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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF PHENOL-FORMALDEHYDE RESIN BLENDED WITH SULPHONATED *Sapindus mukorossi KAERTN* CARBON

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ABSTRACT

Phenol-Formaldehyde Resin (PFR) is blended with *Sapindus mukorossi KAERTN* Carbon (SSMC) in various proportions by weight percentage (0-50%*w/w*). A few composite cation-exchangers were prepared by varying the amount of SSMC (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 optimized. 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 SSMC in the blend. The composites up to 20% *(w/w)* blending retains all the essential properties of the original PFR, since the *Sapindus mukorossi KAERTN,* is the low cost, freely available plant material. Therefore, the composites could be used as low cost ion-exchangers, when SSMC partly replaces the original PFR up to 20% *(w/w)* blending without affecting the properties of PFR.

Keywords: Phenol formaldehyde Resin, Sulphonated *Sapindus mukorossi KAERTN* Carbon, Cation Exchange Capacity, Composite resin, low cost ion exchangers.

INTRODUCTION

Industrialized 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], *Egyptian bagasse pith*[10].*Achyranthes aspera*[11]and *Eugenia jambolana.*[12]

The aims and objectives of the present work are to synthesize, characterize (by IR, TGA and SEM studies) the new composite ion exchangers of PhOH-HCHO type blended with sulphonated *Sapindus mukorossi KAERTN* carbon (SSMC) and to estimate the physico - chemical properties including cation exchange capacity (CEC) for some selective metal ions.

EXPERIMENTAL

Materials

The raw/plant material used was *Sapindus mukorossi KAERTN* (In Tamil; Boondikottai and in English Soapnut) 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.

Methods

Sapindus mukorossi KAERTN. (500g) was carbonized and sulphonated by con. Sulphuric acid, washed to remove excess free acid and dried at 70^0C for 12 h. It was labeled as SSMC.

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[3,6-8,13]. 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 SSMC in the blend / composites, respectively were labeled as SM1, SM2, SM3, SM4 and SM5. A separate sample of SSMC was also subjected to the characterization, instrumental and physico -chemical studies.

Characterization of Samples

Instrumental Studies

FT-IR spectral data of pure resin (PFR), 20% *(w/w)* composite and pure Sulphonated *Sapindus mukorossi KAERTN* carbon (SSMC) 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*) SSMC and the pure SSMC as model ion exchangers were obtained using Hitachi Scanning Electron Microscope (Model S-450) Japan.

Physico - Chemical Characteristics

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

The values of cation exchange capacity CEC were determined by using standard titration technique as per the literature method[14-15]. The effect of initial concentration of metal ions, particle size, chemical and thermal stability of the resin on CEC was determined[16].

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.

RESULTS AND DISCUSSION

The experimental and theoretical compositions of SSMC in the composites (SM1-SM5) 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 (SM1-SM5) are more reliable and reproducible.11.5ml of formaldehyde, 12.5ml of Con. Sulphuric acid and 11ml of phenol are found to be optimum.[7-13] FT-IR studies are used to confirm the ion exchangeable groups based on various stretching frequencies[17-19]. Fig.-1 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 20% SSMC and pure SSMC, 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 20% (*w/w*) SSMC in PFR and pure SSMC.

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.

