrus aurantifolia* is locally available in all part of India, especially in Tamil Nadu. This material was locally collected, washed, dried and cut into small pieces of about 0.5cm length. Peel of *Citrus aurantifolia* was carbonised and sulphated by con. Sulphuric acid (500mL) and kept at room temperature (30±1°C) for 24h. Then it was heated at 90°C in a hot air-oven for 6 hours. It was then cooled, washed with distilled water several times and finally with double distilled (DD) water in order to remove excess of free acid and dried at 70°C for 12 h. It was labelled as SCAC.

Concentrated sulphuric acid (12.5mL) was slowly added in drop wise to Phenol (10mL) with constant stirring by placing it in an ice-bath at 0-5°C. The reaction mixture was heated to about 70°C for 3h in a hot air-oven and then cooled immediately in ice-cold water. It was kept overnight. It was then polymerised with formaldehyde solution (11.5 mL) at 80°C and the product was placed in a hot air-oven for 3h. A brown coloured chunky solid mass was obtained. It was then ground, washed with distilled water and finally with double distilled (DD) water to remove free acid, dried, sieved (210-300 micron size) using Jayant Sieves (India) and preserved for characterisation. It was labelled as PFR. A known amount of PFR was mixed various % (w/w) of sulphonated *Citrus aurantifolia* carbon (SCs). The compositions of SCAC were fixed as 10, 20, 30, 40 and 50 % (w/w). In the composites the following formula was used[14].

$$\text{Required \%} = b / (a + b)$$

Where,

a = mass of PFR (in g); b = mass of the SCAC required (in g)

The percentage of SCAC in composites was used to calculate in terms of weight of materials and their actual % in the yields is presented in Table 1. The mixture was polymerised with formaldehyde solution (11.5mL) at 80°C and the product was cured in a hot air-oven for 3h. A brown chunky solid mass was obtained. It was then ground, washed, dried and preserved for characterisation. The product with 10, 20, 30, 40 and 50 % (w/w) of SCAC in the blend/composites, separately were labelled as SCAC1, SCAC2, SCAC3, SCAC4 and SCAC5.

Table 1 Quantity of reagent utilized and yield of PFR, Condensates (SCAC1-SCAC5) prepared by blending of PFR with various % (w/w) of SCAC

Sample	% Of SCAC In IER (cal.)	Quantity of Reagent used					% of SCAC in IER (abs)
		Phenol (ml)	HCHO (ml)	Con.H ₂ SO ₄ (ml)	SCAC (g)	Yield (g)	
PFR	0	10	11.5	12.5	0	19.00	0.00
SCAC1	10	10	11.5	12.5	2.11	21.00	10.05
SCAC2	20	10	11.5	12.5	4.75	23.94	19.84
SCAC3	30	10	11.5	12.5	8.14	27.42	29.69
SCAC4	40	10	11.5	12.5	12.32	30.90	39.87
SCAC5	50	10	11.5	12.5	18.5	36.87	50.18
SCAC	100	-	-	-	-	-	100.00

Physico-chemical factors like absolute density, gravimetric swelling and attrition breaking of PFR, Composites and pure SCAC were determined as per the literature methods[9,11]. The solubility of the sample was tested by various organic solvents and inorganic reagents.

PFR, SCAC2 and pure SCAC were converted into their corresponding H⁺ form by washing the resin with 2M Hydrochloric acid and then washed with DD water in order to remove excess of free acid. The test column was

prepared by packing the graduated burette with the IER samples using glass wool plug. In this column 40 mL of 0.1N of various metal ions (Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Mg^{2+} , Zn^{2+} and Pb^{2+}) were used as effluents. The rate of effluent was adjusted to 1mLmin^{-1} . The cation exchange capacity (CEC) values were determined by using Standard titration method as per literature[15,16].

The samples of PFR and composite SCAC2 were treated with 40mL of 0.1M solution of Mg^{2+} . Now, the H^+ form of the samples was converted to Mg^{2+} form and then 40mL of NaCl solutions of different concentrations such as 0.05, 0.10, 0.15 and 0.20M were added. The effluents were collected at a rate of flow of 1mL min^{-1} . The amount of Mg^{2+} ions of the effluent was determined and reported.

