Synthesis, Characterization, and Application of New Low-Cost Ion Exchangers

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Received 24 February 2005; accepted 20 June 2005
DOI 10.1002/app.23432

ABSTRACT: This paper represents a simple method for preparing and characterizing of low-cost ion exchangers of sulfonated carbon prepared from *Terminalia Chebula*-Retz., (family–combretaceae) as a source of cheap plant material blended with phenol-formaldehyde as a crosslinking agent. The prepared ion exchange resins (IERs) are characterized by infrared (IR) spectral and thermal studies. All the important physicochemical properties of the ion exchangers have been determined. The synthesized resins have cation exchange capacity upto 1.84 mmol g^{-1}. The rational thermodynamic equilibrium constant (ln *K*) are calculated for H^+ and Zn^{2+} exchanges on the resin having various amount of sulfonated *Terminalia Chebula* Retz. carbon (STCC). The thermodynamic parameters were calculated, and suitable explanations are given. It is concluded from the present study that PFR sample could be blended with 20% (w/w) of STCC, without affecting its physicochemical, spectral, and thermal properties. Hence blending with STCC will definitely lower the cost of the ion exchange resin. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4104–4113, 2006

Key words: synthesis; phenol formaldehyde resin; composites; blending; swelling; FTIR; TGA; selectivity; waste water treatment

INTRODUCTION

The ion exchange process is a relatively ancient discovery, which allows us to remove undesirable ions and replace them with less objectionable ions, like H^+, Na^+ and OH^-, Cl^- ions. The process and commercial application for ion exchange are less than 100 years old.[1] The modern ion exchange resins (IERs) used to date for water and wastewater treatment is about 50 years old. Although one can discover new ways to use these resins, the basic chemistry has not changed in half-a-century.[2]

The first synthetic cation exchange resin was obtained by Adams and Holmes.[3] It was shown that strongly acidic groups ($\text{—}SO^-{}_3\ H^+$) may be introduced either by sulfonation or by substitution of phenol sulfonic acid for phenol. The resultant resin could be used as IER at acidic pH value. The IER could be used in the hydrogen form.

Many investigators have introduced composite resin that is used as an IER. Phenolic resin, sulfonated phenol–formaldehyde, sulfonated polystyrene–divinyl benzene, and polyacrylonitrile are the major organic binding matrices that are used for preparing such composite resins.[4,5]

Many ion-exchangers owe their origin to petroleum products, and there is a continual increase in their cost. Hence, there is a timely need to synthesize low-cost ion exchange resins (IERs) and lower the cost of IERs by blending it with sulfonated carbons prepared from plant materials. Earlier reports available in literature revealed that the cheaper composite ion-exchangers could be prepared by partially blending the phenol-formaldehyde matrices with sulfonated carbons from coal,[6] saw dust,[7] spent coffee,[8] cashew nut husk,[9] wheat husk,[10] turmeric plant,[11] spent tea, gum tree bark,[12] *Accacia nilotica*,[13] and Egyptian bagasse pith.[14]

Ion exchange process is suitable in the treatment of wastewater containing metal ions discharged from plating and other industries.[15,16] Also, it is a convenient way to concentrate and remove the ions of valuable metals like, copper, zinc, and chromium. Special processes using selective IERs are also available for the recovery of precisious noble metals like gold, platinum, and silver.[17]

The present study is aimed at to synthesize and characterize new composite ion exchangers of PhOH—HCHO type, blended with sulfonated *Terminalia chebula*-Retz carbon (STCC) and to determine the column/cation exchange capacity (CEC) or ion exchange capacity (IEC) for some selective metal ions.

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Journal of Applied Polymer Science, Vol. 101, 4104–4113 (2006)

EXPERIMENTAL

Materials

Phenol and formaldehyde used in the present study were from Fischer reagents (India). LR grade of con. sulfuric acid (Specific gravity = 1.82) was used. *Terminalia chebula*-Retz. (family-combretaceae) plant materials, especially fruits, were locally collected and cleaned before use.

Methods

Terminalia chebula-Retz. fruits (500g) were cut into small pieces, then carbonized and sulfonated using concentrated sulfuric acid (500 mL) and kept at room temperature (30 ± 1°C) for 24 h and then heated at 90°C in a hot air-oven for 6 h. It was then cooled, washed several times with distilled water and finally with double distilled (DD) water to remove excess free acid, and dried at 70°C for 12 h. It was then labeled as STCC. The phenol formaldehyde resin (PFR) and the composites containing various percentage (w/w) of sulfonated *Terminalia chebula*-Retz. carbon (STCC; 0, 10, 20, 30, 40, and 50 (w/w))in the total blend, respectively, were prepared[7,10–13] and labeled as PFR, TC1, TC2, TC3, TC4, and TC5. These resin and composites were sieved to 210–300 μm (Jayant sieve, India) for further characterization.

Instrumental studies

The FTIR spectral data of pure resin (PFR), 10% (w/w) composite, and pure STCC were recorded with a JASCO FT-IR 460 plus FTIR 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.

