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SYNTHESIS AND CHARACTERISATION OF CATIONIC MATRICES BLENDED WITH SULPHONATED *MELIA COMPOSITA BENTH.* CARBON

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ABSTRACT

Phenol – formaldehyde resin (PFR) was prepared and blended with sulphonated charcoals (SCs) prepared from a plant material. Composite ion exchange resins (IERS) were prepared by varying the amount of SCs (10-50%w/w) in the blends. All the important physico-chemical properties have been analysed. Composites up to 30% (w/w) blending retain almost all the essential characteristics and Cation Exchange Capacity (CEC) of the original PFR. It is concluded that blending of PFR by SCs will reduce the cost of IERS.

Key words: *Phenol – formaldehyde Resin – Sulphonated Mella composite carbon. – Cation Exchange Capacity –Composite resins – Ion Exchangers*

INTRODUCTION

Developed and industrialised nations of the world are taking active measures to control and prevent the environmental pollution caused by chemicals and developing countries begin to follow it. In the wastewater treatment, usually a decreasing level of pollutants is achieved. **Ion exchange** is an appropriate technique, which could be employed under field condition for the removal of ionic materials from water and wastewater[1]. Ion-exchange process finds a valuable place in the treatment of metal wastes from plating and other industrial processes.

Many commercial resins (CRs) 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 (SCs) prepared from carbonaceous materials. Such types of low-cost ion exchangers can be prepared by blending cheaper and freely available plant materials containing phenolic groups. Attempts have also been made to prepare cheaper cationic resins from waste materials and natural products. Earlier studies have shown that the cheaper condensate ion exchangers could be

prepared by partially blending the macroporous phenol-formaldehyde sulphonic acid resin (PFR or PFSAR) matrix by sulphonated carbon (SCs) prepared from coal[2-5], jute[6], Egyptian corn cop[7], baggase charcoal[8], *Accacia nilotica* [9], *Egyptian bagasse pith*[10], ground nut shell[11], wheat husk[12], spent tea[13], mangroves bark[14], starch[15], cashew nut shell[16] and lignin[17].

The aims and objectives of the present work are to synthesise and characterise (by IR, TGA and SEM studies) the new condensate / low-cost ion exchangers of PhOH – HCHO type blended with Sulphonated *Melia Composita* Benth. Carbon(SMCC). And to estimate the physico - chemical properties including cation exchange capacity (CEC) for some selective metal ions, to determine thermal and chemical stability, to find out its solubility. Further to investigate the effect of particle size, and the regeneration level of Mg^{2+} ions loaded IERs by using NaCl, for the above ion exchange process.

EXPERIMENT AND MATERIALS

Materials

The raw/plant material used was *Melia Composita* (.MC). This plant material MC is freely available in Tamil Nadu, India. It belongs to the family ‘Meliaceae’ and called ‘Malaivembu’ in Tamil and ‘Mountain Neem in English and Pahaadee Neem in Hindi.. Phenol and formaldehyde used were of Fischer reagents (India). AR 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.

Methods

Melia Composita (500g) have been carbonized and sulphonated by con. sulphuric acid, washed with distilled water to remove excess free acid(tested with $BaCl_2$ solution) and dried at $70^{\circ}C$ for 12 h. It was labeled as SMCC.

Pure phenol – formaldehyde resin was prepared according to the literature method [18-20]. It was then ground, washed with distilled water and finally with double distilled (DD) water to remove excess free acid (tested with $BaCl_2$ solutions), dried, sieved (210 – 300 μm) using Jayant sieves (India) and preserved for characterisation [9, 11-14, 18]. It was labeled as PFR.

The condensates were obtained as per the method reported in literature [11-14, 18]. The products with 10, 20, 30, 40 and 50% (*w/w*) of SMCC in the condensates, respectively were labeled as MC1, MC2, MC3, MC4 and MC5. A separate sample of SMCC was also subjected to the characterisation (instrumental and physico - chemical) studies.

Characterisation of Samples

Instrumental Studies

FT-IR SMCC spectral data of pure resin (PFR), condensate with 30% (*w/w*) of SMCC and pure SMCC were determined with a JASCO FT-IR 460 plus FT-IR SMCC spectrophotometer by using KBr pellets. To establish the thermal degradation of the samples,

TGA and DTA traces were obtained for PFR and condensate with 30% (w/w) of SMCC by using TZSCH- Geratebau GmbH Thermal analyser. SEM photos of pure resin (PFR), condensate with 30% (w/w) of SMCC and pure SMCC were obtained using Hitachi Scanning Electron Microscope (Model S-450), Japan.

