

Removal of some Metal Ions by Low-Cost Composite Ion-Exchangers

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ABSTRACT

Phenol – Formaldehyde Resin (PFR) is the basic unit for blending of Sulphonated Centalla Asiatica carbon (SCAC). A few novel composite ion-exchangers were prepared by varying the amount of SCAC in the blends of PFR- SCAC from 0 to 50% (w/w). Optimum principal reaction conditions for the preparation were obtained. The important Physico - chemical properties of PFR, composites and SCAC are also determined.

The synthesized composites are stable in water, organic solvents, thermal treatment and mineral acid (1M) like HCl but soluble to some extent in 20% (w/v) NaOH solution. It was found that the Cation Exchange Capacity (CEC) of the composite resins decreased with increasing the percentage of blending PFR matrix with SCAC.

The composites up to 20% (w/w) blending of Phenol-formaldehyde resin (PFR) with SCAC retains almost all the essential properties of the original PFR, including CEC since the Centalla Asiatica.,(CA) is the low cost, and freely available plant material. Therefore, the blended composites of PFR with SCAC could be used as low cost ion-exchangers, when SCAC partly replaces the original PFR up to 20% (w/w) blending without affecting thermal, physico – chemical properties and CEC values of PFR. Hence, blending of PFR with 20% (w/w) of SCAC will definitely lower the cost of ion exchange resin.

Keywords: Synthesis, Phenol formaldehyde resin-blended with sulphonated carbon, spectral, Physico – chemical, properties, Cation exchange capacity, Composite resin.

1. INTRODUCTION

Industrialized nations of the world are taking active measures to control the environmental pollution caused by chemicals. 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 the removal and recovery, as it is employed in the separation and concentration of ionic materials from liquids [1]. Ion exchange process finds a valuable place in the treatment of metal wastes from plating and other industrial processes.

Many commercial ion exchangers originate from 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 its cost by blending it with sulphonated carbons prepared from plant materials. Such types of low cost ion exchangers can be prepared by blending cheaper and freely available plant materials containing phenolic groups. Ion-exchange process finds a valuable place in the treatment of metal wastes from plating and other industrial processes. Attempts have also been made to prepare cheaper cationic resins from waste materials and natural products.

Earlier studies have shown that the cheaper composite ion exchangers could be prepared by partially blending the macro porous phenol-formaldehyde sulphonacid resin matrix by sulphonated charcoals prepared from coal [2], saw dust[3], spent coffee [4,] cashew nuthusk [5], wheat husk [6] , turmeric plant[7], spent tea, gum tree bark [8], *accacia nilotica* [9], *Egyptian bagassepith* [10]. *Achyranthes aspera* [11] and *Eugenia jambolana*. [12]The aims and objectives of the present work are to synthesize, characterize the new composite ion exchangers of PhOH-HCHO type blended with sulphonated *Centalla Asiatica* carbon (SCAC) and to estimate the physico - chemical properties including cation exchange capacity.

2. EXPERIMENTAL

2.1. Materials

The raw/plant material used was *Centalla Asiatica* Family:Apiaceae in Tamil; Vallarai ; in English Indian Pennywort : in Hindi Gotu Kola) 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 cut into small pieces of about 0.5cm length. The other chemicals / reagents used were of chemically pure grade (AnalaR) procured from SD fine chemicals, India.

2.2. Methods

Centalla Asiatica (500g) was carbonized and sulphonated by con. Sulphuric acid, washed to remove excess free acid and dried at 700C for 12 h. It was labeled as SCAC. Pure phenol – formaldehyde resin 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 characterization[3,6-8,13]. 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 SCAC in the blend / composites, respectively were labeled as CA1, CA2, CA3,CA4 and CA5. A separate sample of SCAC was also subjected to the characterization, instrumental and physico -chemical studies and Cation Exchange Capacity (CEC) for some selective metal ions.

2.3. Physico - Chemical Characteristics

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 to find out the values of absolute density, percentage of gravimetric swelling and percentage of attritional breaking [3,7,8]. The solubility of these samples was tested by using various organic solvents and inorganic reagents. The values of CEC were determined by using standard titration technique as per the literature method [14-15]. The effect of initial concentration of metal ions, particle size, chemical and thermal stability of the resin on CEC was determined [16].

3. RESULTS AND DISCUSSION

The experimental and theoretical compositions of SCAC in the composites (CA1-CA5) are in good agreement with each other (Table-1). The results are similar to those obtained by others [2-4]. This indicate that the preparative method adopted for the synthesis of PFR and its composites (CA1-CA5) are more reliable and reproducible.

