

Original paper

## Synthesis and characterization of low-cost ion-exchange resins used for the removal of metal ions

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## ARTICLE INFO

## Article history:

Received 17 February 2016

Received in revised form 16 April 2016

Accepted 30 April 2016

## Keywords:

Phenol-formaldehyde resin  
Sulphonated Abutilon indicum carbon  
Cation exchange capacity  
Composites resin  
Low cost ion exchangers  
Endothermic

## ABSTRACT

Phenol-formaldehyde resin (PFR) is used as a protecting agent in blending of different percentage by weight of Sulphonated Abutilon indicum, Linn. carbon (SAIC). We provide a synopsis of current developments in the use of ion exchange techniques in wastewater treatment. The prepared materials (PFR, composites, and SAIC) were characterized by FT-IR spectra, SEM and thermal (TGA) studies. The low cost ion exchangers (IERS) are used for the removal of some selective metal ions such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup>. Thermodynamic equilibrium constants (ln K<sub>c</sub>) are calculated for Zn<sup>2+</sup>-H<sup>+</sup> ion exchanges using the composite resins and also the thermodynamic parameters such as  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  are evaluated from Van't Hoff plot. The cation exchange capacity (CEC) of the composites were found to decrease with the increasing percentage of SAIC in PFR matrix. It was observed that the composites up to 20% (w/w) blending of SAIC retain all the properties of original PFR. Hence, the blended composites could be used as low cost ion exchangers when SAIC partially replaces the original PFR up to 20% (w/w) SAIC blending without affecting the physico-chemical, thermal, spectral properties and CEC values of PFR.

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## 1. Introduction

The quality of water is of fundamental concern to mankind, since it is directly linked with human benefit. The water pollution and its impact on the environment are currently the focus of international attention. In developed nations are using dynamic methods to manage and prevent the environmental pollution caused by chemicals, but the developing countries are beginning to follow it. Most of the industries discharge the wastewater from some stage of their manufacturing processes. The indiscriminate disposal of untreated wastewater from various industries into the rivers or onto the domestic invariably pollutes surface/ground water and land. The contaminants in wastewater vary depending on the type of industry and nature of processes. The universal pollutants encountered in the industrial wastewater are soluble organics/inorganics, suspended solids, heavy metals, volatile materials, nitrogen, phosphorous, oil and greases. In the wastewater treatment, usually a decreasing level of pollutants is achieved. A large number of methods have been used for the removal of harmful organic and inorganic constituents from wastewater. The available systems to treat wastewater can be broadly classified into physico-chemical and biological treatments. The selection of wastewater treatment process depends upon the nature of pollutants present in wastewater and quality of water required after the treatment process.

Ion exchange method is an appropriate technique, which could be employed under field condition for the removal of ionic materials from water and wastewater (Bolto et al. 1987). Ion-exchange process finds a valuable place in the treatment of metal wastes from plating and other industrial processes. Many viable resins are originated 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 (SCs) prepared from carbonaceous materials. Such types of low-cost ion exchangers can be prepared by blending cheaper and freely available

plant materials containing phenolic groups. Attempts have also been made to prepare cheaper cationic resins from waste materials and natural products. The application of low-cost adsorbents obtained from agricultural by-products is widely used in the recent research as a replacement for costly conventional methods of removing heavy metal ions from wastewater (Homagai. 2012). Earlier studies have shown that the cheaper condensate ion exchangers could be prepared by partially blending the macroporous phenol-formaldehyde sulphonic acid resin (PFR or PFSAR) matrix by sulphonated carbon (SCs) prepared from coal (Sharma et al. 1980), Egyptian corn cop (Metwally et al. 1992), bagasse charcoal (Swamiappan et al. 1984), Egyptian bagasse pith (Metwally et al. 1994), ground nut shell (Chandrasekaran et al. 1987), wheat husk (Dheiveesan et al. 1988), spent tea and mangroves bark (Krishnamoorthy et al. 1997), starch (Farag et al. 1995), jute (Hassan. 2003), Accacianilota (Kannan et al. 2003), cashew nut shell (Bato et al. 2003) and lignin (Zoumpoulakis et al. 2001). A careful literature survey revealed that no work has been done with Abutilon indicum. Abutilon indicum (local name; peelybooti or karandi) is a rigid, timbered, shrubby plant. It is widely distributed in the tropical countries (Kirtikar et al. 1980). It is known as "Atibala" in Hindi and found in the outer Himalayan tracts from Jammu to Bhutan up to an altitude of 1500m and extending through the whole of northern and central India (Rajurkar et al. 2009).

The present work is to synthesize and characterize (by IR, TGA, and SEM studies) the new condensate / low-cost ion exchangers of PhOH-HCHO type blended with sulphonated Abutilon indicum, Linn. Carbon (SAIC) and to estimate the physico-chemical properties including the cation exchange capacity (CEC) for some selective metal ions. The effect of particle size of selective metal ions, regeneration level of Mg<sup>2+</sup> ions loaded IERS by using NaCl and to find out thermodynamic parameters for the above ion exchange process.

## 2. Materials and methods

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## 2.1. Materials

Abutilon indicum, Linn. (AI) was used as a plant material and it is easily available in India. It belongs to the family Malvaceae and called 'Karandi' in Tamil and Atibalain Hindi. The plant material was nearby collected, cleaned, dried and cut into small pieces of about 0.5cm length. Phenol and formaldehyde (AR) were purchased from Fischer reagents (India). Concentrated sulphuric acid (Sp.gr. = 1.82) and other chemicals/reagents used were produced from SD fine chemicals, India.

