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Removal of Selective Metal Ions by Using Phenolic Resin Blended with Sulphonated *Solanum xantho carbum*, Link. Carbon

V. Maheshkumar[1*], R. K. Seenivasan[2] and P. Selvapandian[1]

1. Post Graduate and Research Department of Chemistry, Raja Doraisingam Government Arts College,
Sivagangai – 630 561, Tamil Nadu, **INDIA**
2. Department of Chemistry, Government Arts College, Melur – 625 106, Tamil Nadu, **INDIA**

Email: maheshmalar72@gmail.com

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ABSTRACT

In the present study, the removal of some selective metal ions was studied by using Ion Exchange Resins (IERs) synthesized from phenol formaldehyde resin (PFR) blended with sulphonated Solanum xantho carbum, Linn. Carbon (SXCC). In a new composite, ion exchanges were prepared by using different amount of SXCC in the blend of 0% to 100% (w/w). The CEC (Cation Exchange Capacity) of the composite was found to decrease with increasing the percentage of SXCC in PFR matrix. The synthesized ion exchange resins (IERs) are characterized by IR spectral, SEM images and thermal studies. All significant physico-chemical properties of ion exchangers were determined. The thermodynamic equilibrium constants are calculated by Mg^{2+} - H^{+} *and* Zn^{2+} - H^{+} *ion exchanges on the resin having different amount of SXCC. It was concluded that the PFR sample could be blended with 30% (w/w) of SXCC, without affecting physico-chemical and thermal properties. Hence the blending with SXCC will absolutely lower cost of the ion exchange resin.*

Keywords: Phenol formaldehyde resin, Composites resin, Cation exchange capacity, Sulphonated Solanum xantho carbum Charcoal.

INTRODUCTION

Phenolic resins, which are the condensation product of phenol and formaldehyde, have been used commercially for over 90 years. Phenolic resins are used in areas such as adhesives [1], coatings [2], wood binders and laminates [3].The ion exchange process is a relatively ancient discovery, which allows us to remove undesirable ions and replace them with less objectionable ions, like H^{+}, Na^{+} and OH^{-}, Cl^{-} ions. The commercial use for ion exchange is less than 100 years old [4].

The modern ion exchange resins (IERs) used to time for water and wastewater treatment is about 50 years old. Although one can discover a new technique to use these resins, the basic chemistry has not changed in half-a-century [5]. Many investigators have been done composite resin that has been used as an IER. Phenolic resin, sulphonated phenol–formaldehyde, sulphonated polystyrene–divinyl benzene, and polyacrylonitrile are the major organic binding matrices that are used for making such composite resins

[6]. Plant materials such as: *Phyllanthusemblica,* Linn. (PE), *Eugenia jambolana*, Lam.(EJ), Terminalia*chebula*, Retz. (TC), Terminalia *bellarica*, Roxb. (TB) and *Achyranthesaspere*, Linn. (AA) [7], *Accacianilotica* [8] activated carbons obtained from agricultural wastes [9], *Terminalia chebula* Retz., Carbon [10], *Achyranthesaspera,* Linn. Carbon [11], *Eugenia jambolana,* Lam. Carbon [12] have been used for the synthesis of IERs. Heavy metals are also removed by bamboo activated carbon, natural clinptitolite, titanatenanoflowers and polyhydroxyethyal methacrylate/Malonic acid) hydro gel [13-15] *Terminalia bellerica* [16], Mimosa pudica [17] and Aegle marmelos [18].

Ion exchange process is suitable in the treatment of wastewater containing metal ions satisfied from plating and other industries [19]. It is also a useful way to concentrate and remove the ions of valuable metals like, copper, zinc, and chromium. Special processes using selective IERs are also available forthe recovery of precious noble metals like gold, platinum, and silver [20]. A careful literature survey has revealed that no such studies have been made on the phenolic resin blended with sulphonated S*olanum xantho carbum,* Linn.Carbon. Those prompt us to take this investigation.

Accordingly the objective of this research work is to synthesize and characterize new composite ion exchangers of PhOH-HCHO type, blended with sulphonated *Solanum xantho carbum,* Linn. Carbon (SXCC) and to determine the column / cation exchange capacity (CEC) or ion exchange capacity (IEC) for some selective metal ions.

MATERIALS AND METHODS

Phenol and formaldehyde used were of Fischer reagents (India). A.R grade of Con. Sulphuric acid (Sp.gr. = 1.82) was used. Sulphonated carbon (SC) is obtained from plant materials *Solanum xantho carbum,* Linn., which is chiefly available in southern part of India, mainly in Tamil Nadu. These plant materials were washed, dried and cut into small bits of about 0.5cm length.

Preparation of Sulphonated Carbons (SC): Solanum xantho carbum, Linn. (400g) were carbonized and Sulphonated by con. sulphuric acid (400 mL) and kept at room temperature (30 ± 10^0C) for 24 h and then heated at 90^0C in a hot air-oven for 6 h. It was then cooled, washed with distilled water for several times and finally with double distilled (DD) water in order to remove excess free acid (tested with $BaCl_2$ solution) and dried at 70^0C for 12 h. They were labelled as SXCC.

