

SYNTHESIS AND CHARACTERISATION OF NEW LOW-COST ION-EXCHANGERS PREPARED FROM PLANT MATERIAL ENICOSTAMA AXILLARE , LAM.

R.K.SEENIVASAN¹, P.BHUVANESWARI², D.RAGAVAN³

¹Department of Chemistry, Government Arts College, Melur, Madurai, Tamilnadu

² Department of Chemistry, E.M.G Yadhava Women's college, Madurai, Tamilnadu,

³Department of Chemistry, Raja Doraisingam Government Arts College, Sivgangai, Tamilnadu,

ABSTRACT

A low cost activated Sulphonated Enicostama Axillare, Lam. (SEAC) were blended with Resorcinol- Formaldehyde resin (RFR) in varying amount of percentage weight by using of an ion exchange techniques in aqueous solutions. The low cost ion exchangers (IERs) are used for the removal of some selective metal ions such as Na⁺, Ca²⁺, Cu²⁺, Mg²⁺, Zn²⁺, Cd²⁺ and Pb²⁺. The properties of the blends were determined and compared with the parent resin without SEAC content. It was found that the ion-exchange capacity or cation exchange Capacity (CEC) of the composite resins decreased with increasing the percentage of blending PFR matrix with SEAC. The prepared materials (PFR, composite sand SEAC) were characterized by FT-IR spectra. The composites up to 30% (w/w) blending of PFR with SEAC retain almost all the essential properties of the original PFR (parent resin). Since Enicostama Axillare a freely available plant material, the blended composites of PFR with SEAC could be used as low cost ion exchangers without affecting the physicochemical, CEC, thermal and spectral properties of the original parent CR viz., PFR.

INTRODUCTION

Many investigators have introduced condensate resin which is used as an IER. Phenolic resin, sulphonated phenol-formaldehyde, sulphonated resorcinol-formaldehyde sulphonated polystyrene-divinyl benzene and polyacrylonitrile are the major organic binding matrices which are used for preparing such condensate resins [1, 2]. Many ion-exchangers are of petroleum origin and hence there is a continual increase in their cost. Hence, there is a timely need to synthesise low-cost ion exchange resins (IERs) and lower the cost of IERs by blending it with sulphonated carbons (SCs) prepared from plant materials. Earlier studies in literature 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 [3], saw dust [4], spent coffee [5], cashew nut husk [6], wheat husk [7], turmeric plant [8], spent tea, gum tree bark [9], *Accacia nilotica* [10], and Egyptian bagasse pith [11]. Similarly, the research studies have also been reported in which substituted phenol-formaldehyde resin matrix was blended with sulphonated charcoal obtained from coconut fiber (resorcinol-formaldehyde) [12], coconut shell (p-cresol-formaldehyde) [13] and *curcuma longa* (resorcinol-formaldehyde) [14]

The present study is aimed at to synthesise and characterise new condensate ion exchangers of resorcinol-formaldehyde ($C_6H_4(OH)_2 - HCHO$ type) cationic matrices blended with Sulphonated Enicostama Axillare,, Carbon (SEAC) and to determine the column / cation exchange capacity (CEC) or ion exchange capacity (IEC) for some selective metal ions. The effect of particle size and chemically and thermally treated IER on CEC was studied. Regeneration level was studied with NaCl (brine) solution..

MATERIALS

Resorcinol and formaldehyde used in the present study were of Fischer reagents (India). AR grade of con. sulphuric acid (Sp.gr.= 1.82) was used. The plant *Enicostama Axillare*, is freely available in India. The Stick of the plant was locally collected, cleaned, dried and cut into small pieces of about 0.5 cm length.