Physico-chemical Characteristics

Samples were ground and sieved into a particle size of 210 – 300 μm using Jayant sieves (India). This is used for further characterisation by using standard procedures [9, 11-14] to find out the values of absolute density (wet and dry), percentage of gravimetric swelling and percentage of attritional breaking. The solubility of these IERs was tested with various organic solvents and inorganic reagents.

The values of cation exchange capacity (CEC) were determined by using standard titration technique [19-21] as per the literature method [22-24]. The effects of initial concentration of metal ions, particle size, chemical and thermal stability of the resin on CEC are determined [9, 11-14].

After the exchange of H^+ ions by the Mg^{2+} ions, the regeneration level of the condensates loaded with Mg^{2+} ions was determined by using NaCl (brine) solution.

RESULTS AND DISCUSSION

Preparation

The experimental (obs) and theoretical (cal) composition of SMCC in the condensates (MC1 – MC5) are in good agreement with each other (Table.1). The results are similar to those obtained by others [2 - 4, 11-14].

Table .1 Amount of reagent used and yields of PFR and its condensates prepared from SMCC

SAMPLE	% OF SMCC IN IER	AMOUNT OF REAGENTS USED			SMCC (G)	YIELD (G)	% OF SMCC IN IER(OBS)
		PHENOL (G)	HCHO (ML)	CON.H ₂ SO ₄ (ML)			
PFR	0	10	11.5	12.5	0	19.50	0
MC1	10	10.0	11.5	12.5	1.94	18.00	9.26
MC2	20	10.0	11.5	12.5	4.38	22.18	20.28
MC3	30	10.0	11.5	12.5	7.50	25.83	30.99
MC4	40	10.0	11.5	12.5	11.66	29.72	40.77
MC5	50	10.0	11.5	12.5	17.50	36.08	51.54
SMCC	100	-	-	-	-	-	100.00

This indicates that the preparative methods adopted for the synthesis of PFR and its condensates (MC1 - MC5) are more reliable and reproducible. Exactly 11.5mL of formaldehyde, 12.5mL of con. sulphuric acid and 10mL of phenol are found to be optimum.

Instrumental Studies

FT-IR studies are used to confirm the ion exchangeable groups present in the IERs based on various stretching frequencies [25-26]. Table .2 and Fig.1(a and b) indicates the appearance of absorption bands at $1033 - 1049 \text{ cm}^{-1}$ (S = O str.), $1149 - 1206 \text{ cm}^{-1}$ (SO_2 sym. str.) and $586 - 611 \text{ cm}^{-1}$ (C - S str.) in pure resin (PFR), condensate resin with 30%(w/w) of SMCC (MC3) and pure SMCC, which confirm the presence of sulphonic acid group.

Table.2 FT-IR spectral data of PFR, condensate with 30% (w/w) of SMCC and pure SMCC (in cm^{-1})

Group	PFR	Composites MC3	Pure SMCC
S = O str.	1049	1042	1033
SO_2 sym. str.	1168	1149	1206
C – S str.	611	609	586
Bonded OH str.	3385	3395	3274
CH_2 – def.	1473	1454	1505
C – C str.	1641	1611	1618
C - H def.	887	888	776
C-C def.	858	868	802
SO_2 assy.	1338	1365	1374

The appearance of broad absorption band at $3274 - 3395 \text{ cm}^{-1}$ (bonded –OH str.) indicates the presence of phenolic and –OH group of in sulphonic acid group the samples. The appearance of absorption band at $1611 - 1641 \text{ cm}^{-1}$ (C-C str.) confirms the presence of aromatic ring in PFR, condensate resin, MC2 and pure SMCC. The absorption band at $1454 - 1505 \text{ cm}^{-1}$ (CH_2 def.) concludes the presence of – CH_2 group in the samples. The weak absorption band at $776 - 888 \text{ cm}^{-1}$ (C-H def.) in the samples indicates that the phenols are tetra substituted.

Thermogravimetric analysis (TGA) is used for rapidly assessing the thermal stability of various substances [27-28]. TGA traces shown in Fig.2 (A, B and C) reveals that there is a very small loss in weight (5%) both for PFR and condensate resin with 30% (w/w) of SMCC up to 80°C . This is due to the loss of moisture absorbed by the PFR resin and condensate with 30% (w/w) of MC3. Upto 200°C there is approximately 23.3% weight loss in PFR and 22% loss in weight in condensate with 30% (w/w) of SMCC. Upto 350°C , approximately 28% loss in weight in PFR and approximately 38% weight loss in condensate with 30% (w/w) of SMCC is observed..