Preparation of PFR: Phenol (10 mL) and Con. Sulphuric acid (12.5 mL) were mixed slowly with constant stirring and cooling in an ice bath. The mixture was then heated to 80^oC for 3 h, cooled immediately in ice bath and kept it for overnight. It was then polymerized with formaldehyde solution (12.5 mL) at 80^0C for 3 hours and the product was cured at room temperature. A reddish brown coloured chunky solid obtained. It was crushed, washed with distilled water to remove the free acid, dried, sieved and preserved for characterization.

Preparation of Composites: A known amount of phenol was sulphonated with conc. Sulphuric acid by the above method and calculated quantities of sulphonated *Solanum xantho carbum,* Linn. Carbon (SXCC) were added Subsequently to it so as to keep the percentage substitution by itself at 10, 20, 30, 40 and 50 percentage respectively. Each mixture was then polymerized with Formaldehyde solution at 80^oC and the product was further cured for 3 hours. It was then ground, washed to remove the free acid, dried, sieved and preserved for characterization. The experimental and theoretical yields of the composite are reported in table 1.

Table 1: Amount of reagent utilized and yield of PFR, Condensates (SXC1-SXC5) prepared by blending of PFR with several percentage (w/w) of pure SXCC

Sample	% Of SXCC in IER (cal.)	Amount of Reagent used					
		PhOH (mL)	HCHO (mL)	Con.H_2SO_4 (mL)	SXCC (g)	Yield (g)	% of SXCC in IER (obs.)
PFR	0	10	11.5	12.5	0	19.00	0.00
SXC1	10	10	11.5	12.5	2.11	20.20	10.45
SXC2	20	10	11.5	12.5	4.75	23.53	20.19
SXC3	30	10	11.5	12.5	8.14	26.47	30.75
SXC4	40	10	11.5	12.5	12.36	30.31	40.78
SXC5	50	10	11.5	12.5	17.3	34.35	50.36
SXCC	100	-	-	-		-	100.00

Cation Exchange Capacity: A known weight (2g) of the sample (SXCC) was converted into H^+ form by washing it with 2 M HCl acid and washed with distilled water and finally rinsed with Doubly Distilled water in order to remove excess free acid. The test column was set by using graduated burette with glass-wool plug and the slurry of treated resin/composite sample. 40 mL of 0.1 M solutions of different metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+} and Pb^{2+} ions) were used as effluents. The rate of flow of effluent was adjusted to 1mL min^{-1}. The sample exchanged its H^+ ion to the corresponding metal ions. The total amount of cation exchanged with the resin was determined by using standard titration techniques [21]. The values of cation exchange capacity (CEC) were determined as per the literature method [22]. The effect of initial concentration of metal ions, particle size, chemical and thermal stability of the resin on CEC was also determined [23, 24] and reported.

Regeneration Level: Most of the commercial ion exchangers are in Na^+ ionic form. Hereafter, the exchange of H^+ ion by the metal ions, the regeneration level of the composites loaded with a metal ions were determined by using NaCl (brine) solution. The test samples of IERs (PFR and composites) were first treated with 40 mL of 0.1M solution of Mg^{2+} ion. Hence, H^+ form of test samples was converted into Mg^{2+} form. Then, 40 mL of NaCl solution of several concentrations like, 0.05, 0.10, 0.15 and 0.20M was added and the effluents were collected at a rate of flow of 1mL min^{-1}. The amount of Mg^{2+} ions present in each of the effluent with different concentrations of Mg^{2+} ions was estimated [22]. The Percentage of restoration level was determined and reported.

Instrumental Studies: The FT-IR spectra of pure PFR, Composite obtained by blending of PFR with 30% (w/w) of SXC3 and pure SXCC were recorded with FT-IR spectrometer using KBr pellets. Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) traces were obtained for PFR and composite obtained by blending of PFR with 30% (w/w) of SXC3. The scanning electron microscope analysis of Pure resin, 30% (w/w) composite (SXC3) and pure carbon (SXCC) were recorded.

Physico-Chemical Properties: The Samples were ground and sieved into a size of 210–300 μm using Jayant sieves (India). This was used for further characterization. By using standard procedures [25- 27], the values of absolute density (wet and dry in water and toluene respectively), percentage of gravimetric swelling and percentage of attritional breaking were determined. The solubility of these samples was also tested in various organic solvents and inorganic reagents.

Absolute Density (Dry and Wet): The absolute density of the samples was determined in both dehydrated and hydrated states with the help of a specific gravity bottle in toluene and water media, respectively. The samples were completely washed with toluene solvent for removal of water (dehydrated) and dried. A empty weighed (W_1) specific gravity bottle of 25 mL capacity is filled with the dried samples (PFR, SXC1, SXC2, SXC3, SXC4, SXC5 and SXCC) are packed well by tapping it with a rubber stopper. The weight of the specific gravity bottle were filled with the samples is weighed (W_2). The weight of the samples was determined by the difference in the weight (W_2-W_1). The weight of the samples (in g) divided by the volume (in ml), resulted in the absolute density (in gm L^{-1}) of the adsorbent. The different samples (PFR, SXC1, SXC2, SXC3, SXC4, SXC5 and SXCC) were treated with water (hydrated). The similar procedure (in toluene medium) mentioned above was also followed by this experiment.