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 were determined according to the literature.[7,10,12,17,18] The cation exchange capacity (CEC) and the regeneration level were studied using brine (NaCl) solutions, following the method reported in literatures.[19–24]

Equilibrium constant

The equilibrium constants (K_{eq}) of ion exchange reaction between metal ions (Zn^{2+}) and IERs were obtained according to the methods in literature.[25] The reaction equilibrium is represented as[26] follows:

$$\mathrm{R{-}SO_3^{-}H^{+}} + \mathrm{Zn^{2+}} \leftrightarrows (\mathrm{R{-}SO_3}^{-})_2 - \mathrm{Zn^{2+}} + 2\mathrm{H^{+}} \quad (1)$$

where, $\mathrm{R{-}SO_3H}$ and $(\mathrm{R{-}SO_3}^{-})_2\ \mathrm{Zn}^{2+}$ represent the free IER and metal bonded IER, respectively. Zn^{2+} is unbound metal ion concentration in solution (i.e. influent), which was measured titrimetrically.[19] The concentration of IER, i.e., total IER concentration, in eq. (1) was equal to $(\mathrm{R{-}SO_3}^{-}\mathrm{H}^{+})_{total,}$ and number IER attached to metal ions was proportional to n (n = 2)

$$[\mathrm{R{-}SO_3^{-}H^{+}}]_{total} = [\mathrm{R{-}SO_3^{-}H^{+}}]_{free} + 2[(\mathrm{R{-}SO_3^{-}})_2\mathrm{Zn^{2+}}] \quad (2)$$

$$[(\mathrm{R{-}SO_3})_2^{-}\mathrm{Zn^{2+}}] = [\mathrm{Zn^{2+}}]_{influent} - [\mathrm{Zn^{2+}}]_{effluent} \quad (3)$$

The equilibrium constant (K_{eq}) of the ion exchange reaction was calculated using the Klotz equation, from eqs. (1), (2), and (3).

$$\frac{1}{r} = \frac{[\mathrm{R{-}SO_3^{-}H^{+}}]_{total}}{[(\mathrm{R{-}SO_3^{-}})_2\mathrm{Zn^{2+}})]} = \frac{[\mathrm{RSO_3^{-}H^{+}}]_{free} + 2[(\mathrm{RSO_3^{-}})_2\mathrm{Zn^{2+}}]}{[(\mathrm{R{-}SO_3^{-}})_2\mathrm{Zn^{2+}}]} \quad (4)$$

$$\frac{1}{r} = \frac{[\mathrm{RSO_3^{-}H^{+}}]_{free}}{[(\mathrm{R{-}SO_3^{-}})_2\mathrm{Zn^{2+}})]} + 2$$

$$K_{eq} = \frac{[(\mathrm{R{-}SO_3^{-}})_2\mathrm{Zn^{2+}}][\mathrm{H^{+}}]^2}{[\mathrm{R{-}SO_3^{-}H^{+}}]_{free}[\mathrm{Zn^{2+}}]} \quad (5)$$

By substituting eq. (5) in eq. (4), we obtain

$$\frac{1}{r} = \frac{[(\mathrm{R{-}SO_3^{-}H^{+}})]_{free}[\mathrm{H^{+}}]^2}{K_{eq.}[\mathrm{R{-}SO_3^{-}H^{+}}]_{free}[\mathrm{Zn^{2+}}]_{free}} + 2 \quad (6)$$

when n = 2, according to law of mass action, $[\mathrm{H}^{+}]^2 = [(\mathrm{R{-}SO_3}^{-})_2\ \mathrm{Zn}^{2+}]$ from eq. (1)

$$\frac{1}{r} = \frac{[(\mathrm{R{-}SO_3^{-}})_2\mathrm{Zn^{2+}}]}{K_{eq.}[\mathrm{Zn^{2+}}]_{free}} + 2 \quad (7)$$

where, $(1/r) = [\mathrm{R{-}SO_3}^{-}\mathrm{H}^{+}]_{total}/[(\mathrm{R{-}SO_3}^{-})_2\ \mathrm{Zn}^{2+}]$. Batch ion exchange experiments were carried out at 303, 313, 323, and 333 K, using 20, 30, 40, 50, 60, and 70 mL of 0.1M stock solution of Zn^{2+} ions. From the initial and equilibrium concentrations, $(1/r)$ values were determined. From the plots of $(1/r)$ versus $[(\mathrm{R{-}SO_3}^{-})_2\ \mathrm{Zn}^{2+}]/[\mathrm{Zn}^{2+}]_{free}$ (plots not shown), K_{eq} was obtained from the slope value (slope = $1/K_{eq}$), and intercept value = 2. Thermodynamic parameters (ΔG^0, ΔH^0, and ΔS^0) were calculated by using van't Hoff isotherm, van't Hoff and Gibbs Helmholtz equation, respectively.

TABLE I
Amount of Reagents Used and Yields of the Composites (*Terminalia chebula* Retz.)

Sample	% of STCC in PFR (theoretical)	Amount of reagents used: Phenol (mL)	Formaldehyde (mL)	Con. H_2SO_4 (mL)	STCC (g)	Yield (g)	% of STCC in PFR (observed)
PFR	0	10.0	11.5	12.5	0.00	17.00	0.00
TC1	10	10.0	11.5	12.5	1.89	18.93	9.98
TC2	20	10.0	11.5	12.5	4.25	20.96	20.28
TC3	30	10.0	11.5	12.5	7.29	24.31	29.97
TC4	40	10.0	11.5	12.5	11.33	28.02	40.45
TC5	50	10.0	11.5	12.5	17.00	33.64	50.54
STCC	100	—	—	—	—	—	100

$$\Delta G^0 = -RT \ln K_{eq.} \tag{8}$$

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \tag{9}$$

$$\Delta S^0 = (\Delta G^0 - \Delta H^0)/T \tag{10}$$

RESULTS AND DISCUSSION

Synthesis of IERs

The data given in Table I reveal that the experimental and theoretical composition of STCC in the composites (TC1–TC5) are in good agreement with each other. The results are similar to those obtained by Sharma et al.[6] This indicate that the methods adopted for the synthesis of PFR and composites (TC1–TC5) are more reliable and reproducible.