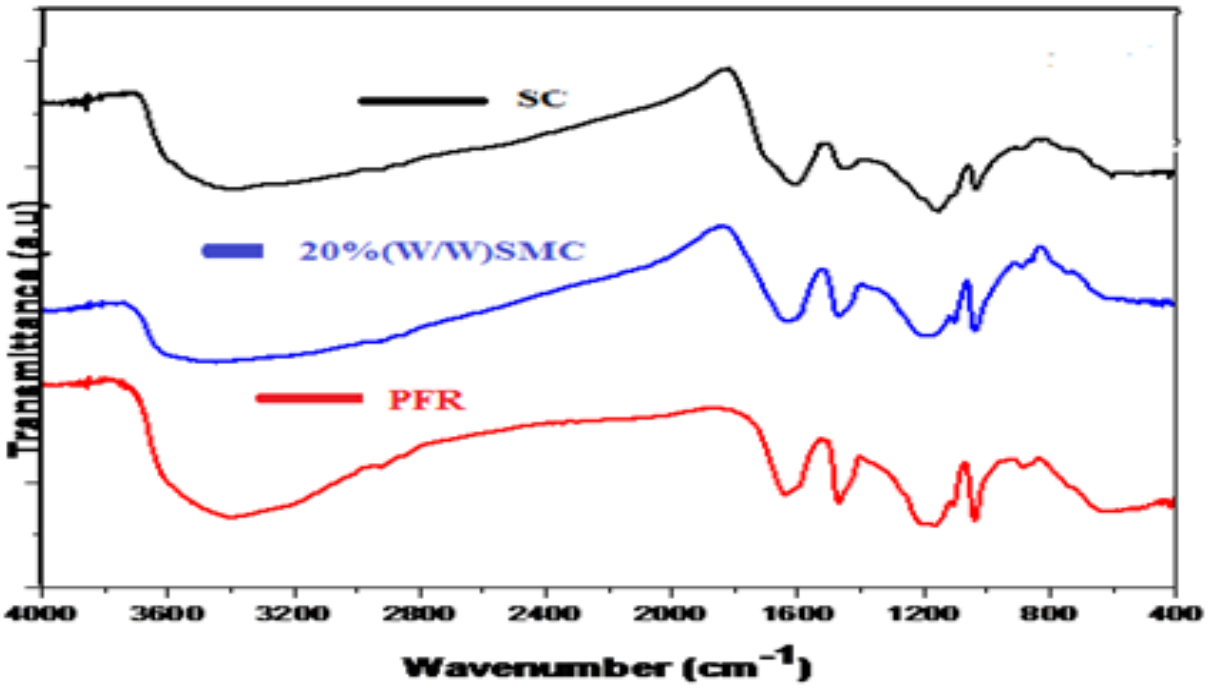


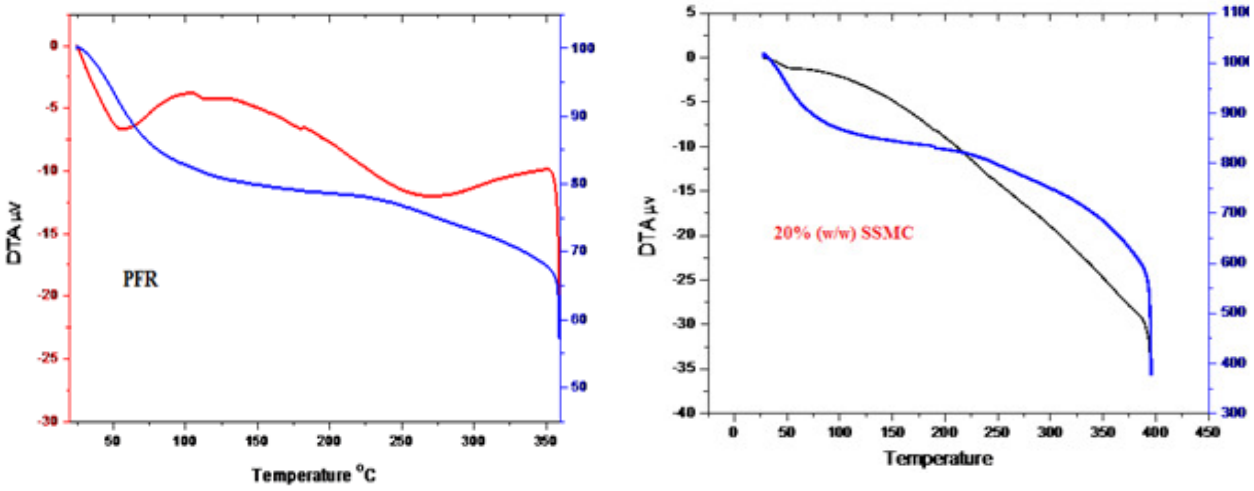
Fig.-1: FT-IR Spectra of PFR, composite resin with 20 % (w/*w*) SSMC and Pure SSMC

Thermo gravimetric analysis (TGA) is used for rapidly assessing the thermal stability of various substances[18]. TGA traces shown in Figures-2a and b reveal that there is a very small loss in weight (5%) for both PFR and composite resin with 20% (*w/w*) SSMC up to 60^{0}C. This is due to the loss of moisture absorbed by the PFR resin and composite resin with 20% (*w/w*) SSMC. Up to 180^{0}C there, is approximately 18% weight loss in PFR and 16% loss in weight in composite resin with 20% (*w/w*) SSMC. Up to 300^{0}C, approximately 32% loss in weight in PFR and approximately 29% weight loss in composite resin with 20% (*w/w*) SSMC was observed.

