Synthesis and Characterization of New Ion-Exchange Resin Prepared from the plant Morinda Citrifolia

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Abstract

The simple method of prepare the cationic resins (CRs) from polycondensation of sulphonated *Morinda citrifolia* Carbon (SMCC) with Phenol-Formaldehyde resin (PFR) as a cross linking agent has been reported. A few composite ion exchangers were prepared by varying the amount of SMCC in the blends from 0 to 100% *(w/w)*. The properties of the blends were determined and compared with the parent resin without SMCC 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 SMCC.

The composites up to 20% *(w/w)* blending of PFR with SMCC retain almost all the essential properties of the original PFR (parent resin). Since *Morinda citrifolia* a freely available plant material, the blended composites of PFR with SMCC could be used as low cost ion exchangers without affecting the physicochemical, CEC, thermal and spectral properties of the original parent CR viz., PFR.

1.0 INTRODUCTION

Some of the chemicals and non-biodegradable / toxic heavy metal ions will penetrate into the environment where a certain number of them will eventually affect all the forms of life including human beings. Many heavy metal ions will enter into water sources, because of the existing inadequate treatment and disposal methods. Considering the industrial wastewater treatments, **ion exchange** is an appropriate technique for the removal and recovery of heavy metal ions, as it is employed in the separation and concentration of ionic materials from liquids [1]. Many commercial resins (CRs) owe their origin to petroleum products and there is a continual increase in their cost owing to the scarcity of petroleum reserves. Difficulty also exists in its procurement. Therefore, there is an urgent need to find out the new low-cost ion exchange resins (IERs) and reduce the cost of IERs. Such types of low-cost ion exchangers could be obtained by blending the IER with SC obtained from cheaper and freely available plant materials containing phenolic groups in it. Attempts have been made in earlier studies to prepare cheaper condensate cationic resins (CRs) by partially blending the macroreticular phenol-formaldehyde sulphonic acid resin (PFSAR) *viz.,* the cationic matrices (CMs) with SCs prepared from natural products like, coal [2], saw dust [3], spent coffee [4], cashew nut husk [5], wheat husk [6], turmeric plant [7] , spent tea, gum tree bark [8], *Accacia nilotica* [9] and Egyptian bagasse pith [10-14]. Special processes using selective IERs are also available in literature for the removal and recovery of precious metals [15].

The aims and objectives of the present work are to determine the optimum conditions for the preparation of condensates obtained by blending CMs of PFSAR with various % (*w/w*) of Sulphonated *Morinda citrifolia* Carbon (SMCC) to characterize the new condensate of sulphonated cationic exchangers (CEs) and to estimate the column / cation exchange capacity (CEC) or ion exchange capacity (IEC) for some selective metal ions. The effect of particle size, chemical, treatment on CEC has been studied. The regeneration level of Ca^{2+} loaded resin is studied with NaCl (brine) solution.

2.1 EXPERIMENTAL

2.1.0 Materials

The raw/plant material used in the present study was *Morinda citrifolia*, in English-Indian Mulberry, in Tamil-Manjanathi and in Hindi-Achi. This is a plant material freely available in Tamil Nadu, India. 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 and reagents were of chemically pure grade (AnalaR) procured from Fisher chemicals, India.

2.1.1 Methods

Morinda citrifolia. (500g) have been carbonised and sulphonated by con. sulphuric acid, washed to remove excess free(tested with $BaCl_2$ solution) acid and dried at 70^0C for 12 h. It was labeled as SCNC. The method followed was similar to the reported one for preparing SCs from plant materials [6-8].

Pure phenol - formaldehyde resin (PFR) was prepared according to the literature method [3, 6 - 8]. It was then ground, washed with distilled water and finally rinsed with double distilled (DD) water to remove excess free acid, dried, sieved (210 - 300 μm) using Jayant sieves (India) and preserved for characterisation [3,6-8,11]. The phenol-formaldehyde resin (100 % pure resin) was labeled as PFR.

The condensates of PFR with various % (*w/w*) of SMCC were obtained as per the method reported in literature [3, 6 - 8]. The products with 10, 20, 30, 40 and 50% (*w/w*) of SMCC in the condensates, respectively are labeled as MC1, MC2, MC3, MC4 and MC5. A separate sample of SMCC (100 % pure) was also subjected to the characterisation studies.

2.1.2 Characterization of Samples

FT-IR spectral data of pure resin (PFR), condensate obtained by blending of PFR with 20% *(w/w)* of SMCC and SMCC (100 % pure) were recorded by using PerkinElmer, Make: Spectrum RX I with KBr pellets. To establish the thermal degradation of the samples, TGA and DTA traces were obtained for PFR and condensate (MC2) by using Perkin Elmer Pyris 1TGA. The surface morphologies of synthesized IERs were studied using a scanning electron microscope (SEM, JEOLJSM 6390). . Characterisation of samples was carried out, following the methods reported in literature [3, 6-11].

