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A NEW LOW-COST ION EXCHANGERS

P. Selvarani [1], J.Jeyaseeli [2], Rane Caroleena Ganesh [3], and R.K. Seenivasan [4*]

[1] Research and Development Centre, Bharathiar University, Coimbatore, Tamil Nadu, India

[2]Department of chemistry, M.V.M Government Arts College for Women, Dindigul, Tamilnadu

[3] Head, Department of Chemistry, Sidharth College, Badlapur, Mumbai, India

[4] Department of chemistry, Government Arts College, Melur, Madurai-625007, Tamilnadu

ABSTRACT

Resorcinol – Formaldehyde Resin (RFR) is the prepared base for cross linking agent for blending of Sulphonated *Psidium Guajava L.*Charcoal (SPGC). A few composite cation-exchangers were prepared by varying the amount of SPGC (sulphonated carbon prepared from a source of cheap and renewable plant material) in the blends from 0 to 100% *(w/w).* Optimum principal reaction conditions for the preparation of blends were determined. All the important physico-chemical, and thermal properties of the composites resins have been determined and analysed. The composites are insoluble in various organic solvents and reagents. The composites are thermally stable and stable towards various reagents. It was found that the ion-exchange capacity (IEC) of the composite resins, decreased with the increasing percentage of SPGC in the blend.. The composites up to 30% *(w/w)* blending retains the essential properties of the original RFR, since the *Psidium Guajava L.*, is the low cost, freely available plant material. Therefore, the composites could be used as low cost ion-exchangers, when SAMC partly replaces the original RFR up to 30% *(w/w)* blending without affecting the properties of RFR.

Keywords: Resorcinol – formaldehyde Resin – Sulphonated *Psidium Guajava L.*Charcoal – Cation Exchange Capacity – Composite resins – Ion Exchangers .

1. INTRODUCTION

Industrialised 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 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. 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 prepared from plant materials. Earlier studies show that the cheaper composite ion-exchangers could be prepared by partially blending the macro porous phenol-formaldehyde sulphonic acid resin matrix by sulphonated charcoals 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]. activated carbons obtained from agricultural wastes[11], *Terminalia chebula* Retz., Carbon[12] *Achyranthes aspera,*Linn., Carbon[13], *Eugenia jambolana,* Lam, Carbon[14], Heavy metals are also removed by bamboo activated carbon, natural clinptitolite, titanate nanoflowers and poly(Hydroxy ethyal methacrylate/Malemic acid) hydro gel[15-18].Attempts have been made to prepare cheaper cationic resins from natural products. Ion-exchange process finds a valuable place in the treatment of metal wastes from plating and other industrial processes.

The aims and objectives of the present work are to synthesise, characterise the new composite ion exchangers of Resorcinol – Formaldehyde Resin (RFR) type blended with sulphonated *Psidium Guajava L.*charcoal (SPGC) and estimate the column exchange capacity for some selective metal ions.

II. MATERIALS AND METHODS

2.1 Chemicals

The raw/plant material used was *Psidium Guajava L.*. 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

500 g of *Psidium Guajava L.* (In Tamil: Koyya In English: Guava) was carbonised and sulphonated by con. sulphuric acid, washed to remove excess free acid and dried at 70^0C for 12 h. It was labeled as SPGC.

Pure Resorcinol – 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 characterisation [3,6-8,19]. It was labeled as RFR.

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 SPGC in the blend / composites, respectively were labeled as PG1, PG2, PG3, PG4 and PG5. A separate sample of SPGC was 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, percentage of gravimetric swelling and percentage of attritional breaking. The solubility of these samples were tested by using various organic solvents and inorganic reagents.The values of cation exchange capacity (CEC) were determined by using standard titration techniques [20] as per the literature method [21]. The effect of initial concentration of metal ions, particle size, chemical and thermal stability of the resins on CEC were determined [22-24].

III. RESULTS AND DISCUSSION

In Table 1 the experimental and theoretical compositions of SAMC in the composites (AM1 – AM5) are in good agreement with each other. 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 (AM1 – AM5) are more reliable and reproducible.

The data given in Table 2 show that the values are absolute density are decreased from pure resin to highest percentage of composite resin and then finally to pure SPGC. The values of absolute density of composite resin in dry and wet forms depend upon the structure of resins and its degree of cross linking and ionic form [25]. Generally the absolute density decreased with increase in SPGC content in the resin. The high value of absolute density indicates 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 resins 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.