Percentage of Gravimetric Swelling: Swelling measurements were made by allowing the samples to equilibrate in water overnight. The weight of the swollen sample (wet weight) was taken as M_w and the corresponding dry weight M_d was determined after drying the same lot at 70°C for 12 h and then Gravimetric swelling percentage was determined using the formula,

$$\text{Percentage of swelling} = M_w - M_d / M_d \times 100$$

Percentage of Attritional Breaking: The samples were initially sieved to give sets of particles of size greater 210 micron sieve. A known amount of the samples (w_1 g) was swollen in water and shaken continuously f hours. The wet sample was separated by filtration, dried, sieved on a 210 micron sieve and the amount of samples retained by the sieve was weighed (w_2 g).

The percentage of Attritional breaking $= W_1 - W_2 / W_1 \times 100$

RESULTS AND DISCUSSION

Cation Exchange Capacity: CEC or IEC values are shown in table 2. It indicates that, the CEC value decreases when the % (w/w) of SXCC content in the condensate increases. The relative ion exchange capacity (IEC) of specific metal ions depends upon the atomic number or atomic radius [28]. Although the CEC values also depends upon the anionic part of the metal salt i.e., inter ionic forces of attraction between the anions and cations, which also plays a vital role in deciding the CEC values for a particular salt solutions [29-30].

Table 2: Cation exchange capacity of PFR, Condensate (SXC3) and pure SXCC (H^+) form of 0.1M solution of selective metal ions at 303K

Sample	**% of SXCC in IER**	**Cation exchange capacity, in m. mol. g^{-1} 0.1M solution**						
		Na^+	**K^+**	**Ca^{2+}**	**Cu^{2+}**	**Mg^{2+}**	**Pb^{2+}**	**Zn^{2+}**
PFR	0	1.4864	1.6216	1.6875	1.6934	1.8111	1.7052	1.8345
SXC1	10	1.1323	1.2251	1.5554	1.3988	1.5705	1.4241	1.6059
SXC2	20	1.0882	1.1274	1.52	1.3837	1.5554	1.3938	1.5857
SXC3	30	0.9853	1.0049	1.4746	1.3029	1.5251	1.3433	1.5554
SXC4	40	0.9558	0.9560	1.419	1.2271	1.4544	1.2221	1.5251
SXC5	50	0.9019	0.897	1.1867	1.0958	1.3837	1.1766	1.4241
SXCC	100	0.3333	0.2549	0.7171	0.9494	0.9797	1.0302	0.909

From the table 2 CEC values of samples is found to decrease in the following order.

$$\mathbf{Zn^{2+} > Mg^{2+} > Ca^{2+} > Pb^{2+} > Cu^{2+} > Na^{+} > K^{+}}$$

On comparing the CEC values of condensates with that of PFR taking it as 100% (Figure 1), it is found that blending of SXCC with PFR decreases its CEC value in table 2. In PFR blended with 10% (w/w) of SXC1 has CEC values 75.54 – 92.17 for exchange of H^+ ions with Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} ions compared to that of PFR. In addition, it is noted that the composites up to 30% (w/w) blending of PFR with SXC2 in polymeric resin leads to 61.96 – 87.38% of CEC of PFR, while blends with 40% (w/w) of SXC4 have CEC values in the range of 58 – 84% of CEC of PFR (Figure 1). Therefore, it may be concluded that PFR could be blended upto30% (w/w) of SXC3 and thus the condensate thus obtained can be used as a new and low cost IERs for water and wastewater treatment, especially for the removal of metal ions from industrial sewage.

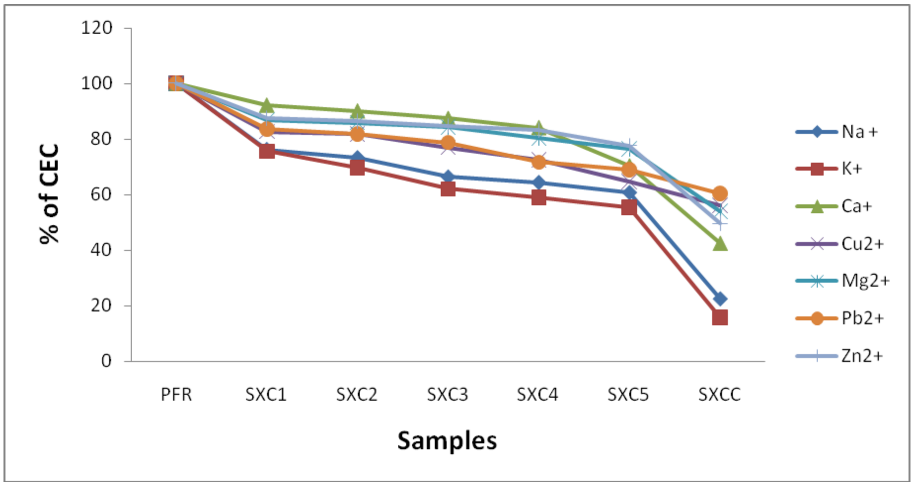

Figure 1: Cation Exchange Capacities of H^+ form of PFR, condensates (SXC1 –SXC5) and SXCC

Selectivity of metal ions: The selectivity order of metal ions is based on CEC value and is also depends upon the ionic potential of the metal ions in solutions [31]. The ion exchange system of the different mental ions is not unique in the order of exchange affinity. Hence, in dilute conditions obeyed Hofmeister series [32] and it is different from high concentration [33]. It is observed that the concentration of the effluent metal ion solutions are comparatively high and also due to the selectivity of the metal ions [34].

