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Synthesis and Characterization of New Composite Ion Exchangers

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The charcoals obtained by sulphonating the tannin-rich spent tea dust and gum tree bark were used separately to replace the polymeric matrix of phenolformaldehyde cation exchanger, varying the substituent content from 0 to 100%. All the important characteristics of the composites have been determined. It is observed that the composites up to 30% substitution with the charcoals of the said tannin-rich materials are economical, since the composites obtained retain all the essential properties of the pure phenolic cationite.

INTRODUCTION

Synthesis and characterization of ion exchangers is of interest because of the large-scale use in hydrometallurgy, pharmaceutical preparations, sugar industry, pollution control, analytical chemistry and particularly in water-softening. Since the current commercial exchangers owe their origin to the products of petroleum, there is a phenomenal increase in the cost of these exchangers.

Hence there is an urgent need now either to find out entirely new resins which are cheaper than the existing exchangers or to prepare composite exchangers by partly replacing the polymeric content of the current exchangers to a considerable extent while the important characteristics of the parent resins are being retained. The composite would be very efficient if the substituent itself could act as an exchanger. The works done by previous workers[1–6] show that cheaper composite exchangers could be prepared by partially substituting the macroporous phenol-formaldehydesulphonic acid matrix by sulphonated charcoals from coal[1], saw dust[2], spent coffee[3], cashew nut[4], wheat husk[5] and ground nut[6].

In the above-said direction, the present work deals with the preparation and characterization of composite cation exchangers obtained by incorporating the sulphonated charcoals from the following two tannin-rich materials into the macroporous phenolformaldehydesulponic acid matrix:

1. Spent tea dust (*Camellia sinensis* (L.) Kuntz.)
2. The bark of the gum tree (*Acacia arabica* Willd.)

EXPERIMENTAL PROCEDURES

Materials and reagents used were the above-said tannin-rich materials, phenol

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(BDH grade), formaldehyde solution (37–40%) (BDH grade) and conc. sulphuric acid (sp. gr. 1.82).

Preparation of phenolformaldehyde resin

Phenol (10 g) and conc. sulphuric acid (23 g) were mixed solwly with constant stirring and cooling in ice. The mixture was then heated to 80°C for 3 h on a water bath, cooled immediately in ice and kept overnight. Then it was polymerised with formaldehyde solution (12.5 g) at 80°C and the product was cured at the same termperature for 3 h. The brown coloured chunky solid obtained was ground, washed with distilled water to remove the free acid, dried, sieved and preserved for property-studies. It constituted the sample R.

Preparation of the composites

The spent tea dust (*ca.* 500 g) was carbonised and sulphonated with conc. sulphuric acid (*ca.* 100 g), kept at ambient temperature for 24 h and heated to 90°C in a hot air over for 6 h. It was then cooled, washed free of acidity and dried (sample SC_1). The same procedure was repeated to get sulphonated gum tree bark charcoal (sample SC_2). A known amount of phenol was sulphonated with conc. sulphuric acid by the said method and calculated quantities of SC_1 were added to it so as to keep the percentage substitution of the sulphonated charcoal at 10, 20, 30, 40 and 50. Each mixture was then polymerised with formalin at 80°C and the product was cured at the same temperature for three more hours. It was then ground, washed free of acidity, dried, sieved and preserved for characterisation. These products constituted the samples 1A to 1E. The same procedure was repeated for the charcoal SC_2 and the products constituted the samples 2A to 2E. Since sulphuric acid is relatively costly, it was tried to sulphonate phenol and introduce the powdered gum tree bark into it directly, so that the residual acid could carbonise and sulphonate the raw material and it was followed by polymerization with formalin, making the composite 20% (sample 2F). The experimental and theoretical yields of the composites are reported in Tables 1.1 and 1.2.