Characterization of IERs

Ir spectral studies

The IR spectral data are given in Table II. It indicates the appearance of absorption bands at 1038–1052 cm^{-1} (S═O str.), 1163–1191 cm^{-1} (SO_2 sym str.), and 575–755cm^{-1} in pure resin (PFR), 10% composite resin, and pure STCC, confirming the presence of sulfonic acid group [Fig. 1(a–c)]

TABLE II
FTIR Spectral Data of PFR ,Composites (TC1), and STCC (ν in cm^{-1})

Group	Pure resin (PFR)	10% (w/w) STCC in PFR (AA1)	Pure STCC
S═O str.	1039	1038	1052
SO_2 sym. str.	1163	1167	1191
C—S str.	575	601	755
Bonded OH str.	3409	3405	3169
C—O str./—OH def.	1210	1210	1212
CH_2— def.	1471	1470	1443
C—C str.	1624	1642	1612
C—H def.	902	888	918

The appearance of broad absorption band at 3169–3409 cm^{-1} (bonded —OH str.) indicate the presence of phenolic and sulfonic —OH group in the samples. The appearance of absorption band at 1612–1624 cm^{-1} (C—C str.) confirms the presence of aromatic ring in PFR, 10% blending of STCC in PFR and pure STCC. The absorption band at 1443–1471 cm^{-1} (—CH_2 def.) confirms the presence of —CH_2 group in the samples. The weak absorption band at 888–918 cm^{-1} (—C—H def.) in samples indicate that the phenols are tetra substituted.

Thermal studies

TGA curves shown in Figures 2(a) and 2(b) revealed that there is a very small (6%) loss in weight for both PFR and STCC upto 80°C. This is due to the loss of moisture absorbed by resin and STCC. Between 50 and 190°C there is 20% weight loss in PFR and 15% weight loss in STCC was observed. Up to 450°C, ~57% weight loss in PFR and up to 340°C, ~35% weight loss in STCC was observed.

In Figure 2(a), DTA curve shows that two exothermic peaks were obtained for PFR, at ~80 and 466°C, respectively. At 80°C, the presence of broad peak was observed, which indicates dehydration process of resin (PFR). A peak at 466°C, indicates chemical changes of pure resin, which reflects ~57% weight loss in PFR.

DTA curve of STCC [Fig. 2(b)] shows two exothermic peaks obtained at 99 and 522°C, respectively, similar to those of PFR. Again, the first broad peak indicates the dehydration of STCC and the second moderate sharp peak indicates the chemical changes of STCC. From Figures 2(a,b), it is concluded that the limiting temperature for the safer use of PFR and STCC as ion exchangers was 80°C, since the resin degrade thermally after 80°C.

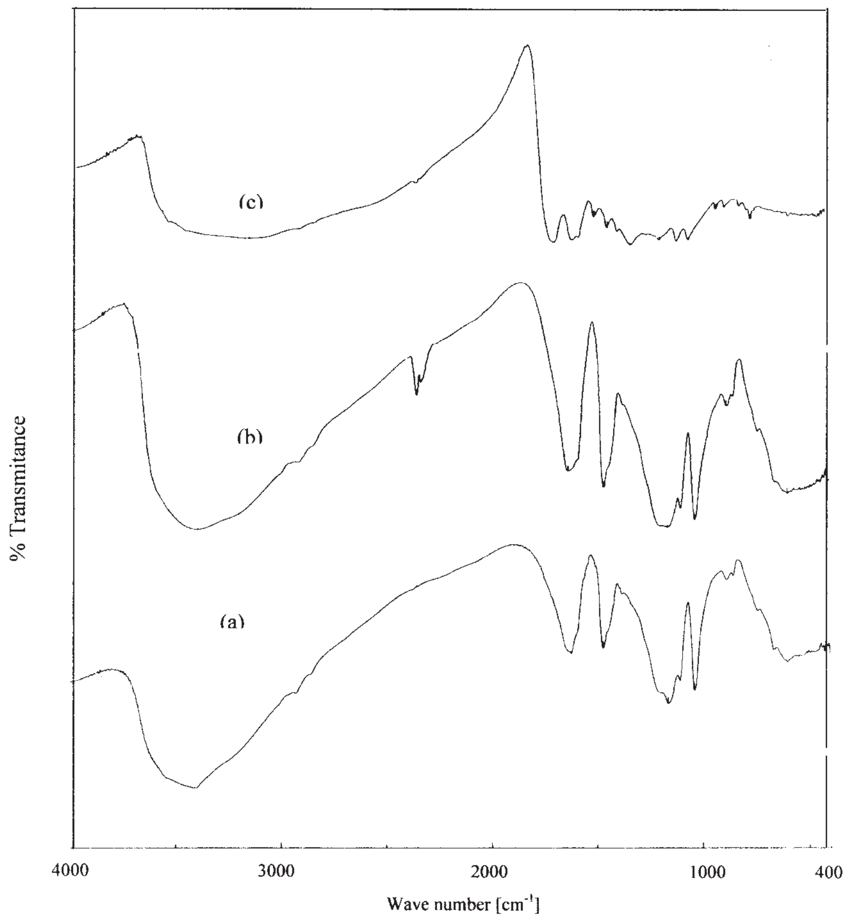

Figure 1 FTIR spectra of (a) PFR, (b) 10% (W/W) STCC in composite, and (c) pure STCC.