The values of cation exchange capacity (CEC) were determined by using standard titration techniques as per the literature method [16, 17]. The effect of particle size, chemical and thermal stability of the PFR and condensates on CEC was also determined [18].

After the exchange of H^+ ion by the metal ions, the regeneration level of the condensates loaded with a metal ion (especially Ca^{2+}) were determined by using NaCl (brine) solution.

3.0 RESULTS AND DISCUSSION

3.1. Synthesis of Condensates

The experimental (obs) and theoretical (cal) composition of SMCC in the condensates (MC1 –MC5) are in good agreement with each other (Table 3.1). The results are similar to those obtained by Sharma *et al.* [2]. This indicates that the preparative methods adopted for the synthesis of PFR and its condensates (MC1 –MC5) are more reliable and reproducible.

Table 3.1 Amount of reagent used and yield of PFR, condensates (MC1 –MC5) prepared by blending of PFR with SMCC

Sample	% of SMCC in IER	Amount of reagents used			SMCC (g)	Yield (g)	% of SMCC in IER(Obs)
		Phenol (g)	Formaldehyde (mL)	Con.H_2SO_4 (mL)			
PFR	0	10.0	11.5	12.5	0	17.5	0
MC1	10	10.0	11.5	12.5	1.94	18.20	10.51
MC2	20	10.0	11.5	12.5	4.38	21.11	20.28
MC3	30	10.0	11.5	12.5	7.50	23.40	30.99
MC4	40	10.0	11.5	12.5	11.66	27.02	40.77
MC5	50	10.0	11.5	12.5	17.50	33.68	51.54
SMCC	100	-	-	-	-	-	100

3.2. Characterization by Instrumental Studies

FT-IR spectral studies are used to confirm the stretching frequencies of various functional groups and to identify the ion exchangeable groups [19] present in IER. The appearance of absorption bands at 1036-1049 cm^{-1} (S = O str.) 1152-1228 cm^{-1} (SO_2 sym. str.) and 572-611 cm^{-1} (C – S str.) in PFR (pure resin), condensate MC2 and pure SMCC (100 %) confirm the presence of sulphonic acid group (Fig. 3.1A, B and C). The relevant data are given in Table 3.2. The data also indicate the presence of phenolic groups.

Table 3. 2 FT-IR spectral data of PFR, condensate with 20% (*w/w*) of SCNC and pure SCNC (in cm^{-1})

Group	PFR	Composites CN2	Pure SCNC
S = O str.	1049	1037	1036
SO_2 sym. str.	1168	1152	1228
C – S str.	611	609	572
Bonded OH str.	3385	3392	3063
CH_2 – def.	1473	1467	1596
C – C str.	1641	1625	1718
C - H def.	887	891	642
C-C def.	858	856	781

SO_2assy.	1338	1364	1315

The appearance of a broad absorption band at 3063-3392 cm^{-1} (bonded –OH str.) indicates the presence of phenolic and sulphonic-OH (due to -SO_3H) groups in the samples. The appearance of an absorption band at 1641-1718cm^{-1} (C-C str.) confirms the presence of aromatic ring in PFR, condensate MC2 and pure SMNC. The absorption band at 1467 – 1596 cm^{-1} (-CH_2-def.) confirms the presence of –CH_2 group in the samples. The weak absorption band at 642 – 891cm^{-1}(-CH def.) noted in samples indicate that the phenols are tetra substituted.

