SYNTHESIS, CHARACTERISATION AND APPLICATION OF NEW LOW-COST COMPOSITE ION EXCHANGERS

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ABSTRACT

This article represents a simple method for preparing and characterising of low cost ion exchangers of sulphonated carbon prepared from Tribulus Terrestris Linn., (Family– Zygophyllaceae) - as a source of cheap plant material blended with phenol-formaldehyde as a cross – linking agent.

All the important physico-chemical, thermal and spectral properties of the ion exchangers have been determined. The synthesised resins having a cation exchange capacity upto $1.96 \text{ m.mol.g}^{-1}$.

KEYWORDS: *Synthesis, Phenol Formaldehyde Resin, Composites, Blending, Swelling, FT-IR-TGA, Selectivity & Waste*

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1. 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 old¹. The modern ion exchange resins (IERs) used to-day 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 a half-a-century².

The first synthetic cation exchange resin was obtained by Adams and Holmes³. It was shown that strongly acidic groups ($-\text{SO}_3 \text{H}^+$) may be introduced either by sulphonation or by substitution of phenol sulphonic 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 which is used as an IER. Phenolic resin, sulphonated phenol – formaldehyde, sulphonated polystyrene – divinyl benzene, and polyacrylonitrile are the major organic binding matrices which 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 synthesise low cost ion exchange resins (IERs) and lower the cost of IERs by blending it with sulphonated 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 sulphonated carbons from coal⁶, saw dust⁷, spent coffee⁸, cashew nut husk⁹, wheat husk¹⁰, turmeric plant¹¹, spent tea, gum tree bark¹², *Accacia nilotica*¹³, and Egyptian bagasse pith¹⁴.

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 process using selective IERs are also available in the recovery of

precious nobel metals like gold, platinum and silver¹⁷.

The present study is aimed at to synthesise and characterise new composite ion exchangers of PhOH – HCHO type, blended with Sulphonated *Tribulus Terrestris* - Linn Carbon (STTC) and to determine the column / cation exchange capacity (CEC) or ion exchange capacity (IEC) for some selective metal ions.

2. EXPERIMENTAL

Materials

Phenol and formaldehyde used in the present study were of Fischer reagents (India). LR grade of con. sulphuric acid (Sp.gr.= 1.82) was used. *Tribulus Terrestris* - Linn., (family- Zygophyllaceae) plant materials especially fruits were locally collected and cleaned before use.

Methods

Tribulus Terrestris: Linn.,, thorn (500g) were cut into small pieces, 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 hours. It was then cooled, washed with distilled water several times and finally with double distilled (DD) water in order to remove excess free acid and dried at 70°C for 12 h. It was labeled as STCC.

The phenol formaldehyde resin (PFR) and the composites containing various percentage (w/w) of sulphonated *Tribulus Terrestris* - Linn.,, carbon (STTC) in the total blend as 0, 10, 20, 30, 40 and 50 (w/w), respectively were prepared^{7, 10-13} and labeled as PFR, TT1, TT2, TT3, TT4 and TT5. These resin and composites were sieved into 210 – 300 micron (Jayant sieve, India) for further characterisation. 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 as per the literature methods^{7,10,12,17,18}. The cation exchange capacity (CEC) and the regeneration level was studied with brine (NaCl) solutions following the method reported in literature¹⁹⁻²⁴.

Instrumental Studies

The FT-IR spectral data of pure resin (PFR), 30% (w/w) composite and pure sulphonated *Tribulus Terrestris* - Linn.,carbon (STTC) 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 30% (w/w) composite resin by using TZSCH- Geratebau GmbH Thermal analysis. The surface morphologies of synthesized IERs were studied using a scanning electron microscope (SEM, JEOLJSM 6390).

3. RESULTS AND DISCUSSIONS

The data given in Table 1 reveal that the experimental and theoretical composition of STTC in the composites (TT1 – TT5) 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 (TT1 – TT5) are more reliable and reproducible.

The data given in Table 2 and show that the absolute density values in both hydrated and dehydrated states decrease steadily from pure resin to 50 % of (w/w) STTC in composite resin and then finally to pure STTC. This indicates that PFR and the composites (TT1 – TT5) are more closely packed⁷⁻¹⁴. It is found that the absolute density of 100% STTC possess only 48.58% and 43.56% of density of PFR in hydrate (wet) and dehydrate (dry) states, respectively. This result

indicates that STTC also has closely packed structure^{17,18}.