Table .1 AMOUNT OF REAGENT USED AND YIELD OF RFR, CONDENSATES (PG 1 – PG5) PREPARED BY BLENDING OF RFR WITH VARIOUS %(*W/W*) OF SPGC

Sample	%of SPGC in IERs (cal)	Amount of reagents used					
		Resorcinol (ml)	HCHO (ml)	Con. H_2SO_4 (ml)	SPGC (g)	Yield (g)	% of SPGC in IERs (obs)
RFR	0	10	11.5	12.5	0	19.5	0
PG 1	10	10	11.5	12.5	2.17	21.91	9.9
PG 2	20	10	11.5	12.5	4.75	22.89	20.75
PG 3	30	10	11.5	12.5	8.36	28.19	29.65
PG 4	40	10	11.5	12.5	13	32.86	39.55
PG 5	50	10	11.5	12.5	19.5	39.87	48.9
SPGC	100	-	-	-	-	-	100

The data given in Table 2 indicate that the swelling percentage decreases from RFR (98.258%) to SpgC (20.81%). The value of average % of swelling decreased with increasing SPGC content. The This indicates that up to 30% (*w/w*) SPGC could be mixed with the RFR. The rigidity of the resin matrix was thus concluded from the swelling measurements. Therefore, these cationic resins with increasing SPGC content showed lower swelling which revealed much lower rigid shape, and the rigidity decreased with the increase in % of SPGC. It indicates that, pure resin and composites are rigid with non - gel macro porous structure [19].

The values of attritional breaking (Table 2) increase with increase in SPGC content (*w/w)* in the resins, representing the stability of the resin, which decreases from pure resin to SPGC. Therefore, the mechanical stability is good upto 20 - 30% *(w/w)* substitution of SPGC in pure resin. This observation also shows that, the capillaries of the resin may be occupied by the sulphonated carbon (SPGC) particles [6-8].

The chemical stability of the samples in terms of its CEC in various solvents was determined. It reveals that RFR, composites and SPGC are practically insoluble in almost all the solvents. Hence, they can be used as ion exchangers for treating non-aqueous effluents. At the same time, the samples were found to be partially soluble in 20% NaOH solution which indicate the presence of phenolic groups. Hence, these ion exchange materials cannot be used for the treatment of industrial effluents having high alkalinity (pH > 7). The insolubility of the samples even in the trichloroacetic acid expresses the rigidity *i.e.,* having high degree of cross-linking in them.

Table 3.3 PHYSICO - CHEMICAL PROPERTIES OF RFR, SPGC AND CONDENSATES (PG1- PG 5)

Sample	% of SPGC	Density (gL^{-1})		Percentage of	
		Wet	Dry	Gravimetric Swelling	Attritional Breaking
RFR	**0**	**1.952**	**1.910**	**98.25**	**7.96**
PG 1	**10**	**1.586**	**1.647**	**75.33**	**9.31**
PG 2	**20**	**1.504**	**1.576**	**66.52**	**9.98**
PG 3	**30**	**1.433**	**1.333**	**62.31**	**11.59**
PG 4	**40**	**1.382**	**1.293**	**58.00**	**14.80**
PG 5	**50**	**1.118**	**1.192**	**55.40**	**17.09**
SPGC	**100**	**0.996**	**1.010**	**36.16**	**20.81**

CEC data shown in Table 3 indicate that, the CEC values (for 0.1M solution of metal ions) decrease when the SPGC % content *(w/w)* in RFR increases. The relative value of CEC of individual metal ions depends upon the atomic radius or atomic number [26]. 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 [23,24].

From the CEC data given in Table 4, the cation exchange capacity of the samples was found to decrease in the following order.

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

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 [24]. The order of exchange affinities of various metal ions is not unique to ion exchange system. Only under dilute conditions Hofmeister or lyotropic series [25] is obeyed. But, under high concentration it is different [25]. 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 [27]. The observed order in the present study is different from that of the Hofmeister or lyotropic series [25]. 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 3, conclude that, upto 30% *(w/w)* blending of SPGC with RFR retains 80 – 95.7% of CEC for all metal ions. Hence, 30% (*w/w*) blending of SPGC in RFR reduce the cost of original resin. It is observed that there is a continuous decrease in cation exchange capacity (CEC), as the percentage of SPGC content in the blend increases. Hence, any chemical methods requiring ion exchangers of small ion exchange capacity, 30% (*w/w*) blended SPGC –RFR resin could be used. SPGC can be inexpensively prepared from the plant materials, *Psidium Guajava L.*, which is freely available in plenty, in India.This indicates that the composites can partially replace commercial IERs in making the ion exchangers for industrial applications.