Two peaks are obtained in DTA curve of PFR, one approximately at 80°C and another one at 380°C , respectively (Fig.2A). At 80°C , the presence of a broad peak is observed, due to the dehydration process of resin (PFR). A peak at 380°C , indicates, the chemical changes of pure resin, which reflects approximately 28% weight loss in PFR.

DTA curves of condensate with 30% (w/w) of SMCC (Fig .2B) show that, the same two peaks are obtained at 103^oC and at 526^oC, respectively. Again, the first broad peak indicates the dehydration of condensate with 30% (w/w) of SMCC and second moderate sharp peak indicates the chemical changes of condensate with 30% (w/w) of SMCC, which reflect approximately 38% weight loss in condensate with 30% (w/w) of SMCC.

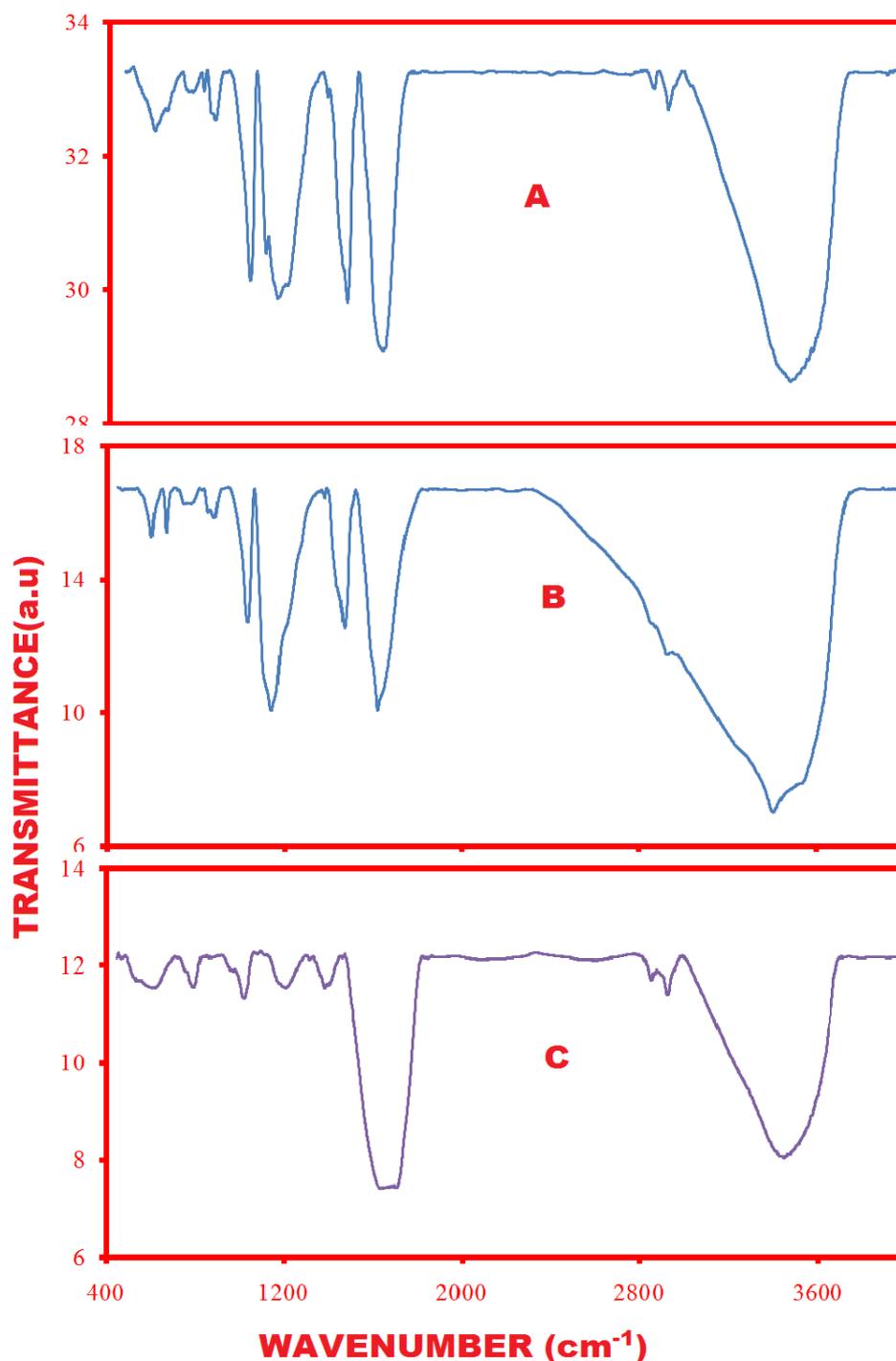


Fig.1 FT-IR Spectra of (a) PFR, (b) MC3 and (c) pure SMC (100%)