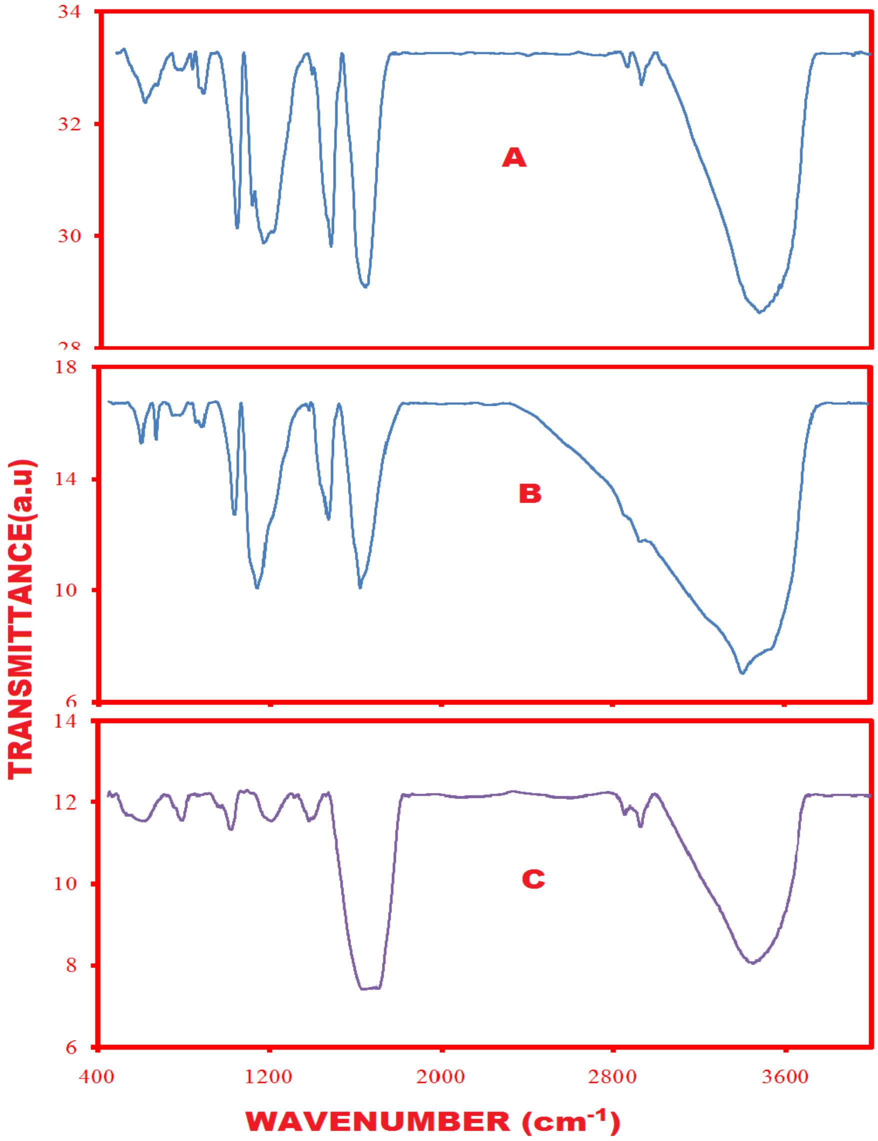

Fig. 3. 1 FT-IR Spectra of (A) PFR, (B) PFR blended with 20 % (*w/w*)

SMCC in condensate(MC2) and (C) SCNC (100% pure)

3. 3. Physico – Chemical Characteristics

The absolute density (Table 4.3) values in both hydrated (in water) and dehydrated (in toluene) states decrease steadily from PFR (100 % pure resin) to 50 % (*w/w*) SMCC in condensate (MC5) and then finally to SMCC (100 % pure SC). This indicates that PFR and the condensates (MC1 – MC5) are more closely packed [3-10]. It is found that the absolute density of 100% SMCC possess only, 42.94% and 45.75% of density of PFR in hydrated (wet) and dehydrated (dry) states, respectively. This indicates that SMCC also has closely packed structure [15] similar to condensate.

The values of density of condensates in dry and wet states depend upon the structure of the basic resin unit (PFSAR), its degree of cross-linking and ionic form [21]. Hence, high-density values are obtained for these IERs. The values of density (both wet and dry forms) presented in Table 3.3, indicate the high degree of cross-linking, and hence the condensate resins are suitable for making columns for treating polar and non-polar effluents. Moreover, the wet and dry density values are close to each other, which indicate that the IER samples may be macro porous in nature. From the data given in Table 3.3, it is clear that there is no considerable decrease in absolute density in both hydrated (wet) and dehydrated (dry) states upto 20% (*w/w*) blending of SMCC with PFR. In the condensates, indicating that they also have similar closely packed structures with high degree of cross-linking and hence they are suitable for making ion exchange columns for polar and non-polar liquids of high density [18].

The percentage of gravimetric swelling (Table 3.3) decreases from PFR (81.16%) to SMCC (42.41%). Condensates have intermediate values of gravimetric swelling (%). It indicates that the values of gravimetric swelling (%) for PFR, and condensates are not as high as compared to conventional gel type IERs, indicating rigidity in the matrix and therefore the pores of condensates are of non-gel type and macro reticular[15]. SMCC has a swelling capacity of only 46.71%, as compared to that of PFR. This extremely low value of percentage gravimetric swelling may be due to certain rigidity in the matrix of the resin. The blending of PFR with 20% (*w/w*) of SMCC has the gravimetric swelling value as 76.55% of that of PFR, thus decreasing 24.45% of swelling compared to that of PFR (100 % for pure resin).