Effect of particle size on CEC: The CEC values are shown in table 3. This indicates that the IERs with a particle size < 210 µm are fine; 300 -500 µm and > 500 µm are common as to cause very low ion exchange capacity as compared to that of 210 – 300 µm particle size. Therefore, for effective ion exchange capacity, the particle size would be maintained between 210 and 300 µm.

Table 3: Effect of particle size on CEC of PFR and condensate obtained by blending PFR with 30% (w/w) of (SXC3) at 30 ^{0}C

Sample	**Particle Size (Micron)**	**Cation exchange capacity, in m. mol. g^{-1} 0.1M solution**			
		Na$^+$	**Ca^{2+}**	**Mg^{2+}**	**Zn^{2+}**
PFR	<200	1.4170	1.6228	1.7698	1.7816
	200-300	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
30%SXCC	<200	1.0774	1.5170	1.5453	1.5756
	200-300	1.0882	1.5200	1.5554	1.5857
	300-500	1.0826	1.5116	1.5352	1.5655
	>500	1.0463	1.4935	1.5150	1.4746

Physico – Chemical Characteristics

Absolute density: The values of absolute density in both hydrated (wet) and dehydrated (dry) states decreases steadily from PFR, condensate resin (SXC1 – SXC5) and then finally to SXCC. This is observed that the absolute density of 100% of pure SXCC possess only 55.75% and 54.47% of hydrated (wet) and dehydrated (dry) states respectively. It clearly shows that PFR, condensates and SXCC are more closely packed structurewith high degree of cross-linking and therefore could develop suitable for making ion exchange columns for polar and non-polar liquids of high density [22 - 24, 35 and 36].

Gravimetric Swelling: The percentage gravimetric swelling of various samples decreases from PFR (80.37%) to SXCC (49.2%) in table 4. It shows that, the values for PFR and condensates are not as high as compared to conventional gel type IERs signifying rigidity in the matrix and hence the pores of condensates are of non-gel type and macro reticular [20]. SXCC has a gravimetric swelling dimension only 49.2% as compared to that of PFR. This tremendously low value may be due to certain rigidity in their matrix. The blending of PFR with 30% (w/w) of SXCC has the gravimetric swelling value (61.82), which is about 80.37% of that of PFR, thus decreasing 18.55% of percentage of gravimetric swelling compared to that of PFR. The decrease in percentage gravimetric swelling is attributed due to the loss of polarity and porosity in the condensates. Thus, the condensates may prove to be useful where they are required to withstand a large osmotic shock [18].

Attritional Breaking: The values of percentage of attritional breaking in Table 3 also illustrate the stability of the resin, which decrease from PFR, condensates to pure SXCC. Thus, the mechanical stability is good up to 30% (w/w) blending of SXCC with PFR. This observation shows the probability of formation of resin in the capillaries of the sulphonated carbon (SXCC) atoms [25].

Table 4: Physicochemical properties of PFR, condensates SXC1-SXC5 and SXCC

Sample	**% of SXCC in IER**	**Density (g mL-1)**		**Percentage**	
		Wet	**Dry**	**Gravimetric swelling**	**Attritional breaking**
PFR	0	1.948	1.926	80.37	9.00
SXC1	10	1.822	1.820	70.05	19.25
SXC2	20	1.678	1.682	63.80	21.00
SXC3	30	1.565	1.553	61.82	25.65
SXC4	40	1.499	1.480	65.23	36.27
SXC5	50	1.107	1.134	56.32	38.00
SXCC	100	1.086	1.053	49.12	42.00

Effect of Stability of IERs on CEC: In order to test the chemical stability of IERs viz. PFR and condensates, the samples were boiled with water, benzene and 20% (w/w) NaOH for an hour. This result all the samples possess CEC value almost similar to that of parent / untreated resins (range: 2 - 8 %). It indicates that all the samples are chemically stable (Table 5).

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

Reagents	**Cation Exchange Capacity (m.mol. g^{-1} 0.1M solution)**					
	PFR	**SXC1**	**SXC2**	**SXC3**	**SXC4**	**SXC5**
CEC (of untreated)	1.855	1.676	1.534	1.453	1.302	1.245
20% (w/w) NaOH	1.745	1.646	1.532	1.367	1.286	1.209
Benzene	1.696	1.606	1.565	1.334	1.310	1.242
Water	1.808	1.696	1.510	1.368	1.336	1.216
Thermal treatment	1.612	1.467	1.432	1.204	1.146	1.089

Regeneration of IERs: All the composite resins and SXCC are effectively regenerates after the exchange with Mg^{2+} ions (Figure 2). It results that the most of the commercial IERs are in Na^+ form and therefore, 40 mL of NaCl solution was used as a regenerator for every 2g of the resin.