Characterization of the samples

Determination of physical properties

The densities of the dry samples (in toluene) and the wet samples (hydrated overnight in water) were determined by a specific gravity bottle. Swelling measurements were made by allowing the samples to equilibrate in water overnight. The wet weight was taken as M_w and the corresponding dry weight M_d was obtained after drying the same samples at 70°C and then exposing to air. The gravimetric swelling precentage, α, was calculated from the equation

$$\alpha = \frac{M_w - M_d}{M_d} \times 100$$

To find out the percentage of attritional breaking, the sample was initially sieved to give particles of > 200 μ size. A known quantity (W_1 g) of the sample was swollen in water and shaken continuously for 6 h. The wet sample was

separated by filtration, dried, sieved on a 200 μ mesh and the amount of the sample remaining on the sieve was weighed (W_2 g). From the above said weights, the percentage of attritional breaking was calculated to be $\frac{W_1 - W_2}{W_1} \times 100$. The above said measurements are presented in Tables-2.1 and 2.2. Uniform particle size was maintained by sieving the samples in 200 μ and 300 μ mesh.

Measurement of column capacity

A known weight (2 g) of the sample was converted into the H^+ form by washing with hydrochloric acid (4 M), followed by distilled water to remove free H^+ ions. Test column was prepared from a graduated burette with glass-wool plugs and the slurry of the treated sample. $Na^+/Mg^{2+}/Zn^{2+}/Ca^{2+}/Cu^{2+}$ solution (40 mL, 0.1 M) was added into the column in several portions. The flow of the effluent was adjusted to be 1–2 mL min^{-1}. The sample exchanged its H^+ ion for $Na^+/Mg^{2+}/Zn^{2+}/Ca^{2+}/Cu^{2+}$ ion in the solution. The total amount of the cation exchanged was found out by using standard titration techniques[7]. From the total amount of the ions exchanged, column capacity was calculated and the values (in mmol g^{-1}) are presented in Tables 3.1 and 3.2. Comparisons of column capacities for the composites are given in representative Fig. 1. To get the Na^+ form of the column, it was washed with NaCl solution (5%) several times and the column capacity was determined with respect to Zn^{2+} ion. The effect of concentration of the cation on the column capacity of the pure resin and the composites (10%) was determined by using Zn^{2+} ion (0.05 M and 0.01 M) and the values are presented in Table-3.3. The effect of particle size on the column capacity of the pure resin with respect to all the five sample ions was studied by making columns of particle sizes < 200 μ and > 1500 μ and determining the column capacities. The values are given in Table-3.4.

Measurement of absolute capacity

The sample was taken in H^+ form and its scientific weight capacity for the exchange of Na^+ ion was determined by pH titration technique[8]. The scientific weight capacity of the sample with respect to $Mg^{2+}/Zn^{2+}/Ca^{2+}/Cu^{2+}$ ion was determined by adopting Kunin's method[9]. A known weight of the sample was converted to the H^+ form with hydrochloric acid (200 mL, 4 M). Then it was rinsed free of excess acid and drained. A portion of the wet sample was dried to find out the percentage dry weight content. Another weighed portion of the wet sample was introduced into a dry 250 mL Erlenmeyer flask. To the sample in the flask standard solution of $Mg^{2+}/Zn^{2+}/Ca^{2+}/Cu^{2+}$ (200 mL, 0.01 M) ion was added. The stoppered sample was allowed to stand for 24 h, for the equilibrium to be established. The sample exchanged its H^+ ion for the said divalent ion. The total H^+ ion exchanged was calculated from the pH change before and after equilibration. The scientific weight capacities for all the composites are finally expressed in mmol g^{-1} dry sample (Table-4). Some scientific weight capacity measurements were also made with sodium hydroxide at pH *ca.* 13.

Determination of thermal stability

To determine the thermal stability, known weights of H^+ forms of the sample were taken at room temperature, heated to constant weight at 50°C, 70°C, 90°C, 110°C and 120°C for 1 h in an air oven, cooled and immediately weighed. Then the samples were exposed to air for 24 h and again weighed. The precentages of the weight loss of the samples are presented in Table-5.