## 2.2. Methods

Abutilonindicum, Linn.plant material (500 g) has been carbonized and sulphonated by using con. sulphuric acid, washed with distilled water to remove excess free acid (tested with BaCl<sub>2</sub> solution) and dried at 70 °C for 12 h. It was labeled as SAIC.

Pure phenol-formaldehyde resin was prepared according to the literature method (Ramachandran et al. 1984; Radhakrishnan et al. 1990). It was then ground, washed with distilled water and finally with double distilled (DD) water to remove the excess acid (tested with BaCl<sub>2</sub> solutions), dried, sieved (210 – 300µm) using Jayant sieves (India) and preserved for characterization ( Kannan et al. 2003;Dheiveesan et al. 1988). It was labeled as PFR.

The condensates were obtained as per the method reported in the literature (Krishnamoorthy et al. 1997). The products with 10, 20, 30, 40 and 50 % (w/w) of SAIC in the condensates were labeled as SAIC1, SAIC2, SAIC3, SAIC4, and SAIC5 respectively. A separate sample of SAIC was also subjected to the characterization (instrumental and physico - chemical) studies.

## 2.3. Characterization of samples

### 2.3.1. Instrumental studies

FT-IR spectral data of pure resin (PFR), condensate with 20 % (w/w) of SAIC2 and pure SAIC were recorded with a JASCO FT-IR 460 plus FT-IR spectrophotometer by using KBr pellets. To establish the thermal degradation of the samples, TGA and DTA traces were obtained by using the thermal analyzer. SEM analysis of pure resin (PFR), condensate with 20 % (w/w) of SAIC2 and pure SAIC were obtained using Hitachi Scanning Electron Microscope (Model S-450), Japan.

### 2.3.2. Physico-chemical characteristics

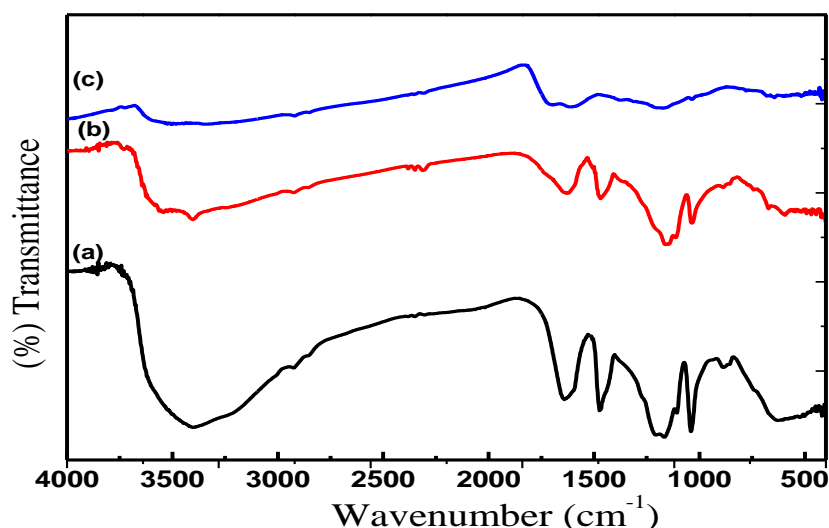


Fig.1. FT-IR spectra of (a) PFR (b) condensate resin with 20 % (w/w) of SAIC2 and (c) pure SAIC (100 %).

The appearance of broad absorption band at 3332 - 3404 cm<sup>-1</sup> (H-bonded -OH str.) indicates the presence of phenolic and -OH group of in sulphonic acid group of the samples. The appearance of absorption

Samples were crushed and sieved into a particle size of 210 – 300 µm using Jayant sieves (India). This was used for further characterization by using standard procedures (Kannan et al. 2003; Chandrasekaran et al. 1987) to find out the values of absolute density (wet and dry), the percentage of gravimetric swelling and percentage of attritional breaking. The solubility of these IERs was tested with various organic solvents and inorganic reagents.

The values of cation exchange capacity (CEC) were determined by using standard titration technique (Ramachandran et al. 1984), as per the reported method (Raghunathan et al. 1984; Bassett et al. 1989). The effects of initial concentration of metal ions, particle size, chemical and thermal stability of the resin on CEC were determined (Kannan et al. 2003; Chandrasekaran et al. 1987; Krishnamoorthy et al. 1997).

After the exchange of H<sup>+</sup> ions by the Mg<sup>2+</sup> ions, the regeneration level of the condensates loaded with Mg<sup>2+</sup> ions were determined by using NaCl (brine) solution. The equilibrium constant (K<sub>eq</sub>) of an exchange reaction between H<sup>+</sup> ions (bound resin) and Zn<sup>2+</sup> ions (in aqueous solution) were obtained as per the literature method (Bato et al. 2003). Thermodynamic parameters (ΔG°, ΔH° and ΔS°) were computed by following the standard procedure and interpretation.

## 3. Results and discussion

### 3.1. Synthesis of composites

The experimental (observed) and theoretical (calculated) composition of SAIC in the condensates (SAIC1 – SAIC5) is in good agreement with each other. The results are similar to those obtained by others (Vasudevan et al. 1978; Sharma et al. 1980). This indicates that the preparative methods adopted for the synthesis of PFR and its condensates (SAIC1 – SAIC5) are more dependable and reproducible. Exactly 11.5mL of formaldehyde, 12.5mL of conc. Sulphuric acid and 10mL of phenol are found to be optimum.

