



REMOVAL OF MONO/DIVALENT METAL IONS FROM CATIONIC MATRICES BLENDED WITH SULPHONATED CASSIA ANGUSTIFOLIA VAHL CARBON FOR LOW COST ION EXCHANGE RESINS

A. Palanimurugan

Assistant Professor, Research and PG Department of Chemistry, Raja Doraisingam Government Arts College, Sivagangai - 630 561, India.

D. Ragavan*

Assistant Professor, Research and PG Department of Chemistry, Raja Doraisingam Government Arts College, Sivagangai - 630 561, India. *Corresponding Author

ABSTRACT New Phenol formaldehyde resins efficiently blended with 20% (w/w) of sulphonated cassia angustifolia vahl carbon (SCAC). The physico-chemical, spectral, morphological and thermal properties including cation exchange capacity (CEC) have discussed. The blending of PFR with 20 % (w/w) of SCAC (CA2) and the cationic matrices blended in the 20 % (w/w) of SCAC have used as low cost IERs for water and waste water treatment especially for the removal of metal ions.

KEYWORDS : Phenol formaldehyde resins; SCAC; Cationic matrices; SEM; DTA/TG curves.

1. INTRODUCTION

Senna (*Cassia angustifolia*) which is used as medicinal plant and also have strong laxative effect. Phenol formaldehyde resins were the first commercial synthetic resins (plastics). The process and commercial application for ion exchange are nearly good for the purposes of purification [1]. Phenolic resin, sulphonated phenol formaldehyde, sulphonated polystyrene divinyl benzene and polyacrylonitrile are the major organic binding matrices which are used for preparing such kind of condensate resins [2]. Earlier reports revealed that the cheaper condensate ion-exchangers could be prepared by partially blending the phenol-formaldehyde resin (PFR) matrices/cationic matrices with SCs derived from coal, saw dust, spent coffee, cashew nut husk, wheat husk, turmeric plant, spent tea, gum tree bark, *Accacia nilotica* and Egyptian bagasse pith [3]. It is a convenient way to concentrate, remove and recover the ions of important metals like copper, zinc, chromium, etc. Special process using selective IERs are also available in the recovery of some expensive metals like gold, platinum and silver [4-12].

The present study is aimed to synthesis, characterization of the new condensate ion exchangers of PhOH – HCHO type, cationic matrices blended with Sulphonated *Cassia Angustifolia Vahl* Carbon (SCAC) and to determine the column/cation exchange capacity (CEC) and/or ion exchange capacity (IEC) for some selective metal ions.

2. EXPERIMENTAL

TABLE 1 Amount of reagent used and yield of PFR, condensates (CA1 - CA5) prepared by blending of PFR with various % (w/w) of SCAC

IERs	% of SCAC in IERs (Theoret.)	Amount of reagents used			SCAC (g)	Yield (g)	% of SCAC in IERs (Obs)
		Phenol (mL)	HCHO (mL)	Con. H ₂ SO ₄ (mL)			
PFR	0	10.0	11.5	12.5	0	16.5	0
CA-1	10	10.0	11.5	12.5	1.83	18.13	10.09
CA-2	20	10.0	11.5	12.5	4.12	20.51	20.08
CA-3	30	10.0	11.5	12.5	7.07	23.63	29.91
CA-4	40	10.0	11.5	12.5	11.00	25.14	43.75
CA-5	50	10.0	11.5	12.5	16.50	31.00	53.22
SCAC	100	-	-	-	-	-	100

3.2 CHARACTERISATION OF IERS

3.2.1 IR SPECTRA

IR spectra indicated that the appearance of absorption band at 1039 - 1024 cm⁻¹ (S=O str.), 1184 - 1118 cm⁻¹ (SO₂ sym str.) and 623 - 512 cm⁻¹ (C-S Str.) in PFR (pure resin), condensate resin blended with 20% (w/w) SCAC (CA2) and pure (100 %) SCAC proved that the presence of sulphonic acid group. A broad absorption band which appeared at 3328 - 2921 cm⁻¹ (bonded -OH str.) indicates the presence of phenolic and sulphonic acid -OH group in the IERs. The appearance of absorption band at 1641 - 1603 cm⁻¹ (C=C str.) confirms the presence of aromatic ring in PFR, condensate with 20% (w/w) blending of SCAC in PFR and pure SCAC. The band at 1478-1467 cm⁻¹ (-CH₂ def.) confirms the presence of -CH₂ group in the prepared samples. The weak absorption band at 858 - 781 cm⁻¹ (-CH- def.) which indicated that the phenols are tetra substituted [16].

