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Research Paper

Studies On The Removal Of Metal Ions Using Resins Blended With Mimosa Pudica Sulphonated Carbon

Chemistry

KEYWORDS :Synthesis, Cationic exchangers, Sulphonated Mimosa pudica Carbon, Cation Exchange Capacity, Composite resin.

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ABSTRACT

This paper deals with the study of Sulphonated Carbon derived from plant viz., Mimosa pudica (Thottaccurungi - stem) (MP) has been prepared and blended with Phenol – Formaldehyde Cation Exchanger (PFCE) by varying the percentage of blending (w/w) and Physico-chemical parameters like, density, gravimetric swelling (%), attritional breaking (%) and Cation Exchange Capacity (CEC) of various metal ions have been determined. For a given metal ion, CEC decreases with the increase in percentage of blending MP with PFCE. The blending of PFCE upto 30% (w/w) of MP retains almost all the essential physico-chemical characteristics including CEC, as compared to that of the PFCE. It is concluded that the sulphonated Mimosa pudica Carbon (SMPC) could be used as blending material in the PFCE to lower the cost of the ion-exchange resin for water and wastewater treatment, especially for the removal of hardness in particles.

1. 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 metals ions will enter into water resources, 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]. Since the current commercial ion-exchangers owe their origin to Petroleum products and there is a continual increase in their cost. Hence, there is an urgent need to find out the new low-cost Ion-Exchange Resins (IERs) and reduce the cost of IERs by blending it with Sulphonated Carbons (SCs) prepared from plant materials. Such types of low cost ion-exchangers could be obtained by blending the IER with SC obtained from cheaper and freely available plant material containing Phenolic groups in it. Ion exchange may be defined as the reversible interchange of ions between a solid phase (resin) and a liquid phase. In earlier studies Phenol–Formaldehyde Resins (PFR) have been modified with Sulphonated Carbon 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]. The ion-exchange process finds a valuable place in the treatment of wastewater containing heavy metal ions discharged from electroplating and other industries. In addition, ion exchange is a convenient way to concentrate, remove and recover the ions of valuable metals. The aims and objectives of the present work are to determine the optimum conditions for the preparation of composites obtained by blending Cationic Matrices (CMs) of PFR with various % (w/w) of Sulphonated Mimosa pudica Carbon (SMPC), to characterize the new composite/blends 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, chemically and thermally treated IERs on CEC was studied.

2. Experimental

Preparation of PFR

The raw/plant material used in the present study was Mimosa pudica (Thottaccurungi - stem). This is a plant material freely available in Tamil Nadu, India. Phenol (BDH Sample), Formaldehyde solution (37 to 40 percent, SD fine reagent) and conc. Sulphuric acid (sp.gr. 1.82).

The powdered Mimosa pudica stem (1kg) was carbonized with sulphonated by con. Sulphuric acid (600ml), washed to remove excess free acid and dried at 110oC for 12 hours. It was labelled as MPC. This method followed was similar to the reported one for preparing SCs from plant materials [6-8].

Phenol (10ml) and Con.Sulphuric acid (12.5ml) were mixed slowly with constant stirring and cooling in an ice bath. The mixture was then heated to 80oC for 3 hours, cooled immediately in ice bath and kept it for overnight. It was then polymerized with Formaldehyde solution (12.5ml) at 80oC for 3 hours and the product was cured at room temperature. A reddish brown coloured chunky solid obtained was ground, washed with distilled water to remove the free acid, dried, sieved and preserved for characterization. It was labeled as PFR.

Preparation of Composites

The dried Mimosa pudica (Thottaccurungi – stem d 1kg) was carbonized and sulphonated with Conc.Sulphuric acid (600ml) kept at ambient temperature for overnight, and heated to 80oC in a hot air oven for 3 hours. It was then cooled, washed free of excess acid and dried (MPC). A known amount of phenol was sulphonated with conc. Sulphuric acid by the above method and calculated quantities of sulphonated Mimosa pudica Charcoal (SMPC) were added to it. So as to keep the percentage substitution by sulphonated Mimosa pudica Charcoal at 10,20,30,40 and 50 respectively. Each mixture was then polymerized with Formaldehyde solution at 80oC and the product was further cured for 3 hours. It was then ground, washed to remove the free acid, dried, sieved and preserved for characterization. The experimental and theoretical yields of the composite are reported in table 1.