RESULTS AND DISCUSSION

The FT-IR spectral data are shown in the Table 2. It indicates the appearance of absorption band at $1028\text{-}1039\text{ cm}^{-1}$ (S=O str.), $1118\text{-}1172\text{ cm}^{-1}$ (SO_2 sym. str.), $1315\text{-}1364\text{ cm}^{-1}$ (SO_2 assy.) and $623\text{-}682\text{ cm}^{-1}$ (C=S str.) in pure resin (PFR), composites blended with 20% (w/w) SCAC2 and pure SCAC (100%) which confirm the presence of sulphonic acid group (Fig.1a,1b and 1c). The appearance of broad absorption band at $3194\text{-}3427\text{ cm}^{-1}$ (bonded -OH str.) indicates the presence of phenolic and sulphonic -OH group (due to SO_3H group). The appearance of absorption band at $1467\text{-}1478\text{ cm}^{-1}$ (- CH_2 def.) shows the presence of - CH_2 group in the samples. The absorption band at $1519\text{-}1656\text{ cm}^{-1}$ (-C-Cstr.) and at $760\text{-}858\text{ cm}^{-1}$ (C-C def.) are confirms the presence of aromatic ring in PFR, composites blended with 20% (w/w) (SCAC2) and pure SCAC (100%). The weak absorption bands at $642\text{-}887\text{ cm}^{-1}$ (-C-H str.) indicate that the phenols are tetra substituted.

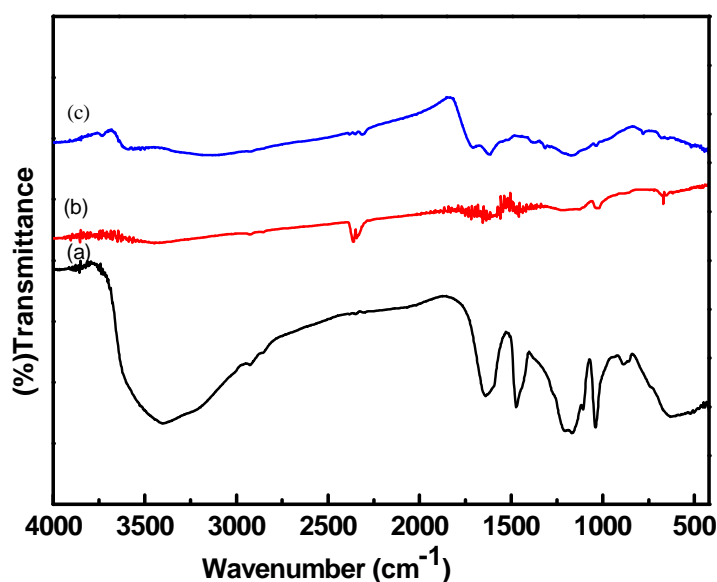


Fig.1. FT-IR spectra of (a) PFR, (b) condensate resin with 20 % (w/w) of SCAC2 and (c) pure SCAC (100%)

Table 2. FT-IR spectral data of PFR condensate with 20% (w/w) SCAC2 and Pure SCAC (in cm^{-1})

Group	PFR	Composites with 20% (w/w) SCAC2	Pure SCAC
S = O str.	1039	1028	1037
SO_2 sym. str.	1118	1130	1172
C - S str.	623	671	682
Bonded OH str.	3404	3427	3194
CH_2 - def.	1469	1467	1478
C - C str.	1629	1656	1519
C - H def.	887	895	642
C-C def.	858	760	781
SO_2 assy.	1338	1364	1315

The results of TGA curves are shown in Fig.2. From the TG data profile, there is a 16% weight loss for PFR up to 90°C and for PFR blended with 20% (w/w) of (SCAC2) there is 15% weight loss for up to 90°C . It is clearly observed that the loss of moisture absorbed by the resin and composite SCAC2. The temperature between 100°C - 300°C there is 27% weight loss in PFR and 29% weight loss for SCAC2. Up to 360°C , approximately 43% loss of

weight was observed for both PFR and SCAC2. Thermal studies indicate that the IERs are thermally stable up to 100°C.

