



## ENCROACHMENT OF NATURAL CATION EXCHANGER FOR THE BEHAVIOR OF UNI/DIVALENT METAL IONS FROM AQUEOUS SOLUTION

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**ABSTRACT** Phenol-Formaldehyde Resins (PFR) blended with sulphonated Aerva lanata (L.) Juss.ex Schult Carbon (SALC) was used for the removal of various metal ions from aqueous solutions. SALC could be used as blending material in the PFR to lower the cost of the ion exchange resin for water and wastewater treatment, particularly for the removal of heavy metal ions.

**KEYWORDS :** Phenol formaldehyde resins; Cation exchange capacity; FTIR; SEM.

### 1. Introduction

Ion exchange resins (IERS) are polymers that are capable of exchanging particular ion within the polymer with ions in a solution that is passed through them. They are classified as cation exchangers, whom it has positively charged movable ions available for exchange and anion exchangers [1]. Both anion and cation resins are made from the same basic organic polymers [2]. Ion exchange is also effectively used in the industry for the removal of heavy metals from wastewater and process streams [3-5].

Earlier, it could be prepared by partially blending the macro porous phenol-formaldehyde sulphonic acid resin (PFR) matrix with SCs obtained from cassia auriculata[6], vilvam skin waste [7], tannin materials [8], cellulose acetate [9], lignin from the black liquor [10], sugar cane bagasse lignin [11], Terminalia bellerica [12] and Tung oil [13]. A careful literature survey has revealed that no report is available with SALC [14-32]. The aim of this work are synthesized, characterization of new low cost IERS obtained by blending PFR with various composition of sulphonated *A.lanata* Carbon and to estimate the CEC for some selective metal ions from aqueous solutions.

### 2. Experimental

#### 2.1. Materials and Methods

The plant material used in the present study was *Aerva lanata* (L.) Juss.ex Schult (Tamil: Siru pulley and English: Mountain knotgrass). The other materials like Phenol (BDH Sample), Formaldehyde solution (37 to 40 percent, Sd fine reagent) and con. Sulphuric acid (SG 1.82) were also used.

#### 2.2. Preparation of Sulphonated Carbon, PFR and its composites

It was prepared as per literature and well-preserved for characterization. The experimental and theoretical yields of the composite are presented [33].

#### 2.3. Characterization of samples

The samples were characterized by using technique like FT-IR, DTA/TGA and SEM. It was carried out and determined the values of cation exchange capacity (CEC) by using standard titration techniques as per the literature method [34].

### 3. Results and Discussion

#### 3.1 FT-IR Analysis

FT-IR studies are used to confirm the various ion exchangeable groups [35] and their spectral data (frequencies) are given in Table 1.

**Table 1 FT-IR spectral data of PFR, 20% (w/w) of SALC and pure SALC ( $\nu$  in  $\text{cm}^{-1}$ )**

Group	PFR	20% (w/w) SALC	Pure SALC
S = O str.	1039	1041	1037
SO <sub>2</sub> sym. str.	1118	1163	1112
C – S str.	623	680	678
OH str.	3404	3446	3290
CH <sub>2</sub> – def.	1469	1469	1490
C – C str.	1629	1649	1512

C - H def.	887	886	875
C-C def.	858	742	717
SO <sub>2</sub> assy.	1338	1358	1338

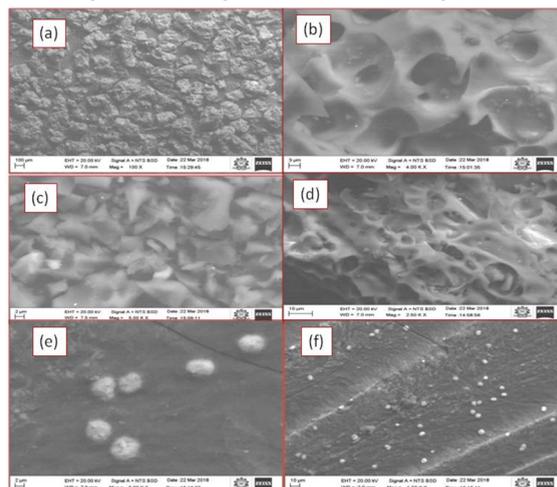
#### 3.2. DTA and TGA studies

TGA data exposed that there is a small (16%) loss in weight for PFR and blend with 20% (w/w) of SALC2 upto 90°C. This is due to the loss of moisture absorbed by resin and composite with 20% (w/w) of SALC2. At the temperature between 100-300°C there is 27% weight loss in PFR and 24.5% loss in weight in blend with 20% (w/w) of SALC2. Upto 360°C approximately 43% loss in weight in PFR and approximately 42% weight loss in composite with 20% (w/w) of SALC2 was observed. Two exothermic peaks were obtained in PFR, approximately at 50°C and at 270°C respectively. At 50°C, the presence of broad peak indicates the dehydration process of PFR. A peak at 270°C indicates the chemical changes which occur due to thermal degradation of PFR which reflect approximately 43% weight loss in PFR [36].