Table.1 Amount of reagent used and yield of PFR, condensates (CA1 –CA5) prepared by blending of PFR with SCAC

Sample	% of SCAC in IER	Amount of reagents used			SCAC (g)	Yield (g)	% of SCAC in IER(Obs)
		Phenol (g)	Formaldehyde (mL)	Con.H ₂ SO ₄ (mL)			
PFR	0	10.0	11.5	12.5	0	17.5	0
CAC1	10	10.0	11.5	12.5	1.94	19.52	9.94
CA2	20	10.0	11.5	12.5	4.38	21.66	20.22
CA3	30	10.0	11.5	12.5	7.50	24.98	33.3
CA4	40	10.0	11.5	12.5	11.66	30.2	38.41
CA5	50	10.0	11.5	12.5	17.50	35.32	49.54
SCAC	100	-	-	-	-	-	100

The density of composite resin in dry (dehydrated) and wet (hydrated) form depends upon the structure of resin, degree of cross linking and its ionic nature [17]. As expected the values of absolute density decrease with the increase in SCAC content (% w/w) in the composite. The value of high absolute density (in both dry and wet condition) indicates high degree of cross linking, and hence suitable for making columns for treating polar and non polar effluents liquids of high density. The values of absolute densities of the resins in the hydrated states are higher than that of the dehydrated state. Moreover, the values of absolute density in wet and dry states are close to each other, indicating that the pores of the sample may be macroporous in nature [18].

Table 2. Physico-chemical properties of PFR, SCAC and condensates (CA1-CA5)

IERS	% of SCAC in IER	Density (g/mL)		Percentage	
		Wet	Dry	Gravimetric swelling	Attritional breaking
PFR	0	2.02	1.98	81.16	9.24
CA1	10	1.90	1.88	75.60	10.32
CA2	20	1.72	1.65	68.32	19.2
CA3	30	1.35	1.33	60.02	32.41
CA4	40	1.21	1.17	51.03	41.20
CA5	50	0.95	0.88	44.89	49.51
SCAC	100	0.74	0.68	33.35	62.32

The value of gravimetric swelling percentage (Table-2) decreases from PFR (81.16%) to SCAC (33.35%). The average % of gravimetric swelling of the resin decreased with increasing SSMC content in the composite. The values of gravimetric swelling percentage are found to be 75.60, 68.32 and 60.02 respectively, for 10, 20 and 30% (w/w) blending of SCAC with the parent resin, viz., PFR. This indicates that up to 20% (w/w) SCAC could be mixed with the PFR without affecting its property.

The rigidity of the resin matrix was proved from the swelling measurements. Therefore, the cationic resins with higher SCAC content showed lower swelling which revealed much lower rigid shape, and the rigidity decreased with the increase in % of SCAC content in the composite. It indicates that, pure resin and composites are rigid with non gel macro porous structure [11]. Attritional breaking values (Table-2) increase with the increase in SCAC content in the resins, representing the stability of the resin, which decreases from pure resin to SCAC.

Therefore, the mechanical stability is good upto 20%(w/w) substitution of SCAC with pure resin. This observation indicates that, the capillaries of the resin may occupy by the sulphonated carbon (SCAC) particles [6-8].

CEC data are given in Table-3, which indicate that, the CEC values decrease (for 0.1M solution of metal ions) when the %(w/w) content of SCAC in PFR increases 0 - 100. The relative value of CEC of individual metal ion depends upon its atomic radius or atomic number [19]. 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 a particular metal salt solution [15, 16]. From the CEC data given in Table-3, 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 [16]. The order of exchange affinities of various metal ions is not unique for all the ion exchange systems. Only under dilute conditions, Hofmeister or lyotropic series is applicable [17]. But, under high concentration the order is different [17]. It is equally important to note that the relative behaviour of these ions for other ionic phenomena is different from the affinity order under the same experimental conditions [20-24]. The observed order in the present study is different from that of the Hofmeister or lyotropic series [17]. 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.

Table 3.4. Cation exchange capacities of PFR, condensates (CA1-CA5) and SCAC for selective metal ions (0.1 M) at 303 K

IERS	% of SCAC	Cation Exchange Capacity m mol/g						
		Ca ²⁺	Zn ²⁺	Mg ²⁺	Cu ²⁺	Pb ²⁺	Na ⁺	K ⁺
PFR	0	1.489	1.832	1.670	1.922	1.755	1.260	1.111
CA1	10	1.345	1.800	1.589	1.711	1.702	1.200	1.002
CA2	20	1.289	1.693	1.457	1.601	1.625	1.165	0.947
CA3	30	1.184	1.432	1.300	1.354	1.421	1.021	0.878
CA4	40	1.111	1.321	1.192	1.241	1.287	0.975	0.779

CA5	50	0.987	1.154	1.002	1.054	1.065	0.865	0.701
SCAC	100	0.832	1.112	0.899	0.988	1.002	0.789	0.659

Also, the CEC data given in the Fig.-4, conclude that, the composite up to 20% (w/w) mixing of SCAC with PFR retains 92.409 –85.24% of CEC for all metal ions. Hence, 20% (w/w) blending of SCAC in PFR will reduce the cost of original resin. It is observed that there is a continuous decrease in cation exchange capacity (CEC), as the percentage of SCAC content in the composite increases. Hence, any chemical method requiring ion exchangers of low value of CEC, 20% (w/w) blended SCAC –PFR resin could be used. SCAC can be inexpensively prepared from the corresponding plant materials, which is freely available in plenty, in this study area viz., Tamil Nadu, India.

4. CONCLUSION

It is concluded from the present study that PFR sample could be blended up to 20% (w/w) of SCAC without affecting its physico -chemical properties. The effect of CEC values of various metal ions, reveal that the resin substituted with 20% (w/w) SCAC was very close to the original PFR resin. Hence, blending of PFR with SCAC will definitely lower the cost of IER.

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