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Studies on Composites of Resorcinol-Formaldehyde resin blended with Sulphonated Aegle marmelos(L) Correa

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ABSTRACT

Resorcinol – Formaldehyde Resin (RFR) is the prepared base for cross linking agent for blending of Sulphonated Aegle Marmelos Charcoal (SAMC). A few composite cation-exchangers were prepared by varying the amount of SAMC (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, thermal and spectral 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 SAMC in the blend.. The composites up to 30% (w/w) blending retains the essential properties of the original RFR, since the Aegle Marmelos, 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 Aegle Marmelos 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 ***Aegle Marmelos*** charcoal (SAMC) and estimate the column exchange capacity for some selective metal ions.

Materials and methods

2.1 Chemicals

The raw/plant material used was ***Aegle Marmelos***. 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 ***Aegle Marmelos*** (In Tamil: Vilvam, In English: Beatel Tree) 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 SAMC.

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 SAMC in the blend / composites, respectively were labeled as AM1, AM2, AM3, AM4 and AM5. A separate sample of SAMC 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].After the exchange of H^+ ion by the metal ions, the regeneration level of the composites loaded with a metal ions were determined by using NaCl (brine) solution.

The FT-IR spectral data of pure resin (RFR), 30% *(w/w)* composite and pure sulphonated ***Aegle Marmelos*** charcoal (SAMC) were recorded with a JASCO FT-IR 460 plus FT-IR spectrometer by using KBr pellets. To establish the thermal degradation of the samples, TGA and DTA traces were obtained for resorcinol – formaldehyde resin (RFR) and 30% *(w/w)* composite resin by using TZSCH- Geratebau GmbH Thermal analysis.

3. 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 SAMC. 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 SAMC 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.

The data given in Table 2 indicate that the swelling percentage decreases from RFR (88.08%) to SAMC (42.13%). The value of average % of swelling decreased with increasing SAMC content. The This indicates that up to 30% (*w/w*) SAMC 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 SAMC content showed lower swelling which revealed much lower rigid shape, and the rigidity decreased with the increase in % of SAMC. 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 SAMC content (*w/w)* in the resins, representing the stability of the resin, which decreases from pure resin to SAMC. Therefore, the mechanical stability is good upto 20 - 30% *(w/w)* substitution of SAMC in pure resin. This observation also shows that, the capillaries of the resin may be occupied by the sulphonated carbon (SAMC) particles[6-8].

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

CEC data shown in Table 3 indicate that, the CEC values (for 0.1M solution of metal ions) decrease when the SAMC % 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 3, 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 [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 SAMC with RFR retains 78.43 – 95.72% of CEC for all metal ions. Hence, 30% (*w/w*) blending of SAMC 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 SAMC content in the blend increases. Hence, any chemical methods requiring ion exchangers of small ion exchange capacity, 30% (*w/w*) blended SAMC –RFR resin could be used. SAMC can be inexpensively prepared from the plant materials, ***Aegle Marmelos***., 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.

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 – 4.8% reduction in CEC value was noted. A higher decrease was observed for resin containing 50% of SAMC. Upon treatment of resins with various organic solvents, the loss in CEC value was 1.4 - 3.5%. 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[28,29]. Hence, for the effective CEC, the bed size and particle size are be maintained and the recommended particle size is 200 – 500μm (mesh size is 0.2mm to 1.4mm)

The regeneration data with forty ml of 0.2M brine solution (NaCl) reveal that it effectively regenerates all composite resin and SAMC (Fig.1). Most of the commercial IERs are in Na^+ form and hence 40ml of 0.2M NaCl was used as a regeneration agent for every 2g of the resin.

In Table 6 shows FT-IR studies to confirm the various stretching frequencies and to identify the ion exchangeable groups [29]. Fig.2 indicate the appearance of absorption band at 1068 – 1073 cm^{-1} (S = 0 str.) 1160 – 1161 cm^{-1} (SO_2 sym str) and 588 – 603 cm^{-1} (C – S str.) in pure resin (RFR), 30% composite resin and pure SAMC confirm the presence of sulphonic acid group[30] .

The appearance of broad absorption band at 3207 – 3317 cm^{-1} (bonded –OH str.) Indicate the presence of phenolic and sulphonic –OH group in the samples. The appearance of absorption band at 1610 – 1612 cm^{-1} (C-C str.) confirms the presence of aromatic ring in RFR, 30% blending of SAMC in RFR and pure SAMC. The absorption band at 1365 – 1475 cm^{-1} ($-CH_2$.def.) confirms the presence of $–CH_2$ group in the samples. The weak absorption band at 887 – 970 cm^{-1} (-C-H def.) in the samples indicate that the phenols are tetra substituted[31].