The value of absolute density of composite resin in dry and wet form depends upon the structure of resin and its degree of cross linking and ionic form²⁵⁻²⁷. Hence, the high density values are obtained for the composite resins. The values of density (both wet and dry densities) presented in Table 2 indicate the high degree of cross linking, and hence the composite resins are suitable for making columns for treating polar and non - polar effluent liquids. Moreover, the wet and dry density values are close to each other, which indicate that the samples may be macro porous in nature. From the data, it is clear that there is no considerable decrease in absolute density in both hydrated and dehydrated states up to 30% blending of PFR with STTC in the condensates, indicating 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 liquids of high density²²⁻²⁴.

The data given in Table 2 indicate that the percentage of swelling decreases from PFR (87.42%) to STTC (39.37%). 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 non-gel type and macroreticular¹⁷. STTC has a swelling capacity of only 39.90% as compared to that of PFR. This extremely low value may be due to certain rigidity in their matrix. The blending of PFR with 30% (w/w) of STTC reduces the gravimetric swelling value as 68.55% of that of the pure PFR, thus decreasing 20.87% of percentage of swelling compared to that of the 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 stand a high osmotic shock¹⁸.

The values of attritional breaking presented in Table 2 also represent the stability of the resin, which decrease from pure resin to STTC. Therefore, the mechanical stability is good up to 20% (w/w) substitution of STTC in pure resin. This observation also shows the possibility of formation of resin in the capillaries of the sulphonated charcoal (STTC) particles^{10 - 12}.

Solubility data indicate the chemical stability of the samples in various solvents. It reveals that PFR, composites and STTC are practically insoluble in almost all the solvents like con. H₂SO₄, HCl, HNO₃, CH₃COOH, CCl₃COOH, CH₃OH, C₂H₅OH, CH₃CHO, CHCl₃, CCl₄, CS₂, C₆H₆ and C₆H₅ CH₃, except 20% (w/v) NaOH solution. Therefore, it may concluded that PFR, and the composites are having high degree of cross linking 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 non-aqueous effluents also¹³. 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 the trichloroacetic acid express the rigidity *i.e.*, having high degree of cross linking in them.

Cation / column exchange capacity (CEC) or Ion exchange capacity (IEC) data shown in Table 3 indicate that, the CEC value decreases when the content of STTC% (w/w) in PFR increases. Fig.1 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 number^{25 - 29}. 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 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.1) it is found that 10% blending of PFR by STTC decreases its CEC to about 10% (Table 3) blending of PFR by STTC retains CEC values above 90% for the exchange of H^+ ions in the Na^+ , K^+ , Cu^{2+} , Ca^{2+} , Mg^{2+} , Zn^{2+} and Pb^{2+} ions. Also it is noted that the composites up to 30% of STTC retains above 90% of CEC of PFR for the exchange of Zn^{2+} , Pb^{2+} and Na^+ and retains 80 – 88% of CEC for the exchange of Ca^{2+} , Cu^{2+} , Mg^{2+} and K^+ ions (Fig.1). The maximum value of % of relative ion exchange capacity of composites is for Zn^{2+} ions and for Na^+ ions. This is due to the reason that the blending of STTC upto 50% (w/w) does not affect the value for Zn^{2+} and Na^+ ions to a greater extent. Hence, it is more suitable for Zn^{2+} and Na^+ ions compared to other ions. However, PFR could be blended up to 30% (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 metal ions in general. It is useful in industrial applications, especially for the treatment of industrial effluent.

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

The order of metal ions based on % of CEC of metal ions compared with PFR. 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 solution²⁶. The order of exchange affinities of various metal ions is not unique to ion exchange system. Only under dilute conditions Hofmeister or lyotropic series²⁸ is obeyed. But, under high concentration it is different²⁸. It is equally important to note that the relative behaviour of these ions for other ionic phenomena deviates the affinity order under the same condition^{30, 31}. The observed order in the present study is different from that of the Hofmeister or lyotropic series²⁸. 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 ions²⁷. Finally this indicates that the these composites can partially replace commercial IERs in making the ion exchangers for industrial applications.