### 3.2. Characterization by instrumental studies

FT-IR studies were used to confirm the ion exchangeable groups present in the IERs based on various stretching frequencies. Fig.1 (a and b) indicates the appearance of absorption bands at 1033 - 1035 cm<sup>-1</sup> (S = O str.), 1118 - 1186 cm<sup>-1</sup> (SO<sub>2</sub> sym. str.) and 623 - 673 cm<sup>-1</sup> (C-Sstr.) in pure resin (PFR), condensate resin with 20 % (w/w) of SAIC2 and pure SAIC, which confirm the presence of sulphonic acid group.

band at 1610 – 1629 cm<sup>-1</sup> (C-C str.) confirms the presence of aromatic ring in PFR, condensate resin with 20 % (w/w) of SAIC2 in PFR and pure SAIC. The absorption band at 1469 – 1581 cm<sup>-1</sup> (-CH<sub>2</sub> def.)

concludes the presence of  $-CH_2$  group in the samples. The weak absorption band at  $887 - 894\text{ cm}^{-1}$  ( $-C-H$  def.) in the sample indicates that the phenols are tetra substituted.

Thermogravimetric analysis (TGA) is used for rapidly assessing the thermal stability of various substances (Sharma et al. 2001). The consequences of TGA curves are shown in Fig.2. From the TG data summary, the 16 % weight loss of PFR sample and the 14 % weight loss 20 % (w/w) of SAIC2 for up to  $90^\circ\text{C}$  observed. It is clearly shown that the loss of moisture absorbed by the resin and composite SAIC2. The temperature between  $100^\circ\text{C}$ - $300^\circ\text{C}$  there is 27 % weight loss in PFR and 30 % weight loss for SAIC2. Up to  $360^\circ\text{C}$ , approximately 44 % loss of weight was observed for both PFR and SAIC2. It is cleared observed that up to  $100^\circ\text{C}$  weight loss of resin is due to the removal of water content present in the resin. Beyond this temperature, a gradual

chemical degradation of PFR and composite resin (PFR-SAIC2) occurs in  $100 - 300^\circ\text{C}$  and up to  $360^\circ\text{C}$  temperature range. Thermal studies indicate that the IERs are thermally stable up to  $10^\circ\text{C}$ .

In Fig. 2a DTA curve shows that there are two peaks obtained in PFR, approximately at  $60^\circ\text{C}$  and  $280^\circ\text{C}$ . At  $60^\circ\text{C}$  the presence of broad peak indicates the dehydration process of PFR. A peak at  $280^\circ\text{C}$  shows the chemical changes, which occur due to thermal dehydration of PFR and reflects approximately 44 % weight loss in PFR. DTA curves of composite with 20 % (w/w) of SAIC2 (Fig. 2b) show that the two exothermic peaks are obtained at  $70^\circ\text{C}$  and  $290^\circ\text{C}$  respectively, which is comparable to PFR. The first peak shows the dehydration of SAIC2 and second sharp peak indicates the chemical changes arising because of thermal degradation of the condensate SAIC2.

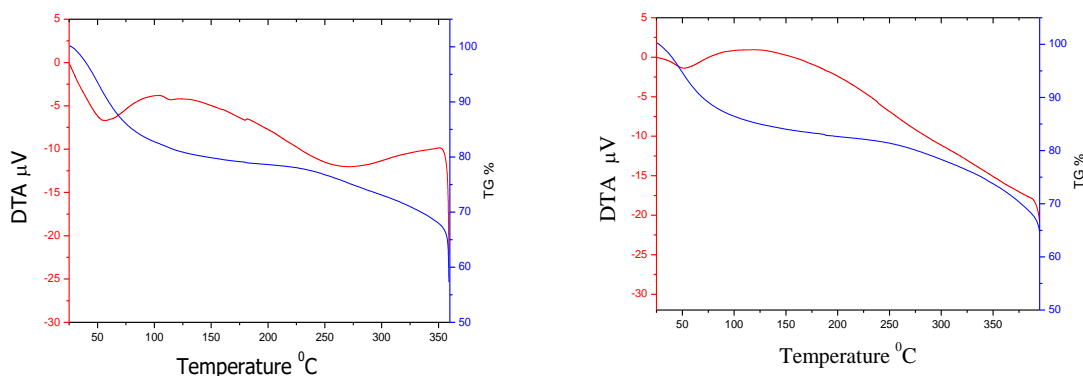
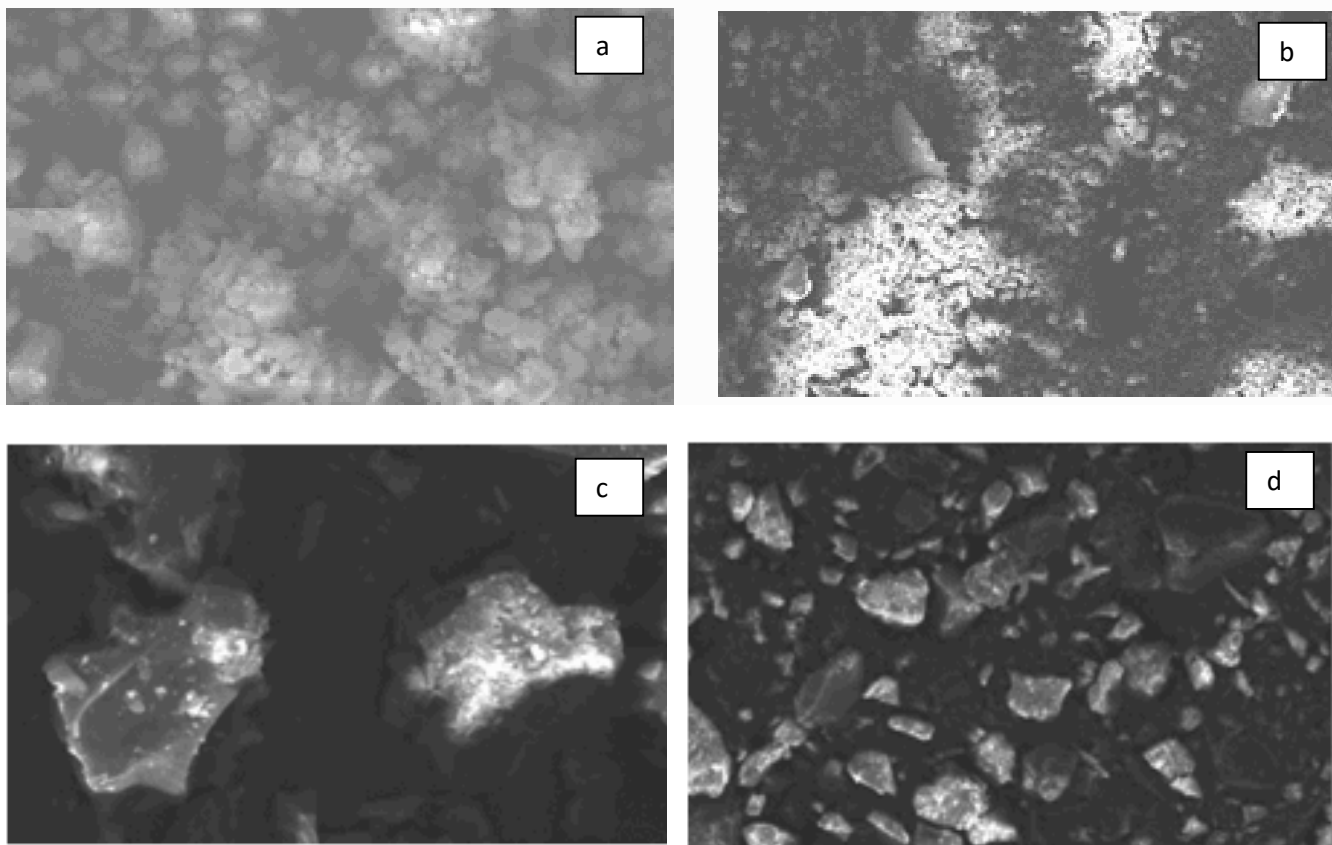