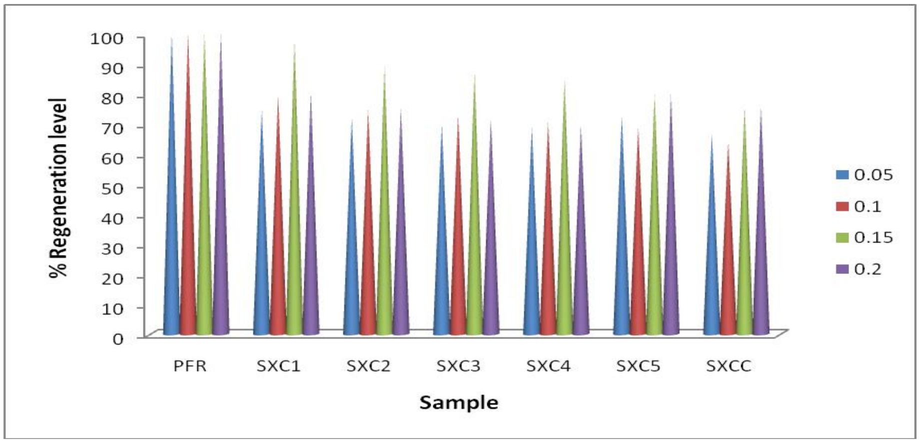

Figure 2: Regeneration level for PFR, condensates and SXCC by using NaCl after exchange with Mg^{2+} ions

FT IR Spectral Studies: The IR spectral data are given in table 6. This indicates the appearance of absorption band at 1033-1039 cm^{-1} (S=O str.), 1118-1200 cm $^{-1}$ (SO_2 sym. str.) and 623-680 cm^{-1}(C – S str.) in pure resin (PFR), 30% (w/w) SXC3 of condensate resin and pure carbon (100%) SXCC confirms the presence of sulphonic acid group (Fig.3a, 3b and 3c). The appearance of broad absorption band at 3338-3404 cm^{-1} (bonded -OH str.) shows the presence of phenolic and sulphonic -OH group in the samples. The appearance of absorption band at 1595-1629 cm^{-1} (C-C str.) confirms the presence of aromatic ring in PFR, 30% (w/w) blending of SXC3 in PFR and pure SXCC. The absorption band at 1467-1480 cm^{-1} (-CH_2 def.) confirms the presence of -CH_2 group in the samples. The weak absorption bands at 885-898 cm^{-1} (-C-H def.), 740 -858 cm^{-1}C-C (def.) in samples show that the phenols are tetra substituted.

Table 6: FT-IR spectral data of PFR condensate with 30% (w/w) SXC3 and pure SXCC ($\bar{\nu}$ in cm^{-1})

Group	PFR	30% (w/w) SXC3	Pure SXCC
S = O str.	1039	1033	1037
SO_2 sym. str.	1118	1184	1200
C – S str.	623	671	680
Bonded OH str.	3404	3338	3352
CH_2 – def.	1469	1467	1480
C – C str.	1629	1595	1612
C - H def	887	885	898
C-C def.	858	740	777
SO_2assy.	1338	-	1371

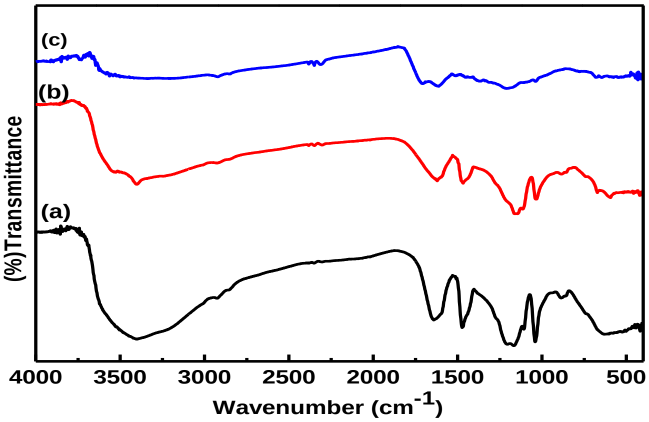

Figure 3: FT-IR spectra of (a) PFR (b) condensate resin with 30 % (w/*w*) of SXC3 and (c) pure SXCC (100%)

Thermal Studies: TGA and DTA traces are used for quickly assessing the thermal stability of various substances [37]. TGA curves shown in fig.4 a and b disclose that there is very small (6.5%) weight loss for PFR and 9.5% weight loss for 30% of SXC3 up to 50^0 C. It is due to the loss of moisture absorbed by resin and condensate with 30% (w/w) of SXC3.At the temperature between 50^0C - 200^0 C there is 21% weight loss for both PFR and SXC3. Up to 360^0 C, approximately 43% loss weight in PFR and 41% weight loss in condensate with 30% (w/w) of SXC3 is observed. This shows that IERs are thermally stable upto 100^0 C. DTA curve (Figure 4a) shows that two exothermic peaks were obtained in PFR, nearly at 50^0C and at 270^0C respectively. At 50^0C the presence of broad peak was observed, which indicates the dehydration process of resin (PFR). A peak at 270^0C indicates the chemical changes of pure resin.