The pure resin and the composites (20%) were kept at 120°C for 1 h and cooled (samples RG, 1G and 2G) and their column capacities were found out. The results are presented in Tables 3.1 and 3.2.

Determination of chemical stability

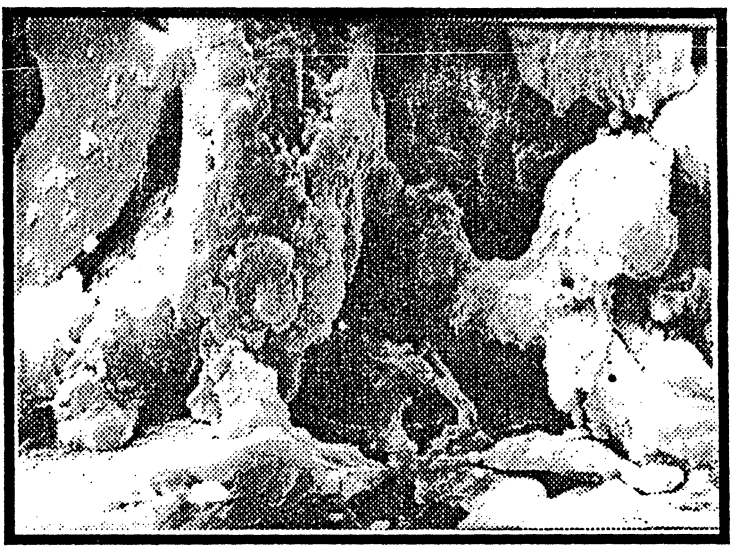
To test the chemical stability, the resin and the composites (30%) were separately boiled with water and very dil. solution of sodium hydroxide for 1 h hour and the resulting samples were filtered, dried, weighed and their column capacities were determined. The results showed no change in the capacity values from those of the untreated samples. Hence these are chemically stable.

Spectral data

The FT-IR spectra of the pure resin and the composites (20%) and the pure charcoals were obtanied in KBr pellets by a Bruker IFS 66v spectrophotometer. The frequency data are given in Table-6.

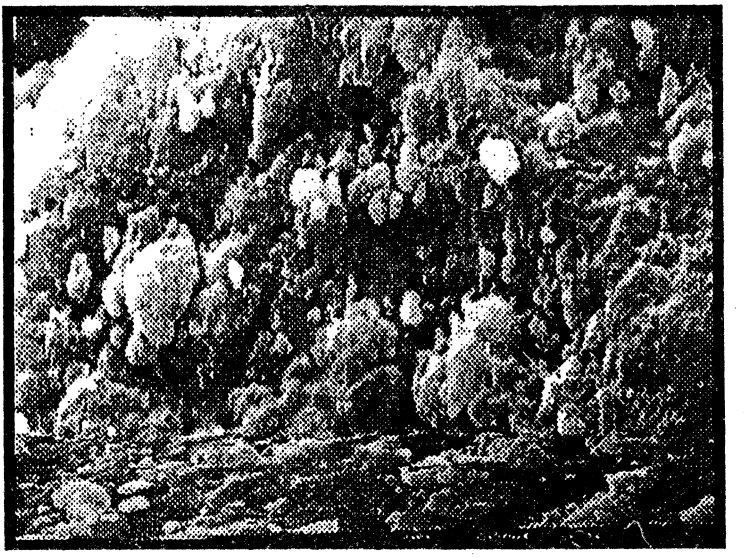
SEMS

The scanning electron micrographs (SEMS) of the samples—pure resin, IB and SC_1—were obtained using a JEOL JSM-5300 SEM and the micrographs are produced in photos 1–3.



SEM (1) Of SC_1 (X 5000)

SEM (2) Of pure resin (X 10,000)



SEM (3) of 1B (X 5000)

Test for tannins

The samples except the pure resin were separately boiled with hydrochloric acid (2M) for $\frac{1}{2}$ h. The red colour produced turned yellowish green on adding neutral ferric chloride solution and again turned red on adding sodium bicarbonate solution[9].