Physicochemical characteristics

Absolute density

The data given in Table III show that the absolute density values in both hydrated (wet) and dehydrated (dry) states decrease steadily from pure resin to 50% of (w/w) STCC in composite resin and then finally to pure STCC. This indicates that PFR and the composites (TC1–TC5) are more closely packed.[7–14] It is found that the absolute density of 100% STCC possess only 55.84 and 48.78% of density of PFR in hydrated (wet) and dehydrated (dry) states, respectively. This result indicates that STCC also has closely packed structure.[17,18]

The values of absolute density of composite resin in dry and wet form depend upon the structure of resin and its degree of crosslinking and ionic form.[25–27] Hence, the high density values are obtained for the composite resins. The values of density (both wet and dry densities) presented in Table III indicate the high degree of crosslinking, and hence the composite resins are suitable for making columns for treating polar and nonpolar effluent liquids. Moreover, the wet and dry density values for each sample are some what (within 10%) close to each other, which indicates that the samples may be macro porous in nature.[28] From the data, it is clear that there is no considerable decrease in the absolute density in both hydrated and dehydrated states up to 20% blending of PFR, with STCC in the condensates, indicating that they also have closely packed structures with high degree of crosslinking, and hence could be more suitable for making ion exchange columns for polar and nonpolar liquids of high density.[22–24]

Gravimetric swelling

The data given in Table III indicate that the percentage of gravimetric swelling decreases from PFR (85.6%) to STCC (39.7%). It indicates that the values for pure resin and composites 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 nongel type and macroreticular.[17] STCC has a gravimetric swelling capacity of only 46.4% as compared to that of PFR. This extremely low value may be due to certain rigidity in their matrix. The blending of PFR with 20% (w/w) of STCC reduces

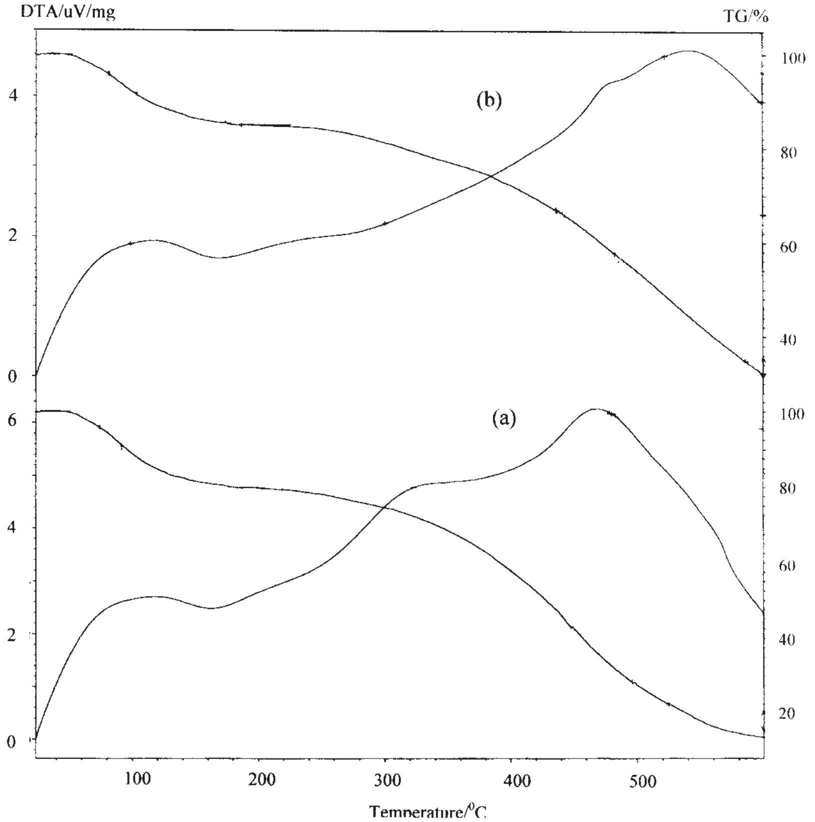

Figure 2 Thermal studies of (a) PFR, (b) 20% (W/W) STCC in composite.

the gravimetric swelling value to 84.3% of that of the pure PFR, thus decreasing 15.7% of percentage of gravimetric swelling compared to that of the pure PFR. The decrease in percentage 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 stand as a high osmotic shock.[18]

Attritional breaking

The values of attritional breaking presented in Table III also represent the stability of the resin, which decrease from pure resin to STCC. Therefore, the mechanical stability is good up to 20% (w/w) substitution of STCC in pure resin. This observation also shows the possibility of formation of resin in the capillaries of the sulfonated charcoal (STCC) particles.[10–12]

Solubility of IERs

Solubility data indicate the chemical stability of the IERs in various solvents. It reveals that PFR, composites, and STCC are practically insoluble in almost all the solvents like con. H_2SO_4, HCl, HNO_3, CH_3COOH, CCl_3COOH, CH_3OH, C_2H_5OH, CH_3CHO, $CHCl_3$, CCl_4, CS_2, C_6H_6, and $C_6H_5CH_3$, except 20% (w/v) NaOH solution. Therefore, it may be concluded that PFR and the composites

TABLE III
Physico-Chemical Properties of IERs (*Terminalia chebula*-Retz.)