Two exothermic peaks were obtained in the DTA curve of PFR, one approximately at 50^{0}C and another one at 180^{0}C, respectively (Fig.-2a). At 50^{0}C, the presence of a broad peak was observed, due to the dehydration process of resin (PFR). A peak at 180^{0}C, indicates, the chemical changes of pure resin, which reflect approximately 18% weight loss in PFR.

DTA curves of composite resin with 20% (*w/w*) SSMC (Fig.-2b) show that, the same two exothermic peaks were obtained at 60^{0}C and at 300^{0}C, respectively. Again the first broad peak indicates the dehydration of composite resin with 20% (*w/w*) SSMC and second moderate sharp peak indicates the chemical changes of composite resin with 20% (*w/w*) SSMC, which reflect approximately 16% weight loss in composite resin with 20% (*w/w*) SSMC.

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



(a) (b)

Fig.-2: Thermal studies of (a) PFR and (b)condensate with 20%(*w/w*) of SSM

SEM photos of PFR (Fig.-3a and b), composite resin with 20% (*w/w*) SSMC (Fig.-3c and d) with different the magnification by 50 and 500 times respectively. Scanning electron microscope (SEM) photos reveal that all these samples are macroporous in nature[18]. The high macro porous charcoal obtained from *Sapindus mukorossi KAERTN* 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*) SSMC (Fig.-3c and d) as compared to pure SSMC. Therefore, composite resin with (20% (*w/w*) SSMC) having high mechanical stability and low attritional breaking (Table-2) compared to pure SSMC. At the same time, increasing the percentage amount of SSMC 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 SSMC. Absolute density values (Table-2) decrease from pure resin to the composite resin containing highest % (*w/w*) of SSMC and then finally to pure SSMC.

Table-1: Amounts of reagents used and yield of PFR condensates (SM1-SM2) prepared by blending PFR with various % (*w/w*) of Sulphonated *Sapindus mukorossi KAERTN*Carbon (SSMC)

Sample	% of SSMC in IER	Amount of reagents used			SSMC (g)	Yield (g)	%of SSMC in IER
		Phenol(g)	Formaldehyde (mL)	Con.H_2SO_4 (mL)			
PFR	0	10	11.5	12.5	0	16.05	0
SM-1	10	10	11.5	12.5	1.83	19.01	9.62
SM-2	20	10	11.5	12.5	4.12	20.62	19.95
SM-3	30	10	11.5	12.5	7.07	23.27	30.38
SM-4	40	10	11.5	12.5	11.00	27.60	39.85
SM-5	50	10	11.5	12.5	16.50	32.00	51.56
SSMC	100	-	-	-	-	-	100.00

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[19]. As expected the values of absolute density decrease with the increase in SSMC 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[20].

Table-2: Physico - chemical properties of PFR and its Composites prepared from Sulphonated *Sapindus mukorossi KAERTN* Carbon (SSMC)

Sample	% of SSMC in IER	Density (g/mL)		Percentage	
		Wet	Dry	Gravimetric swelling	Attritional breaking
PFR	0	2.45	2.24	83.16	8.50
SM-1	10	1.60	1.91	72.04	21.00
SM-2	20	1.54	1.87	68.72	24.63
SM-3	30	1.48	1.80	63.50	26.57
SM-4	40	1.37	1.72	51.44	28.00
SM-5	50	1.14	1.31	45.56	31.72
SSMC	100	1.12	1.14	43.10	39.00

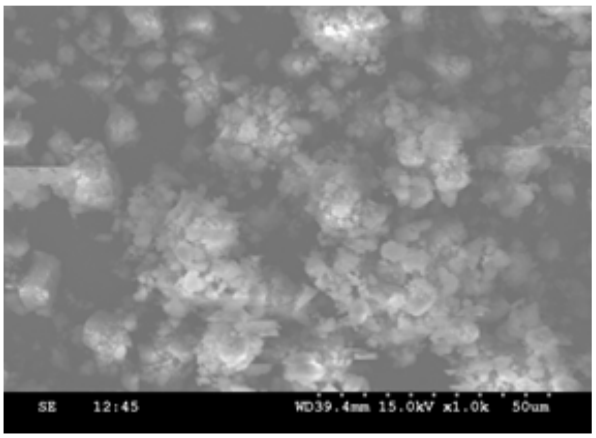


Fig.-3a: SEM images of PFR (X 50)