3.2.2 THERMAL STUDIES

2.1 MATERIALS

Phenol and formaldehyde used were procured from Fischer reagents (India). Analytical grade of concentrated H₂SO₄ (Oil of Vitriol) was used. *Cassia Angustifolia Vahl* (Family-Fabaceae) plant materials which were powdered by well cleaned and dried.

2.2 PREPARATION OF IERS

The phenol formaldehyde resin (PFR) and the condensates containing various percentages (w/w) of sulphonated *Cassia Angustifolia Vahl* carbon (SCAC) as 0, 10, 20, 30, 40 and 50 % (w/w) respectively were prepared as per the standard method of procedure [13].

2.3 INSTRUMENTATION TECHNIQUES

FT-IR spectral data of PFR (pure resin, 100%), condensate containing 20% (w/w) of SCAC (CA2) and pure sulphonated *Cassia Angustifolia Vahl* carbon (SCAC) were recorded with a Perkin Elmer, RX1 FT-IR spectrophotometer by KBr pellets as standard. To establish the thermal degradation of the samples, TGA and DTA traces were obtained for PFR (phenol - formaldehyde resin) and condensate containing 20% (w/w) of SCAC (CA2) by Perkin Elmer Pyris 1TGA. The different physico-chemical properties have been determined [14].

3. RESULTS AND DISCUSSION

3.1 SYNTHESIS OF IERS

It indicates that the methods adopted for the synthesis of PFR and condensates (CA1 - CA5) (Table 1) are more reliable and reproducible [15].

TGA results revealed that there is a very small (13%) loss in weight for both PFR and blend with 20% (w/w) of SCAC (CA2) upto 70°C. This is due to the loss of moisture absorbed by PFR and condensate with 20% (w/w) SCAC. Between 70 and 200°C, there is 22% weight loss in PFR and 16.5% loss of weight in CA2 have been observed. Upto 350 °C, ~32% loss of weight in PFR and then at 340°C, ~29% weight loss in condensate with 20% (w/w) SCAC has been observed

DTA results showed that two exothermic peaks are obtained in PFR, approximately at 50°C and 270°C respectively. At 270°C, the presence of broad peak is observed which indicates that the dehydration process of PFR, it reflects ~29% weight loss in PFR. DTA curve of condensate with CA2 shows that the same two types of exothermic peaks are obtained at 51°C and at 270°C respectively similar to PFR [17]. Again, the first broad peak indicates the dehydration of condensate (CA2) and second moderate sharp peak indicates the chemical changes arising because of thermal degradation of the condensate with CA2. From

data, it is concluded that the limiting temperature for the safer use of PFR and the condensate as ion exchangers is a temperature of 100°C, since the resin degrade thermally after 100°C.

3.2.3 SEM IMAGES

SEM images of PFR (Fig. 1a & b), condensate with CA2 (Fig. 1c & d) and pure SCAC (Fig. 1e & f) with different magnifications are given. SEM images revealed that all these samples are macro porous in nature. The high macro porous carbon obtained from *Cassia angustifolia, vahl.*, carbon form the reservoir in which the phenol-formaldehyde sulphonic acid particles are deposited [18]. Hence, the pore diameter decreases in condensate with CA2 as compared to pure SCAC.