DTA data of composite with 20% (w/w) of SALC2 show that the same two types of exothermic peaks were obtained at 70°C and at 260°C respectively similar to PFR. Again, the first broad peak showed the dehydration and second moderate sharp peak specifies the chemical changes occurring due to thermal degradation of the PFR blended with 20% (w/w) of SALC2. It is concluded that the limiting temperature for the use of PFR and composite resins as ion exchangers was 90°C since the IERS degrade thermally after 100°C.

#### 3.3. Scanning Electron Microscope

The surface morphology of the samples (20% (w/w) composite and SALC) were recorded by Scanning Electron Microscope (SEM) is as shown in Fig. 1. All The images show that different magnifications.



**Fig. 1 SEM photos of PFR (a and b), condensate resin with 20% (w/w) of SALC2 (c and d) and pure 100% SALC (e and f)**

SEM analysis studies are proved that the number and size of pores in 20% (w/w) SALC2 with PFR are greater than pure SALC. The Physico-chemical properties like percentage of gravimetric swelling, absolute density and CEC are very low in pure SALC while compared to the 20% (w/w) of SALC with PFR is attributed to the loss of porosity in pure SALC than 20% (w/w) with PFR [37, 38].

### 3.4. Cation Exchange Capacity

Ion Exchange Capacity (IEC) of particular metal ions depends upon the atomic radius or atomic number [39]. The composites SALC1-SALC5 with PFR decreases the CEC values for the exchange of H<sup>+</sup> ions with that Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions. Also, it is noted that the composites up to 20% (w/w) of SALC retains nearly 97-92% of CEC of PFR, while 30% (w/w) blending of SALC with PFR only leads to 91-79% of CEC of PFR for all the metal ions. Therefore, it may be concluded that PFR could be blended up to 20% (w/w) of SALC will absolutely reduce the cost of the IER Fig. 2a. These are mainly used in industrial for the treatment of industrial sewage. The cation exchange capacity of the prepared samples was decreased ( $Mg^{2+} > Zn^{2+} > Ca^{2+} > Pb^{2+} > Cu^{2+} > K^{+} > Na^{+}$ ) from the CEC data. The orders of exchange affinities of various metal ions are not unique to ion exchange system. Only Hofmeister or lyotropic series is obeyed under high different concentrations [40]. The percentage values of CEC for exchange of H<sup>+</sup> ions with Na<sup>+</sup>, K<sup>+</sup>, Cu<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> ions in 0.1M solution is about 29-41% for SALC1-SALC5 and almost 50% contrast to pure commercial IERs. This shows that the composites can partly replace commercial IERs in making the novel low cost ion exchangers for industrial uses.

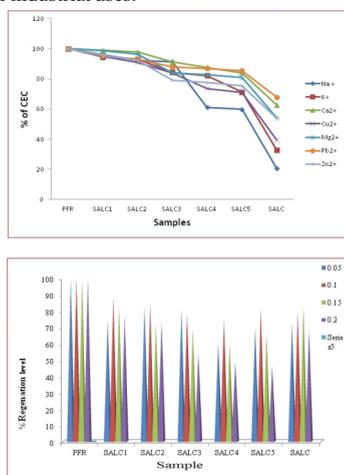


Fig. 2 Cation Exchange Capacities (a) of H<sup>+</sup> form of PFR, condensates (SALC1-SALC5) and pure SALC & Regeneration level (b) for PFR, condensates and pure SALC by using NaCl after exchange with Mg<sup>2+</sup> ions.

The CEC of treated samples possess CEC almost similar to the parent/un-treated resins approximately 3-19% for all the metal ions. This shows that the resin samples are chemically stable. CEC data specified that the particle size of <210 micron are fine, 300-500 micron and >500 micron are coarse, as to cause very low ion exchange capacity compared to IERs of 210-300 micron particle size. Therefore, for the effective IEC, the particle size should be maintained and suggested sieve size is 210-300 micron. The CEC of transition metal ion (Zn<sup>2+</sup>) and alkali metal ion (Na<sup>+</sup>) showed that the values of maximum and minimum. It may be due to the blending of PFR with 20% (w/w) of SALC does not affect these CEC values for the metal ions to a more extent.

### 3.5. Regeneration level

40 mL of 0.1 M brine (NaCl) solution of all the composites, PFR and SALC effectively regenerates after the exchange with the Mg<sup>2+</sup> ions. Most of the commercial IERs are in Na<sup>+</sup> form, and hence 40mL of 0.1M NaCl could be used as a regenerant for every 2g of the resin (Fig. 2b).

### Conclusions

The composites *A. Lanata* charcoal containing up to 20% (w/w) of SALC2 are found to have good thermal stabilities. CEC values of these natural cation exchangers are assessed. These composites are macroporous and low cost. Therefore these ion exchangers can be

useful in element process for the separation of rare earths from industrial to recapture of metals.

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