The regeneration level for the exhausted ion exchangers was found out using brine solution (0.01 M, 0.05 M, 0.1 M, 0.15 M, 0.2 M and 0.25 M, 40 mL each) and the results show that 6 mmol g^{-1} of brine solution is the regeneration level for the exhausted ion exchangers.

RESULTS AND DISCUSSION

TABLE-1.1
AMOUNTS OF REAGENTS USED AND YIELDS OF THE COMPOSITES

Sample	Percentage of SC_1 (theoretical)	Amount of reagents used (g)			SC_1	Yield (g)	Percentage of SC_1 (observed)
		Phenol	Formaldehyde	Conc. sulphuric acid			
R	0	10	12.5	23	0.0000	15.00	0.00
1A	10	10	12.5	23	1.6667	16.60	10.04
1B	20	10	12.5	23	3.7500	18.30	20.49
1C	30	10	12.5	23	6.4286	21.60	29.76
1D	40	10	12.5	23	10.0000	25.10	39.84
1E	50	10	12.5	23	15.0000	30.00	50.00
SC_1	100	–	–	–	–	–	–

TABLE-1.2
AMOUNTS OF REAGENTS USED AND YIELDS OF THE COMPOSITES

Sample	Percentage of SC_1 (theoretical)	Amount of reagents used (g)			SC_2	Yield (g)	Percentage of SC_1 (observed)
		Phenal	Formaldehyde	Conc. sulphuric acid			
R	0	10	12.5	23	0.0000	15.00	0.00
2A	10	10	12.5	23	1.6667	16.66	10.00
2B	20	10	12.5	23	3.7500	18.80	19.90
2C	30	10	12.5	23	6.4286	21.58	29.90
2D	40	10	12.5	23	10.0000	25.00	40.00
2E	50	10	12.5	23	15.0000	30.00	50.00
SC_2	100	–	–	–	–	–	–
2F	20	10	12.5	23	3.7500	18.90	19.84

The data found in Tables 1.1 and 1.2 show that the experimental and theoretical yields of the composites are in good agreement with each other.

TABLE-2.1
ABSOLUTE DENSITIES, GRAVIMETRIC SWELLING PERCENTAGES AND ATTRITIONAL BREAKING OF COMPOSITES (SC_1)

Sample	Percentage of SC_1	Density, g mL^{-1}		Gravimetric swelling %	Attritional breaking %
		wet	dry		
R	0	1.3000	1.3550	60.00	8.10
1A	10	1.4052	1.4486	55.00	10.00
1B	20	1.4455	1.4120	50.00	12.00
1C	30	1.4787	1.4923	45.00	13.50
1D	40	1.4184	1.4295	40.00	15.00
1E	50	1.3440	1.3803	35.00	20.00
SC_1	100	1.4286	1.1748	30.00	15.00

TABLE 2.2
ABSOLUTE DENSITIES, GRAVIMETRIC SWELLING PERCENTAGES AND ATTRITIONAL BREAKING OF COMPOSITES (SC_2)

Sample	Percentage	Density, g mL^{-1}		Gravimetric swelling %	Attritional Breaking %
		wet	dry		
R	0	1.3000	1.3500	60.00	8.10
2A	10	1.4306	1.4852	58.00	10.20
2B	20	1.4472	1.5210	54.00	12.00
2C	30	1.2723	1.3872	52.00	15.00
2D	40	1.4556	1.4248	50.00	19.00
2E	50	1.4574	1.4559	45.40	25.00
SC_2	100	1.3736	1.2741	30.00	26.00
2F	20	1.4450	1.3773	54.00	11.00

The densities of the ion exhangers are fairly high both in dry state and wet state. Hence these are suitable for making columns for treating polar and non-polar liquids of high density. Moreover, the wet and the dry density values for each ion exchanger are close to each other, showing that their pores are so large that they are macroporous. The gravimetric swelling percentage decreases from 60 to 30 and the values are not very high, because the ion exchangers are macroreticular, having nongel pores. Based on the attritional breaking data it is established that the ion exchangers are mechanically stable and the stability is good up to 30% substitution.