Characterization of samples

Samples were ground and sieved into a size of 210-300 µm using Jayant sieves (India). This was used for further characterization by using standard procedures [3,7,8] to find out the values of absolute density (wet and dry in water and toluene respectively), percentage of gravimetric swelling and percentage of attritional breaking. The solubility of these samples was also tested in various organic solvents and inorganic reagents. Characterization of samples was carried out following the meth-

ods reported in literature [3,6-9]. The values of cation exchange capacity (CEC) were determined by using standard titration techniques as per the literature [2,3].

Results and Discussion

Determination of Physical properties

The absolute density of the dry sample (in toluene) and the wet samples (hydrated overnight) was determined by using specific gravity bottles. Swelling measurements were made by allowing the sample to equilibrate in water overnight. The wet weight was taken as Mw and the corresponding dry weight Md was determined after drying the samples at 70oC (343k) and then exposing to air. The gravimetric swelling percentage was calculated as given in equation (1)

α = Mw – Md / Md x 100 ---------- (1)

To find out the percentage of attritional breaking, the sample was initially sieved to give batches of particles of size greater than 200µ sieve. A known quantity (W1g) of the sample was swollen in water and shaken continuously for 6 hours. The wet sample was separated by filtration, dried, sieved on a 200 µ mesh and the amount of the sample which remained on the sieve was weighed (W2g). From the above weights, the percentage of attritional breaking was calculated to be W1–W2/W1 x 100. The values obtained are presented in table 2. Uniform particle size was maintained by sieving the samples in 200µ and 300µ mesh sieves.

Measurement of column capacity

A known weight (2g) of the sample was converted into H+ form by washing with hydrochloric acid (2M), followed by distilled water to remove excess of H+ ions. Test column was prepared by using a graduated burette with glass-wool plugs and the slurry of the treated sample. Na+/Mg2+/Zn2+/Cu2+/Ca2+/Pb2+ solution (40 ml, 0.1M) was added in different portions. The flow of the effluent was adjusted between 1 to 2 ml min-1. The sample exchanged its H+ ion for Na+/Mg2+/Zn2+/Cu2+/Ca2+/Pb2+ ion in the solution. The total amount of the cation exchanged was found using standard titration techniques. From the total amount of the cation exchanged, column capacity was calculated and the values (in meqg-1) are presented in table 3.

Measurement of Thermal Stability

To measure the thermal stability of the sample, known weights of H+ forms of the sample were heated separately at 323K, 343K, 363K, 383K and 393K for 1 hour in an air oven and immediately weighed. The samples were then exposed to air for 24 hours and again weighed. The percentages of the weight loss of the sample are presented in Table 4.

Characterisation of instrumental studies

FT – IR spectral studies are used to confirm the stretching frequencies of various functional groups and to identify the ion – exchangeable groups present in IER. It indicates the appearance of absorption band at 1038-1048 cm-1 (S=O str.) 1163-1202 cm-1 (SO2 sym.str.) and 575-603 cm-1 (C-S str.) in PFR (pure resin). Composite blended with 10% (w/w) MPSC and pure MPSC (100%) confirm the presence of sulphonic acid group (fig 2). The appearance of broad absorption band at 3384-3407 cm-1 (bonded -OH str) indicates the presence of Phenolic and Sulphonic –OH (due to –SO3H) groups in the samples. The appearance of absorption band 1613-1643 cm-1 (C-C str.) confirms the presence of aromatic ring in PFR, composite obtained by 30% (w/w) blending of MPSC with PFR and pure MPSC. The absorption band at 1327-1471 cm-1 (-CH2- def.) confirms the presence of –CH2- group in the samples. The weak absorption band at 888-918 cm-1 (-CH2- def.) in samples indicate that the phenols are tetra substituted.

Thermo gravimetric analysis (TGA) has been widely for rapid assessment of the thermal stability of various substances [4,1]. TGA curves shown in fig 3 reveal that there is a very small (6%) loss in weight for both PFR and blend with 30% (w/w) of MPSC up to 80oC. This is due to the loss of moisture absorbed by resin and composite with 30% (w/w) of MPSC. Between 50-190oc there is 20% weight loss in PFR and 15% loss in weight in blend with 30%(w/w) of MPSC. Up to 450oC approximately 57% loss in weight in PFR and up to 480oC , approximately 56% weight loss in composite with 30% (w/w) of MPSC was observed. Two exothermic peaks were obtained in PFR, approximately at 80oC and at 466oC, respectively fig 3. At 80oC, the presence of broad peak indicates the dehydration process of PFR. A peak at 466oC indicates the chemical changes which occur due to thermal degradation of PFR, which reflect approximately 57% weight loss in PFR.