From Figs.2 (A,B and C), it is concluded that, the limiting temperature for the safer use of PFR, and condensate with 30% (w/w) of SMCC as ion exchangers is 100°C, since the resins degrade thermally after 100°C.

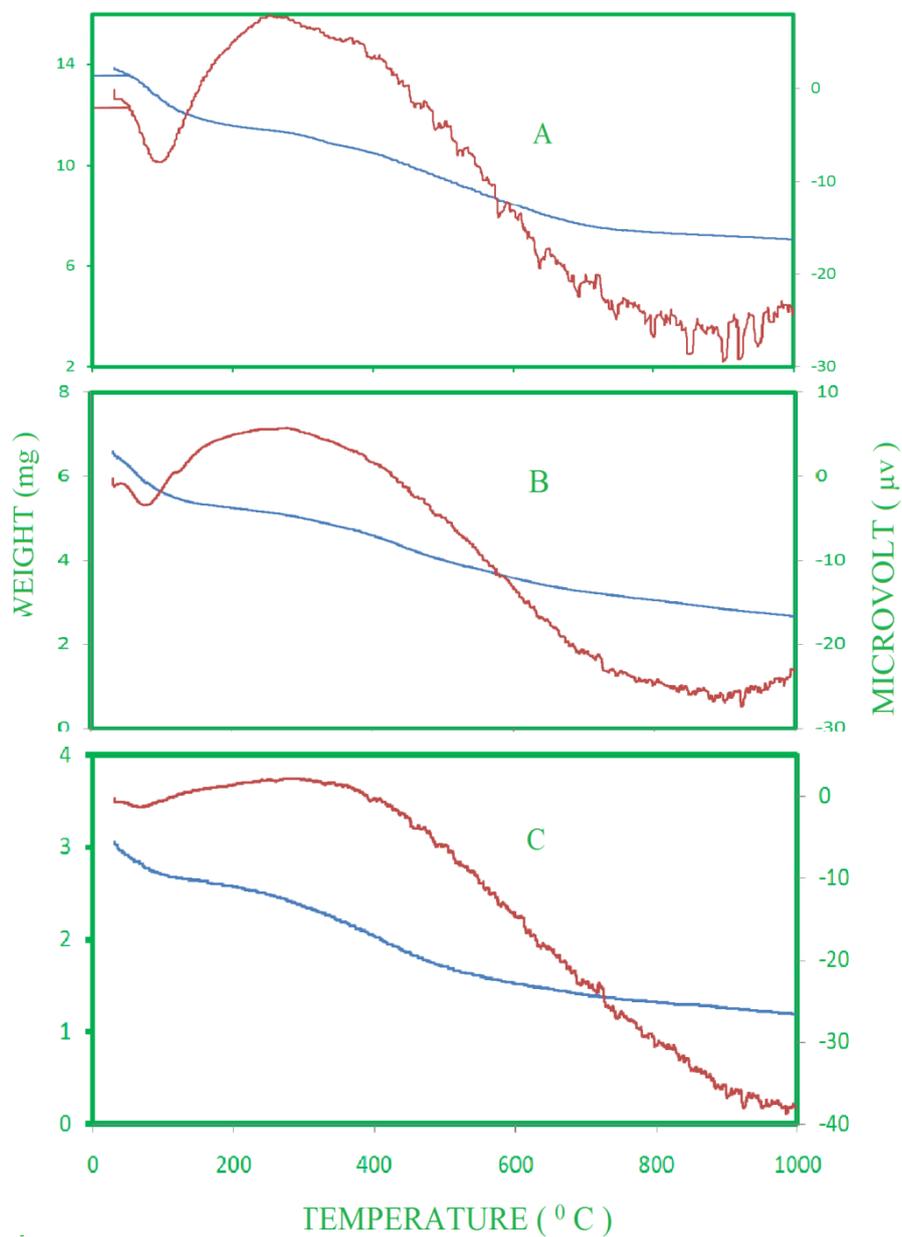


Fig .2 TGA and DTA studies of (A) PFR and (B) MC3 and SMCC

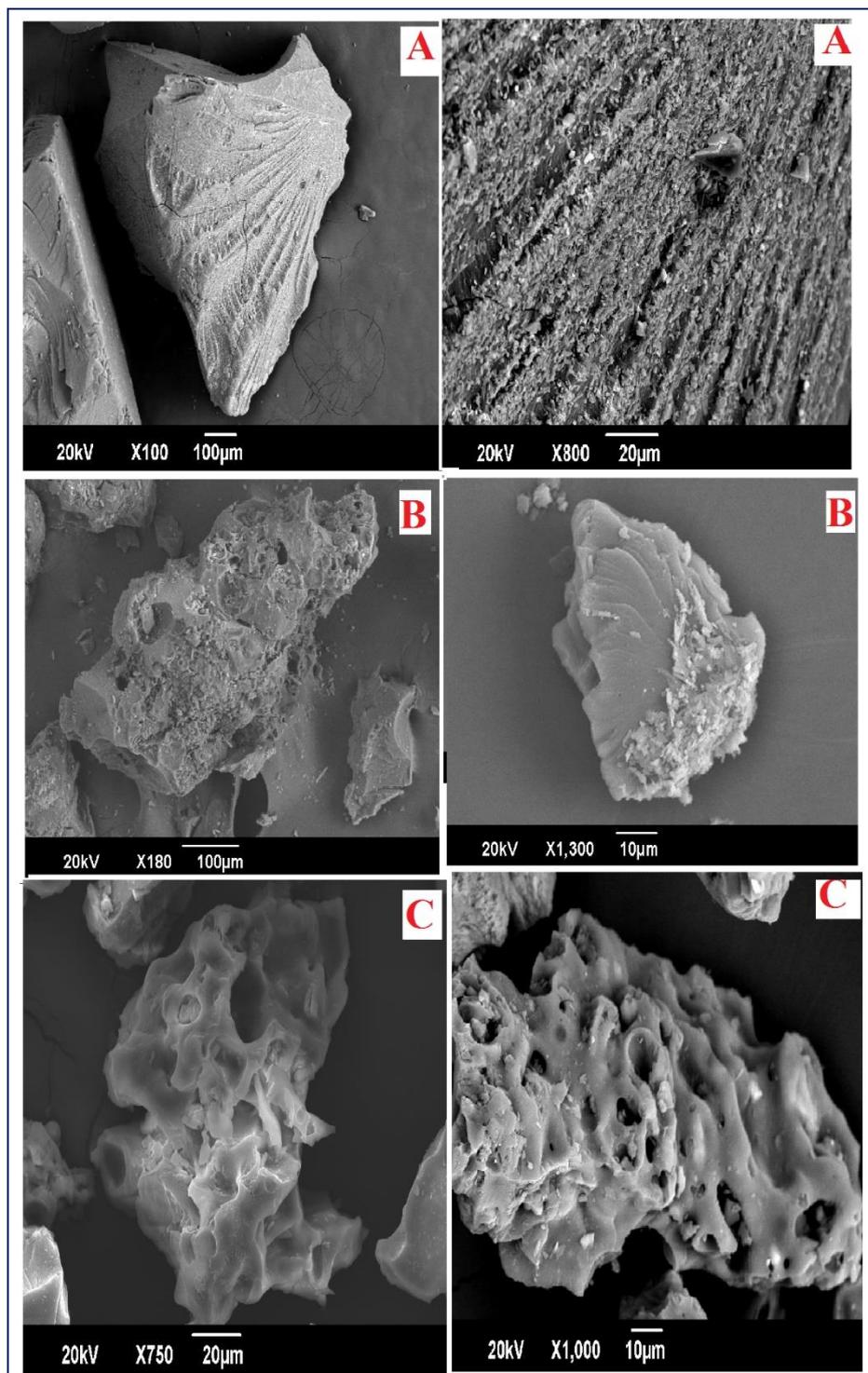


Fig. 3 SEM images of A), PFR B) MC3 and C) pure SMCC

SEM photos of PFR condensate MC3 and pure SMCC (Fig.3 A,B and C) with different magnification are given. SEM photos reveal that all these samples are macroporous in nature. The high macroporous carbon obtained from *Melia Composita*, form the reservoir in which the phenol-formaldehyde sulphonate particles are deposited. Hence, the pore diameter decreases in condensate with 30% (w/w) of SMCC (Fig.3) as compared to pure SMCC.