Table 3. 3. Physico-chemical properties of PFR, SMCC and condensates (MC1-MC5)

IERs	% of SMCC in IER	Density (g/mL)		Percentage	
		Wet	Dry	Gravimetric swelling	Attritional breaking
PFR	0	2.02	1.98	81.16	9.24
MC1	10	1.72	1.70	71.86	15.00
MC2	20	1.60	1.58	62.00	18.23
MC3	30	1.48	1.38	58.25	20.92
MC4	40	1.32	1.26	52.22	26.45
MC5	50	1.28	1.12	48.67	38.63
SMCC	100	1.18	0.98	41.32	47.21

The decrease in % gravimetric swelling is attributed due to the loss of polarity and porosity in condensates. Thus, the condensates may prove to be highly suitable where they are required to withstand a large osmotic shock during its application for the removal of metal ions.

The values of percentage of attritional breaking (Table 3.3) represent the stability of the IER, which increase from PFR to SMCC. The data reveal that the mechanical stability is good upto 20% *(w/w)* blending of SMCC (20.58%) with PFR. This observation also shows the possibility of formation of resin in the capillaries of the sulphonated carbon (SCNC) particles [6-8].

The solubility of the IER samples in various organic solvents and inorganic reagents reveals that PFR, condensates (MC1-MC5) and SMCC are practically insoluble in almost all the solvents and reagents, except in 20 % (*w/w*) NaOH. The insolubility of the resin samples even in the highly polar tricholoroacetic acid express its rigidity *i.e.,* high degree of cross-linking within the molecules. Therefore, it may be concluded that PFR, and the condensates are having high degree of cross-linking in the sample structure *i.e.*, the basic polymer unit has mostly high molecular weight fractions or at least the absence of very low molecular weight fractions in them [15] . Hence, IERs can be used as ion exchangers for treating non-aqueous effluents also [9]. At the same time, the samples are partially soluble in 20% (*w/w*) NaOH solution, which indicates the presence of phenolic groups in them. Hence, these ion exchange materials cannot treat the industrial effluent having high alkalinity (above pH 7).

3. 3. 1 Cation Exchange Capacity

Cation/ Column exchange capacity (CEC) or Ion exchange capacity (IEC) values given in Table 3.4 indicate that, the CEC value decreases when the content of SMNC *(%w/w)* in PFR increases.

Table 3.4. Cation exchange capacities of PFR, condensates (MC1-MC5) and SMCC for selective metal ions (0.1 M) at 303 K

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	1.378	1.694	1.583	1.745	1.663	1.105	0.923
MC2	20	1.211	1.611	1.5215	1.553	1.588	1.122	0.800
MC3	30	1.174	1.401	1.402	1.234	1.420	1.035	0.684
MC4	40	1.100	1.364	1.321	1.143	1.311	1.000	0.514
MC5	50	1.008	1.231	1.264	1.023	1.215	0.940	0.401
SMCC	100	1.000	1.100	1.129	0.954	1.023	0.831	0.300

The relative ion exchange capacity (IEC) of individual metal ions depends upon the atomic radius or atomic number [22]. At the same time, the CEC value also depends upon the valency of the ions, the concentration of metal ion in the influent solution and the anionic part of the metal salt [23]. Inter ionic forces of attraction between anions and cations, which also plays a vital role in deciding the CEC values of metal ions for a given metal salt solution [24,25]. It is found that CEC values of IERs obtained by blending PFR with 20 % (*w/w*) of SCNC in the range of 25.85-63.81% for various metal ions *viz.,* Na^{+}, K^{+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+} and Pb^{2+} ions.

It is also noted that the condensates with 20 % (*w/w*) of SMCC (MC2) have CEC values, which are in the range of 59.05 – 90.87 % of CEC of PFR. Hence, it may be concluded that PFR could be blended upto 20% (*w/w*) of SMCC and the condensates thus obtained could be new / novel and cheap IERs, which could be used for water and wastewater treatment especially for the removal of metal ions. It is also useful in industrial applications, especially for the treatment of industrial effluent containing metal ions or desalination purpose.

From the CEC data given in Table 3.4, the CEC values of IERs are found to decrease in the following order:

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

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 [25]. The order of exchange affinities of various metal ions is not unique to ion exchange system. Only under dilute conditions Hofmeister or lyotropic series [21] is obeyed. However, under high concentration it is different [21]. It is equally important to note that the relative behaviour of these ions for other ionic phenomena deviate the affinity order under the same conditions [26]. The observed order in the present study is different from that of the Hofmeister or lyotropic series [21]. 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.

4. 0 CONCLUSION

It is concluded from the results of the present study that PFR sample could be blended upto 20% (*w/w*) of SMCC in PFR, without affecting its spectral, thermal and physico-chemical properties. CEC values of these CERs are estimated. Hence, blending of PFR with SMCC to get condensates will definitely lower the cost of IER.

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