In Fig.2a DTA curve shows that there is two peaks obtained in PFR, approximately at 60°C and 270°C. At 60°C the presence of broad peak indicates the dehydration process of PFR. A peak at 270°C indicates the chemical changes, which occur due to thermal dehydration of PFR and reflects approximately 43% weight loss in PFR. DTA curves of composite with 20%(w/w) of SCAC(Fig.2b) shows that the two exothermic peaks are obtained at 70°C and 280°C respectively, which is similar to PFR. The first peak indicates the dehydration of SCAC2 and second sharp peak indicates the chemical changes arising because of thermal degradation of the condensate SCAC2.

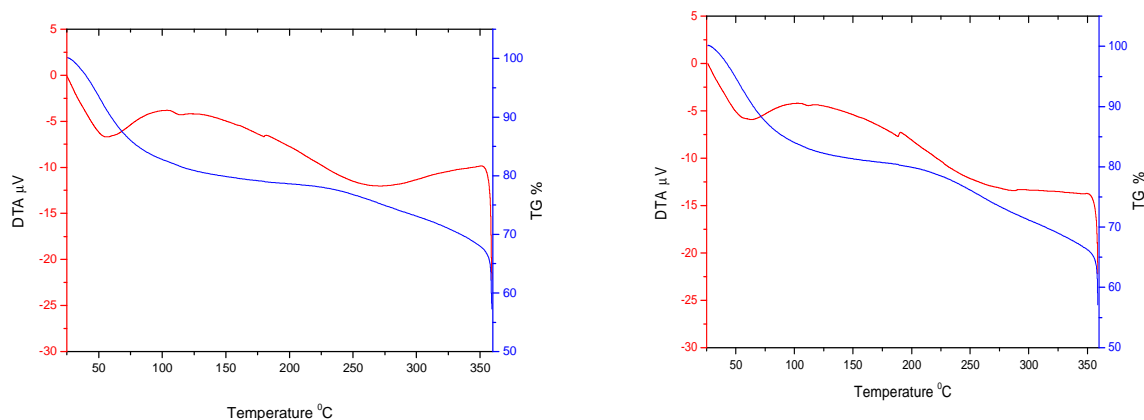


Fig.2. Thermal studies of (a) PFR and (b) condensate with 20%(w/w) of SCAC2

SEM photos of PFR (Fig.3a&3b), condensate SCAC2 (Fig.3c& 3d) and pure SCAC (Fig.3e&3f) with the magnification of 50 μm and 500 μm are given. SEM images reveals that all the samples are macro porous in nature. The high macro porous carbon obtained from Citrus aurantifolia, form the reservoir in which the phenol-formaldehyde sulphonic acid particles are deposited. As a result the pore diameter decreases in condensate SCAC2 as compared to pure SCAC. Therefore, the condensate resin SCAC2 has great mechanical stability and little attritional breaking (Table 3) compare to pure SCAC.

Table 3. Physicochemical properties of PFR, SCAC and condensates SCAC1-SCAC5

Sample	%of SCAC in IER	Density (g/ mL ⁻¹)		%	
		Wet	Dry	Gravimetric swelling	Attritional breaking
PFR	0	1.916	1.907	80.37	9.00
SCAC1	10	1.838	1.822	75.44	17.25
SCAC2	20	1.465	1.433	72.25	20.00
SCAC3	30	1.336	1.335	70.49	22.35
SCAC4	40	1.218	1.277	59.86	28.00
SCAC5	50	1.059	1.061	47.94	34.00
SCAC	100	1.092	1.015	37.31	46.44

The absolute density of both hydrated (wet) and dehydrated (dry) samples decreases steadily from pure PFR to SCAC condensate resin and finally to 100% SCAC. It is clearly observed that PFR and condensate are more closely packed [7,11,12]. It is found that the values of absolute density (100% of SCAC) possess only 56.99% and 53.21% density of PFR in wet and dry states respectively. This indicates both SCAC and condensate resin has similar closely packed structure [14]. The absolute density of PFR and condensate in dry and wet states depends upon the structure of resins [17]. Therefore, the high density values of resin shown in Table 2 indicates, high degree of cross linking structure which may be suitable for making columns for polar and non-polar effluents.

The percentage of gravimetric swelling also decreases from PFR (80.37%) to SCAC (37.31%) indicating the values of pure resins and condensate are not as high as compare to IERs. This due to the rigidity in the matrix SCAC has gravimetric swelling of only 46.42% as that of PFR. The low values may be due to rigidity in their matrix. When 20%(w/w) SCAC2 was blended with PFR the resultant composite has the gravimetric swelling values 89.89% which is nearly about of PFR. The decrease in % of gravimetric swelling is due to the loss of polarity and porosity in the condensate. Therefore, the condensate may be useful where they are required to resist large osmotic shock [18].