Thermal gravimetric analysis (TGA) is used for rapidly assessing the thermal stability of various substances [30]. TGA curves shown in Figs.3 reveal that there is a very small (5-9%) loss in weight for both RFR and resin blended with 30% (*w/w*) SAMC up to 80^0C. This is due to the loss of moisture absorbed by the pure resin and resin blended with 30 (*w/w*) SAMC. Between 80 - 300^0C there is 20% weight loss in RFR and 14% loss in weight in resin blended with 30% (*w/w*) SAMC.

Two exothermic peaks were obtained in PFR, approximately at 80^0C and at 400^0C, respectively (Fig.4). At 80^0C, the presence of broad peak was observed, due to the dehydration process of resin (RFR). A peak at 400^0C, indicates, the chemical changes of pure resin, which reflect approximately 14% weight loss in RFR.

DTA curves of 30% (*w/w*) SAMC (Fig.3) show that, the same two exothermic peaks were obtained at 80^0C and at 400^0C, respectively. Again the first broad peak indicates the dehydration of 30% (*w/w*) SAMC and second moderate sharp peak indicates the chemical changes of 30% (*w/w*) SAMC.

From Figs. 4 it is concluded that, the limiting temperature for the safer use of PFR, and resin blended with 30% (*w/w*) SAMC as ion exchangers was 80^0C, since the resin degrade thermally after 80^0C[32].

The morphological changes in the cross linking agent RFR, blending of 30 %(*w/w*) sulphonated carbon with the adsorbate are clearly visualized from SEM studies. In Fig.5 shows that rough surface of IERs with heterogeneous pores. Fig.4 showed micrographs of the metal ion adsorbed in the pores and the surface of 30% (*w/w*) composite resin relatively smoother.

4. Conclusion

It is concluded from the present study that PFR sample could be blended with 30% (*w/w*) of SAMC, 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*) SAMC were very close to the original RFR resin. Hence, blending of RFR with SAMC will definitely lower the cost of IER.

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IERs	% of SAMC in IERs (Theoret.)	Amount of reagents used			SAMC (g)	Yield (g)	% of SAMC in IERs(obs)
		Resorcinol (mL)	HCHO (mL)	Con.H_2SO_4 (mL)			
RFR	0	10.0	11.5	12.5	0	16.00	0
AM-1	10	10.0	11.5	12.5	1.77	16.98	10.42
AM-2	20	10.0	11.5	12.5	4.00	19.83	20.17
AM-3	30	10.0	11.5	12.5	6.86	23.89	28.71
AM-4	40	10.0	11.5	12.5	10.67	27.42	38.91
AM-5	50	10.0	11.5	12.5	16.00	34.78	46.00
SAMC	100	-	-	-	-	-	---

Table1 Amount of reagent utilized and yield of RFR, Condensates and SAMC

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Table: 2 Physico-chemical properties of RFR and its composites

Sample	% of SAMC in RFR	Density g/mL		% of gravimetric swelling	% of attritional Breaking
		Wet	Dry		
RFR	0	2.52	2.64	88.08	9.45
AM-1	10	1.87	1.98	76.05	14.08
AM-2	20	1.49	1.56	70.15	16.56
AM-3	30	1.40	1.49	68.34	22.08
AM-4	40	1.21	1.38	63.56	26.08
AM-5	50	1.09	1.23	60.34	29.07
SAMC	100	1.02	1.19	42.13	34.67

Table: 3 Cation exchange capacities of RFR, Condensates (AM1-AM5) and pure SAMC for various metal ions at 303K

Sample	% of SAMC in composite resin	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
AM-1	10	0.715	1.678	1.431	1.517	1.634	0.795	1.734

AM-2	20	0.696	1.643	1.398	1.453	1.563	0.654	1.651
AM-3	30	0.609	1.587	1.309	1.432	1.509	0.456	1.553
AM-4	40	0.456	1.345	1.123	1.213	1.432	0.345	1.376
AM-5	50	0.423	1.267	1.096	1.134	1.221	0.213	1.113
SAMC	100	0.065	0.643	0.476	0.698	0.876	0.076	0.978

Table:4 Chemical effect on CEC of RFR and SAMC Condensates for exchange with 0.1M Mg^{2+} ions at 303K

Reagents	**Cation exchange capacity, in mol. g^{-1} 0.1M solution**					
	RFR	**AM1**	**AM2**	**AM3**	**AM4**	**AM5**
CEC (of untreated)	1.545	1.200	1.052	1.080	0.750	0.705
20%(*w/v*) NaOH	1.501	1.089	1.000	0.985	0.683	0.633
Benzene	1.486	1.000	0.933	0.845	0.568	0.541
1M HCl	1.421	0.987	0.888	0.814	0.566	0.511

Table: 5 Effect of particle size on cation exchange capacity of RFR and AM30

Sample	**Particle size**	**Cation exchange capacity mmol/gm**				
		Na^{+}	**Ca^{2+}**	**Mg^{2+}**	**Cu^{2+}**	**Pb^{2+}**
RFR	<210µ	0.723	1.624	1.486	1.613	1.781

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	210-300 µ	0.799	1.701	1.545	1.682	1.832
	300-500 µ	0.654	1.582	1.423	1.547	1.721
	>500 µ	0.628	1.401	1.390	1.393	1.698
AM30	<210µ	0.526	1.534	1.269	1.471	1.501
	210-300 µ	0.609	1.587	1.309	1.509	1.553
	300-500 µ	0.509	1.526	1.232	1.423	1.467
	>500 µ	0.465	1.512	1.116	1.378	1.417

Table 6 FT-IR spectral data of RFR condensate, AM30 and Pure SAMC (υ in cm^{-1}).

