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Studies on Composites of Resorcinol-Formaldehyde resin blended with Sulphonated Cardiosprmum halicababum

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ABSTRACT

Resorcinol – formaldehyde resin (RFR) was prepared and blended with sulphonated charcoals (SCs) prepared from *Cardiosprmum halicababum* 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 have been analysed. Composites up to 30% (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.

1. 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. Further more 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 does 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 *Cardiosprmum halicababum* Carbon (SCHC) and to estimate the column exchange capacity (CEC) for some selective metal ions.

2. EXPERIMENTAL

2.1 Materials

The raw/plant material used was *Cardiosprmum halicababum* (In Tamil: Mudakathan, In English: Indravalli) Carbon (CHC). This is a plant material freely available in Tamil Nadu, India. Resorcinol 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

Cardiosprmum halicababum Carbon (500g) was carbonised and sulphonated by con. sulphuric acid, washed to remove excess free acid and dried at 70^0C for 12 h [6-10]. It was labeled as SCHC.

Pure resorcinol – formaldehyde resin (RFR) 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 RFR.

The composites were obtained as per the method reported in literature [3, 6– 8]. The products with 10 % -- 50 % (*w/w*) of SCHC in the blend / composites, respectively were labeled as CH1, CH2, CH3, CH4 and CH5.

A separate sample of SCHC is also subjected to the characterisation studies.

2.3 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. By employing FT-IR spectra for RFR, 30 %(*w/w*) composite and pure SCHC

The values of cation exchange capacity (CEC) were determined by using standard titration techniques [12], as per the literature method [13].

3. RESULTS AND DISCUSSION

3.1 Synthesis

The experimental and theoretical compositions of SCHC in the composites (CH1 – CH5) 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 RFR and its composites (CH1 – CH5) are more reliable and reproducible. The optimum value of formaldehyde and resorcinol are found to be 11.5mL and 10 mL, respectively.

3.2 Characterisation studies

3.2.1 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 RFR to composite with highest %(*w/w*) of SCHC and finally to pure SCHC. 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 SCHC 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 RFR (88.08%) to SCHC (45.23%). The value of average % of gravimetric swelling decreased with increasing CLC content in the composite. The values of % gravimetric swelling are found to be 75.08%, 73.23% and 68.52% respectively, for 10, 20 and 30% (*w/w*) of mixing of SCHC with RFR compared to that of pure RFR. This indicates that up to 30% (*w/w*) SCHC could be mixed with the RFR. The rigidity of the resin matrix was thus concluded from the % of gravimetric swelling measurements. Therefore, these composite resins with increasing amount of SCHC content in the composites showed lower % of gravimetric swelling which revealed much lower rigid shape, and the rigidity of composites (from CH1 to CH5). It indicates that, pure resin 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 SCHC content in the composite, representing the stability of the resin, which decreases fromRFR to SCHC. Therefore, the mechanical stability is good upto 20 - 30% *(w/w)* substitution of SCHC in pure resin. This observation also shows that, the capillaries of the IER may be occupied by the sulphonated carbon (SCHC) particles [6-8].

3.2.2. Solubility of Ion Exchangers

The chemical stability of ion exchange resins under the present study is established by testing their solubility in a few selected organic solvents and reagents the results are presented in Table 3

The samples tested viz.,, RFR, SCHC and CH1 to CH5 are all practically insoluble in almost all the reagents and polar and organic solvents. It was noted that the resins and condensates (except pure SCHC) 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.

3.2.2 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 SCHC 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.

$$\mathbf{Pb^{2+} > Ca^{2+} > Cu^{2+} > Zn^{2+} > Mg^{2+} > Cd^{2+} > Na^{+}}$$

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. Also, the CEC data given in the Table 4 conclude that, upto 30% *(w/w)* blending of SCHC with RFR retains 87.12 - 95.7% of CEC for all metal ions. Hence, 30% (*w/w*) blending of SCHC with RFR to an extent of 30 %(*w/w*) will reduce the cost of the IER.

3.2. 3. FT- IR Spectral Studies

IR spectral data are shown in Table 5 indicate the appearance of absorption band at 1073-1086 cm^{-1} (S = O str.) 1141 -1161 cm^{-1} (SO_2 sym str.) and 601-658 cm^{-1} (C-S str.) in RFR (pure resin), condensate resin blended with 30% (*w/w*) CH3 and pure (100 %) SCHC confirm the presence of sulphonic acid group (Fig.1).