PREPARATION OF IERS

Enicostama Axillare, (500g) were cut into small pieces and then carbonised and sulphonated by con. sulphuric acid (500mL) and kept at room temperature ($30 \pm 1^{\circ}\text{C}$) for 24 h and heated at 90°C in a hot air-oven for 6 h. It was then cooled, washed with distilled water 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°C for 12 h. It is labeled as SEAC. The Resorcinol Formaldehyde resin (RFR) and the condensates containing various percentages (*w/w*) of sulphonated *Enicostama Axillare*, carbon (SEAC) as 0, 10, 20, 30, 40 and 50 % (*w/w*), respectively were prepared as per the method described in literature [7, 10-13] and labelled as RFR, EA1, EA2, EA3, EA4 and EA5. These resin and condensates were sieved into 210 – 300 micron (Jayant sieve, India) for further characterisation.

INSTRUMENTAL STUDIES

FT-IR spectral data of RFR (pure resin, 100%), condensate containing 30% (*w/w*) of SEAC(EA3) and pure sulphonated *Enicostama Axillare*, carbon (SEAC) were recorded PerkinElmer, Make: Spectrum RX I with KBr pellets.

PHYSICO-CHEMICAL PROPERTIES

The various physico – chemical properties like absolute density – dry (toluene medium) and wet (water medium), percentage of gravimetric swelling, percentage of attritional breaking and CEC

have been determined as per the literature methods [4, 7, 9, 15 16]. The effect of particle size, chemical and thermal stability of the RFR and condensates on CEC was also determined [11].

RESULTS AND DISCUSSION

The data given in Table 1 reveal that the experimental and theoretical composition of SEAC in the condensates (EA1 – EA5) is in good agreement with each other. The results are similar to those obtained by Sharma *et al.*[3]. This indicates that the methods adopted for the synthesis of RFR and condensates (EA1–EA5) are more reliable and reproducible.

IR spectral data are shown in Table 2 indicate the appearance of absorption band at 1022-1082 cm^{-1} (S = O str.) 1161 -1267 cm^{-1} (SO_2 sym str.) and 482-599 cm^{-1} (C-S str.) in RFR (pure resin), condensate resin blended with 30% (*w/w*) SEAC (EA3) and pure (100 %) SEAC which confirm the presence of sulphonic acid group (Fig.1). A broad absorption band which appeared at 3186-3273 cm^{-1} (bonded –OH str.) indicates the presence of phenolic and sulphonicacid –OH group in the IERs. The appearance of absorption band at 1588-1612 cm^{-1} (C-C str.) confirms the presence of aromatic ring in RFR, EA3 and pure SEAC. The absorption band at 1396-1465 cm^{-1} (- CH_2 def.) confirms the presence of – CH_2 group in the samples. The weak absorption band at 880-892 cm^{-1} (-CH- def.) in samples indicate that the phenols are tetra substituted.

The data given in Table. 3 show that the absolute density values in both hydrated (wet) and dehydrated (dry) states decrease steadily from pure resin to 50 % (*w/w*) of SEAC (EA5) in condensate resin and then finally to SEAC (100% pure). This indicates that RFR and the condensates (EA1 – EA5) are more closely packed [4-11]. It is found that the absolute density of 100% SEAC possesses only 42.49 and 40.42% of density of RFR in hydrated (wet) and dehydrated (dry) states, respectively. This result indicates that SEAC also has closely packed structure [15, 16].

The values of absolute density of RFR and condensate in dry and wet form depend upon the structure of resin and its degree of cross-linking and ionic form [17-19]. Hence, the high density values are obtained for the condensate resins. The values of density (both wet and dry densities) presented in Table.3 indicate high degree of cross-linking and hence the condensates are suitable for making columns for treating polar and non-polar effluents.

Moreover, the wet and dry density values for each sample are somewhat (within 6%) close to each other, which indicate that the samples may be macrorous in nature [20]. This also reveals that there is no considerable decrease in absolute density in both hydrated and dehydrated states upto 30% (*w/w*) of blending of SEAC with RFR. It indicates that they also 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 [21-23].