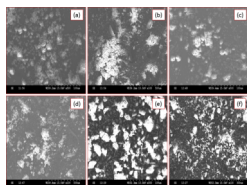


Fig. 1 SEM images of PFR (a & b), CA2 (c & d) and pure SCAC (e & f)

TABLE 2 Physico - chemical properties of PFR, SCAC and condensates (CA1-CA5)

IERS	% of SCAC in IER	Density (g/mL)		Percentage	
		Wet	Dry	Gravimetric swelling	Attritional breaking
PFR	0	2.45	2.24	83.16	8.50
CA-1	10	1.75	1.62	70.31	18.98
CA-2	20	1.54	1.49	65.24	19.53
CA-3	30	1.40	1.34	58.48	21.01
CA-4	40	1.32	1.19	51.71	24.83
CA-5	50	1.00	1.12	40.01	29.17
SCAC	100	0.96	1.10	37.53	49.05

3.3.3 ATTRITIONAL BREAKING

The values of attritional breaking (in %) presented in Table 2 also represent the mechanical stability of the resin which increase from PFR to SCAC. Therefore, the mechanical stability is good upto blending of PFR with CA2. This observation also shows the possibility of filling sulphonated carbon particles in the capillaries of the particles during the blending of cationic matrices (PFR) with SCAC [21].

3.3.4 SOLUBILITY OF IERS

Solubility data indicate the chemical stability of the IERS in various solvents and reagents. It reveals that PFR, condensates and SCAC are practically insoluble in almost all the solvents and reagents except 20% (w/v) NaOH solution. Hence, these condensates can be used as ion exchangers for treating non-aqueous effluents. The insolubility of the IERS even in the trichloroacetic acid express the rigidity i.e., high degree of cross-linking [22].

3.3.5 CATION EXCHANGE CAPACITY

From Fig. 2, it is found that blending of SCAC with PFR decreases its CEC value. Blending of PFR with 20% (w/w) SCAC (CA2) has CEC values 87.63 - 93.38% for the exchange of H⁺ ions with the Na⁺, K⁺, Cu²⁺, Ca²⁺, Mg²⁺, Zn²⁺ and Pb²⁺ ions compared to that of PFR. Then, 20% (w/w) blending of PFR with SCAC in the polymeric resin leads to decrease 6.62-12.3% of CEC of PFR (Fig. 2). The maximum and minimum values of % of relative ion exchange capacity of condensates are for Zn²⁺ and Na⁺ ions respectively. This is due to the reason that the blending of PFR with SCAC upto 20% (w/w), does not affect the CEC value for metal ions to a greater extent. The results conclude that, PFR could be blended up to 20% (w/w) of SCAC and the condensate (CA2) thus obtained could be new and cheap IERS which could be used for water and waste water treatment especially for the removal of metal ions from the industrial effluent.

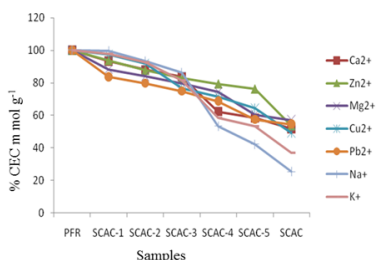


FIG. 2 Cation Exchange Capacity (in %) of H⁺ form of PFR,

3.3PHYSICO-CHEMICAL CHARACTERIZATION STUDIES

3.3.1ABSOLUTE DENSITY

The data given in Table 2 shows that the absolute density values in both hydrated (wet) and dehydrated (dry) states decrease steadily from pure resin to 50 % (w/w) of SCAC (CA5) in condensate resin and then finally to SCAC (100% pure). It indicates that have closely packed structures with high degree of cross-linking and hence could be more suitable for making ion exchange columns for polar and non-polar solutions of high density [19].

3.3.2 GRAVIMETRIC SWELLING

The data given in Table 2 indicates that the percentage of gravimetric swelling decreases from PFR (83.16%) to SCAC (37.53%). SCAC has a gravimetric swelling capacity of only 4.13% as compared to that of PFR. This extremely low value of % swelling may be due to certain rigidity in its matrix. The blending of PFR with 20% (w/w) of SCAC reduces the gravimetric swelling value as 84.55% of that of the (100 % pure) PFR, thus decreasing 15.55% of gravimetric swelling compared to that of the (100% pure) PFR. The decrease in % gravimetric swelling is attributed to the loss of polarity and porosity in condensates. Thus, the condensates may prove to be useful where they are required to withstand a high osmotic shock [20].