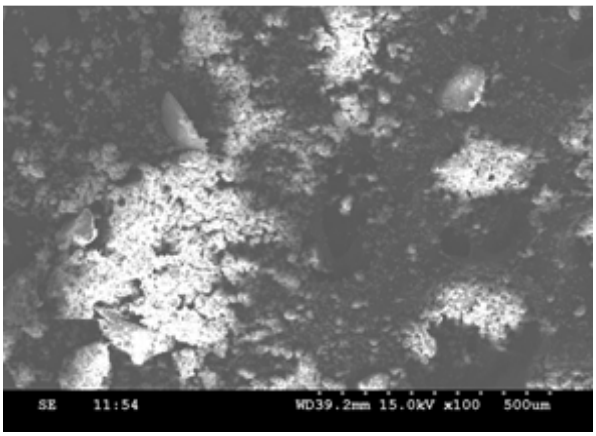


Fig.-3b: SEM images of PFR (x 500)

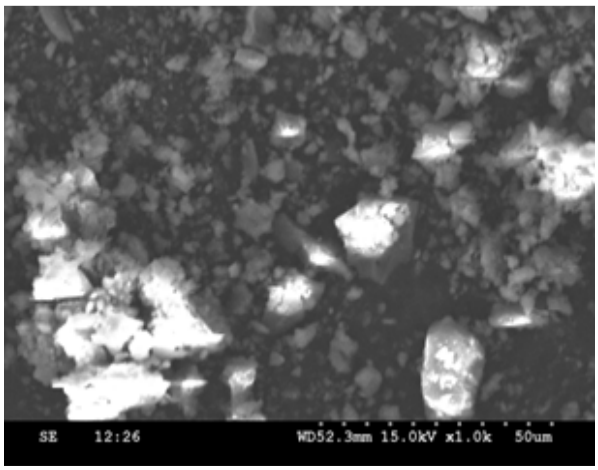


Fig.-3c: SEM images of SSMC (X 50)

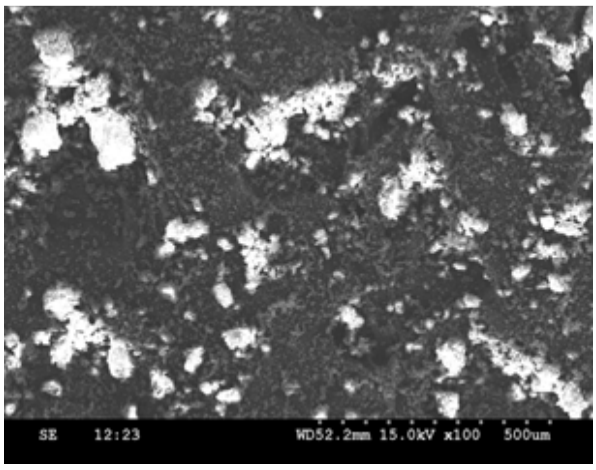


Fig.-3d: SEM images of SSMC (X 500)

The value of gravimetric swelling percentage (Table-2) decreases from PFR (83.16%) to SSMC (43.10%). The average % of gravimetric swelling of the resin decreased with increasing SSMC content in the composite. The values of gravimetric swelling percentage are found to be 72.04, 68.72 and 63.50 respectively, for 10, 20 and 30% (*w/w*) blending of SSMC with the parent resin, *viz*., PFR. This indicates

that up to 20% (*w/w*) SSMC 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 SSMC content showed lower swelling which revealed much lower rigid shape, and the rigidity decreased with the increase in % of SSMC content in the composite. It indicates that, pure resin and composites are rigid with non gel macro porous structure[11].

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

The chemical stability of the samples in terms of its solubility in various solvents and reagents was determined. It reveals that PFR, composites and SSMC 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.

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% SSMC:- 0.1.290 – 0.514 for Na^+ ion; 1.212 – 0.197 for K^+ ion; 1.512 – 0.811 for Cu^{2+} ion; 1.312 – 0.518 for Ca^{2+} ion; 1.770 -0.894 for Mg^{2+}ion; 1.741 – 0.117 for Zn^{2+} ion and 1.723 – 0.918 for Pb^{2+} ion when the *%(w/w)* content of SSMC in PFR increases 0 - 100.

The relative value of CEC of individual metal ion depends upon its atomic radius or atomic number [21]. 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[15, 16.]