The data given in Table.3 also indicate that the percentage of gravimetric swelling decreases from RFR (88.08%) to SEAC (45.23%). It indicates that the % gravimetric swelling values for RFR and condensates are not as high as compared to that of the conventional gel type IERs indicating rigidity in the matrix and therefore the pores of condensates are of non-gel type and macroporous [15]. SEAC has a gravimetric swelling capacity of only 44.77 % as compared to that of RFR. This extremely low value of % swelling may be due to certain rigidity in its matrix. The blending of RFR with 30% (*w/w*) of SEAC reduces the gravimetric swelling value as 76.03% of that of the (100 % pure) RFR, thus decreasing 20.23% of gravimetric swelling compared to that of the (100% pure) RFR. 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 [16].

The values of attritional breaking (in%) presented in Table.3 also represent the stability of

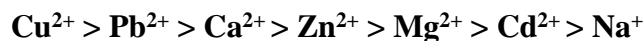
the resin which increase from RFR to SEAC. Therefore, the mechanical stability is good upto blending of RFR with 30% (w/w) SEAC. This observation also shows the possibility of formation of resin in the capillaries of the sulphonated carbon (SEAC) particles [7-9], during the blending of cationic matrices (RFR) with SEAC.

Solubility data indicate the chemical stability of the IERs in various solvents and reagents. It reveals that RFR, condensates and SEAC are practically insoluble in almost all the solvents and reagents like con. H₂SO₄, HCl, HNO₃, CH₃COOH, CCl₃COOH, CH₃OH, C₂H₅OH, CH₃CHO, CHCl₃, CCl₄, CS₂, C₆H₆ and C₆H₅CH₃, except 20% (w/v) NaOH solution. Therefore, it may be concluded that RFR and the condensates are having high degree of cross-linking in the sample structure *i.e.*, the basic polymeric unit has mostly high molecular weight fractions or at least the absence of very low molecular weight fractions in it [15, 21]. Hence, these condensates can be used as ion exchangers for treating non-aqueous effluents also [10]. At the same time the samples are partially soluble in 20% (w/v) NaOH solution. This indicates the presence of phenolic groups in them. Hence, the industrial effluent having high alkalinity cannot be treated by these ion exchange materials. The insolubility of the IERs, even in the trichloroacetic acid express the rigidity *i.e.*, high degree of cross- linking.

Cation / column exchange capacity (CEC) or Ion exchange capacity (IEC) data shown in Table.4 indicate that the CEC value decreases when the % (w/w) or content of SEAC in RFR increases. Fig.2 represents the variations of CEC for various condensates and metal ions. The value of relative ion exchange capacity (IEC) of individual metal ions depends upon the atomic radius or atomic number [24-26]. At the same time the CEC value 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 CEC for a particular metal salt solution [17,18].

On comparing the CEC values of condensates with that of the CEC values of RFR (Fig.2) it is found that blending of SEAC with RFR decreases its CEC value (Table.4). Blending of RFR with 30%(w/w) SEAC(EA3) has CEC values 74.22-88.52% for the exchange of H⁺ ions with the Cu²⁺, Zn²⁺, Pb²⁺, Cd²⁺, Ca²⁺, Mg²⁺ and Na⁺ ions compared to that of RFR. The maximum and minimum values of % of relative ion exchange capacity of condensates are for Cu²⁺ ions and for Na⁺ ions, respectively. This is due to the reason that the blending of RFR with SEAC upto 30% (w/w), does not affect the CEC value for metal ions to a greater extent. The results conclude that, RFR could be blended up to 30% (w/w) of SEAC and the condensates thus obtained could be new and cheap IERs, which could be used for water and wastewater treatment especially for the removal of metal ions from the industrial effluent.

From the CEC data given in Table.4, the cation exchange capacity of the samples for various metal ions was found to decrease in the following order:



The selectivity order of metal ions *i.e.*, orders of CEC value also depends upon the ionic potential and the hydrated atomic radius of the metal ions in solution [18]. The order of exchange affinities of various metal ions is not unique to ion exchange system. Only under dilute conditions Hofmeister or lyotropic series [27] is obeyed. But, under high concentration it is different [27]. It is equally important to note that the relative behaviour of these ions for other ionic phenomena do not obey the affinity order under the same condition [28,29]. The observed order in the present study is different from that of the Hofmeister or lyotropic series [27]. This may be 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 [19]. This indicates that these condensates can partially replace commercial IERs in making the low-cost ion exchangers for industrial

applications.