Fig. 2. Thermal studies of (a) PFR and (b) condensate with 20 % (w/w) of SAIC2.

SEM photos of PFR (Fig.3a and b), condensate SAIC2 (Fig. 3c and d) and pure SAIC (Fig.3e and f) with the magnification of  $50\ \mu\text{m}$  and  $500\ \mu\text{m}$  are given. SEM images that all the samples are macro permeable in nature. The high macro porous carbon obtained from *Abutilon indicum*, from the basin in which the phenol-formaldehyde

sulphonic acid particles are deposited. As a result, the pore diameter decreases in condensate SAIC2 as compared to pure SAIC. Therefore, the condensate resin SAIC2 has a great mechanical strength and little attritional breaking (Fig. 3) compare to pure SAIC.



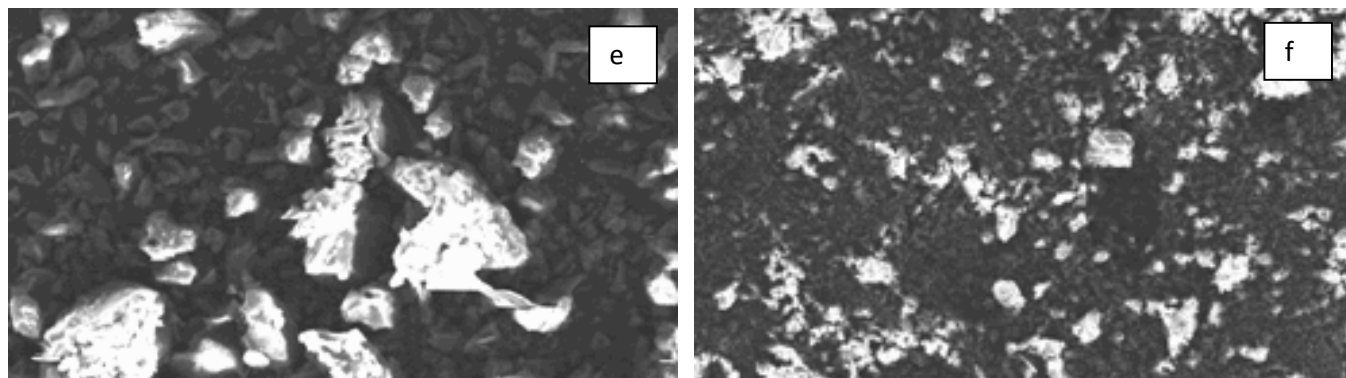


Fig. 3. SEM images of PFR (a & b), condensate resin with 20 % (w/w) of SAIC2 (c & d) and pure 100 % SAIC (e & f).

3.3. Physico-chemical characteristics

3.3.1. Absolute density

Absolute density value (Table 1) decreases from pure resin(PFR) to the condensate containing highest percentage (w/w) of SAIC5 (50 %) and then finally to pure SAIC (100 %). The density of condensate resin in dry (dehydrated) and wet (hydrated) form depends upon the structure of resin, degree of cross-linking and its ionic nature (Sharma et al. 2001). As expected, the value of absolute density decreases with

the increase in SAIC content (% w/w) in the condensate. The value of high absolute density (in both dry and wet condition) indicates a high degree of cross-linking and hence suitable for making columns for treating polar and nonpolar effluents liquids of high density. The values of absolute density of the resins in the dehydrated states are slightly higher than that of the hydrated state, but somewhat close to each other. 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 (Krishnamoorthy et al. 1997) and close packing.