Sample	% of STCC in PFR	Density ($g\ mL^{-1}$)		% of gravimetric swelling	% of attritional breaking
		Wet	Dry		
PFR	0	2.01	2.07	85.56	8.00
TC1	10	1.65	1.78	72.16	18.00
TC2	20	1.58	1.73	63.00	22.00
TC3	30	1.46	1.61	59.39	27.45
TC4	40	1.43	1.26	49.64	28.43
TC5	50	1.34	1.02	42.21	29.00
STCC	100	1.12	1.01	39.68	51.49

TABLE IV
Cation Exchange Capacities of IERs (H^+ Form) for Selective Metal Ions (*Terminalia chebula*-Retz.)

Sample	% of STCC in PFR	Cation exchange capacity in 0.1*M* effluent (mmol g^{-1})						
		Na^+	Fe^{2+}	Cu^{2+}	Ca^{2+}	Mg^{2+}	Zn^{2+}	Pb^{2+}
PFR	0	0.822	1.624	1.835	1.644	1.816	1.779	1.840
TC1	10	0.790	1.175	1.510	1.565	1.702	1.630	1.684
TC2	20	0.778	1.150	1.340	1.511	1.648	1.547	1.636
TC3	30	0.694	1.125	1.260	1.327	1.464	1.440	1.494
TC4	40	0.658	0.950	1.225	1.238	1.339	1.329	1.440
TC5	50	0.634	0.850	1.070	1.208	1.315	1.119	1.416
STCC	100	0.085	0.650	0.815	0.571	0.660	0.702	0.791

are having high degree of crosslinking in the sample structure, i.e., the basic polymeric unit has mostly high molecular weight fractions or atleast the absence of very low molecular weight fractions present in it.[17,18] Hence, they can be used as ion exchangers for treating nonaqueous effluents also.[13] At the same time the samples were partially soluble in 20% (w/v) NaOH solution, which indicate 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 resin samples even in trichloroacetic acid express the rigidity, i.e., having high degree of crosslinking in them.

Cation exchange capacity

Cation/column exchange capacity (CEC) or Ion exchange capacity (IEC) data shown in Table IV indicate