Condensates and SCAC for various metal ions at 303 K

From the CEC data, Zn²⁺ > Mg²⁺ > Cu²⁺ > Pb²⁺ > Ca²⁺ > Na⁺ > K⁺ order may due to the ionic strength of the metal ions, the internal structure of the polymeric matrix and also due to the selectivity of the metal ions [23-32].

3.3.6 EFFECT OF CHEMICAL STABILITY OF IERS ON CEC

The CEC values of the thermally treated resins are found to be almost similar to the untreated IER/parent resin (Table 3 and Fig. 3).

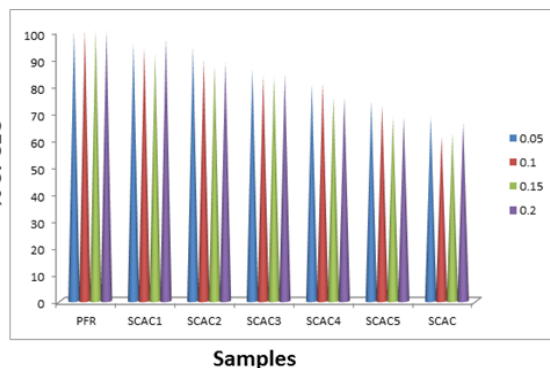


FIG. 3 Regeneration level for PFR, condensates and SCAC- loaded with Mg²⁺ ions by using NaCl solution at 303 K.

TABLE 3 Chemical effect on CEC of PFR and its condensates for exchange with 0.1 M Mg²⁺ ions at 303 K

Reagents	Cation exchange capacity, in mol. g ⁻¹ 0.1 M solution					
	PFR	CA1	CA2	CA3	CA4	CA5
CEC (of untreated)	1.770	1.560	1.486	1.411	1.316	1.070
20% (w/v) NaOH	1.645	1.465	1.382	1.342	1.286	1.026
Benzene	1.768	1.558	1.464	1.404	1.300	1.064
1 M HCl	1.765	1.554	1.456	1.384	1.293	1.045

3.3.7 EFFECT OF PARTICLE SIZE ON CEC

CEC data given in Table 4 indicate that the resin with particle size of < 210 m are fine, 300 - 500 and > 500 m are coarse as to cause very low ion exchange capacity compared to the resin with 210 – 300 m particle size of IER.

TABLE 4 Effect of particle size of PFR and condensate with 20% (w/w) of SCAC (CA2) on CEC at 303 K

IERS	Particle size (μm)	Cation exchange capacity m.mol/g			
		Zn ²⁺	Mg ²⁺	Ca ²⁺	Na ⁺
PFR	< 210	1.261	1.265	0.830	0.979
	210-300	1.741	1.770	1.311	1.290
	300-500	1.175	1.181	0.640	0.882
	>500	0.950	0.480	0.510	0.431
CA2	< 210	0.993	0.789	0.821	0.974
	210-300	1.525	1.485	1.152	1.205
	300-500	0.639	0.771	0.552	0.586
	>500	0.501	0.438	0.416	0.401

3.3.8 REGENERATION OF IERS

40 mL of 0.2 M NaCl (brine) solution effectively regenerates all the condensate resin and SCAC after the exchange with Mg²⁺ ions. The results reveal that 40 mL of 0.2 M NaCl solution could be used as regeneration for every 2 g of the resins.

4. CONCLUSION

It is concluded from the results of the present study that the PFR sample could be blended with 20% (w/w) of SCAC, without affecting its physico-chemical, spectral and thermal properties including CEC. Also the effect of particle size and the initial concentration of Mg²⁺ ions on CEC and its regeneration level by brine solution were studied. CEC values of various metal ions of 20% (w/w) SCAC are very close to that of the PFR resin. Hence, the blending of PFR with 20% (w/w) of SCAC (CA2) will definitely lower the cost of IER. The cationic matrices blended in the 20% (w/w) of SCAC could be used as low-cost IERS for water and waste water treatment especially for the removal of metal ions.