Table 1. Physicochemical properties of PFR, SAIC and condensates SAIC1- SAIC5.

Sample	% of SAIC in IER	Density (g mL <sup>-1</sup> )		Percentage	
		Wet	Dry	Gravimetric Swelling	Attritional Breaking
PFR	0	2.015	2.080	80.37	9.00
SAIC1	10	1.778	1.734	65.68	18.25
SAIC2	20	1.604	1.605	55.82	19.52
SAIC3	30	1.435	1.426	54.29	24.36
SAIC4	40	1.257	1.222	44.71	31.25
SAIC5	50	1.195	1.187	42.20	38.65
SAIC	100	1.025	1.072	35.04	47.00

3.3.2. Gravimetric swelling

The value of gravimetric swelling percentage (Table 1) decreases from PFR (80.37 %) to SAIC (35.04 %). The average percentage of gravimetric swelling of the resin decreased with increasing SAIC content in the condensate. The values of gravimetric swelling percentage are found to be 80.37, 65.68 and 55.82 respectively, for 10, 20 and 30 % (w/w) blending of SAIC with the parent resin, viz., PFR. This indicates that up to 20 % (w/w) SAIC2 could be mixed with the PFR without affecting its property. The rigidity of the resin matrix is proved from the swelling measurements. Therefore, the cationic resin with higher SAIC content shows lower swelling, which reveals much lower rigid shape, and the rigidity decreases with the increase in the SAIC content in the condensate (Krishnamoorthy et al. 1997). It indicates that pure resin and condensates are rigid with non-gel macroporous structure (Bassett et al. 1989; Duraisamy et al.1987).

3.3.3. Attritional breaking

Attritional breaking value in Table 1 percentage increases with the increase in SAIC content in the resins, representing the stability of the resin, which increases from pure resin to SAIC. Therefore, the mechanical stability is good up to 20% (w/w) of SAIC2 with pure resin. This observation indicates that the capillary of the resin may be occupied by the sulphonated carbon (SAIC2) particles (Dheiveesan et al. 1988; Krishnamoorthy et al. 1997).

3.3.4. Solubility of IERs

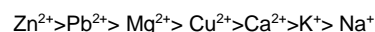
The chemical stability of the samples in terms of its solubility in various solvents and reagents was determined. It reveals that PFR,

condensates, and SAIC are practically insoluble in almost all the solvents and reagents. Therefore, these samples could be used as ion exchangers for treating non-aqueous effluents. However, the samples are found to be partially soluble in 20 % (w/w) NaOH solution, which indicates the presence of phenolic groups. Hence, these ion exchange materials cannot be used for the treatment of industrial effluents having high alkalinity. The insolubility of the samples even in the trichloroacetic acid express the rigidity, i.e., the high degree of cross-linking.

3.3.5. Cation exchange capacity

CEC data are given in Table 2. The CEC values decrease with the increase in the percentage (w/w) of SAIC in PFR for 0.1M solution of metal ions. CEC range (in m. mol. g<sup>-1</sup>) for condensates 0-100 % (w/w) of SAIC with PFR: 1.4864 - 0.1791 for Na<sup>+</sup> ion; 1.6216- 0.2786 for K<sup>+</sup> ion; 1.6875 - 0.8484 for Ca<sup>2+</sup> ion; 1.6934 – 1.1968 for Cu<sup>2+</sup> ion; 1.8111 -0.6464 for Mg<sup>2+</sup> ion; 1.7052 – 1.01 for Pb<sup>2+</sup> ion and 1.8343 – 1.1312 for Zn<sup>2+</sup> ion. Fig.4 shows the percentage CEC for various IERs-metal ion systems.

The Value of CEC for individual metal ion depends upon its atomic radius or atomic number. At the same time, the CEC value 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 deciding the value of CEC for a particular metal salt solution (Natarajan et al. 1993; Dimov et al. 1990; Son et al. 2001). From the CEC data given in Table 2, the CEC of the samples is found to decrease in the following order.



3.3.6. Selectivity of metal ions

The selectivity order of metal ions, i.e., orders of CEC value also depend upon the ionic potential and the hydrated atomic radius of the metal ions in solution (Dimov et al. 1990). The order of exchange affinities of various metal ions is not unique for all the ion exchange systems. Only under dilute conditions, Hofmeister series is applicable. But, under high concentration the order is different (Kunin, et al. 1958). It is equally important to note that the relative behavior of these ions for other ionic phenomena is different from the attraction order under the

same experimental condition (Bonner et al.1995). The observed order in the present study is different from that of the Hofmeister or lyotropic series. This may be due to the concentration of the metal ion in effluent solution, which is relatively high and also due to the selectivity of the metal ions. Therefore, each composite resin (prepared from plant material) system has its own specific selectivity of the particular metal ion.