The density, swelling and attritional breaking data for the 2B and 2F samples (both 20% composites) closely agree indicating the fact that the two different methods adopted for the preparation of the composites give the same quality products. Hence it is established that instead of sulphonated charcoal, the powdered raw material could be directly mixed with the sulphonated phenol and then polymerised, resulting in saving of large quantity of conc. sulphuric acid.

TABLE-3.1

COLUMN CAPACITIES OF THE $\frac{H^+}{Na^+}$ FORM OF THE SAMPLES

Sample	Percentage of SC_1	Column capacity, mmol g^{-1}					
		Na^+ 0.1 M	Mg^{2+} 0.1 M	Zn^{2+} 0.1 M		Cu^{2+} 0 1 M	Ca^{2+} 0. 1M
				H^+ form	Na^+ form		
R	0	2.24	1.23	1.27	1.18	1.18	1.18
1A	10	2.08	1.23	1.18	1.17	1.18	1.13
1B	20	2.08	1.23	1.27	1.18	1.18	1.17
1C	30	2.00	1.20	1.20	1.08	1.06	1.00
1D	40	1.64	1.10	1.06	0.99	0.95	0.95
1E	50	1.39	0.95	0.96	0.93	0.86	0.84
SC_1	100	0.72	0.47	0.42	0.36	0.40	0.39
RG	0	1.88	1.02	0.96	–	0.92	0.94
1G	20	2.04	1.20	1.27	–	1.00	1.16

TABLE-3.2

COLUMN CAPACITIES OF THE H^+ FORM OF THE SAMPLES

Sample	Precentage of SC_2	Column Capacity, mmol g^{-1}				
		Na^+ 0.1M	Mg^{2+} 0.1 M	Zn^{2+} 0.1 M	Cu^{2+} 0.1 M	Ca^{2+} 0.1 M
R	0	2.24	1.23	1.27	1.18	1.18
2A	10	2.17	1.15	1.12	1.18	1.12
2B	20	2.16	1.10	1.05	1.08	1.06
2C	30	2.14	1.05	1.04	1.00	1.02
2D	40	1.86	1.05	1.02	0.95	1.00
2E	50	1.67	0.94	0.87	0.85	0.86
SC_2	100	0.52	0.50	0.45	0.47	0.41
2F	20	2.06	1.20	1.13	1.08	1.16
2G	20	2.06	0.99	0.93	0.91	0.93

It is seen (Tables 3.1 and 3.2) that the pure resin has a consistent column exchange capacity of 2.24 mmol g^{-1} which is comparable to the capacity values of commercial ones such as Amberlite IR-1, Amberlite IR-100, Zeo Karb 215, Zeo Karb 315, Wofatit P and Wofatit K. It is also seen that in all the composites, the column capacity is greater for the Na^+ ion than that for the divalent ions. This may be due to the preferential uptake of the monovalent Na^+ ion by the highly cross-linked and moderately sulphonated phenolformaldehyde system. Among the divalent ions the column capacity decreases in the following order:

$Mg^{2+} \geq Zn^{2+} > Cu^{2+} \geq Ca^{2+}$, the important factor in concentrated solutions for the above-said trend being ionic size [Mg^{2+}, 0.65 Å; Zn^{2+}, 0.74 Å; Cu^{2+}, 0.93 Å;

and Ca^{2+}, 0.99 Å—data provided by Pauling[10]]. It is also observed (Table 3.1) that the Na^+ form of the ion exchangers has a slightly lower capacity value than that for the H^+ form. This fact is as expected, since ion exchange is mainly diffusion controlled; the bigger Na^+ ion lags behind the smaller H^+ ion in diffusion.