CONCLUSION

It is concluded from the results of the present study that RFR could be blended upto 30% (w/w) of SEAC, without affecting its spectral, thermal and physico-chemical properties. CEC values of these CERs are estimated. CEC values of various metal ions of condensates upto 30% (w/w) SEAC are found to be very close to the RFR. Hence, blending of RFR with SEAC to get condensates will definitely lower the cost of IER.

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TABLE 1 AMOUNT OF REAGENTS USED FOR RFR AND COMPOSITE RESINS

| Sample | % of SEAC In IER (cal) | Amount of reagent used | | | | Yield (gm) | % of SEAC in IER (obs) |
|--------|------------------------|------------------------|-----------|---|-----------|------------|------------------------|
| | | Resorcinol (ml) | HCHO (ml) | Conc. H ₂ SO ₄ (ml) | SEAC (gm) | | |
| RFR | 0 | 10.0 | 11.5 | 12.5 | 0 | 16.00 | 0 |
| EA1 | 10 | 10.0 | 11.5 | 12.5 | 1.77 | 17.06 | 10.37 |
| EA2 | 20 | 10.0 | 11.5 | 12.5 | 4.00 | 20.47 | 19.54 |
| EA3 | 30 | 10.0 | 11.5 | 12.5 | 6.86 | 25.32 | 27.09 |
| EA4 | 40 | 10.0 | 11.5 | 12.5 | 10.67 | 30.34 | 35.16 |
| EA5 | 50 | 10.0 | 11.5 | 12.5 | 16.00 | 34.69 | 46.12 |
| SEAC | 100 | ----- | ---- | ---- | ---- | ---- | ---- |

TABLE 2 FT-IR SPECTRAL DATA OF RFR, EA3 AND SEAC ($\bar{\nu}$ in cm⁻¹)

| Group | RFR | EA3 | SEAC |
|---------------------------|------|------|------|
| S = O str. | 1022 | 1074 | 1082 |
| SO ₂ sym. str. | 1161 | 1207 | 1267 |
| C – S str. | 599 | 646 | 482 |
| Bonded OH str. | 3273 | 3186 | 3200 |
| CH ₂ – def. | 1465 | 1460 | 1396 |
| C – C str. | 1612 | 1612 | 1588 |

TABLE.3 PHYSICO CHEMICAL PROPERTIES OF CATIONIC EXCHANGE RESINS AND PURE CARBON SEAC

| IERS | % of SEAC in RFR | Density g/mL | | % of gravimetric swelling | % of attritional Breaking |
|-------|------------------|--------------|------|---------------------------|---------------------------|
| | | Wet | Dry | | |
| RFR | 0 | 2.52 | 2.64 | 88.08 | 9.45 |
| EA1 | 10 | 1.92 | 2.16 | 75.08 | 11.57 |
| EA 2 | 20 | 1.48 | 1.73 | 73.23 | 13.31 |
| EA 3 | 30 | 1.34 | 1.67 | 68.52 | 19.78 |
| EA 4 | 40 | 1.21 | 1.66 | 61.78 | 23.08 |
| EA 5 | 50 | 1.16 | 1.23 | 53.08 | 27.67 |
| SEA C | 100 | 1.05 | 1.14 | 45.23 | 31.24 |