In order to test the chemical stability of IER *viz.*, PFR-composites, the samples were boiled with water, benzene and dilute NaOH for an hour. The CEC of the resulting acid boiled, benzene boiled and alkali boiled samples possess CEC almost similar to the parent/ untreated resins (range 1-2%). This indicates that these samples are chemically stable (Table 4). In order to test the thermal stability of IER *viz.*, PFR –composites the samples were heated to 100⁰ 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 100⁰ 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 4).

CEC data given in Table 5, indicate that the particle size of < 210 μ m are fine, 300 - 500 μ m and > 500 μ m are coarse as to cause very low ion exchange capacity compared to 210 – 300 μ m particle size. Hence, for the effective IEC, the particle size should be maintained and recommended mesh size is 210 - 300 μ m. Forty ml of 0.2M brine solution (NaCl) effectively regenerates all the composite resin and STCC after the exchange with the Mg^{2+} ions. Most of the commercial IERs are in Na^+ form and hence 40ml of 0.2M NaCl could be used as a regenerant for every 2g of the resin²⁶ (Fig.2).

The IR spectral data are shown in Table 6. It indicates the appearance of absorption band at 1038 – 1051 cm^{-1} (S = 0 str.) 1152 – 1192 cm^{-1} (SO_2 sym str.) and 597 - 608 cm^{-1} (C-S str)- in pure resin (PFR), 30% composite resin and pure

STTC(ST3) confirm the presence of sulphonic acid group (Fig.3)

The appearance of broad absorption band at $3396 - 3447\text{ cm}^{-1}$ (bonded $-\text{OH}$ str.) indicate the presence of phenolic and sulphonic $-\text{OH}$ group in the samples. The appearance of absorption band at $1603 - 1639\text{ cm}^{-1}$ (C-C str.) confirms the presence of aromatic ring in PFR, 30% blending of STTC in PFR and pure STTC. The absorption band at $1431 - 1488\text{ cm}^{-1}$ ($-\text{CH}_2$ def.) confirms the presence of $-\text{CH}_2$ group in the samples. The weak absorption band at $878 - 888\text{ cm}^{-1}$ ($-\text{C-H}$ def.) in samples indicate that the phenols are tetra substituted.

TGA curves shown in Fig.4 revealed that there is a very small (6%) loss in weight for both PFR, ST3 and STTC upto 80°C . This is due to the loss of moisture absorbed by resin and STTC. Between $50 - 190^\circ\text{C}$ there is 20% weight loss in PFR and 15-20% loss in weight in ST3 and STTC was observed. Upto 450°C , approximately 57% loss in weight in PFR and upto 340°C , approximately 35-42 % weight loss in ST3 and STTC was observed.

In Fig.4, DTA curve shows that two exothermic peaks were obtained in PFR, approximately at 80°C and at 466°C , respectively. At 80°C , the presence of broad peak was observed, which indicates the dehydration process of resin (PFR). A peak at 466°C , indicate, the chemical changes of pure resin, which reflect approximately, 57% weight loss in PFR.

DTA curve of ST3 and STTC (Fig.4) shows that, the same two exothermic peaks were obtained at 99°C and at 522°C , respectively similar to PFR. Again the first broad peak indicates the dehydration of ST3 and STTC and second moderate sharp peak indicates the chemical changes of ST3 and STTC.

From Figs.4 is concluded that, the limiting temperature for the safer use of PFR and ST3 as ion exchangers was 80°C , since the resin degrade thermally after 80°C .

SEM photos of RFR and ST3 and STTC with different magnification (by 100, 500 and 1000 times respectively) are given Fig 5. SEM photos reveal that all these samples are macroporous in nature. The high macroporous carbon obtained from *Enicostema axillare* form the reservoir in which the resorcinol-formaldehyde sulphonic acid particles are deposited. Hence, the pore diameter decreases in ST3.

4. CONCLUSIONS

It is concluded from the present study that PFR sample could be blended with 30% (w/w) of STTC, without affecting its physico-chemical, thermal properties. Also the effect of particle size and on CEC, its regeneration level by using NaCl, spectral properties and the CEC values of various metal ions of 30% (w/w) STTC were very close to the original PFR resin. Hence, blending with STTC will definitely lower the cost of IER.

