

**SYNTHESIS AND CHARACTERISATION OF PHENOL-
FORMALDEHYDE COMPOSITE RESIN PREPARED FROM *BASSIA
LONIFOLIA KOEN***

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ABSTRACT

Phenol – formaldehyde resin (PFR) was prepared and blended with sulphonated charcoals (SCs) prepared from a plant material. 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 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.

Key words: *sulphonated charcoals, Phenol – formaldehyde resin (PFR), Cation Exchange Capacity (CEC), Ion exchange resins (IERS)*

1. INTRODUCTION

It is necessary duties of industrialized nations to protect our environment from various pollutants caused by toxic metal ions. Many of the industry reduce their polluted level and not to get valuable metal ions. It is very important to recovery and recollect of various metal ios from solution [1]

Since petroleum based Ion-exchangers (IERS) are very high cost, low cost ion exchange method was adopted. So it is important to prepare low cost IERS from plant materials by mixing their sulphonated carbon form with Phenol-Formaldehyde polymeric matrix. Early study showed that Phenol-Formaldehyde polymeric matrix blended with Sulphonated Carbons (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].

Number of methods has been adopted for preparing low cost IERs which is used to remove metal ions from solution. 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 *Bassia Lonifolia Koen* Carbon (SBLC) and to estimate the column exchange capacity (CEC) for some selective metal ions.

2. EXPERIMENTAL

2.1 Materials

Bassia Lonifolia Koen Carbon (BLC) is enormous source of plant material and easily 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. Plant material was collected, cleaned and cut into small pieces of about 0.5cm length and then dried. All other chemicals / reagents obtained from SD fine chemicals, India.

2.2 Methods

Bassia Lonifolia Koen Carbon (500g) was carbonised and sulphonated by con. sulphuric acid. Excess of free acid is washed number of times by doubled distilled water. Then heated at 70⁰C for 12 h [6-10] and then dried. The powdered form of sulphonated carbon named as BLC.

PFR was obtained as per literature method [3, 6 – 8]. Solid PFR was grinded. Excess sulphuric acid was removed by double (DD). Then dried and sieved by Jayant sieves (India) to get 210 – 300 μm size. It is preserved for further characterisation [3,6-8,11].

As per literature method all composite IERs were obtained.[3,6– 8]. Composites with 10, 20,30,40 and 50% (w/w) of BLC respectively were labeled as BL1,BL2,BL3,BL4 and BL5.

2.3 Characterisation of samples

All IERs converted into a size of 210 – 300 μm using Jayant sieves (India). Using slandered methods, the IERs were characterised [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. Solubility of all IERs in organic and inorganic solvents were tested. As per the literature method [13] and using standard titration techniques [12] the values of cation exchange capacity (CEC) were determined.

3. RESULTS AND DISCUSSION

3.1 Synthesis

The experimental and theoretical compositions of BLC in the composites (BL1 – BL5) 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 (BL1 – BL3) are more reliable and reproducible. The optimum value of formaldehyde and phenol are found to be 10mL and 11.5 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 PFR to composite with highest %(w/w) of BLC

and finally to pure BLC. 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 BLC 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 (87.42%) to BLC (40.11%). The value of average % of gravimetric swelling decreased with increasing BLC content in the composite. The values of % gravimetric swelling are found to be 80.21%, 76.27% and 69.54% respectively, for 10, 20 and 30% (w/w) of mixing of BLC with PFR compared to that of pure PFR. This indicates that up to 20% (w/w) BLC 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 BLC content in the composites showed lower % of gravimetric swelling which revealed much lower rigid shape, and the rigidity of composites (BL1 – B15). 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 BLC content in the composite, representing the stability of the resin, which decreases from PFR to BLC. Therefore, the mechanical stability is good upto 20 - 30% (w/w) substitution of BLC in pure resin. This observation also shows that, the capillaries of the IER may be occupied by the sulphonated carbon (FBC) particles [6-8].

3.2.2. 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.

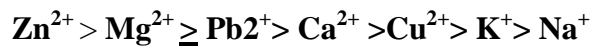
The samples tested viz., PFR, SC and BL1 – BL5 are all practically insoluble in almost all the reagents and polar and organic solvents. It was noted that the resins and condensates (except BLC) are partially soluble (5 - 10%) in 20% NaOH solution. This is because these samples have phenolic groups in 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 BLC 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. Also, the CEC data given in the Fig.1, conclude that, upto 20% (*w/w*) blending of BLC with PFR retains 82.23 – 92.45% of CEC for all metal ions. Hence, 20% (*w/w*) blending of BLC with PFR to an extent of 20 %(*w/w*) will reduce the cost of the IER.