Physico-chemical Characteristics

Absolute Density

Absolute density value (Table.3) decreases from pure resin to the condensate containing highest % (w/w) of SMCC and then finally to pure SMCC. The density of condensate resin in dry (dehydrated) and wet (hydrated) form depends upon the structure of resin, degree of cross-linking and its ionic nature [28]. As expected, the value of absolute density decreases with the increase in SMCC content (% w/w) in the condensate. 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 density of the resins in the dehydrated states are slightly higher than that of the hydrated state, but somewhat close to each other. 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 macroporous in nature[13,14] and close packing.

Gravimetric Swelling

The value of gravimetric swelling percentage (Table.3) decreases from PFR (98.25%) to SMCC (39.24%). The average % of gravimetric swelling of the resin decreased with increasing SMCC content in the condensate. The values of gravimetric swelling percentage are found to be 72.15, 63.56 and 57.54 respectively, for 10, 20 and 30% (w/w) blending of SMCC with the parent resin, viz., PFR. This indicates that up to 30% (w/w) SMCC could be mixed with the PFR without affecting its property. The rigidity of the resin matrix is proved from the swelling measurements. Therefore, the cationic resin with higher SMCC content shows lower swelling, which reveals much lower rigid shape, and the rigidity decreases with the increase in % of SMCC content in the condensate[13, 14]. It indicates that pure resin and condensates are rigid with non-gel macroporous structure [23, 24].

Table.3 Physico - chemical properties of PFR, condensates SMC1-MC5 and SMCC

IERS	% of SMCC in IER	Density (g/mL)		Percentage	
		Wet	Dry	Gravimetric swelling	Attritional breaking
PFR	0	1.952	1.910	98.25	7.96
MC1	10	1.74	1.69	72.15	16.21
MC2	20	1.59	1.54	63.56	20.15
MC3	30	1.43	1.36	57.54	24.65
MC4	40	1.36	1.24	51.30	29.46
MC5	50	1.24	1.18	46.15	37.45

SMCC	100	1.12	0.96	39.24	49.24
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Attritional Breaking

Attritional breaking value in % (Table.3) increases with the increase in SMCC content in the resins, representing the stability of the resin, which increases from pure resin to SMCC. Therefore, the mechanical stability is good upto 30% (w/w) of SMCC with pure resin. This observation indicates that the capillaries of the resin may be occupied by the sulphonated carbon (SMCC) particles [9, 12-14].

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, condensates and SMCC 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 are found to be partially soluble in 20% (w/v) NaOH solution, which indicates 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 express the rigidity *i.e.*, high degree of cross-linking.

Cation Exchange Capacity

CEC data are given in Table .4, which indicate that, the CEC values decrease with the increase in the % (w/w) of SMCC in PFR for 0.1M solution of metal ions. CEC range (in m mol g⁻¹) for condensates 0-100% (w/w) of SMCC with PFR: 1.260 - 0.874 for Na⁺ ion; 1.111- 0.314 for K⁺ ion; 1.922 - 0.988 for Cu²⁺ ion; 1.489 – 1.004 for Ca²⁺ ion; 1.670—1.103 for Mg²⁺ ion; 1.832 – 1.162 for Zn²⁺ ion and 1.755 – 1.102 for Pb²⁺ ion. Fig.4 gives the CEC value for various IERs-metal ion system.

The relative value of CEC for individual metal ion depends upon its atomic radius or atomic number [29]. At the same time, the CEC value 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 deciding the value of CEC for a particular metal salt solution [25, 28].

From the CEC data given in Table 5.4, the CEC of the samples are found to decrease in the following order.



Table.4 Cation exchange capacity of H⁺ form of the PER, condensates MC1- MC5 and SMCC for various metal ions at 30⁰C

IERs	% of SMCC	Cation exchange capacity m mol/g						
		Ca ²⁺	Zn ²⁺	Mg ²⁺	Cu ²⁺	Pb ²⁺	Na ⁺	K ⁺
PFR	0	1.489	1.832	1.670	1.922	1.755	1.260	1.111

MC1	10	1.345	1.712	1.541	1.745	1.615	1.160	0.946
MC2	20	1.210	1.652	1.462	1.612	1.521	1.121	0.815
MC3	30	1.165	1.541	1.358	1.416	1.411	1.020	0.722
MC4	40	1.102	1.388	1.264	1.264	1.362	1.003	0.614
MC5	50	1.020	1.245	1.194	1.102	1.256	0.965	0.462
SMCC	100	1.004	1.162	1.103	0.988	1.102	0.874	0.314