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ANNEXURES

Table 1: Amount of reagent used and yield of PFR, condensates (TT1 – TT5) prepared by blending of PFR with various %(w/w) of STTC

Sample	% of STTC in IER (theory)	Amount of reagents used			STTC (g)	Yield (g)	% of STTC in IER(obs)
		Phenol (g)	HCHO (mL)	Con.H ₂ SO ₄ (mL)			
PFR	0	10.0	11.5	12.5	0	18.80	0
TT1	10	10.0	11.5	12.5	2.08	20.95	9.93
TT2	20	10.0	11.5	12.5	4.70	23.98	19.60
TT3	30	10.0	11.5	12.5	8.06	27.02	29.83
TT4	40	10.0	11.5	12.5	12.53	30.88	40.58
TT5	50	10.0	11.5	12.5	18.8	37.14	50.62
STTC	100	-	-	-	-	-	100.00

Table 2: Physico - chemical properties of PFR, STTC and condensates (TT1-TT5)

IERs	% of STTC in IER	Density (g/mL)		Percentage	
		Wet	Dry	Gravimetric swelling	Attritional breaking
PFR	0	2.12	2.02	87.42	8.52
TT1	10	1.83	1.79	77.32	9.88
TT2	20	1.70	1.64	74.34	11.72
TT3	30	1.64	1.60	68.55	16.33
TT4	40	1.48	1.31	52.08	20.77

TT5	50	1.25	1.12	43.12	29.88
STTC	100	1.03	0.88	39.33	44.55

Table 3: Cation exchange capacities of PFR, condensates (TT1-TT5) and STTC for selective metal ions (0.1 M) at 303 K

IERS	% of STTC	Cation exchange capacity m mol/g						
		Ca ²⁺	Mg ²⁺	Zn ²⁺	Pb ²⁺	Cu ²⁺	Na ⁺	K ⁺
PFR	0	1.536	1.956	1.735	1.988	1.784	1.327	1.121
TT1	10	1.426	1.725	1.700	1.735	1.688	1.201	1.102
TT2	20	1.388	1.600	1.674	1.667	1.601	1.185	1.000
TT3	30	1.222	1.523	1.587	1.589	1.488	1.116	0.927
TT4	40	1.104	1.141	1.435	1.457	1.392	0.988	0.854
TT5	50	0.991	1.198	1.299	1.264	1.183	0.884	0.765
STTC	100	0.853	1.044	1.000	1.022	1.000	0.764	0.687

Table 4: Chemical effect on CEC of PFR and its condensates for exchange with 0.1M Zn²⁺ ions at 303 K

Reagents	Cation exchange capacity, in mol. g ⁻¹ 0.1M solution					
	PFR	TT1	TT2	TT3	TT4	TT5
CEC (of untreated)	1.735	1.700	1.674	1.587	1.435	1.299
20%(w/v) NaOH	1.561	1.534	1.421	1.322	1.188	1.000
Benzene	1.624	1.587	1.498	1.388	1.239	1.145
1M HCl	1.612	1.565	1.475	1.392	1.245	1.267

Table 5: Effect of particle size on CEC of PFR and condensates (TT 3) at 303K

Sample	Particle Size	Cation exchange capacity (m. mol. g ⁻¹)		
		Zn ²⁺	Mg ²⁺	Pb ²⁺
PFR	<210	1.661	1.821	1.855
	210-300	1.735	1.956	1.988
	300-500	1.689	1.854	1.857
	>500	1.598	1.762	1.1.789
TT 3	<210	1.298	1.444	1.527
	210-300	1.587	1.523	1.589
	300-500	1.454	1.500	1.547
	>500	1.381	1.483	1.511

Table 6: FT-IR spectral data of PFR, condensates TT3 and pure STTC ($\bar{\nu}$ in cm⁻¹)

Group	PFR	Composites TT3	Pure STTC
S = O str.	1051	1044	1038
SO ₂ sym. str.	1152	1187	1192
C – S str.	608	598	597
Bonded OH str.	3396	3447	3427

CH ₂ – def.	1488	1468	1431
C – C str.	1639	1603	1614
C - H def.	880	878	888
C-C def.	862	844	839
SO ₂ assy.	1332	1327	1316

Figure 1: CEC of PFR, TT1-TT5 and STTC for selective metal ions (0.1 M) at 303 K

Figure 2: Regeneration level for PFR, TT1-TT5 and STTC- loaded with Zn²⁺ ions by using NaCl solution at 303 K.

Figure 2: FT-IR spectral of PFR, condensates TT3 and pure STTC ($\bar{\nu}$ in cm^{-1})

Figure 3: TGA and DTA curves of PFR, condensates TT3 and pure STTC

Figure 4: SEM images with different magnification