

STUDIES ON LOW-COST ION-EXCHANGERS

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Abstract

Phenol - formaldehyde resin (PFR) was prepared and blended with sulphonated charcoals (SCs) prepared from Arappu Thool Carbon. Composite ion exchange resins (IERS) were prepared by varying the amount of SCs (10-50%w/w) in the blends. All the important physico - chemical properties and FT-IR spectral analysis have been done. Composites up to 20% (w/w) blending retain almost all the essential characteristics and Cation Exchange Capacity (CEC) of the original PFR. It is concluded that blending of PFR by SCs will reduce the cost of IERS.

Keywords: SCs, PFR, IERS, CEC, PFSAR, ATC

Introduction

Industrialised nations of the world are taking active measures to control the environmental pollution caused by the hazardous chemicals especially toxic metal ions. In the wastewater treatment, usually a decreasing level of pollutants is achieved, rather than the selective removal and recovery. Ion exchange is an appropriate technique for removal and recovery, as it is employed in the separation and concentration of ionic materials from liquids [1].

Many ion exchangers owe their origin to petroleum products and there is a continual increase in their cost. Furthermore the difficulty also exists in its procurement due to the scarcity of petroleum resources. Hence, there is an urgent need to find out the new low - cost ion exchange resin (IERS) and reduce the cost of IERS by blending it with sulphonated carbons (SCs) prepared from plant materials containing phenolic groups. Earlier studies show that the cheaper composite ion-exchangers could be prepared by partially blending the macro porous / macro reticular phenol-formaldehyde sulphonic acid resin (PFSAR) matrix by SCs prepared from 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].

Attempts have been made to prepare cheaper cationic resins (CRs) from natural products. Ion-exchange process finds a valuable place in the treatment of waters and waste water discharged from plating and other industrial processes containing metal ions.

The aims and objectives of the present work are to synthesise, characterise the new composite ion exchangers of PhOH - HCHO type/cationic matrices blended with sulphonated Arappu Thool Carbon (ATC) and to estimate the column exchange capacity (CEC) for some selective metal ions.

Experimental

Materials

The raw/plant material used was (Albizia Amara; Botanical name) Arappu Thool Carbon (ATC-in Tamil)). This is a plant material freely available in Tamil Nadu, India. Phenol and formaldehyde used were of Fischer reagents (India). LR grade of con. sulphuric acid (Sp.gr.= 1.82) was used. The plant material was locally collected, cleaned, dried and then powdered. The other chemicals / reagents used were of chemically pure grade (AnalaR) procured from SD fine chemicals, India.

Methods

Arappu Thool Carbon (500g) was carbonised and sulphonated by con. sulphuric acid, washed to remove excess free acid and dried at 70°C for 12 h [6-10]. It was labeled as ATC. 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 with double distilled (DD) water to remove free acid, dried, sieved (210 - 300 µm) using Jayant sieves (India) and preserved for characterisation [3,6-8,11]. It was labeled as PFR. The composites were obtained as per the method reported in literature [3,6- 8]. The products with 10, 20, 30,40 and 50% (w/w) of ATC in the blend / composites, respectively were labeled as AT,AT2,AT3,A and AT5. A separate sample of ATC was also subjected to the characterisation studies.

Characterisation of samples

Samples were ground and sieved into a size of 210 - 300µm using Jayant sieves (India). This was used for further characterisation 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 tested by using various organic solvents and inorganic reagents. The values of cation exchange capacity (CEC) were determined by using standard titration techniques [12], as per the literature method [13]. Ft-IR spectral data was recorded for PFR, 20%(w/w) ATC and pure ATC.

RESULTS AND DISCUSSION

Synthesis

The experimental and theoretical compositions of ATC in the composites (AT1 - AT5) are in good agreement with each other (Table 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 composites (AT1 - AT5) are more reliable and reproducible. The optimum value of formaldehyde and phenol are found to be 10mL and 11.5 mL, respectively.

Characterisation studies

Physico - chemical properties

The data given in Table 2 show that the values are absolute density (wet and dry in water and toluene respectively) are decreased from PFR to composite with highest %(w/w) of ATC and finally to pure ATC. The values of absolute density of composite in dry and wet forms depend upon the structure of the resins and its degree of cross linking and ionic form [14]. Generally the absolute density decreased with increase in ATC content in the composite.

The high value of absolute density indicates a high degree of cross linking, and hence suitable for making columns for treating polar and non - polar effluent liquids of high density. The values of absolute densities for the different composites in the dehydrated states are higher than the hydrated states. Moreover, the values of wet and dry density are close to each other indicates that the pores of the sample may be macro porous in nature. The data given in Table 2 indicate that the % of gravimetric swelling decreases from PFR (83.16%) to ATC (28.41%). The value of average % of gravimetric swelling decreased with increasing CLC content in the composite. The values of % gravimetric swelling are found to be 75.17%, 68.32%, 53.41%, 48.62% and 42.01% respectively, for 10, 20,30,40 and 30% (w/w) of mixing of ATC with PFR compared to that of pure PFR. This indicates that up to 20% (w/w) ATC could be mixed with the PFR. The rigidity of the resin matrix was thus concluded from the % of gravimetric swelling measurements. Therefore, these composite resins with increasing amount of ATC content in the composites showed lower % of gravimetric swelling which revealed much lower rigid shape, and the rigidity of composites (from AT1 to AT5). It indicates that, pure resin and composites are rigid with non - gel macro porous structure [11].