Figs. 1 shows that the column capacities do not fall appreciably up to the composites (30%). This observation supported by other data like density, swelling, attritional breaking, chemical and thermal stabilities points to the fact that the composites (30%) are as good as the pure resin itself. Moreover, spent tea dust and gum tree bark are freely available in plenty. Hence it may be concluded that the pure phenolformaldehyde sulphonic acid resin could be substituted by spent tea dust and gum tree bark charcoals up to 30% which would form cheap composite ion exchangers.

TABLE-3.3
EFFECT OF CONCENTRATION OF ION ON COLUMN CAPACITY OF ION EXCHANGERS

Sample	Percentage of charcoals	Column capacity, m mol g^{-1}		
		Zn^{2+} 0.1 M	Zn^{2+} 0.05 M	Zn^{2+} 0.01 M
R	0	1.27	0.70	0.170
1A	10	1.18	0.64	0.125
2A	10	1.12	0.13	0.030

TABLE-3.4
EFFECT OF PARTICLE SIZE ON COLUMN CAPACITY OF ION EXCHANGERS

Sample with Size	Column capacity, m mol g^{-1}				
	Na^+ 0.1 M	Mg^{2+} 0.1 M	Zn^{2+} 0.1 M	Ca^{2+} 0.1 M	Cu^{2+} 0.1 M
R					
< 200 μ	1.96	1.16	1.22	0.93	1.07
200–300 μ	2.24	1.23	1.27	1.18	1.08
> 1500 μ	1.86	1.06	1.12	0.83	0.97

It is seen (Table-3.3) that when the concentration of Zn^{2+} ion decreases, the capacity of ion exchangers also decreases. It is in accordance with the Le-Chatelier-Braun principle. It is also seen (Table-3.4) that in the case of finer and coarser particles, the column capacity has low values. Hence to maintain the exchange capacity at optimum level, the recommended size of the particles is 0.2 mm to 1.4 mm.