DTA curve of composite resin obtained by blending PFR with 30% (w/w) SXC3 (Fig. 4b) shows that the same two exothermic peaks were obtained at 60^0 C and at 230^0 C, respectively similar to PFR. Again the first broad peak indicates the dehydration of SXC3 and second moderate sharp peak indicates the chemical changes of SXC3 in the condensate. It is concluded that, the limiting temperature for the safer use of PFR and composite with 30% (w/w) of SXC3 as ion exchangers was 100^0 C, since the resin/composite degrade thermally after 100^0 C.

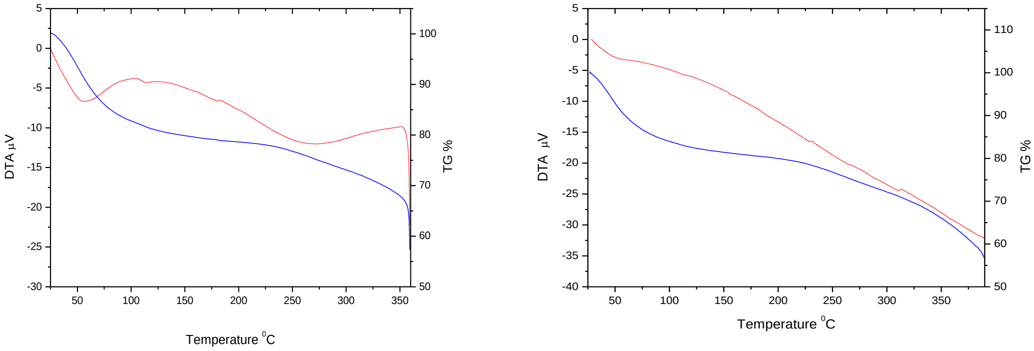

Figure 4: Thermal studies of (a) PFR and (b) condensate with 30% (*w/w*) of SXC3

SEM Studies: The surface morphology of the PFR (a & b), condensate resin with 30% (w/w) of SXC3 (c & d) and pure 100% SXCC (e & f) was examined by Scanning Electron Microscope (SEM) and the images are given in figure 5. All the SEM images were taken at two different magnifications such as, 50 µm and 500 µm. The images show that all the samples have well defined micrometric structure. SEM analysis studies are also proved that the size of pores in 30% (w/w) of SXC3with PFR is greater than in pure SXCC. The SEM images also confirm the physicochemical properties like % of gravimetric swelling, absolute density and CEC are very low value in pure 100% SXCC while compared to the 30% (w/w) of SXC3 with PFR is attributed to the loss of porosity in pure SXCC than 30% (w/w) of SXC3 with PFR.