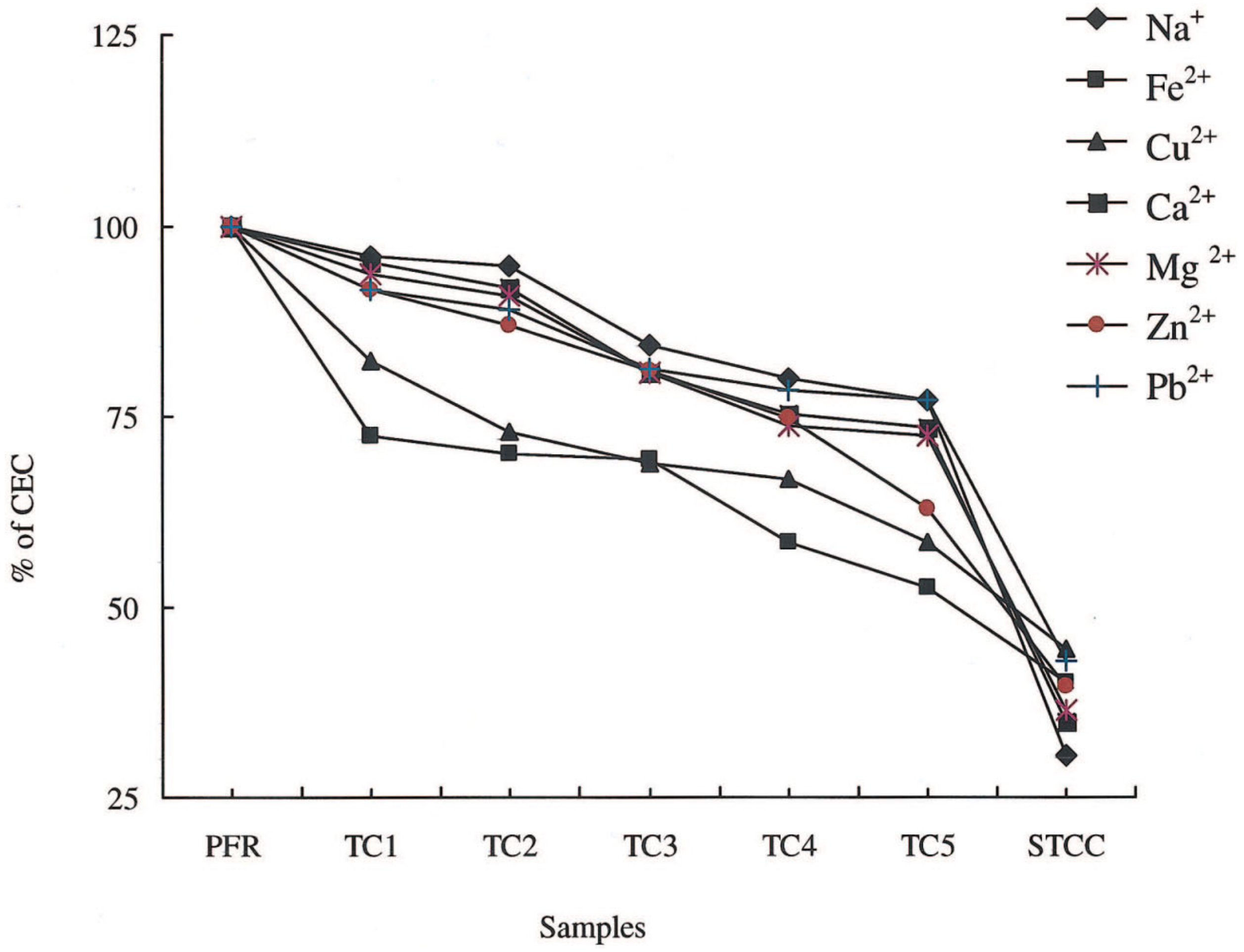

Figure 3 CEC of H^+ form of IERs for various metal ions relative to PFR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].

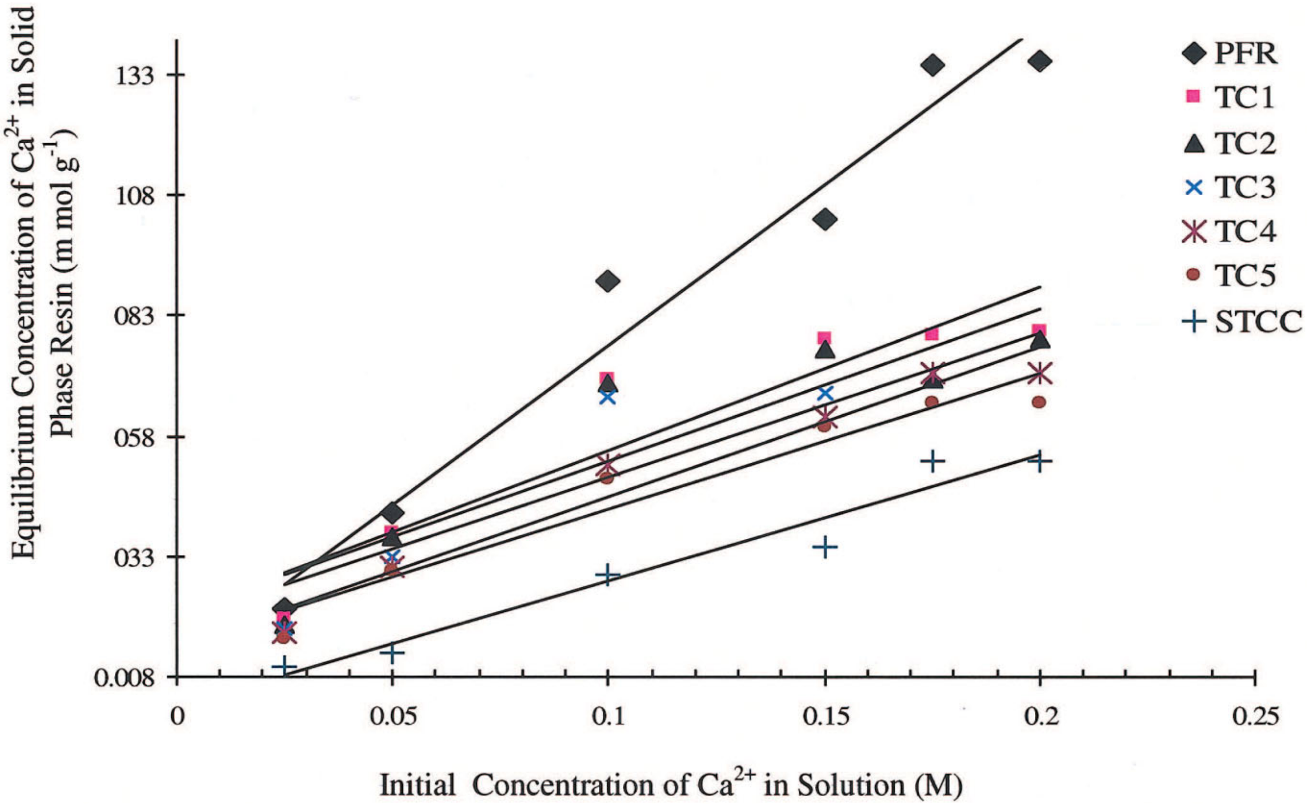

Figure 4 Effect of concentration of Ca^{2+} ions on PFR composites and STCC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].

that, the CEC value decreases when the content of STCC% (w/w) in PFR increases. Figure 3 represents the variations in percentage column capacity for various composites and metal ions.