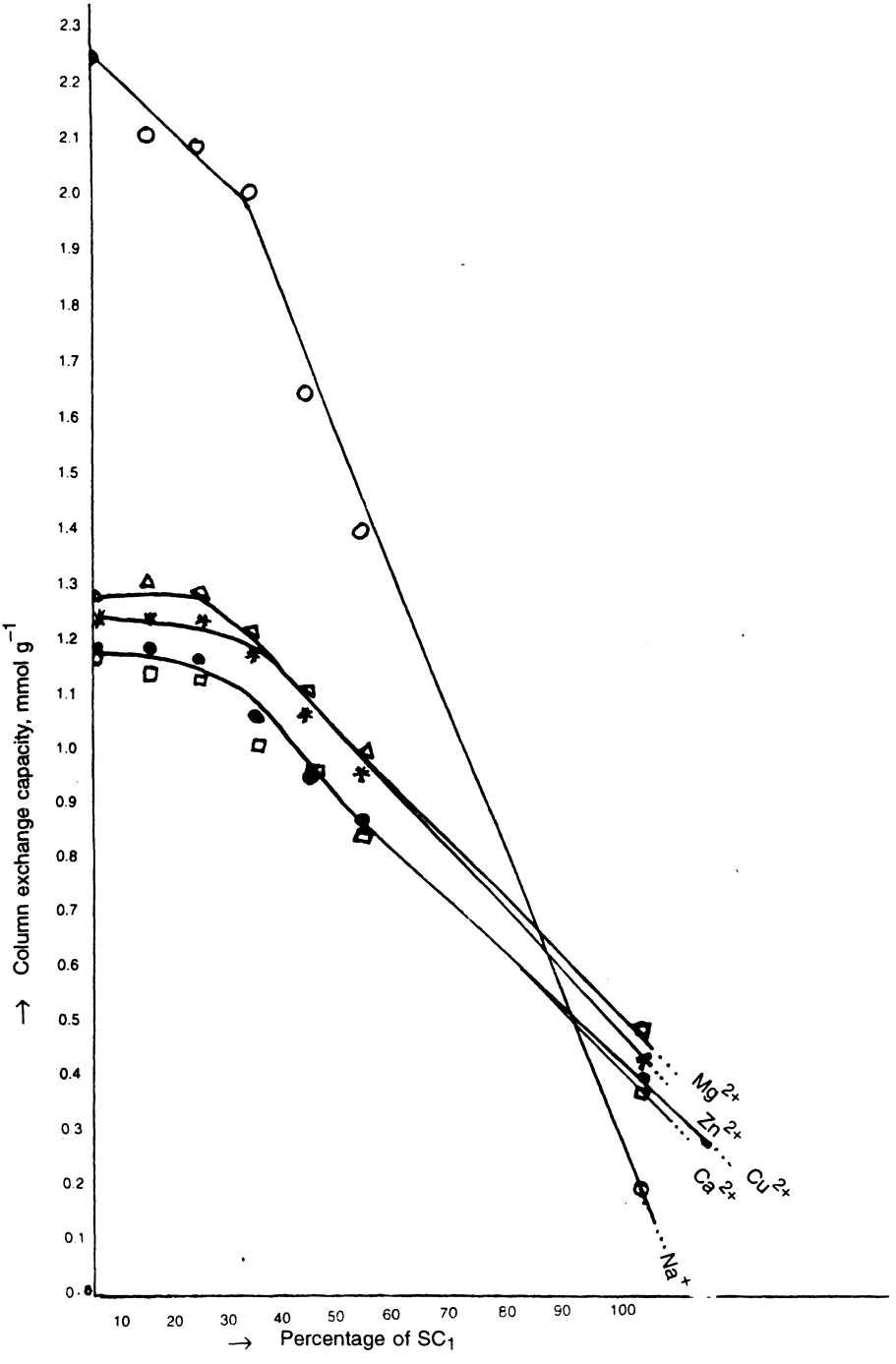


Fig. 1 Column capacity of spent tea dust charcoal composites
[Na^+, Mg^{2+}, Zn^{2+}, Cu^{2+}, Ca^{2+} Ions, 0.1 M]

TABLE-4
SCIENTIFIC WEIGHT CAPACITY OF ION EXCHANGERS

Sample	Percentage of charcoal	Scientific Weight Capacity, m mol g^{-1}					
		Na^+ 0.1 M pH 4.5–10	Na^+ 0.1 M pH ~ 13	Mg^{2+} 0.01 M	Zn^{2+} 0.01 M	Cu^{2+} 0.01 M	Ca^{2+} 0.01 M
R	0	2.25	7.35	1.26	1.26	1.76	2.00
1B	20	2.75	7.82	1.26	1.26	1.76	2.00
1C	30	–	–	1.26	1.26	1.76	2.00
2B	20	2.75	7.93	1.26	1.26	1.76	2.00
2C	30	–	–	1.26	1.26	1.76	2.00
SC_1	100	1.20	–	–	–	–	–
SC_2	100	1.30	–	–	–	–	–

It is seen (Tables-3.1 and 3.4) that the scientific weight capacity of the pure resin matches the column capacity with respect to Na^+ ion in 0.1 M concentration indicating attainment of rapid equilibrium in the column. It is also seen that the total capacity of the charcoals is more than one-third of the capacity of the pure resin. Hence charcoals themselves can be used to make columns for the treatment of effluents containing heavey metal ions. The total capacities of the composites are higher than that of pure resin (0.5 mmol g^{-1}). This may be due to ionizable phenolic —OH groups (at pH 4.5–10) present in the charcoals which are obtained from tannin-rich materials. At pH *ca.* 13, the composites have higher capacity for Na^+ from NaOH. This may be due to all the phenolic groups present in the composites in addition to the sulphonic acid groups. Among the divalent ions in 0.01 M concentration, the total capacity increases in the following order:
$Mg^{2+} = Zn^{2+} < Cu^{2+} < Ca^{2+}$, the major factor being hydrated ionic radii[11]