The percentage values of attritional breaking decreases from PFR, condensate to pure SCAC. The mechanical stability is good up to the condensate of PFR blended with 20%(w/w) SCAC2 which shows the possibility of the formation of resins in the capillaries of the sulphonated carbon (SCAC) particles[9].

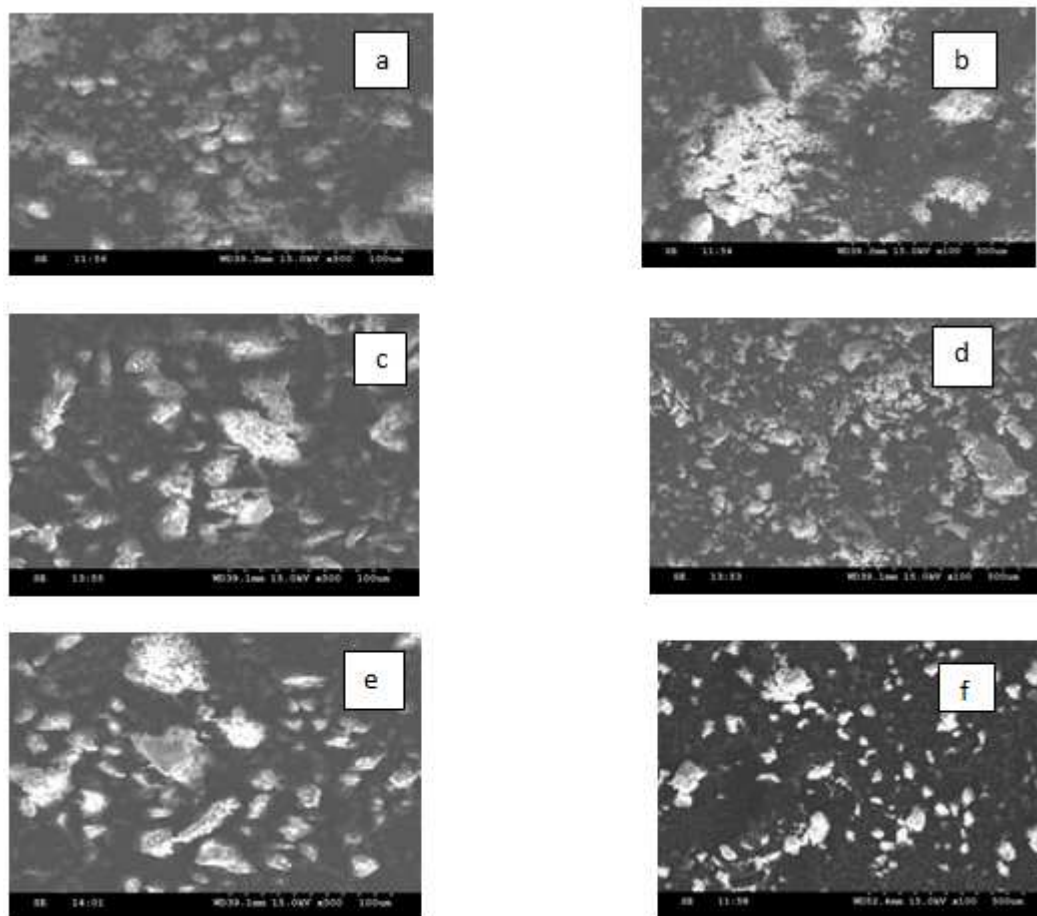


Figure 3. SEM images of PFR (a & b), condensate resin with 20%(w/w) of SCAC2 (c & d) and pure 100%SCAC (e &f)

Cation/Column exchange capacity (CEC) or Ion exchange capacity (IEC) data shown in Table 4 indicate that the CEC value decreases as the%(w/w) of SCAC in condensate increases. The relative IEC of separate metal ions depends upon the atomic radius or atomic number[17,19]. At the similar time the CEC value also depends upon the valance of the ions, the concentration of metal ion in the solution which is transferred into the resin and also the anionic part of the metal salt, i.e., inter ionic forces of attraction between anions and cations, which also plays a vital role in CEC values of metal ion in a given metal salt solution[20,21].