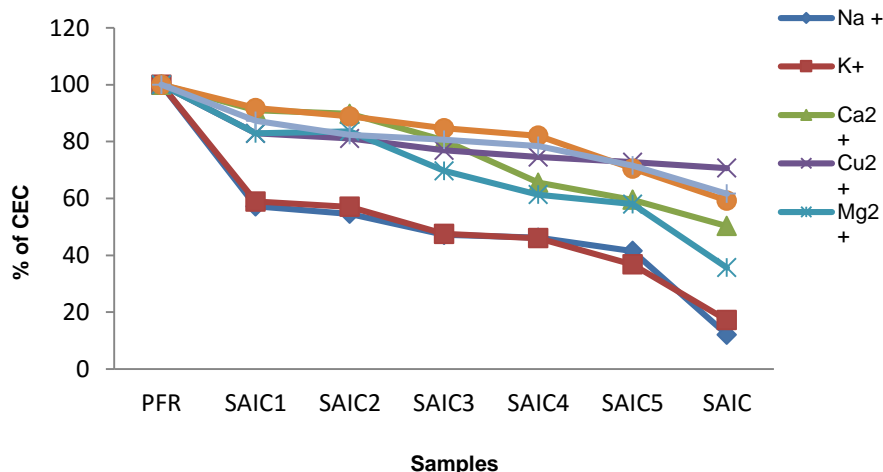
**Table 2.** Cation exchange capacity of PFR, pure SAIC and condensate SAIC1 – SAIC5 (H<sup>+</sup>) form of 0.1 M solution of selective metal ions at 303K.

Sample	% of SAIC in IER	Cation exchange capacity, in m. mol. g <sup>-1</sup> 0.1 M solution						
		Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Cu <sup>2+</sup>	Mg <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
PFR	0	1.4864	1.6216	1.6875	1.6934	1.8111	1.7052	1.8343
SAIC1	10	0.8509	0.9552	1.5352	1.4039	1.5009	1.5655	1.6008
SAIC2	20	0.8109	0.9253	1.515	1.3736	1.515	1.515	1.5099
SAIC3	30	0.7014	0.7711	1.3584	1.3029	1.2625	1.4443	1.4796
SAIC4	40	0.6865	0.7462	1.1059	1.2625	1.111	1.3988	1.4392
SAIC5	50	0.6169	0.597	1.0049	1.2322	1.0504	1.2019	1.313
SAIC	100	0.1791	0.2786	0.8484	1.1968	0.6464	1.01	1.1312

Also, the CEC data given in Fig 4, conclude that the condensate up to 20 % (w/w) mixing of SAIC with PFR (SAIC2) retains nearly 81.11–90.95 % of CEC bivalent metal ion and 54.45-58.90 for monovalent metal ions. Hence, 20% (w/w) blending of SAIC2 in PFR will reduce the cost of original resin. It is observed that the CEC decreases as the percentage of SAIC content in the condensate increases. Hence, any chemical method requiring ion exchangers of the low value of CEC, 20 % (w/w) blended SAIC –PFR resin could be used. SAIC can be inexpensively prepared from the corresponding plant material (Abutilon

indicum), which is freely available in plenty, in this study area viz., Tamil Nadu, India.

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 are about 56-65 % for SAIC1 - SAIC5 compared to pure commercial resin(CRs) (100 %). As an average, the condensates SAIC1 - SAIC5 retain nearly 60 % of CEC of CRs. This indicates that the condensates can partially replace commercial resins (CRs) in making the ion exchangers for industrial applications.



**Fig. 4.** Cation Exchange Capacities of H<sup>+</sup> form of PFR, condensates and Pure SAIC.

**3.3.7. Effect of stability of IERs on CEC**

The effect of different reagents and heat on the values of CEC for Mg<sup>2+</sup> ions for various cationic resins is shown in Table 5. On treatment with 20 % (w/v) NaOH solution, 1.0 – 2.2 % reduction in CEC value is noted. Upon treatment of the resins with an organic solvent like benzene, the loss in CEC is noted to be 1.0 – 3.0 %. The decrease in

CEC value on treatment with boiling water is 0.4 – 1.5 %, for condensates with different amounts of SAIC in the resin. When the resins are heated for 10 h at 100 °C the value of CEC decreases (8 – 18 %) compared to the resins, which are not heated. All these observations reveal that the condensates have good thermal and chemical stability.

**Table 3.** Chemical and thermal effect on CEC of PFR and condensates for exchange with 0.1 M Mg<sup>2+</sup> ions at 303 K.

Reagents	Cation exchange capacity, in m. mol. g <sup>-1</sup> 0.1M solution					
	PFR	SAIC1	SAIC2	SAIC3	SAIC4	SAIC5
CEC (of untreated)	1.855	1.714	1.535	1.413	1.345	1.287
20% (w/v) NaOH	1.745	1.613	1.514	1.343	1.243	1.285
Benzene	1.696	1.656	1.525	1.315	1.287	1.225
1M HCl	1.768	1.635	1.498	1.356	1.298	1.204
Water	1.808	1.723	1.541	1.334	1.302	1.214
Thermal treatment	1.616	1.532	1.386	1.132	1.102	1.006



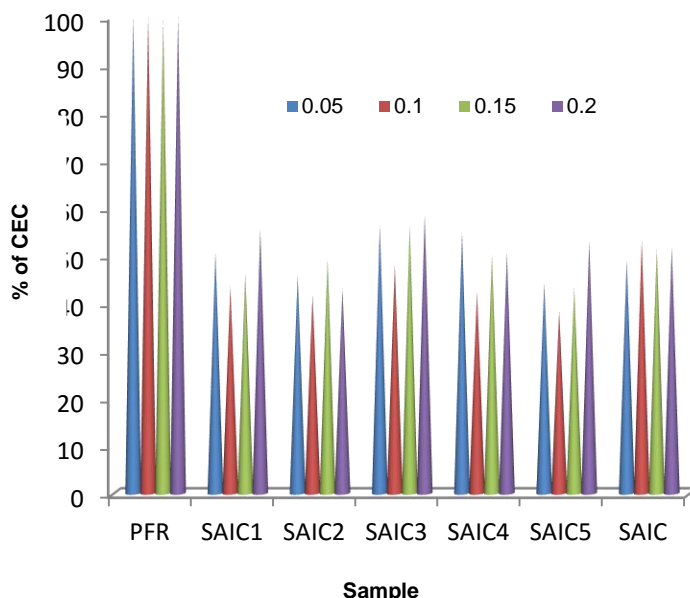
CEC data given in Table 3, describe that the particle size of IERs < 210 μm are fine, 300 – 500μm and > 500 μm are common as to cause very low value of CEC compared to 210 – 300μm particle size. Hence, in order to have the effective CEC, the bed size and particle size of IER should be maintained and the recommended particle size of IER is 210 – 300μm for preparing columns for in ion exchange studies.