A broad absorption band which appeared at 3307-3322 cm^{-1} (bonded –OH str.) indicates the presence of phenolic and sulphonicacid –OH group in the IERs. The appearance of absorption band at 1617-1614 cm^{-1} (C-C str.) confirms the presence of aromatic ring in RFR, condensate with 30% (*w/w*) blending of SCHC in RFR and pure SCHC. The absorption band at 1475-1548 cm^{-1} (-CH_2 def.) confirms the presence of –CH_2 group in the samples. Weak absorption band at 970-1024 cm^{-1} (-CH- **def**.), shows that the phenols are tetra substituted.

3.3. Conclusion

It is concluded from the result of the present study that RFR sample could be blended with 30% (*w/w*) of SCHC, without affecting its physico-chemical and ion exchange properties. Hence, blending of RFR with 30% (*w/w*) of SCHC will definitely lower the cost of IER for the treatment of industrial effluent for the removal of metal ions.

3.4 REFERENCE

1. B.A. Bolto and L. Pawlowsk, *Waste Water Treatment by Ion-exchange*, Oxford & IBH Publ. Co., New Delhi, (1987).
2. V. Maheshkumar R.K. Seenivasan and P. Selvapandian, *J.Chem. Pharm. Res*., **8(6)**, 104, (2016)
3. M.Thenmozhi , M.Karpagavalli and R.K.Seenivasan, *Rasayan .J*. **9(4)**, 849,(2016).
4. G.J. Mohan Rao and S.C. Pillai, *J. Indian Inst .Sci*., **36A,** 70 (1954)
5. Shahha and S.L. Batna , *J. Appl. Chem. Lond*., **8,** 335 (1953)

6. Rane Caroleena Ganesh and R.K.Seenivasan, , *Inter. J. Adv. Res. Sci.Engin*.,**7**, 333, (2018)

7. D. Kathiresapandian and S. Krishnamoorthy, Indian. *J. Technol*.,**29,** 487 (1991)
8. A. Mariamichel and S. Krishnamoorthy, *Asian J. Chem*., **9(1),** 136 (1997)
9. N. Kannan, R.K. Seenivasan and R. Mayilmurugan, *Indian J. Chem. Technol*., **10,** 623 (2003)
10. M.S. Metwally, N.E. Metwally and T.M. Samy, *J. Appl. Poly. Sci*., **52**, 61 (1994)
11. M. Natarajan and S. Krishnamoorthy, *Res. Ind*., **38,** 278 (1993)
12. 12. G.H. Bassett, J. Jeffery, J. Mendham and R.C. Denney, *Vogel's Text Book of Quantitative Chemical Analysis*, 5th Edn. Longman Group Ltd., London, (1989)

13. V.Maheshkumar, R.K.Seenivasan and K.Ananthakumar,*Indian J. Environ. Protect*, 36 (5), 412, (2016).

14. R. Kunin, *Ion Exchange Resin*, Wiley, Newyork and London, 2nd Edition, (1958)
15. S. Mattson, *Ann. Agric. Coll., Sweden*, **10,** 56 (1942)
16. W.K. Son, S.H. Kim and S.G. Park, *Bull.Korean Chem.Soc*., **22 (1) ,** 53 (2001)
17. D.K. Dimov, E.B. Petrova, I.M. Panayotov and Ch.B.Tsvetanov, *Macromolecules*, **21**, 2733 (1990)

18. O. Bonner, G. Easterling, D. Weit and V. Holland, *J.Am.Chem.Soc*. **77**, 242 (1955).

Table 1 Amount of reagents used for RFR & Composite resins preparation.

Sample	**% of SCHC In IER (cal)**	**Amount of reagent used**					
		Resorcinol (ml)	**HCHO (ml)**	**Conc. H_2SO_4 (ml)**	**SCHC**	**Yield (gm)**	**% of SCHSC in IER (obs)**
RFR	0	10.0	11.5	12.5	0	16.00	0
CH1	10	10.0	11.5	12.5	1.77	17.34	10.21

CH2	20	10.0	11.5	12.5	4.00	21.03	19.02
CH3	30	10.0	11.5	12.5	6.86	24.23	28.31
CH4	40	10.0	11.5	12.5	10.67	29.34	39.37
CH5	50	10.0	11.5	12.5	16.00	33.96	47.11
SCHC	100	-----	----	----	----	----	----

Table: 2 Physico chemical properties of cationic exchange resins and pure carbon SCHC