From the CEC values as shown in Table 4, the cation exchange capacity of the samples is found to decrease in the following order:

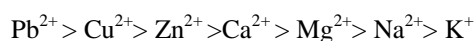


Table 4: Cation exchange capacities of PFR, Condensates (SCAC1-SCAC5) and SCAC for various metal ions (0.1M) at 303K

Sample	%of SCAC in IER	Cation exchange capacity, in mol. g ⁻¹ 0.1M solution						
		Na ⁺	K ⁺	Ca ⁺	Mg ²⁺	Cu ²⁺	Pb ²⁺	Zn ²⁺
PFR	0	1.4864	1.6216	1.6875	1.8111	1.6934	1.7052	1.8345
SCAC1	10	0.9652	1.0989	1.6783	1.6984	1.5175	1.6934	1.7989
SCAC2	20	0.9405	1.0642	1.2864	1.2411	1.4271	1.4572	1.3316
SCAC3	30	0.9306	1.0197	1.226	1.005	1.2813	1.407	1.2663
SCAC4	40	0.9157	0.8415	1.1859	0.9698	1.2462	1.2763	1.177
SCAC5	50	0.792	0.7425	0.8994	0.9045	1.1658	1.206	1.1055
SCAC	100	0.3564	0.396	0.7587	0.804	1.1256	1.1004	0.8693

The CEC values of PFR, condensates and pure SCAC are shown in Fig.4. In order to the blending of PFR with 20%(w/w) of SCAC has the CEC values 63.27 - 85.45%for the exchange of H^+ ions with the Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Mg^{2+} , Pb^{2+} and Zn^{2+} ions compared to that of PFR. Then, 30%(w/w) blending of PFR with SCAC2 in the polymeric resin leads to 55.4-77.66%of CEC of PFR. The maximum and minimum values of percentage of ion exchange capacity of condensates are Pb^{2+} and Na^+ for ions respectively. This is due to that the blending of PFR with SCAC up to 20%(w/w) does not affect the CEC values for the metal ions. It results the PFR could be blended up to 20%(w/w) of SCAC2 and condensates thus be new and cheap IERs, which should be used for waste water treatment for the removal of metal ions from the industrial effluent.

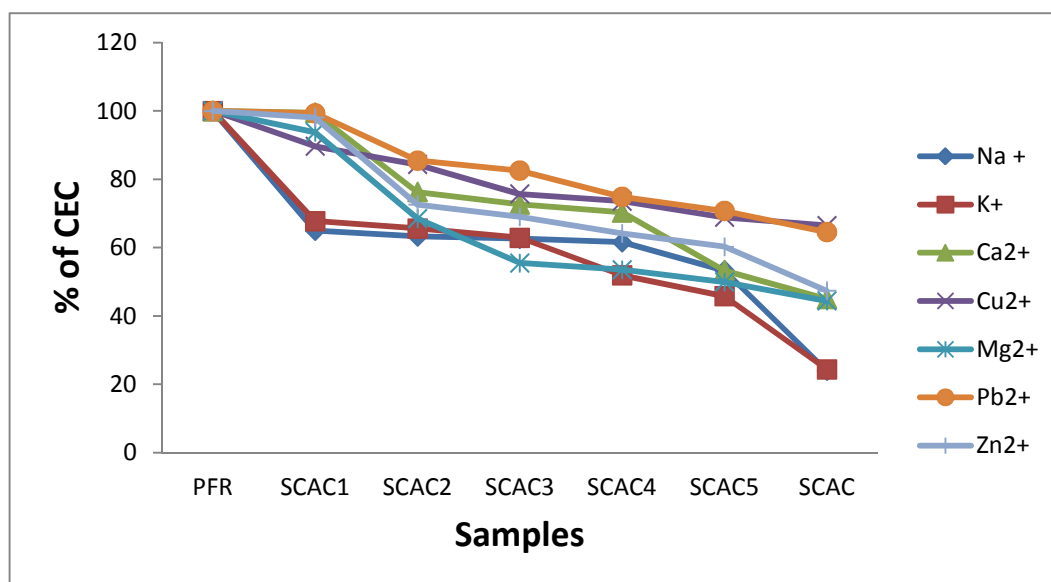


Fig. 4 Cation Exchange Capacities of H^+ form of PFR, condensates and pure SCAC

The data are shown in Table 4. The results indicate that the resin samples are almost soluble in all the solvents except 20% NaOH. Therefore, resins can be used as a better ion exchanger for treating non aqueous effluent aside from in alkaline condition (PH > 7)