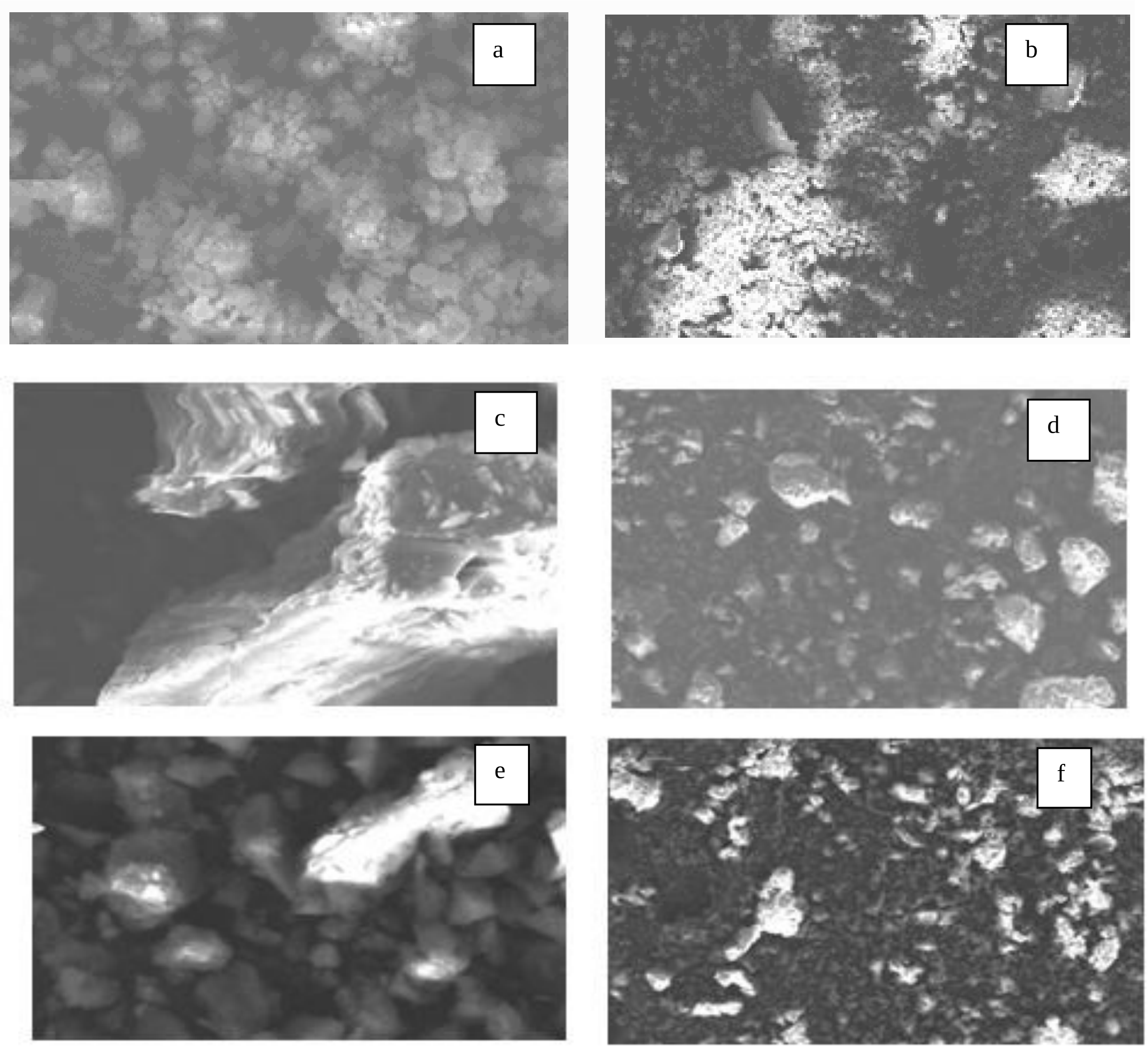

Figure 5: SEM photos of PFR (a, b), condensate resin with 30% (*w/w*) of SXC3(c, d) and pure 100% SXCC (e, f)

Thermodynamic Studies: To determine the effect of temperature on the ion exchange capacity of resin for the exchange of metal ion, experiments were conducted at 303, 308, 313 and 318 K and the results are shown in figure 6. The thermodynamic parameters such as free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) can be calculated using equilibrium constants changing with temperature. The values of thermodynamic parameters were calculated using the following relationships:

$$\Delta G^o = - RT \ln K$$

$$\log K = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT}$$

Where R is the gas constant, K is the equilibrium constant and T is the solution temperature in Kelvin. The thermodynamic parameters can be calculated from plot of log K versus1/T (Figure 6). The observed thermodynamic values are given in table 7. The negative values of ΔG^o indicated the feasibility and spontaneity of the ion exchange process. The positive values of ΔH^o showed endothermic nature of the overall ion exchange process.

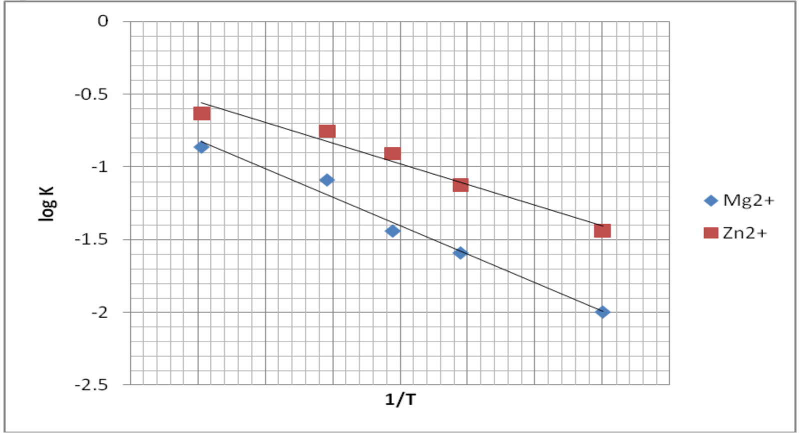

Figure 6: Plot of log K versus 1/T for ion exchange of the Mg^{2+} and Zn^{2+}metal ion onto SXC3

The positive entropy change may be attributed to the increasing disorder because the number of water molecules surrounding metal ion decreases and thus the degree of freedom of the water molecules increases.

Table7. The observed thermodynamic values

Metal ion	ΔH^o	ΔG^o	ΔS^o
Mg^{2+}	**50248.26**	**-13,382.25**	**210.04**
Zn^{2+}	**54480.9**	**-13,975.89**	**225.93**

APPLICATIONS

The prepared resin is applied for removal of metal ions like copper, zinc, lead, calcium, magnesium, sodium and potassium of single and binary metal ions from water and waste water and it is cheaper in cost.

CONCLUSIONS

From the results of the present study, it is concluded that, the single low cost IERs are found to be suitable for removal of metal ions like copper, zinc, lead, calcium, magnesium, sodium and potassium of single and binary metal ions from water and waste water. The composite containing *Solanum xantho carbum*,Linn. Carbon (SXC3) upto 30 percent is found to have high density values, good swelling behaviour, comparable attritional resistance, effective column and absolute dimensions, adequate thermal stability, and is mainly macro porous and cheap. Therefore, blending of PFR with 30 % (w/w) SXC3 to get composite will definitely lower the cost of IER.

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REFERENCES

[1] Pizzi, K.L. Mital, K.L., Handbook of Adhesive Technology, Marcel Dekker, Inc., New York, **1994.**

[2] P. Kopf, The Encyclopedia of Polymer Science, **1998**, 11, 45.

[3] A. Pizzi, Wood Adhesives Chemistry and Technology, Vol. 1, Marcel Dekker, New York, **1983**.