The relative ion exchange capacity (IEC) of individual metal ions depends upon the atomic radius or atomic number.[29–32] At the same time, the CEC value also depends on the anionic part of the metal salt, i.e., interionic forces of attraction between anions and cations, which play a vital role in the CEC of particular metal salt solution.[25,26] On comparing the CEC of composites with the CEC values of PFR (taking it as 100%; Fig. 3), it is found that 10% blending of PFR by STCC decreases its CEC to about 10% (Table IV) and blending of PFR by STCC retains CEC values above 90% for the exchange of H^{+} ions in the Na^{+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, and Pb^{2+} ions and 70–83% for the exchange of Fe^{2+} and Cu^{2+} ions. Also, it is noted that the composites up to 20% of STCC retains above 90% of CEC of PFR for the exchange of Na^{+}, Ca^{2+}, and Mg^{2+} and retains 70–88% of CEC for the exchange of Fe^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} ions. Then 30% substitution by STCC in the polymeric resin leads to 68–84% of CEC of PFR (Fig. 3). The maximum value of percentage of relative ion exchange capacity of composites is for Na^{+} ions and not for Pb^{2+} ions. This is due to the reason that the blending of STCC upto 50% (w/w) does not affect the value for Na^{+} ions to a greater extent. Hence, it is more suitable for Na^{+} ions compared to other ions. However, PFR could be blended up to 20% (w/w) of STCC and the composites thus obtained would be new and cheap IERs, which could be used for water and wastewater treatment for the removal of all metal ions in general. It is useful in industrial applications, especially for the treatment of industrial effluent.

From the CEC data given in Table IV, the CEC of the samples for various metal ions was found to decrease in the following order:

$$Pb^{2+} \geq Mg^{2+} > Zn^{2+} > Ca^{2+} > Cu^{2+} > Fe^{2+} > Na^{+}$$

The selectivity order of metal ions, i.e., order of CEC values, also depends upon the ionic potential and the hydrated atomic radius of the metal ions in solution.[26] The order of exchange affinities of various metal ions are not unique to ion exchange system. Only under dilute conditions Hofmeister or lyotropic series[29] is obeyed. But under high concentration it is different.[29] It is equally important to note that the relative behavior of these ions for other ionic phenomena deviates the affinity order under the same condition.[33,34] The observed order in the present study is different from that of the Hofmeister or lyotropic series.[29] This may

TABLE V
Correlation Analysis on the Concentration of Ca^{2+} Ion by PFR, Composites, and STCC.

Sample	Correlation Coefficient	Slope	Intercept
PFR	0.988	0.700	0.0125
TC1	0.931	0.341	0.0209
TC2	0.931	0.335	0.0202
TC3	0.913	0.298	0.0198
TC4	0.975	0.306	0.0147
TC5	0.971	0.283	0.0143
STCC	0.979	0.262	0.0013

TABLE VII
Effect of Particle Size on Cation Exchange Capacity of PFR, Composites, and STCC (*Terminalia chebula*-Retz.)

Sample	Particle size micron	Column capacity (m mol g^{-1})			
		Na^{+}	Mg^{2+}	Ca^{2+}	Zn^{2+}
PFR	<210	0.785	1.409	1.047	1.325
	210–300	0.822	1.816	1.644	1.779
	300–500	0.793	1.475	1.562	1.680
	>500	0.780	1.350	1.432	1.651
TC2	<210	0.713	1.057	1.211	1.122
	210–300	0.778	1.648	1.511	1.547
	300–500	0.760	1.115	1.509	1.434
	>500	0.655	0.952	1.159	1.123

be due to the ionic strength of the metal ions, the internal structure of the polymeric matrix, and also the selectivity of the metal ions.[27]

The percentage values of CEC of pure commercial (SD) resin (100%) for exchange of H^{+} ions with Na^{+}, Fe^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, and Pb^{2+} ions in 0.1*M* solution are about 46–59% for TC1–TC5 and nearly 50% as compared to that of the pure commercial resin. This indicates that these composites can partially replace commercial IERs for making ion exchangers for industrial applications.

Effect of initial concentration of Ca^{2+} ions on CEC

The CEC increases with increase in the concentration of Ca^{2+} ion from 0.025 to 0.20*M*.(Fig. 4) It is in accordance with le Chatlier –Braun principle. For PFR, composites, and STCC, the value of IEC increases with increase in concentration of Ca^{2+} ions from 0.025 to 0.20*M*. Figure 4 shows the effect of initial Ca^{2+} concentration on the equilibrium concentration of Ca^{2+} in solid phase (resin).[35] The equilibrium load of Ca^{2+} ion in unit mass of resin linearly increases with increase in the initial concentration of Ca^{2+} ion in solution from 0.025 to 0.15*M*. Linear plots were obtained between the initial concentration (in solution) and equilibrium concentration (in resin) of Ca^{2+} ions. The values of slope, intercept, and correlation coefficient are given in Table V. Beyond 0.15*M*, a leveling effect for the values of CEC (i.e., a constant CEC value) is noticed for the metal ion at high concentrations above 0.15*M*. Hence, upto 0.15*M* concentration of solution of metal ions, the composite resins could be applied, since they act as good ion-exchangers.