Table 5: Chemical and thermal effect on CEC of PFR and SCAC Condensates for exchange with 0.1M Mg^{2+} ions at 303K

Reagents	Cation exchange capacity, in mol. g ⁻¹ 0.1M solution					
	PFR	SCAC1	SCAC2	SCAC3	SCAC4	SCAC5
CEC (of untreated)	1.855	1.722	1.523	1.404	1.345	1.264
20%(w/v) NaOH	1.745	1.605	1.512	1.312	1.286	1.206
Benzene	1.696	1.644	1.534	1.324	1.286	1.234
1M HCl	1.768	1.654	1.556	1.324	1.293	1.145

CEC values shown in Table 6 indicate that the IERs with a particle size of <210 micron are fine; 300–500 micron and >500 micron are rigid, as to cause very low CEC compared to that of IERs of 210–300 micron particle size. Therefore, for the effective CEC, the particle size of the IER should be maintained in the range 210–300 micron. The CEC of metal ions like Zn^{2+} and Na^+ shows maximum and minimum values. It may be due to the blending of PFR with SCAC up to 20%(W/W) of SCAC2 does not affect these CEC values for the metal ions to a more extent.

From the Table 6, the CEC of the samples the affinity of metal ions decreases in the order Zn^{2+} , Mg^{2+} , Ca^{2+} and Na^+ .

Table 6: Effect of particle size on CEC of PFR and condensate obtained by blending PFR with 20%(w/w) of (SCAC2) at 30 °C

Sample	Particle size	Cation exchange capacity (m.mol. g ⁻¹)			
		Na ²⁺	Ca ²⁺	Mg ²⁺	Zn ²⁺
PFR	<210	1.4170	1.6228	1.7698	1.7816
	210-300	1.4864	1.6875	1.8333	1.8345
	300-500	1.3288	1.5934	1.7522	1.7934
	>500	1.2936	1.4994	1.6346	1.4935
20%SCAC2	<210	0.9375	1.2700	1.2322	1.2978
	200-300	0.9405	1.2864	1.2411	1.3316
	300-500	0.9324	1.2759	1.2221	1.2625
	>500	0.9220	1.2524	1.2019	1.2302

A known volume of 0.2 M NaCl (brine solution) is used for the regeneration of all the composites, unblended resin (PFR) and SCAC after exchange with the Mg^{2+} ions (Fig. 5). Most of the commercial IERs are in Na^+ form and 0.2M NaCl solution could be used as a regenerator for every 2g of the resin.

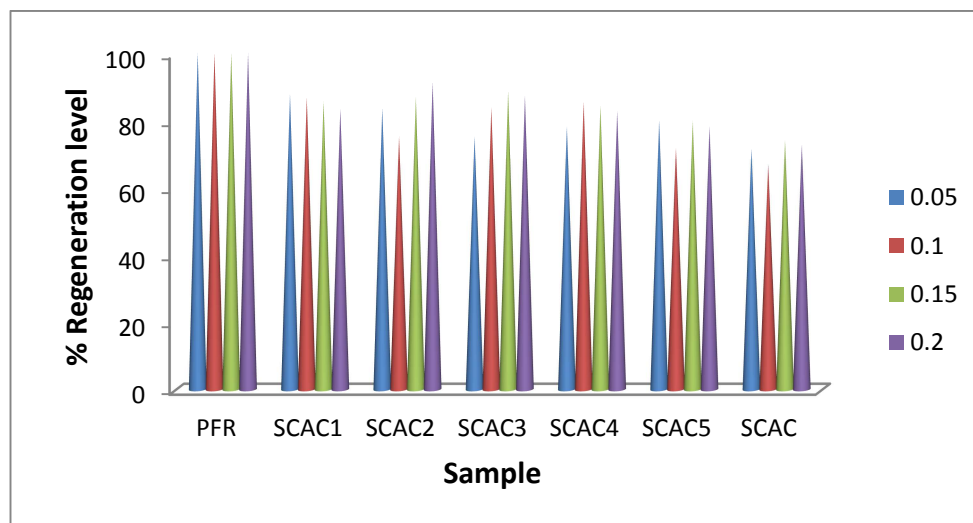


Fig.5: Regeneration level for PFR, Condensates and SCAC by using NaCl after exchange with Mg^{2+} ions