Selectivity of Metal Ions

The selectivity order of metal ions *i.e.*, orders of CEC value also depend upon the ionic potential and the hydrated atomic radius of the metal ions in solution [25]. 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 [29] is applicable. But, under high concentration the order is different [29]. 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 condition [29]. The observed order in the present study is different from that of the Hofmeister or lyotropic series [29]. This may be due to the concentration of the influent metal ion solution, which is relatively high and also due to the selectivity of the metal ions.

Also, the CEC data given in the Fig.6.4, conclude that the condensate upto 30% (*w/w*) mixing of SMCC with PFR (MC3) retains nearly 28.26- 73.67% of CEC for all the studied metal ions. Hence, 30% (*w/w*) blending of SMCC in PFR will reduce the cost of original resin. It is observed that the CEC decreases as the percentage of SMCC content in the condensate increases. Hence, any chemical method requiring ion exchangers of low value of CEC, 30% (*w/w*) blended SMCC –PFR resin could be used. SMCC can be inexpensively prepared from the corresponding plant material (MC), 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⁺, K⁺, Cu²⁺, Ca²⁺, Mg²⁺, Zn²⁺ and Pb²⁺ ions in 0.1M solution are about 52-66% for MC1 - MC5 compared to pure commercial (SD's) resin (100%). As an average, the condensates MC1-MC 5 retain nearly 60% of CEC of CR. This indicates that the condensates can partially replace commercial resins (CRs) in making the ion exchangers for industrial applications.

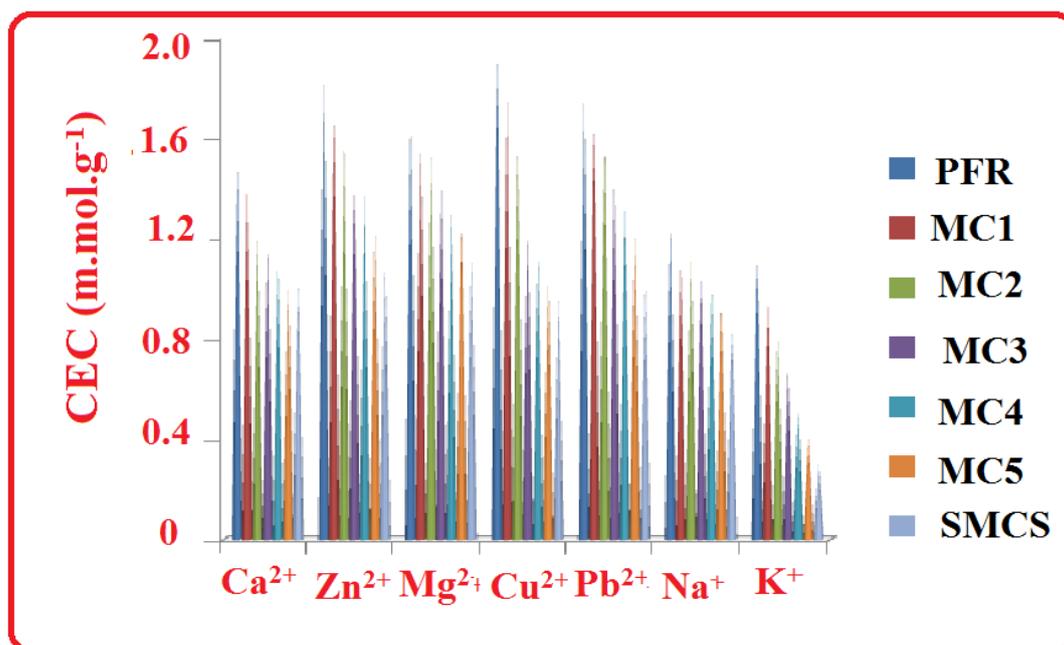


Fig. 4 Cation Exchange Capacities of H⁺ form of PFR, condensates and SMCC Effect of Stability of IERs on CEC

The effect of different reagents and heat on the values of CEC for Mg²⁺ ions for various cationic resins is shown in Table.6. On treatment with 20% (w/v) NaOH solution, 1.6 – 3.0% reduction in CEC value is noted. Upon treatment of the resins with organic solvent like benzene, the loss in CEC is noted to be 1.2 – 2.2%. The decrease in CEC value on treatment with boiling HCl is 1.2 – 1.9 %, for condensates with different amounts of SMCC in the resin. All these observations reveal that the condensates have good chemical stability.