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

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

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[16]. 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 is applicable[19]. But, under high concentration the order is different[19]. 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[22-25]. The observed order in the present study is different from that of the Hofmeister or lyotropic series[19]. 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.

Table-3: Cation exchange capacity of H^+ form of the IERs prepared from SSMC for various metal ions

Sample	% of SSMC	Cation exchange capacity m mol/g						
		Cu^{2+}	Zn^{2+}	Pb^{2+}	Mg^{2+}	Ca^{2+}	Na^+	K^+
PFR	0	1.5107	1.7408	1.7254	1.7702	1.3109	1.2904	1.2108
SM-1	10	1.240	1.618	1.571	1.498	1.168	1.091	0.724
SM-2	20	1.145	1.502	1.430	1.321	1.112	1.011	0.618
SM-3	30	1.102	1.413	1.317	1.235	1.063	0.918	0.571
SM-4	40	1.079	1.332	1.201	1.117	0.788	0.776	0.436
SM-5	50	1.010	1.201	1.115	1.102	0.639	0.630	0.366
SSMC	100	0.811	1.170	0.918	0.894	0.518	0.514	0.197

Also, the CEC data given in the Fig.-4, conclude that, the composite up to 20% *(w/w)* mixing of SSMC with PFR retains 82.99 –60.00% of CEC for all metal ions. Hence, 20% (*w/w*) blending of SSMC 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 SSMC content in the composite increases. Hence, any chemical method requiring ion exchangers of low value of CEC, 20% (*w/w*) blended SSMC –PFR resin could be used. SSMC 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^+, K^+, Cu^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+} and Pb^{2+} ions in 0.1M solution are about 75-65% for SM1-SM5 compared to pure PFR resin (100%). This indicates that the composites can partially replace commercial IERs in making the ion exchangers for industrial applications.

Table-4: Effect of initial concentration of Zn^{2+} on CEC value of PFR, SSMC and condensates.

Sample	0.05 M	0.1M	0.15M	0.2M
PFR	1.65	1.52	1.47	1.31
SM-1	1.50	1.43	1.39	1.25
SM-2	1.46	1.37	1.30	1.21
SM-3	1.33	1.28	1.26	1.18
SM-4	1.24	1.13	1.21	1.12
SM-5	1.10	1.10	1.15	1.09
SSMC	1.07	1.04	1.10	1.01

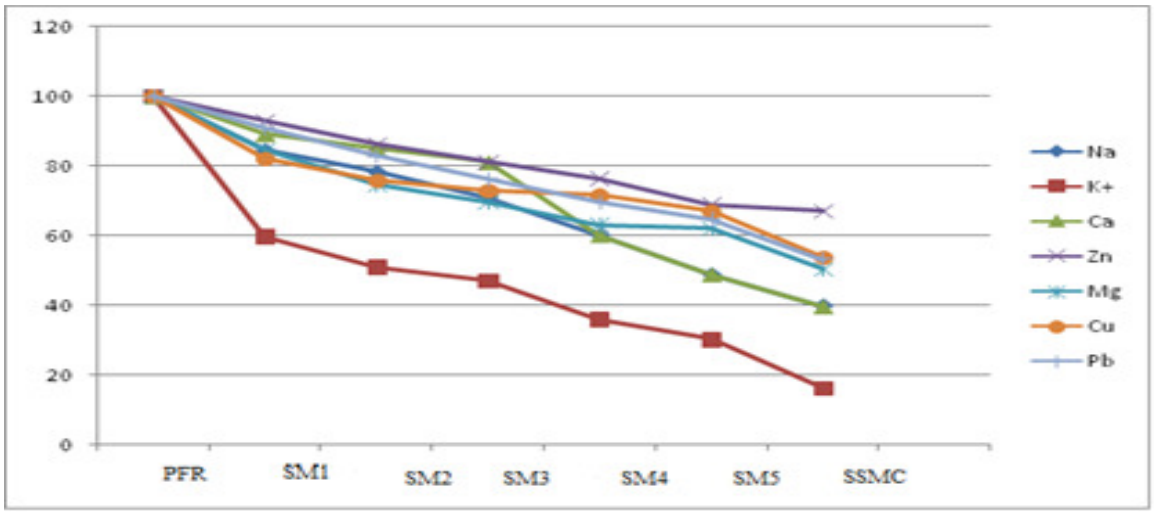


Fig.-4: Cation Exchange Capacities of H^+ form of PFR, Composites and SSMC forSelective metal ions

The values of cation exchange capacity (CEC) increase with the increase in the concentration of Zn^{2+} ions. The equilibrium load of Zn^{2+}ions in unit mass of resin linearly increases with the increase in the initial concentration of Zn^{2+}ions in solution from 0.025M to 0.15M[26]. The values of CEC with initial concentration of $Zn^{2+}$are given in Table-4. Beyond 0.15M, there is a leveling 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.