Table 3 CATION EXCHANGE CAPACITIES OF RFR, CONDENSATES (PG1-PG5) AND SPGC FOR SELECTIVE METAL IONS (0.1 M)AT 303 K

Sample	% of SPGC in IER	Cation exchange capacity(m mol g^{-1})							
		Na^{+}	K^{+}	Pb^{2+}	Cu^{2+}	Cd^{2+}	Zn^{2+}	Mg^{2+}	Ca^{2+}
RFR	**0**	**1.35**	**1.58**	**1.47**	**1.56**	**1.58**	**1.62**	**1.82**	**1.88**
PG 1	**10**	**.87**	**1.47**	**1.37**	**1.48**	**1.43**	**1.53**	**1.63**	**1.60**
PG 2	**20**	**0.83**	**1.45**	**1.34**	**1.39**	**1.37**	**1.49**	**1.59**	**1.53**
PG 3	**30**	**0.74**	**1.39**	**1.30**	**1.31**	**1.28**	**1.33**	**1.51**	**1.43**
PG 4	**40**	**0.72**	**1.33**	**1.13**	**1.22**	**1.18**	**1.27**	**1.41**	**1.35**
PG 5	**50**	**0.70**	**1.24**	**1.07**	**1.20**	**1.06**	**1.19**	**1.32**	**1.26**
SPGC	**100**	**0.33**	**0.52**	**0.70**	**0.74**	**0.72**	**0.76**	**0.98**	**0.89**

The effects of different reagents on the values of CEC of various cationic resins are shown in Table 4. On treatment with 0.2M NaOH 1.0 – 3.2% reduction in CEC value was noted. A higher decrease was observed for resin containing 50% of SPGC. Upon treatment of resins with various organic solvents, the loss in CEC value was 1.4 – 4.1%. All these observations reveal that the composites have high thermal and chemical stability.

CEC data given in Table 5, described that the particle size of <200 µm are fine and > 500µm are coarse compared to a particle size of 200 - 500µm to cause very low ion Exchange capacity.

TABLE 3.5 CHEMICAL EFFECT ON CEC OF RFR AND ITS CONDENSATES FOR EXCHANGE WITH 0.1M Zn^{2+} IONS AT 303 K

Reagents	**Cation Exchange Capacity(m.mol.g^{-1})**					
	RFR	**PG 1**	**PG 2**	**PG 3**	**PG 4**	**PG 5**
CEC(untreated IER)	**1.620**	**1.530**	**1.490**	**1.330**	**1.270**	**1.190**
20%NaOH	**1.603**	**1.424**	**1.316**	**1.278**	**1.112**	**1.010**
Benzene	**1.571**	**1.425**	**1.376**	**1.325**	**1.102**	**1.008**
Boiling water	**1.604**	**1.470**	**1.391**	**1.317**	**1.121**	**1.015**
1M HCl	**1.603**	**1.431**	**1.422**	**1.330**	**1.138**	**0.959**
Thermal Treatment	**1.491**	**1.316**	**1.320**	**1.207**	**1.067**	**0.954**

Table 3.7 Effect of particle size on CEC of RFR and condensates (S3) at 303K

Sample	**Particle Size (micron)**	**Cation Exchange Capacity(m.mol.g^{-1})**		
		Cd^{2+}	**Zn^{2+}**	**Mg^{2+}**
RFR	**<210**	**1.37**	**1.40**	**1.63**
	210-300	**1.58**	**1.62**	**1.82**
	300-500	**1.53**	**1.55**	**1.79**
	>500	**1.51**	**1.53**	**1.75**
PG 3	**<210**	**1.18**	**1.19**	**1.34**
	210-300	**1.28**	**1.33**	**1.51**
	300-500	**1.20**	**1.21**	**1.36**
	>500	**1.14**	**1.13**	**1.32**

IV. CONCLUSION

It is concluded from the present study that PFR sample could be blended with 30% (*w/w*) of SPGC, without affecting its physico-chemical, thermal properties. Also the effect of particle size, its regeneration level by using NaCl, spectral properties and the CEC values of various metal ions of resins blended with 30% (*w/w*) SPGC were very close to the original RFR resin. Hence, blending of RFR with SPGC will definitely lower the cost of IER.

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