**3.3.8. Regeneration of IERs**

The regeneration data obtained with 40 mL of 0.2 M NaCl (brine) solution conclude that it effectively regenerates PFR, condensate resins, and pure SAIC. Exactly 40 mL of 0.2M brine solution effectively acts as a regenerating agent for original PFR (Fig. 5). Most of the CRs are in Na<sup>+</sup> form and hence 40mL of 0.2 M NaCl is to be used as a regenerator for every 2 g of the resin.

**Table 4.** Effect of particle size on CEC of PFR and condensate obtained by blending PFR with 20 % (w/w) of SAIC at 30 °C.

Sample	Particle Size(micron)	Cation exchange capacity,in m.mol. g <sup>-1</sup> 0.1M solution			
		Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Zn <sup>2+</sup>
PFR	<200	1.4170	1.6228	1.7698	1.7816
	200-300	1.4864	1.6875	1.8333	1.8345
	300-500	1.3288	1.5934	1.7522	1.7934
	>500	1.2936	1.4994	1.6346	1.4935
SAIC2	<200	0.8080	1.3994	1.1413	1.4998
	200-300	0.8109	1.5150	1.5150	1.5099
	300-500	0.7977	1.4347	1.4847	1.4897
	>500	0.7770	1.3641	1.4594	1.4746



**Fig. 5.** Regeneration level for PFR condensates and SAIC by using NaCl after the exchange with Mg<sup>2+</sup> ions.

**3.3.9. Equilibrium Constant and Thermodynamic Parameters**

In order to determine the effect of temperature on the exchange of Zn<sup>2+</sup> by SAIC2, experiments were carried between 303 K and 333 K. The thermodynamic parameters for the removal of Zn<sup>2+</sup> by IER (SAIC2) were calculated using the following basic thermodynamic equations.

$$\Delta G^\circ = - RT \ln K_c \tag{1}$$

$$\ln K_c = \Delta S^\circ/R - \Delta H^\circ/RT \tag{2}$$

Where R is the universal gas constant, 8.314 J/mol.K and T, the absolute temperature (K) and ΔH°, ΔG°&ΔS° are the changes in enthalpy (J/mol.), Gibb’s free energy (J/mol.) and entropy (J/K/mol.) respectively. The values of ΔH° and ΔS° could be determined from the slope and intercept of the linear plot of lnK<sub>c</sub>versus 1/T. where R is the gas constant, K<sub>c</sub> is the equilibrium constant and T is the solution temperature in Kelvin. The thermodynamic parameters can be calculated from Vant Hoff plot (Fig. 6). The positive value of ΔH° (6350J/mol.) for the adsorption of Zn<sup>2+</sup> by SAIC2 showed endothermic nature of the overall process. NegativeΔG° value (-882 J mol<sup>-1</sup>)

indicates that the ion exchange reaction is spontaneous (Selvapandian et al. 2015).

**4. Conclusions**

From the current study, it is concluded that the PFR could be blended withupto20 % (w/w) of SAIC2, without affecting its spectral, thermal and physico-chemical properties and also retain the CEC values of PFR. The effect of particle size and initial concentration of Zn<sup>2+</sup> ions on CEC, its regeneration level by NaCl solution was studied. To have the effective CEC, the particle size of IER should be maintained between 210 and 300μm. CEC values of various metal ions of blends up to 20 % (w/w) SAIC2 were found to be very close to that of PFR. Equilibrium studies for the removal of Zn<sup>2+</sup> ion reveal that the process is spontaneous, endothermic and occur with an increased randomness. SEM images have well defined micrometric structures. Therefore, the composites obtained from cationic matrix blending of PFR with 20 % (w/w) of SAIC2 will absolutely lower the cost which can be used in wastewater treatment, especially for the removal of metal ions.

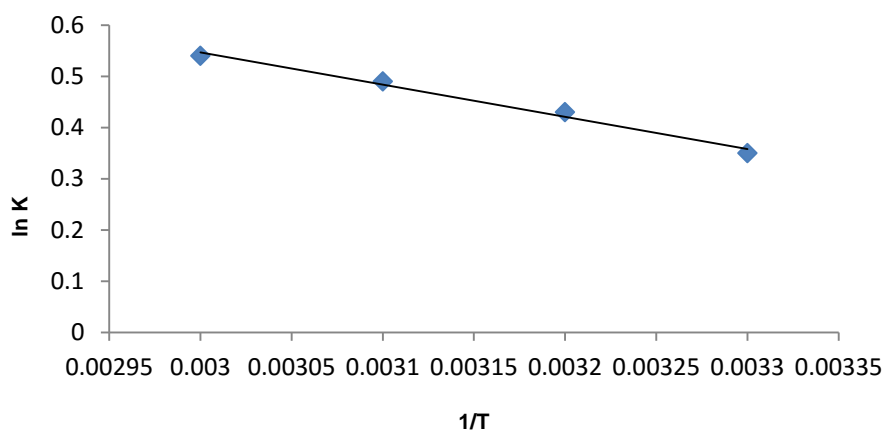


Fig. 6. Vant Hoff plot for the removal of Zn<sup>2+</sup> by SCAC2.