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 - 2.0%.The decrease in CEC value on treatment with boiling water was 0.6 – 1.6, for composites with different amounts of SSMC in the resin. When the resins were heated for 10h at 100^0 C the value of CEC decreased (8-16%) 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 µm are fine, 300 - 500µm and > 500µm 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.[26]

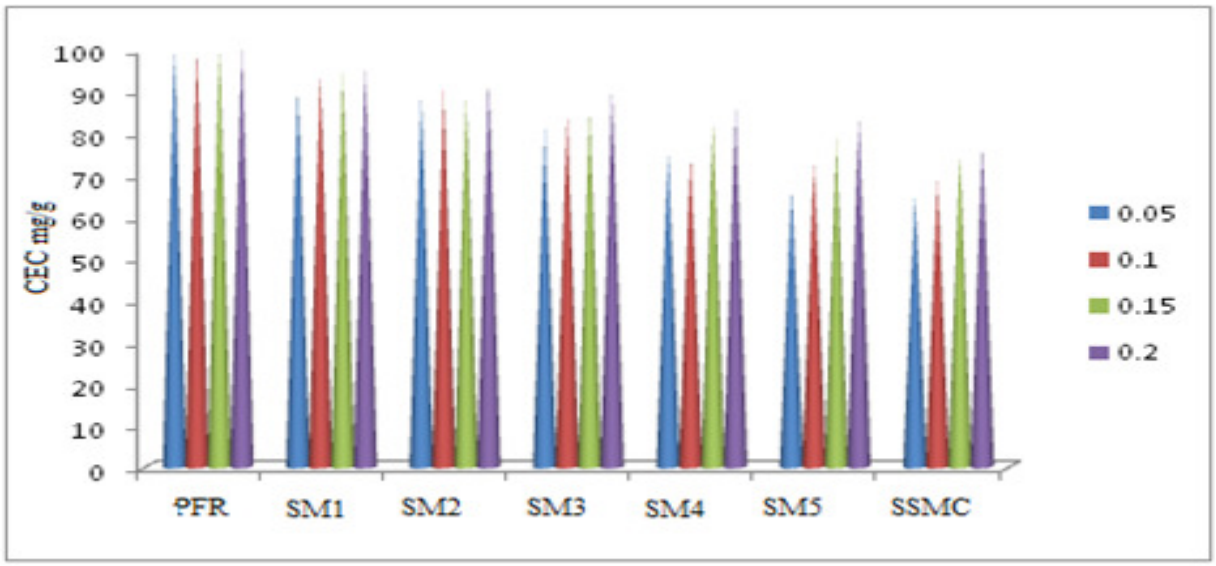


Fig.-5: Regeneration level for PFR, its Composites and SPEC by using NaCl afterexchange with Mg^{2+} ions

Table-5: Chemical and Thermal effect on CEC of PFR and its composites obtained from Sulphonated *Sapindus mukorossi KAERTN Carbon* (SSMC)for exchange with 0.1M Mg^{2+} ions at 30^0C

Reagents	Cation Exchange Capacity m.mol. g^{-1}					
	PFR	SM1	SM2	SM3	SM4	SM5
Original Capacity	1.770	1.498	1.321	1.235	1.117	1.102
0.2M NaOH boiled for 1 h	1.695	1.424	1.301	1.198	1.101	0.978
Benzene boiled for 1h	1.743	1.432	1.318	1.196	1.10	1.000
Boiling water for 1h	1.756	1.488	1.302	1.222	1.113	1.000
Thermal treatment in hot air-oven at 100^0C for 12h	1.532	1.287	1.200	1.185	1.116	1.103

Table-6: Effect of particle size on CEC of PFR and composite obtained by blending PFRwith 20% (*w/w*) of SSMC

Sample	Particle size	Cation exchange capacity m mol/g			
		Zn^{2+}	Mg^{2+}	Ca^{2+}	Na^{+}
PFR	< 210µ	1.2606	1.2653	0.8301	0.9785
	210-300 µ	1.74608	1.7702	1.3109	1.2904
	300-500 µ	1.1753	1.1808	0.6403	0.8821
	>500	0.9501	0.4804	0.5102	0.4310
SM-2	< 210µ	1.022	1.119	0.935	0.871
	210-300 µ	1.502	1.321	1.112	1.011
	300-500 µ	1.314	1.078	0.892	0.931
	>500	1.175	0.938	0.784	0.825

The regeneration data obtained with forty ml of 0.2M brine (NaCl), effectively regenerates all the composite resins and SSMC. 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 regenerator for every 2g of the resin.