DTA curves of composite with 30% (w/w) of HPSC fig 3 show that the same two types of exothermic peaks were obtained at 80oC and at 482oC, respectively similar to PFR. Again, the first broad peak indicated the dehydration of MPSC and second moderate sharp peak indicates the chemical changes occurring due to thermal degradation of the PFR blended with 30% (w/w) of MPSC.

From fig 3, it is concluded that the limiting temperature for the safer use of PFR and composite resins (CRs) as ion exchangers was 80oC since the IERs degrade thermally after 80oC.

Synthesis of Composites

The experimental and theoretical compositions of MPSC in the composites (A -E) are in good agreement with each other. The results given in Table 1 are similar to those obtained by Sharma et al [3]. This indicates that the preparative methods adopted for the synthesis of PFR and its composites (A-E) are more reliable and reproducible.

Spectral data

The FT-IR spectra of pure resin, 30 percent composite and pure charcoal were obtained in KBr pellets by a Bruker 66v spectrophotometer. The frequency data are given in Table 5.

Scanning Electron Microscope

The Sem analysis of 30 percent composite and pure charcoal were obtained using a JEOL JSM-5300 SEM as shown in figure 4. Sem analysis studies are proved that the number and size of pores in 30% (w/w) MPC with PFR are greater than pure SMPC.The Physico-chemical properties like % of gravimetric swelling, absolute density and CEC are very low in pure SMPC while compared to the 30% SMPC with PFR is attributed to the loss of porosity in pure SMPC than 30% with PFR.

Conclusion

Among the composite prepared, the composite containing Mimosa pudica (Thottaccurungi stem) charcoal up to 30 percent is found to have high density values, good swelling behaviour, comparable attritional resistance, efficient column and absolute capacities, sufficient thermal stability, and is particularly macro porous and cheap. Hence, blending of PFR with 30 %(w/w) MPSC to get composite will definitely lower the cost of IER.

Acknowledgement

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Tables

Table captions

Table 1 Amounts of reagents used and yields of condensates

Table 2 Densities, gravimetric swelling percentages and attritional breaking of the composites

Table 3 Column exchange capacity of H+ form of PFR, Condensates & SMPC

Table 4 Measurement of Thermal Stability

Table 5 FT-IR spectral data* ($\bar{\upsilon}$ in cm^{-1})

Table 1
Amounts of reagents used and yields of condensates

Sample	% of SMPC* (Theoretical)	Amounts of reagents used				
		PhoH (ml)	HCHO (ml)	SMPC (g)	Yield (g)	% of SMPC (observed)
PFR	0	10	12.5	0	19.17	0
A	10	10	12.5	1.67	18.62	10.33
B	20	10	12.5	3.75	20.38	22.52
C	30	10	12.5	6.43	23.67	31.83
D	40	10	12.5	10	27.18	41.80
E	50	10	12.5	15.2	32.10	52.10
MPSC	100	_	_	_	_	100
*% of SMPC = % (w/w) of SMPC						

Table 2
Densities, gravimetric swelling percentages and attritional breaking of the composites

Sample	% of SMPC	Absolute Density (g/ml)		% of Gravimetric swelling	% of Attritional breaking
		Wet	Dry		
PFR	0	2.49	2.26	94.20	46.30
A	10	2.29	2.01	86.70	60.35
B	20	1.95	1.58	77.20	68.70
C	30	1.58	1.43	66.80	74.43
D	40	1.59	1.40	60.08	79.5
E	50	1.47	1.12	52.5	80.19
MPSC	100	1.45	1.09	41.3	86.1

Table 3
Column exchange capacity of H+ form of PFR, Condensates & SMPC

Sample	Na^{+}	Ca^{2+}	Mg^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}
PFR	2.314	1.748	1.838	1.837	1.706	1.545
A	2.199	1.707	1.746	1.674	1.577	1.499
B	2.027	1.635	1.710	1.629	1.395	1.294
C	1.98	1.619	1.650	1.578	1.115	1.145
D	1.593	1.558	1.417	1.25	1.038	1.023
E	1.434	1.387	1.244	1.192	1.014	0.858
MPSC	0.344	0.483	0.366	0.944	0.368	0.477