IERs	**% of SCHC in RFR**	**Density g/mL**		**% of gravimetric swelling**	**% of attritional Breaking**
		Wet	**Dry**		
RFR	**0**	**2.52**	**2.64**	**88.08**	**9.45**
CH1	**10**	**1.92**	**2.16**	**75.08**	**11.57**
CH 2	**20**	**1.48**	**1.73**	**73.23**	**13.31**
CH 3	**30**	**1.34**	**1.67**	**68.52**	**19.78**
CH 4	**40**	**1.21**	**1.66**	**61.78**	**23.08**
CH 5	**50**	**1.16**	**1.23**	**53.08**	**27.67**
SCHC	**100**	**1.05**	**1.14**	**45.23**	**31.24**

Table.3 Solubility of pure resin and condensates

Solvent	**RFR**	**CH1-CH5**	**SCHC**
Con.H_2SO_4	X	X	X
Con.HCl	X	X	X
Con.HNO_3	X	X	X

NaOH(20%)	PS	PS	X
Benzene	X	X	X
Toluene	X	X	X
Ethanol	X	X	X
Methanol	X	X	X
Acetaldehyde	X	X	X
Chloroform	X	X	X
Diethyl ether	X	X	X
CCL_4	X	X	X
CS_2	X	X	X

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

Table: 4 CEC of H^+ form of RFR, composite resins and SCHC

Sample	**% of SCHC**	**Cation exchange capacity in m.mol.g^{-1} (0.1Msolution)**						
		Na^+	**Ca^{2+}**	**Mg^{2+}**	**Zn^{2+}**	**Cu^{2+}**	**Cd^{2+}**	**Pb^{2+}**
RFR	0	0.799	1.701	1.545	1.590	1.682	0.845	1.832
CH1	10	0.776	1.653	1.493	1.542	1.654	0.831	1.786
CH 2	20	0.749	1.601	1.463	1.528	1.629	0.781	1.764
CH 3	30	0.684	1.542	1.380	1.487	1.594	0.753	1.607
CH 4	40	0.513	1.314	1.205	1.301	1.481	0.471	1.521
CH 5	50	0.409	1.119	1.181	1.273	1.287	0.463	1.293
SCHC	100	0.078	0.684	0.623	0.658	0.711	0.081	0.792

Table 5 FT-IR spectral data of RFR condensate CH30 and Pure SCHC (υ in cm^{-1}).

Group	RFR	CH30	SCHC
S = O str.	1073	1086	1080
SO_2 sym. str.	1161	1153	1141
C – S str.	601	658	646
Bonded OH str.	3307	3322	3315
CH_2 – def.	1475	1548	1510
C – C str.	1612	1614	1608
C - H def.	970	1011	1024
C-C def.	860	874	888
SO_2assy.	1355	1289	1270

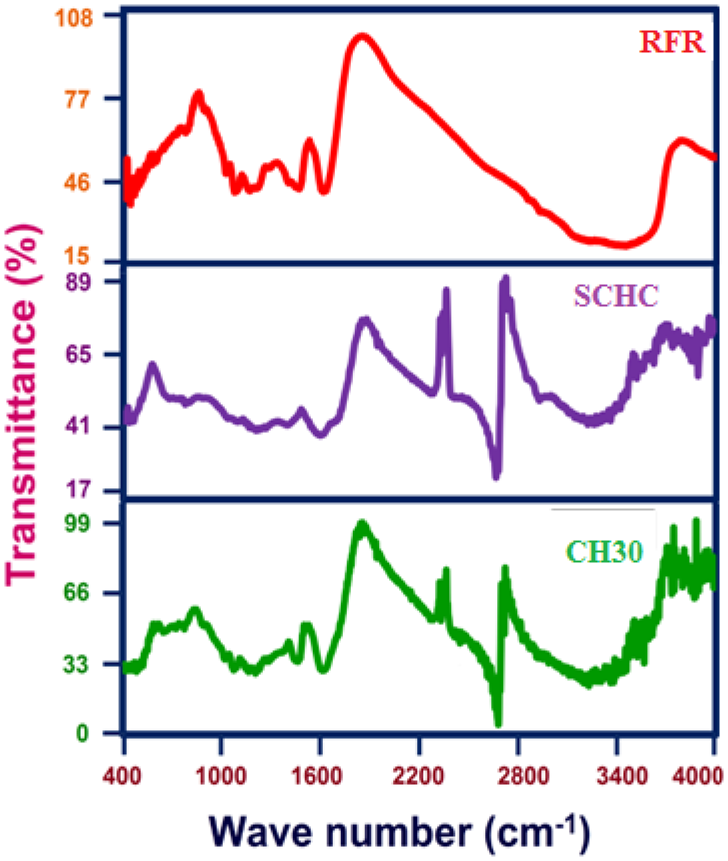

Fig. 1. FT-IR Spectra of RFR, CH30 and SCHC