It is observed that there is a continuous decrease in cation exchange capacity (CEC), as the percentage of BLC content in the blend increases. Hence, any chemical methods requiring ion exchangers of small ion exchange capacity, 20% (*w/w*) blended BLC –PFR resin could be used. BLC can be inexpensively prepared from the plant materials, which is freely available in plenty, in India, especially in Tamil Nadu.

3.2. 3. FT- IR Spectral Studies

IR spectral data are shown in Table 5 indicate the appearance of absorption band at 1020-1511 cm^{-1} (S = O str.) 1144 -1162 cm^{-1} (SO_2 sym str.) and 587-608 cm^{-1} (C-S str.) in RFR (pure resin), condensate resin blended with 20% (*w/w*) BL2 and pure (100 %) SBLC confirm the presence of sulphonic acid group (Fig.1).

A broad absorption band which appeared at 3396-3414 cm^{-1} (bonded –OH str.) indicates the presence of phenolic and sulphonic acid –OH group in the IERs. The appearance of absorption band at 1580-1639 cm^{-1} (C-C str.) confirms the presence of aromatic ring in RFR, condensate

with 20% (w/w) blending of SBLC in RFR and pure SBLC. The absorption band at 1398-1448 cm^{-1} ($-\text{CH}_2$ def.) confirms the presence of $-\text{CH}_2$ group in the samples. Weak absorption band at 865-892 cm^{-1} ($-\text{CH}$ - def.), shows that the phenols are tetra substituted.

4. Conclusion

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

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ANNEXURE:

Table 1

Amount of reagent used and yield of PFR, condensates (BL1 – BL5) prepared by blending of PFR with various % (w/w) of SBLC

Sample	% of SBLC in IER (theory)	Amount of reagents used			SBLC (g)	Yield (g)	% of SBLC in IER(obs)
		Phenol (g)	HCHO (mL)	Con.H ₂ SO ₄ (mL)			
PFR	0	10.0	11.5	12.5	0	18.80	0
BL1	10	10.0	11.5	12.5	2.08	20.33	10.23
BL2	20	10.0	11.5	12.5	4.70	23.36	20.12
BL3	30	10.0	11.5	12.5	8.06	27.00	29.85
BL4	40	10.0	11.5	12.5	12.53	31.39	39.92
BL5	50	10.0	11.5	12.5	18.8	37.44	50.21
SBLC	100	-	-	-	-	-	100.00

Table 2

Physico - chemical properties of PFR, SBLC and condensates (BL1-BL5)

IERs	% of SBLC in IER	Density (g/mL)		Percentage	
		Wet	Dry	Gravimetric swelling	Attritional breaking
PFR	0	2.12	2.02	87.42	8.52
BL1	10	1.92	1.89	80.21	9.00
BL2	20	1.83	1.74	76.27	10.55
BL3	30	1.74	1.70	69.54	14.32
BL4	40	1.57	1.41	56.32	17.32
BL5	50	1.38	1.22	48.78	26.89
SBLC	100	1.19	1.02	40.11	38.44

Table.3

Solubility of pure resin and condensates

Solvent	RFR	BL1-BL5	SBLC
Con.H₂SO₄	X	X	X
Con.HCl	X	X	X
Con.HNO₃	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
CCL₄	X	X	X
CS₂	X	X	X

Table 4

Cation exchange capacities of PFR, condensates (BL1-BL5) and SBLC for selective metal ions (0.1 M) at 303 K

IERs	% of SBLC	Cation exchange capacity m mol/g						
		Ca²⁺	Mg²⁺	Zn²⁺	Pb²⁺	Cu²⁺	Na⁺	K⁺
PFR	0	1.536	1.956	1.735	1.988	1.784	1.327	1.121
BL1	10	1.382	1.857	1.725	1.888	1.604	1.021	1.006
BL2	20	1.304	1.741	1.700	1.741	1.521	0.954	0.987
BL3	30	1.214	1.631	1.654	1.613	1.346	0.857	0.877
BL4	40	1.125	1.444	1.521	1.456	1.275	0.654	0.722
BL5	50	1.000	1.283	1.387	1.324	1.111	0.589	0.599
SBLC	100	0.913	0.888	1.123	1.011	0.979	0.456	0.452

Table 5
FT-IR spectral data of PFR, Condensates BL2 and pure SBLC ($\bar{\nu}$ in cm^{-1})

Group	PFR	Composites BL2	Pure SBLC
S = O str.	1051	1033	1020
SO ₂ sym. str.	1152	1162	1144
C – S str.	608	588	587
Bonded OH str.	3396	3401	3414
CH ₂ – def.	1488	1412	1398
C – C str.	1639	1588	1580
C - H def.	880	865	892
C-C def.	862	840	847
SO ₂ assy.	1332	1333	1325

Fig. 1
Cation Exchange Capacity of H⁺ form of PFR, Composites (BL1-BL5) and SBLC for various metal ions at 303 K