TABLE.4 CATION EXCHANGE CAPACITIES OF H⁺ FORM OF RFR, COMPOSITE RESINS AND SEAC

| Sample | % of SEAC in composite resin | Cation exchange capacity in m.mol.g ⁻¹ (0.1Msolution) | | | | | | |
|--------|------------------------------|--|------------------|------------------|------------------|------------------|------------------|------------------|
| | | Na ⁺ | Ca ²⁺ | Mg ²⁺ | Zn ²⁺ | Cu ²⁺ | Cd ²⁺ | Pb ²⁺ |
| RFR | 0 | 0.799 | 1.701 | 1.545 | 1.590 | 1.682 | 0.845 | 1.832 |
| EA1 | 10 | 0.776 | 1.653 | 1.493 | 1.542 | 1.673 | 0.831 | 1.654 |
| EA2 | 20 | 0.749 | 1.601 | 1.463 | 1.528 | 1.664 | 0.781 | 1.629 |
| EA3 | 30 | 0.684 | 1.542 | 1.380 | 1.487 | 1.607 | 0.753 | 1.594 |
| EA4 | 40 | 0.513 | 1.314 | 1.205 | 1.301 | 1.521 | 0.471 | 1.481 |
| EA5 | 50 | 0.409 | 1.119 | 1.181 | 1.273 | 1.293 | 0.463 | 1.287 |
| SEAC | 100 | 0.078 | 0.684 | 0.623 | 0.658 | 0.792 | 0.081 | 0.711 |

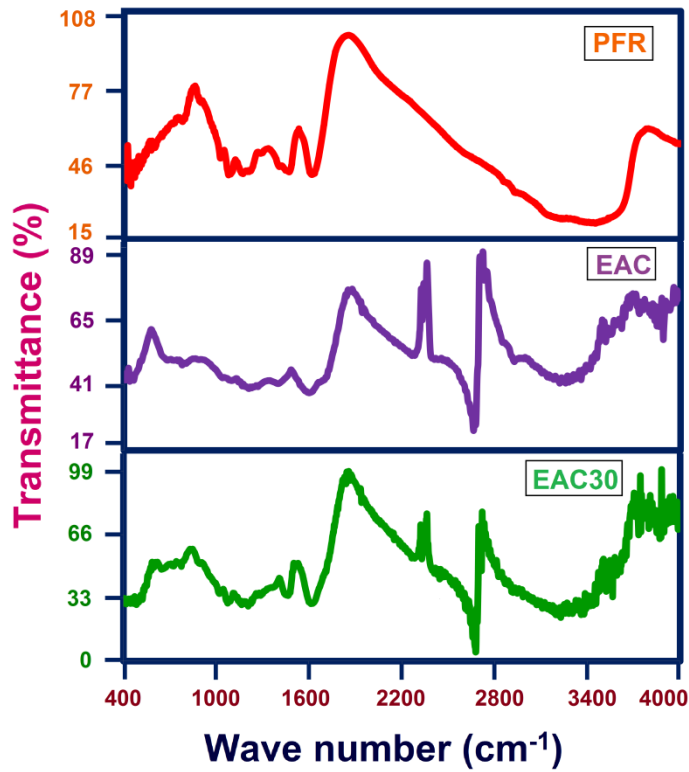


FIG.1 FT-IR SPECTRA OF RFR, BLENDED WITH 30% (W/W) OF SEAC (EA3) AND PURE SEAC

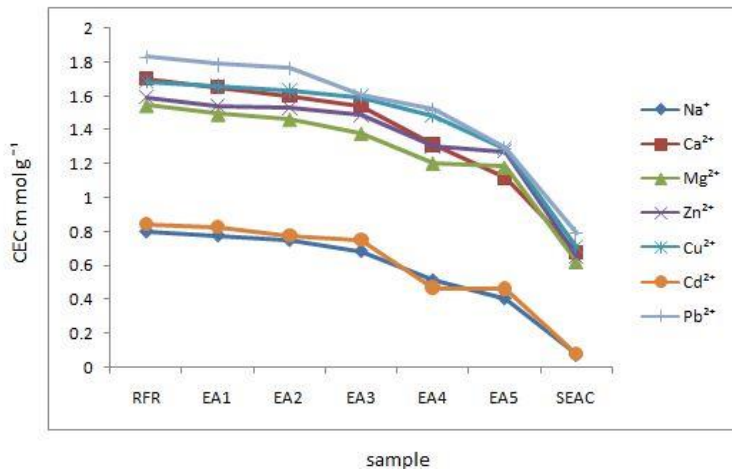


FIG.2 CATION EXCHANGE CAPACITY OF H⁺ FORM OF RFR, (EA1-EA5) AND SEAC FOR VARIOUS METAL IONS AT 303 K