5. REFERENCES

- P. Vasudevan, N. L. M. Sharma, *J. Appl. Poly. Sci.*, 23 (1979) 1443.
- V. Maheshkumar, R. K. Seenivasan, K. Ananthakumar, *Indian J. Env. Prot.*, 36 (2016) 5.
- D. Ragavan, R. K. Seenivasan, *Shanlax Inter. J. Arts, Sci. Hum.*, 3 (4) (2016) 169.
- R. K. Seenivasan, D. Ragavan, A. Girija, R. Muthuramalingam, *J. Adv. Chem.*, 9 (2) (2014) 1921.
- H. A. Shnawa, I. K. Ibraheem, A. A. Shenta, *Nat. Resources*, 6 (2015) 503.
- A. P. Singh, A. Nuryawan, B. D. Park, *Microscopy Res.*, 1 (2013) 1.
- M. Sadiq, M. Ilyas, *Modern Res. Cat.*, 1 (2012) 23.
- Z. Liu, Y. Zhang, X. Wang, D. Rodrigue, *Mat. Sci. Appl.*, 6 (2015) 567.
- N. Kannan, R. K. Seenivasan, R. Mayilmurugan, *Indian J. Chem. Technol.*, 10 (2003) 623.
- M. S. Metwally, N. E. Metwally, T. M. Samy, *J. Appl. Poly. Sci.*, 52 (1994) 61.
- M. Natarajan, S. Krishnamoorthy, *Res. Ind.*, 38 (1993) 278.
- P. Vasudevan, M. Sing, S. Nanda, N. L. N. Sharma, *J. Poly. Sci.*, 16 (1978) 2545.
- W. K. Son, S. H. Kim, S. G. Park, *Bull. Korean Chem. Soc.*, 22 (1) (2001) 53.
- D. K. Dimov, E. B. Petrova, I. M. Panayotov, B. Tsvetanov, *Macromolecules*, 21 (1990) 2733.
- A. Mariamichel, S. Krishnamoorthy, *J. Sci. Ind. Res.*, 56 (1997) 680.
- R. Kumin, 'Ion Exchange Resin', Wiley, Newyork and London, 2nd edn., 15 (1958) 320.
- J. G. Grantham, 'Ion Exchange Resin: Testing', Duolite International Ltd., 14 (1982) 60.
- S. Mattson, *Soil Sci.*, 33 (1932) 41.
- S. Mattson, *S. Ann. Agric. Col. Sweden*, 10 (1942) 56.
- O. Bonner, A. Davidson, W. Argersinger, *J. Am. Chem. Soc.*, 74 (1952) 1047.
- O. Bonner, G. Easterling, D. Weit, V. Holland, *J. Am. Chem. Soc.*, 77 (1955) 242.
- Y. K. Kim, K. J. Lee, *J. Nucl. Sci. Technol.*, 38 (9) (2001) 785.
- [23] G. E. Boyd, S. Lendenbaum, *J. Phys. Chem.*, 69 (1965) 2374.
- R. P. Bhatnagar, S. N. Sharma, *J. Indian Chem. Soc.*, 51 (1974) 852.
- G. E. Boyd, F. Vaslov, S. Lendenbaum, *J. Phys. Chem.*, 68 (1964) 590.
- P. U. Singare, R. S. Lokhande and Rochelle D. Souza, *Rasayan J. Chem.*, 2(2) (2009) 507.
- G. Tripathi, D. Srivastava, *International J. Org. Chem.*, 1 (2011) 105.
- J. Wei, C. Wei, L. Su, J. Fu, J. Lv, *J. Mat. Sci. Che. Engg.*, 3 (2015) 56.
- S. Muhammad, A. Fatima, *J. Biosci. Med.*, 2 (2014) 37.
- D. Wang, X. Zhang, S. Luo, S. Li, *Adv. Mat. Phy. Chem.*, 2 (2012) 63.
- I. M. Hamouda, H. A. Elkader, F. Manal, Badawi, *J. Biomat. Nanobiotech.*, 2 (2011) 329.
- E. Paulsamy, P. Ayyappan, R. K. Seenivasan, *J. Chem. Pharma. Res.*, 7(10) (2015) 165.