CONCLUSION

It is concluded from the present study that PFR sample could be blended up to 20% (*w/w*) of SSMC, without affecting its spectral, thermal and texturaland physico 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 Zn^{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*) SSMC was very close to the original PFR resin. Hence, blending of PFR with SSMC will definitely lower the cost of IER.

REFERENCES

1. B.A. Bolto, L. Pawlowsk, Waste Water Treatment by Ion-exchange, Oxford & IBH Publ. Co., New Delhi, 1987.
2. N.L.N. Sharma, Joseph Mary and Padma Vasudevan, *Res. Ind.*, **21,**173 (1976).
3. Padma Vasudevan and N.L.N. Sarma, *J.Appl. Poly. Sci.*, **23,** 1443 (1979).
4. G.J. Mohan Rao and S.C. Pillai, *J. Indian Inst. Sci.*, **36A,** 70 (1954).
5. Shahha and S.L. Batna, *J. Appl. Chem. Lond.*, **8,** 335 (1953).
6. T. Dheiveesan and S. Krishnamoorthy, *J. Indian Chem. Soc.*, **65**,731 (1988).
7. D. Kathiresapandian and S. Krishnamoorthy, *Indian. J. Technol.*, **29,**487 (1991).
8. A. Mariamichel and S. Krishnamoorthy, *Asian J. Chem.*, **9(1),**136 (1997).
9. N. Kannan, R.K. Seenivasan and R. Mayilmurugan, *Indian J. Chem. Technol.*,**10,**623 (2003).
10. M.S. Metwally, N.E. Metwally and T.M. Samy, *J. Appl. Poly. Sci.*, **52,**61 (1994)
11. N.Kannan, and R.K.Seenivasan, *J. Ion Exchange.*,**16**,164 (2005)
12. N.Kannan, and R.K.Seenivasan, *Desalination.*,**216**, 77 (2007)
13. M. Natarajan and S. Krishnamoorthy, *Res. Ind.*, **38**, 278 (1993).
14. G.H.Bassett, J.Jeffery, J. Mendham and R.C. Denney, Vogel's Text Book ofQuantitative Chemical Analysis, 5th Edn. Longman Group Ltd., London, 1989.
15. S. Ramachandran and S. Krishnamoorthy, *Indian J. Technol.*, **22**, 355 (1984).
16. M.B. Chandrasekaran and S. Krishnamoorthy, *J. Indian Chem. Soc.*,**64,**134 (1987).
17. W.K. Son, S.H. Kim and S.G. Park, *Bull.Korean Chem.Soc.*,**22 (1)**,53 (2001).
18. V.Maheshkumar, R.K.Seenivasan and K. Ananthakuamar, *Indian J. Environ.Protect.*,**36(5)**, 412(2016).
19. P. Vasudevan, M. Sing, S. Nanda and W. L. N. Sharma, *J. Poly. Sci.*,**16**, 2545 (1978).
20. D.K. Dimov, E.B. Petrova, I.M. Panayotov and Ch.B.Tsvetanov, *Macromolecules*, **21**,2733 (1990).
21. A.A. Zagorodni, D.L. Kotova and V.F. Selemenev, *Reac. Func. Poly*., **53**,157 (2002).
22. H.C. Anderson, SPETrans. **1**,(1962).
23. R. Kunin, Ion Exchange Resin, Wiley, Newyork and London, 2nd Edition (1958).
24. A. Mariamichel and S.Krishnamoorthy, *J.Sci.Ind.Res.*,**56**, 680 (1997).
25. S. Mattson, *Ann. Agric. Coll. Sweden*, **10**, 56 (1942).
26. V.Maheshkumar, R.K.Seenivasan and P.Selvapandian, *J. Appl. Chem.*,**5(4)**, 826 (2016).

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