Effect of stability of IERs on CEC

To test the chemical stability of IER, *viz.* PFR-composites, the samples were boiled with water, benzene, and dilute NaOH for an hour. The resulting water-boiled, benzene-boiled, and alkali-boiled samples possess CEC values almost similar to the parent/untreated resins (range 1–2%). This indicates that these samples are chemically stable (Table VI). To test the thermal stability of IER, *viz.* PFR –composites, the samples were heated to 100°C for an hour. Although the samples lose weight initially on heating, the lost weight is regained after cooling for 24 h and exposing it to air. This indicates that the IERs are thermally stable upto 100°C. The CEC values of the thermally treated resins are found to be almost similar to the untreated IER/parent resin within 1–2% (Table VI)

Effect of particle size on CEC

CEC data given in Table VII indicate that the particle size of <210μm are fine, and 300–500μm and >500μm are coarse as to cause very low ion exchange capacity compared to 210–300μm particle size. Hence, for effective IEC, the particle size should be maintained, and recommended mesh size is 210–300μm.

TABLE VI
Chemical and Thermal Effect on CEC of PFR and its Composites for Exchange with 0.1*M* Mg^{2+} Ions at 303 K

Reagents	Cation exchange capacity (mol g^{-1})					
	PFR	TC1	TC2	TC3	TC4	TC5
Original capacity	1.816	1.702	1.648	1.464	1.339	1.315
0.2*M* NaOH boiled for 1 h	1.798	1.693	1.602	1.412	1.298	1.284
Benzene boiled for 1 h	1.762	1.699	1.621	1.400	1.309	1.299
Boiling water for 1 h	1.800	1.700	1.634	1.420	1.314	1.309
Thermal treatment in hot air-oven at 100°C for 12 h	1.671	1.447	1.385	1.224	1.110	1.078

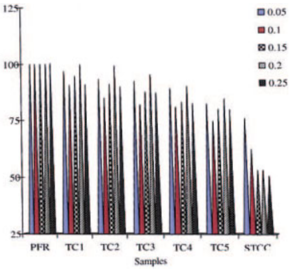

Figure 5 Regeneration level for PFR, its composites, and STCC by using NaCl, after exchange with Mg^{2+} ions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].

Regeneration of IERs

Forty milliliter of 0.2*M* brine solution (NaCl) effectively regenerates all the composite resin and STCC after exchange with Mg^{2+} ions. Most of the commercial IERs are in Na^+ form and hence 40 mL of 0.2*M* NaCl could be used as a regenerant for every 2 g of the resin (Fig. 5).

Equilibrium constants and thermodynamic parameters

The equilibrium constants (in terms of ln *K*) are given in Table VIII for the removal of Zn^{2+} ions using PFR and composites ($R—SO_3^- H^+$). It has been found that the equilibrium constant (ln *K*) for the ion exchange reaction increased with increase in temperature and decreased with the increase in the content of STCC (% w/w) in the blend resin. The standard values of thermodynamic parameters (ΔG^0, ΔH^0, and $\Delta S^{0)}$ were determined and listed in Table IX. ΔG^0 values range from -302 to -1033 J mol^{-1}, which indicate that the ion exchange reaction was spontaneous because of the negative values of Gibbs free energy. The stability of system increased when IER and Zn^{2+} ions bound to each other. The ΔH^0 value was in the range of 1577–9462 J mol^{-1}, which implied that the ion exchange reaction between the IERs and aqueous solution of Zn^{2+} was endothermic. Similarly, it was found that the ΔS^0 value was in the range of 6.2–34.64 J mol^{-1} K^{-1}, which indicates the increased randomness or disorderliness. This may be due to higher amount of Zn^{2+} ion entering into resin and therefore causing much more amount of H^+ ion releasing into the solution. Hence, the increased amount of H^+ ion in solution reflects the randomness/disorderliness, i.e., ΔS^0 values increases from PFR to STCC. The pure PFR is having higher CEC values and therefore possess high positive ΔS^0 value. The results are consistent with the earlier reports.[14,36–38]

TABLE VIII
Thermodynamic Equilibrium Constant (in Terms of ln K) for H^+/Zn^{2+} Exchanges on IERs (*Terminalia chebula*-Retz.)

Samples	% of STCC in PFR	ln *K*			
		303 K	313 K	323 K	333 K
PFR	0	0.41	0.53	0.62	0.70
TC1	10	0.35	0.46	0.54	0.62
TC2	20	0.29	0.36	0.42	0.48
TC3	30	0.26	0.32	0.39	0.44
TC4	40	0.20	0.25	0.29	0.33
TC5	50	0.18	0.22	0.25	0.27
STCC	100	0.12	0.14	0.16	0.17

TABLE IX
Standard Gibbs Free Energy, Enthalpy and Entropy of H^+/Zn^{2+} Ion Exchanges on Various IERs at 303 K

Sample	$-\Delta G^0$ (J mol^{-1})	ΔH^0 (J mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
PFR	1033	9462	34.64
TC1	882	8674	31.54
TC2	731	5520	20.63
TC3	655	4731	17.78
TC4	504	3943	14.68
TC5	454	3154	11.91
STCC	302	1577	6.20

CONCLUSIONS

It is concluded from the present study that PFR sample could be blended with 20% (w/w) of STCC without affecting its physicochemical, spectral, and thermal properties. Also the effect of particle size and the concentration effect of Ca^{2+} ions on CEC, its regeneration level by using NaCl, spectral properties, and the CEC values of various metal ions of 20% (w/w) STCC were very close to the original PFR resin. Equilibrium constant for the removal of Zn^{2+} ion and thermodynamic parameters reveal that the process is spontaneous, endothermic, and occur with randomness. Hence, blending with STCC will definitely lower the cost of IER.

The authors thank the management and principal of their colleges for providing research facilities and constant encouragement.

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