### Acknowledgments

The authors wish to thank the Principal and Head, Department of chemistry, R.D.Govt. Arts College, Sivagangai, for providing research

facilities and encouragement. The authors also thank Department of chemistry, Thiagarajar college of Engineering and Technology, Madurai for recording TGA studies.

### References

- Bassett G. H., Jeffery J., Mendham J., R.C. Denney (eds.), Vogel's Text Book of Quantitative Chemical Analysis, 5<sup>th</sup> Edn., Longman Group Ltd., London, UK, (1989) pp. 186 – 192.
- Bato R. C., Tanayo J. P., Jennifer J., Midred M., FPRDI J., 25 (2003) 115.
- Bolto B. A., Pawlowski L. (eds.), Waste Water Treatment by Ion Exchange, Oxford & IBH Publ. Co., New Delhi, (1987).
- Bonner O., Easterling G., Weit D., Holland V., J Am. Chem. Soc., 77 (1955)
- Chandrasekaran M. B., Krishnamoorthy S., Studies on the removal of metal ions by various cashewnutshell-groundnutshell, Journal of the Indian Chemical Society, 64 (1987) 134.
- Dheiveesan T., Krishnamoorthy S., J. Indian Chem. Soc. LXV (10) (1988) 731.
- Dimov D.K., Petrova E.B., Panayotov I.M., Tsvetanov Ch.B., Macromolecules, 21 (1990) 2733.
- Duraisamy N., Krishnamoorthy S., Journal of the Indian Chemical Society, 64 (1987) 701.
- Farag S., Synthesis and Physicochemical Studies of Starch-Sulphonated Phenol Formaldehyde Cationic Exchangers, Starch 47 (1995) 196.
- Hassan M. L., Egyptian J. Chem 46 (2003) 329.
- Homagai P.L., Development of Natural Cation Exchanger for the Treatment of Lead ions from Aqueous Solution, Journal of Nepal Chemical Society 29 (2012) 34-43.
- Kannan N., Seenivasan R. K., Mayilmurugan R., Phenol-formaldehyde cationic matrices substituted by sulphonated acacia nilotic charcoal, Indian Journal of Chemical Technology 10 (2003) 623.
- Kirtikar K.R., Basu B.D., Indian Medicinal Plants, 2nd Ed., Bishen Singh, Mahendra Pal Singh, India, 1 (1980) 314–15.
- Krishnamoorthy S., Mariamichel A., Synthesis and characterization of new composite ion exchangers, Asian Journal of Chemistry 9 (1997) 136.
- Krishnamoorthy S., Mariamichel A., synthesis and characterization of new composite ion-exchangers, journal of scientific & industrial research, 56 (1997) 680-685.
- Kunin R., Ion Exchange Resin, Wiley, New York and London, 2<sup>nd</sup> edn., (1958).
- Metwally M. B., Metwally N. E., Samy T. M., Synthesis and studies of Egyptian bagasse pith Phenol-formaldehyde cationic exchangers, Journal of Applied Polymer Science 52 (1) (1994) 61.
- Metwally M. S., Metwally N. S., Synthesis and properties of synthetic Egyptian corn-cob-phenol formaldehyde cationic exchangers, Polymer-Plastics Technology and Engineering 31(9-10) (1992) 773.
- Natarajan M., Krishnamoorthy S., studies on p-cresol-formaldehyde cationic resins substituted by coconut shell charcoal, Research and Industry 38 (1993) 278-281.
- Radhakrishnan S., Krishnamoorthy S., Research and Industry 35 (1990) 188.
- Raghunathan J., Krishnamoorthy S., Journal of the Indian Chemical Society 61 (1984) 911.
- Rajurkar R., Jain R., Mataka N., Aswar P., Khadbadi S.S., Anti-inflammatory Action of Abutilon indicum (L.) Sweet Leaves by HRBC Membrane Stabilization, Research Journal of Pharmacy and Technology 2 (2009) 415-416.
- Ramachandran S., Krishnamoorthy S., Resorcinol-formaldehyde cationic resins, Indian journal of technology 22(1984) 355-358.
- Selvapandian P., Ananthakumar K., Removal of methylene blue from aqueous solutions by Cynodondactylon leaf powder 5 (2015) 71-72.
- Sharma N. L. N., Vasudevan P., Indian journal of technology 17 (1979) 450.
- Sharma N. L. N., Vasudevan P., Journal of the Indian Chemical Society 57 (1980) 191.
- Sharma N. L. N., Vasudevan P., Journal of Macromolecular Science A12 (1978) 1401.

Sharma Y.R., Elementary Organic Spectroscopy, Chand S., Co.Ltd., India, Ch. 3 (2001) 100 – 104.

Son W. K., Kim S.H., Park S. G., Synthesis and exchange properties of sulfonated poly(phenylene sulfide) with alkali metal ions in organic solvents, Bulletin of the Korean Chemical Society 22 (2001) 53-58.

Swamiappan N., Krishnamoorthy S., Res. Ind., 29 (1984) 293.

Vasudevan P., Sing M., Satish N., Sharma N.L.N., J. Poly. Sci., Polymery Chemistry, 16 (1978) 2545.

Zoumpoulakis L., Simitzis J., Ion exchange resins from phenol/formaldehyde resin-modified lignin, Polymer International 50 (2001) 277-283.