In order to determine the effect of temperature for the removal of Zn^{2+} and Pb^{2+} by SCAC2, experiments were carried out between 298 K and 323 K. The thermodynamic parameters for the removal of Zn^{2+} and Pb^{2+} by IER (SCAC2) were calculated using the following basic thermodynamic equations.

$$\Delta G^{\circ} = -RT \ln K_c \quad \text{----- (1)}$$

$$\ln K_c = \Delta S^{\circ}/R - \Delta H^{\circ}/RT \quad \text{----- (2)}$$

Where R is the universal gas constant, 8.314 J/mol./K and T, the absolute temperature (K); and ΔH° , ΔG° & ΔS° are the changes in enthalpy (J/mol.), Gibb's free energy (J/mol.) and entropy (J/K/mol.) respectively. The values of ΔH° and ΔS° could be determined from the slope and intercept of the linear plot of $\log K_c$ versus $1/T$. where R is the gas constant, K_c is the equilibrium constant and T is the solution temperature in Kelvin. The thermodynamic parameters can be calculated from Van't Hoff plot (Figure.6). The positive value of ΔH° (75.248KJ/mol., 54.416KJ/mol.) for the adsorption of Zn^{2+} and Pb^{2+} by SCAC2 showed endothermic nature of the overall process.

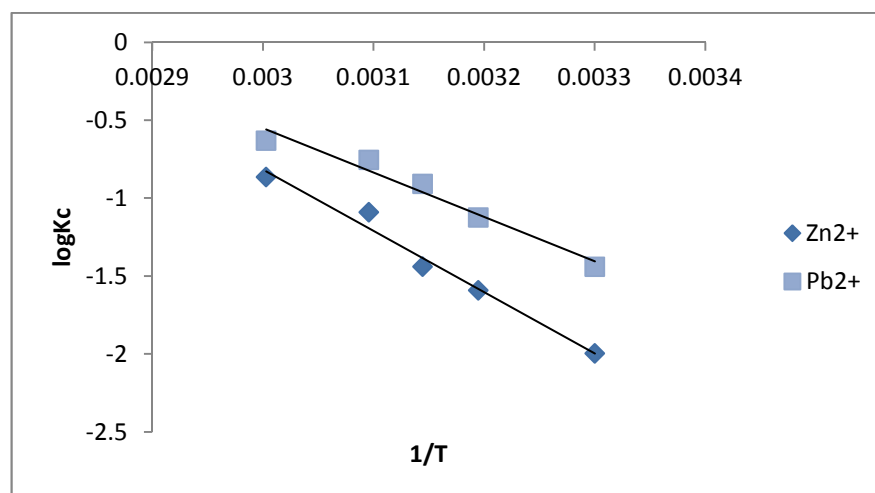


Figure 6. Van't Hoff plot for the removal of Zn^{2+} and Pb^{2+} by SCAC2

CONCLUSION

From the present study, it is concluded that the PFR could be blended with 20% (w/w) of SCAC, without affecting its spectral, thermal and physicochemical properties and also retain the CEC values of PFR. The effect of particle size

and initial concentration of Zn^{2+} ions on CEC, its regeneration level by NaCl solution was studied. CEC values of various metal ions of blends up to 20%(w/w) SCAC2 were found to be very close to the PFR. Equilibrium studies for the removal of Pb^{2+} ion and Zn^{2+} ion reveal that the process is spontaneous, endothermic and occur with increased randomness. SEM images have well defined micrometric structures. Hence, blending of PFR with 20%(w/w) SCAC2 to get composites will definitely lower the cost of IER.

Acknowledgements

The authors thank the principal and Head, Department of chemistry, R.D.Govt. Arts College, Sivagangai, for providing research facilities and encouragement. The authors also thank to Department of chemistry, Thiagarajar College of Engineering and Technology, Madurai, and Alagappa college of Engineering & Technology, Karaikudi for recording TGA and SEM studies.

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