The values of % of attritional breaking (Table 2) increase with increase in % (w/w) of ATC content in the composite, representing the stability of the resin, which decreases from PFR to ATC. Therefore, the mechanical stability is good upto 20 - 30% (w/w) substitution of ATC in pure resin. This observation also shows that, the capillaries of the IER may be occupied by the sulphonated carbon (ATC) particles [6-8].

Solubility of Ion Exchangers

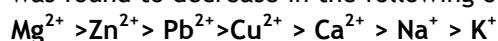
The chemical stability of ion exchange resins under the present study are established by testing their solubility in a few selected organic solvents and reagents the results are presented in Table 3. The samples tested viz., PFR, SC and (AT1-AT5) are all practically insoluble in almost all the reagents and polar and organic solvents. It was noted that the resins and condensates (except ATC) are partially soluble (5 - 10%) in 20% NaOH solution. This is because these samples have phenolic groups in them and hence could not be used in strongly basic medium owing to its solubility. This indicates a high degree of cross-linking in all the samples (*i.e.*) the basic polymer unit is mostly of higher molecular weight fractions or atleast the absence of very low molecular weight fractions in the resins.

Hence, the samples could be used to make cations exchanger column, which could be used acidic neutral and light alkaline medium and treat non-aqueous industrial effluents.

Cation exchange capacity (CEC)

CEC data shown in Table 4 indicate that, the CEC values (for 0.1M solution of metal ions) decrease when the % (w/w) of ATC content (w/w) in the composite increases. The relative value of CEC of individual metal ions depends upon the atomic radius or atomic number [15]. 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 cation exchange capacity of particular metal salt solution [16,17].

From the CEC data given in Table 4, the cation exchange capacity of the samples was found to decrease in the following order.



The selectivity order of metal ions *i.e.*, orders of CEC values also depends upon the ionic potential and the hydrated atomic radius of the metal ions in solution [17]. The order of exchange affinities of various metal ions is not unique to ion exchange system. Only under dilute conditions Hofmeister or lyotropic series [14] is obeyed. But, under high concentration it is different [14]. It is equally important to note that the relative behaviour of these ions for other ionic phenomena deviates the affinity order under the same conditions [18]. The observed order in the present study is different from that of the Hofmeister or lyotropic series [14]. 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 [19]. Also, the CEC data given in the Fig.1, conclude that, upto 20% (w/w) blending of ATC with PFR retains 91.4 - 59.0% of CEC for all metal ions. Hence, 20% (w/w) blending of ATC with PFR to an extent of 20 % (w/w) will reduce the cost of the IER.

FT-IR studies are used to confirm the ion exchangeable groups based on various stretching frequencies [20-21]. Figs.1a and b indicate the appearance of absorption bands at 1028 - 1047 cm^{-1} (S = 0 str.), 1109 - 1156 cm^{-1} (SO_2 sym str) and 588 - 612 cm^{-1} (C - S str.) in pure resin (PFR), composite resin with 20% SATC and pure SATC which confirm the presence of sulphonic acid group.

The appearance of broad absorption band at 31181 - 3289 cm^{-1} (bonded -OH str.) indicates the presence of phenolic and sulphonic -OH group in the samples. The appearance of absorption band at 15895 - 1628 cm^{-1} (C-C str) confirms the presence of aromatic ring in PFR, composite resin with 200% (w/w) SATC in PFR and pure SATC. The absorption band at 1486 - 1420 cm^{-1} (- CH_2 .def) concludes the presence of - CH_2 group in the samples. The weak absorption band at 897 - 911 cm^{-1} (-C-H def.) in the samples indicates that the phenols are tetra substituted.

It is observed that there is a continuous decrease in cation exchange capacity (CEC), as the percentage of ATC content in the blend increases. Hence, any chemical methods requiring ion exchangers of small ion exchange capacity, 20% (w/w) blended CLC -

PFR resin could be used. ATC can be inexpensively prepared from the plant materials, Arappu Thool., which is freely available in plenty, in India, especially in Tamil Nadu.