[4] A.M. Wachinski, J.E. Etzel, Environmental Ion Exchange; Lewis: New York, **1997**.

[5] C.F. Michaud, Technical paper given at water quality association convention, Fort Lauderable, FL, March, **1998.**

[6] J. Lento et al., in the proceedings of water management symposium, **1989.**

[7] A.Girija and R.K. Seenivasan, *Rasayan J. Chem.*, **2013**, 6(3), 212-222.

[8] N. Kannan, R.K. Seenivasan, R. Mayilmurugan, *Indian J. Chem. Technol.,* **2003**, 10, 623-626.

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

[10] N. Kannan, R.K. Seenivasan, *J. Appl. Poly.Sci.,* **2006**, 101, 4104.

[11] N. Kannan, R.K. Seenivasan, *J. Ion Exch.,* **2005**, 16, 164.

[12] N. Kannan, R.K. Seenivasan, *Desalivation.,* **2006**, 216, 77

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

[14] M. Jovanovic, N. Rajic, B.J. Obradovic, *Haz.Mat.*, **2012**, 233, 57.

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

[16] D. Ragavan. A. Girija, B. Kathereen, R.K Seenivasan., *Int. Jour.ofInnov. Res. & Dev.,* **2014**, 3(4), 17–23.

[17] R.Sayeekannan, K.kavitha, M.Ilayaraja, S.Siva., *IJSR.*, **2012**, 1(4), 10-13.

[18] Siva Sundarajan, BeaulahAngelin, Sudharsan Sankaranarayanan, SayeekannanRamaraj, **2014**, 2, 81-93.

[19] F. McGarvey, D. Tamaki, In 26th Annual Liberty Bell Corrosion Course, **1988**, (2), 81-93.

[20] M. Natarajan, S.Krishnamoorthy, *Res. Ind*., **1993**, 38, 278-282.

[21] A. I. Vogel, Text Book of Quantitative Chemical Analysis, (Eds. G. H. Bassett, J. Jeffery, J. Mendham and R. C. Den ney, 5th Edn., Longman Groud Ltd., London, **1989**, 186-192.

[22] S. Ramachandran, S. Krishnamoorthy, *Indian J. Technol.*, **1984**, 22, 355.

[23] J. Ragunathan, S. Krishnamoorthy, *J. Indian Chem. Soc.,* **1984** 61, 911.

[24] M. B. Chandrasekaran, S. Krishnamoorthy, *J. Indian.Chem. Soc.*, **1987**, 64, 134.

[25] P. Vasudevan, N. L. N. Sharma, *J. Appl. Poly*.Sci., **1979**, 23, 1443-1448.

[26] D. Kathiresapandian, S. Krishnamoorthy, *Indian. J. Technol*., **1991,** 29, 487-488.

[27] A. Mariamichel, S. Krishnamoorthy, *Asian J. Chem*., **1997**, 56, 680-685.

[28] H. Kamal, M. Rashid, H. Arafahi, *J. Saudi Chem. Soc*., **2005**, 9, 11-28.

[29] W. K. Son, S. H. Kim, S. G. Park, *Bull Korean Chem. Soc***., 2001**, 22 (1), 53-58.

[30] S. Mustafa, K. H. Shan, A. Naeem, M. Waseem, T. Ahmad, S. Sarfraz , M. Irshad, *Chin. J. Chem*., **2010**, 28, 27-32.

[31] D.K. Dimov, E.B.Petrova, I.M. Panayotov, Ch.B.Tsvetanov, *Macromolecules*, **1990,** 21, 2733.

[32] F. M. Perez, F. A. Castro, J. F. P. Benito, *J. Macromol. Sci*., **1987**, 24, 155-165.

[33] A. A. Zagorodni, D. L. Kotova, V. F. Selemenev, *Reac. Func.Poly*, **2002**, 53, 157-171.

[34] C.E. Harland, Ion Exchange Theory and Practice, Royal Society of chemistry, UK**, 1994**, 4, 320 - 325.
[35] N. Kannan, R. K. Seenivasan, R. Mayilmurugan, *Indian J. Chem. Technol*., **2003**, 10, 623-626.
[36] M. S. Metwally, N. E. Metwally,T. M. Samy, *J. Appl. Poly.Sci*., **1994**, 52, 61-67.
[37] S. K. Srivastava, G. Bhattacharjee, R. Tyagi, N. Pant, N. Paul, *Environ Technol Lett*., **1988**, 9, 1173-1185.

AUTHORS' ADDRESSES

1. **V. Maheshkumar**
Assistant Professor, P. G and Research Department of Chemistry,
Raja Doraisingam Government Arts College,
Sivagangai – 630 561, Tamil Nadu, India.
Mob: 7598249314, Email:maheshmalar72@gmail.com
2**. R. K.Seenivasan**
Assistant Professor, Department of Chemistry,
Government Arts College,
Melur – 625 106, Tamil Nadu, India.
Mob: 9442879521, Email: rkseenivasan@gmail.com
3. **P. Selvapandian**
Assistant Professor, P. G and Research Department of Chemistry,
Raja Doraisingam Government Arts College,
Sivagangai – 630 561, Tamil Nadu, India.
Mob: 9790489343, Email: rajiselva03@gmail.com