Table 4
Measurement of Thermal Stability

Sample	% of SMPC	% of weight loss at	
		383 K	393 K
PFR	0	0	19.21
A	10	0	18.70
B	20	0	16.25
C	30	0	13.93
D	40	0	12.13
E	50	0	11.19
MPSC	100	0	6.13

Table 5
FT-IR spectral data* ($\bar{\upsilon}$ in cm^{-1})

Group	Pure resin PFR	(30%)	SMPC
S = O Str. SO_2 sym str. C –S str. Bonded OH str. C–O str OH def CH_2 str -CH_2 def C – C str -C-H def	1030.8 1155.2 552.5 3400.9 1155.2 2914.5 1467.56 1639.20 882.27 1704	1031.7 1162.9 576.6 3407.6 1162.9 2919.70 1466.60 1626.66 884.20 1702	1031.7 1166.7 594.9 3393.1 1166.7 2923.56 1467 1614.13 884 1701.87

Figures
Figure captions:

Fig 1 Cation Exchange capacity of H+ form of PFR, Condensates & SMPC

Fig 2 FT – IR Spectra of (a) PFR, (b) PFR blended with 30 %(w/w) MPC in composite and (c) S M P C (100% pure)

Fig 3 TGA and DTA curves of (a) PFR and (b) composite with 30% (w/w) SMPC

Fig 4 SEM analysis of (a) Condensate resin of 30% (w/w) and (b) Pure 100% SMPC

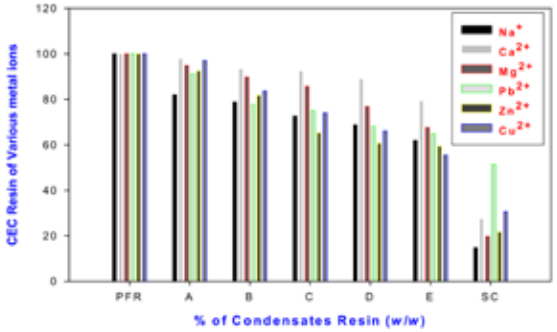

Fig 1 Cation Exchange capacity of H+ form of PFR, Condensates & SMPC

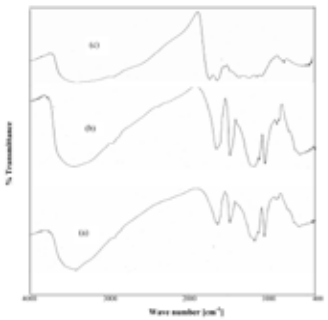

Fig 2 FT – IR Spectra of (a) PFR, (b) PFR blended with 30 %(w/w) MPC in composite and (c) SMPC (100% pure)

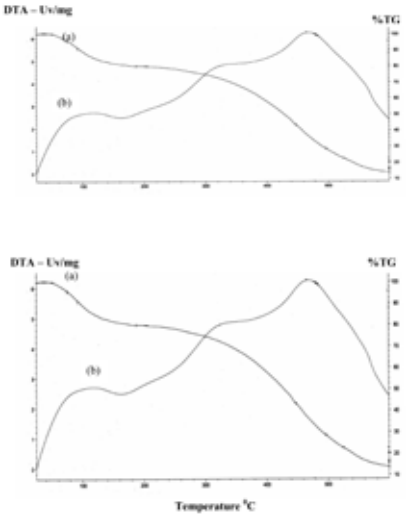

Fig 3 TGA and DTA curves of (a) PFR and (b) composite with 30% (w/w) SMPC

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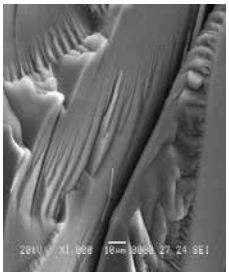
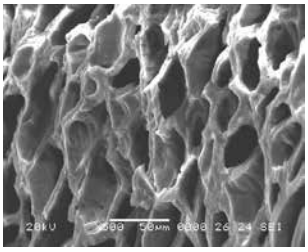
Porosity confirmed by SEM:



(a) 30 % SMPC with PFR



(b) Pure SMPC

Fig 4 SEM analysis of (a) Condensate resin of 30% (w/w) and (b) Pure 100% SMPC

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