CEC data given in Table.7, describe that the particle size of IERs < 210 μm are fine, 300 – 500μm and > 500 μm are coarse as to cause very low value of 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.

Table 6 Chemical effect on CEC of PFR and condensates for exchange with 0.1M Mg²⁺ ions at 303K

Reagents	Cation exchange capacity, in mol. g ⁻¹ 0.1M solution					
	PFR	MC1	MC2	MC3	MC4	MC5
CEC (of untreated)	1.670	1.541	1.502	1.465	1.374	1.221
20%(w/v) NaOH	1.533	1.432	1.395	1.322	1.264	1.188
Benzene	1.600	1.523	1.456	1.354	1.217	1.136

1M HCl	1.602	1.475	1.412	1.384	1.214	1.165
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Table .7 Effect of particle size on CEC of PFR and condensate MC2 at 30°C

Sample	Particle Size (micron)	Cation Exchange Capacity(m.mol.g ⁻¹)		
		Zn ²⁺	Pb ²⁺	Cu ²⁺
PFR	<210	1.700	1.634	1.803
	210-300	1.832	1.755	1.922
	300-500	1.801	1.732	1.887
	>500	1.732	1.686	1.832
MC3	<210	1.541	1.462	1.432
	210-300	1.645	1.621	1.569
	300-500	1.596	1.577	1.541
	>500	1.523	1.523	1.436

Regeneration of IERs

The regeneration data obtained with 40 mL of 0.2M NaCl (brine) solution conclude that it effectively regenerates PFR, condensate resins and pure SMCC. Exactly 40 mL of 0.2M brine solution effectively acts as a regenerating agent for original PFR (Fig.5). Most of the CRs are in Na⁺ form and hence 40mL of 0.2M NaCl is to be used as a regenerant for every 2g of the resin.

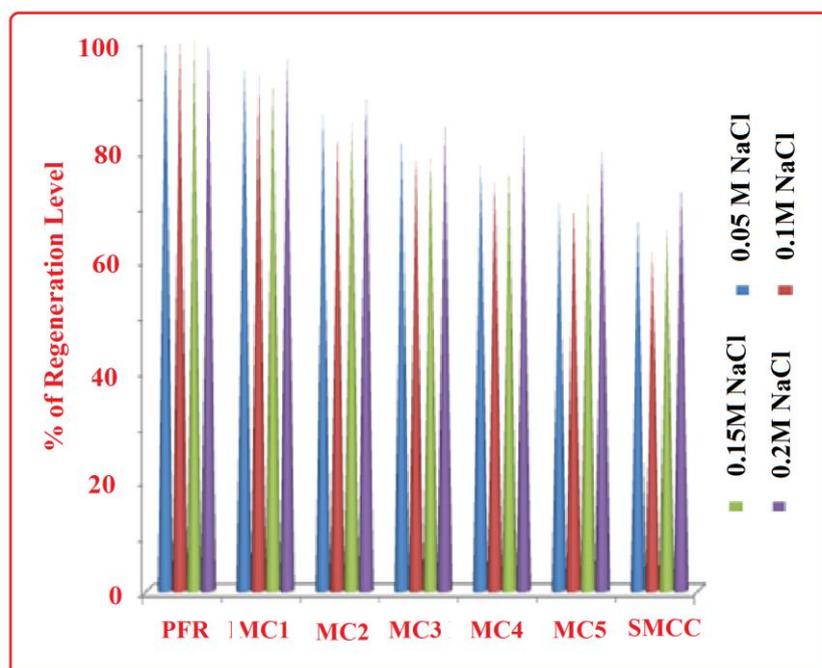


Fig.5 Regeneration level for PFR, condensates MC1-MC5 by using NaCl after exchange with Mg^{2+} ions

CONCLUSION

The following conclusions were arrived from the results of the present study:

- 1) PFR sample could be blended upto 30% (w/w) of SMCC without affecting its SMCC, thermal, textural and physico chemical properties
- 2) The effect of particle size on CEC and its regeneration level by using NaCl has been studied.
- 3) CEC values of various metal ions, reveal that the resin substituted with 30% (w/w) of SMCC has very close to that of the original PFR resin.
- 4) The blending of PFR with SMCC will definitely lower the cost of IER and the condensate can be used as low-cost IERs.

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