TABLE-5
THERMAL STABILITY OF THE COMPOSITES

Sample	Percentage of charcoal	50°C, g		70°C, g		90°C, g		110°C, g		120°C, g	
		Imme-diate	after 24 h	Imme-diate	after 24 h	Imme-diate	After 24 h	Imme-diate	after 24 h	Imme-diate	after 24 h
R	0	0.940	1.000	0.930	1.000	0.930	1.000	0.905	1.000	0.700	0.800
1B	20	0.950	1.000	0.940	1.000	0.940	1.000	0.940	1.000	0.750	0.850
1C	30	0.950	1.000	0.940	1.000	0.940	1.000	0.940	1.000	0.750	0.850
2B	20	0.950	1.000	0.940	1.000	0.940	1.000	0.940	1.000	0.750	0.850
2C	30	0.950	1.000	0.940	1.000	0.940	1.000	0.940	1.000	0.750	0.850
SC_1	100	0.995	1.000	0.995	1.000	0.995	1.000	0.990	1.000	0.800	0.900
SC_2	100	0.995	1.000	0.990	1.000	0.990	1.000	0.990	1.000	0.800	0.900

When the samples are heated up to 110°C, initially they lose some weights but the lost weights are regained after exposure to air for 24 h (Table 5). However at 120°C even after exposure to air, there is a weight loss of 10–20%. This is the reason for the loss of about 10% in column capacity of the samples heated at 120°C (Tables-3.1 and 3.2)

TABLE-6

FT-IR SPECTRAL DATA (cm^{-1}) OF THE COMPOSITES

Sample	Percentage of charcoal	S=O str	SO_2 sym str	–C–H def	C–S str	Bonded O–H str	C–O str / O–H def	CH_2 str	CH_2 def	C–S str
		cm^{-1}								
R	0	1032.0	1163.0	879.1	581.8	3430.7	1209.1	2924.6 2852.9	1472.5	1594.5 1655.6
1B	20	1031.1	1164.1	883.3	581.9	3440.2	1212.2	2922.4 2852.2	1469.5	1596.9 1648.8
2B	20	1032.3	1162.3	884.2	582.9	3414.0	1207.3	2925.2 2854.3	1470.4	1596.1 1649.1
SC_1	100	1025.6	–	–	609.6	3425.8	1231.8	–	–	1615.3
SC_2	100	1034.1	1163.5	–	594.6	3408.9	–	–	–	1616.6

An analysis of the data (Table-6) reveals that the composites have strong absorption bands at 1040–1020 cm^{-1} (S=O str), strong bands at 1165–1162 cm^{-1} (SO_2 sym str) and at 630–580 cm^{-1} (C—S str), confirming the presence of sulphonic acid groups in them. The absorption bands at 2925–2820 cm^{-1} (CH_2 str) and at 1475–1465 cm^{-1} (CH_2 def) confirm the presence of $-CH_2-$ groups in the pure resin and the composites. The appearance of bands at 1600–1590 cm^{-1} (C—C str) confirm the presence of aromatic rings in the composits. The broad absorption bands at 3445–3380 cm^{-1} (bonded O—H str) and sharp bands at 1232–1207 cm^{-1} (O—H def) indicate the presence of phenolic and sulphonic —OH groups in the composites. The weak absorption bands at 885–879 cm^{-1} in the resin and the composites indicate the fact that the phenols are tetrasubstituted.

The SEM photos (1–3) reveal that the charcoals and the pure resin are macroporous, the pore diameter ranging in the region 10^3–10^5 Å and also that the charcoals form the reservoir in which the phenolformaldehydesulphonic acid polymeric particles are deposited.

Conclusions

Among the composites prepared, the composites containing spent tea dust charcoal and gum tree bark charcoal up to 30% are found to have high densities, good swelling behaviour, high attritional resistance, high column and absolute capacities, good thermal and chemical stabilities and particularly, these are macroporous and cheap. Hence these ion exchangers can be applied in unit operations for the separation of rare earths, recovery of metals from industrial

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