Table-1 Amounts of reagents used and yield of PFR condensates (AT1-AT5) prepared by blending PFR with various % (w/w) of SATC

Sample	% of SATC in IER	Amount of reagents used			SATC (g)	Yield (g)	% of SATC in IER(Obs)
		Resorcinol (g)	Formaldehyde (mL)	Con.H ₂ SO ₄ (mL)			
PFR	0	10	11.5	12.5	0	16.05	0
AT-1	10	10	11.5	12.5	1.83	18.43	9.92
AT-2	20	10	11.5	12.5	4.12	19.96	20.64
AT-3	30	10	11.5	12.5	7.07	22.58	31.37
AT-4	40	10	11.5	12.5	11.00	26.87	40.93
AT-5	50	10	11.5	12.5	16.50	28.66	57.56
SATC	100	-	-	-	-	-	100

Table-2 Physico -Chemical properties of PFR, SATC and condensates (AT-1 -- AT-5)

Sample	% of SATC in IER	Density (g/mL)		%	
		Wet	Dry	Gravimetric swelling	Attritional breaking
PFR	0	2.45	2.24	83.16	8.50
AT-1	10	1.93	1.81	75.17	16.89
AT-2	20	1.80	1.76	68.32	18.32
AT-3	30	1.67	1.65	53.41	18.98
AT-4	40	1.53	1.53	48.62	20.01
AT-5	50	1.41	1.42	42.01	24.38
SATC	100	1.21	1.32	39.06	28.41

Table.3 Solubility of pure resin and condensates

Solvent	CR	PFR	R1	R2	R3	SC
Con.H ₂ SO ₄	X	X	X	X	X	X
Con.HCl	X	X	X	X	X	X
Con.HNO ₃	X	X	X	X	X	X
NaOH(20%)	PS	PS	PS	PS	PS	X
Benzene	X	X	X	X	X	X
Toluene	X	X	X	X	X	X
Ethanol	X	X	X	X	X	X
Methanol	X	X	X	X	X	X
Acetaldehyde	X	X	X	X	X	X
Chloroform	X	X	X	X	X	X
Diethyl ether	X	X	X	X	X	X
CCL ₄	X	X	X	X	X	X
CS ₂	X	X	X	X	X	X

Where x - Insoluble and PS - Partially soluble (up to 5 - 10%)

SC - Insoluble in all the solvents and reagent

Table-4 Cation exchange capacities of PFR, SATC and condensates and SATC (H⁺ form) for 0.1M solution of selective metal ions at 303K

Sample	% of SATC	Cation exchange capacity m mol/g						
		Cu ²⁺	Zn ²⁺	Pb ²⁺	Mg ²⁺	Ca ²⁺	Na ⁺	K ⁺
PFR	0	1.5107	1.7408	1.7254	1.7702	1.3109	1.2904	1.2108
AT-1	10	1.304	1.531	1.698	1.721	1.194	1.150	0.812
AT-2	20	1.201	1.412	1.510	1.618	1.150	1.095	0.715
AT-3	30	1.130	1.330	1.415	1.535	1.077	1.015	0.630
AT-4	40	1.075	1.272	1.311	1.410	0.962	0.918	0.515
AT-5	50	1.015	1.118	1.208	1.174	0.810	0.871	0.418
SATC	100	0.898	0.913	1.115	0.941	0.615	0.412	0.211

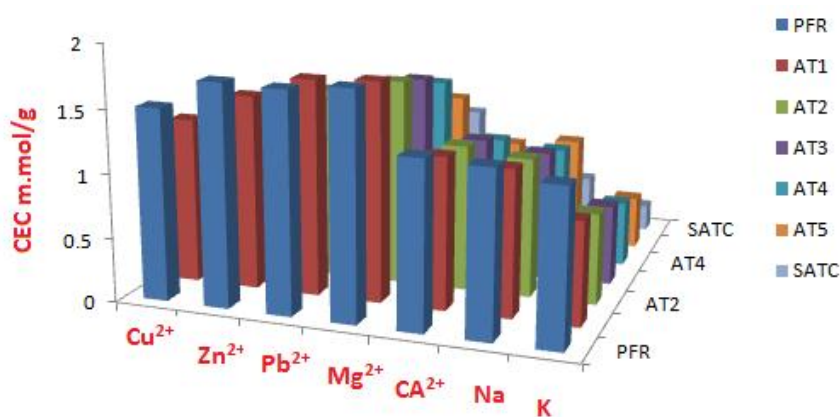
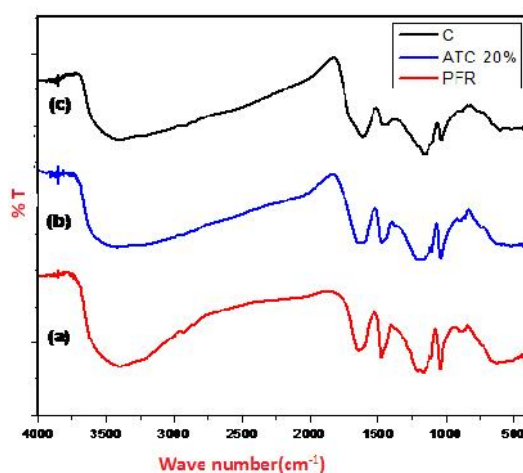


Fig.1 CEC of various metal ions for Various IERs



FT-IR Spectra of (a) PFR, (b) 20%(w/w) SATC and (c) pure SATC

Conclusion

It is concluded from the result of the present study that PFR sample could be blended with 20% (w/w) of ATC, without affecting its physico-chemical and ion exchange properties. Hence, blending of PFR with 20% (w/w) of ATC will definitely lower the cost of IER for the treatment of industrial effluent for the removal of metal ions.

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