Group	**RFR**	**Composites AM30**	**Pure SAMC**
S = O str.	1073	1071	1068
SO_2 sym. str.	1161	1161	1160
C – S str.	601	603	588
Bonded OH str.	3307	3317	3207
CH_2 – def.	1475	1463	1365
C – C str.	1612	1612	1610
C - H def.	970	892	887
C-C def.	860	7800	781
SO_2assy.	1355	1364	1328

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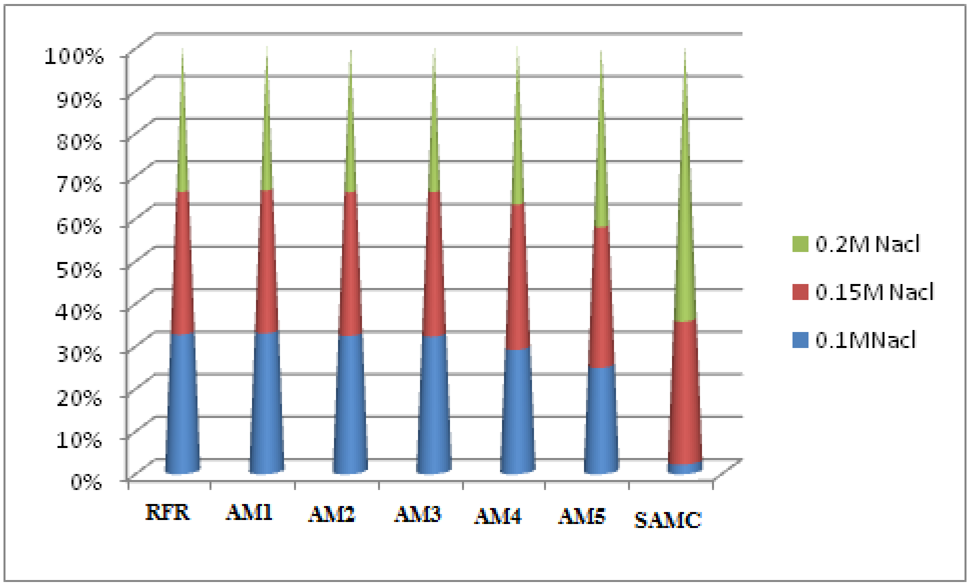

Fig.1: Regeneration level for RFR, Condensates [AM1 – AM5] and SAMC by using NaCl after exchange with Mg^{2+} ion

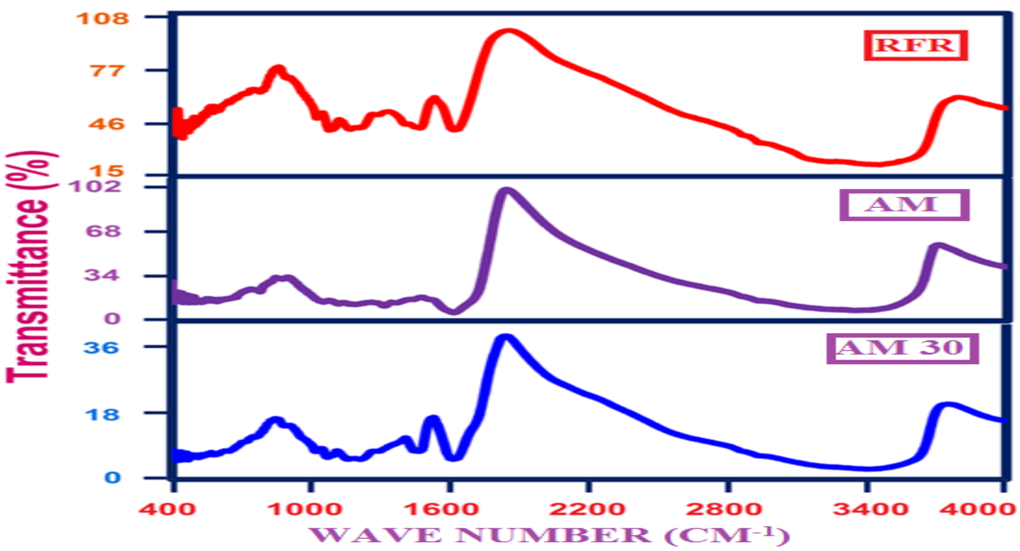

Fig 2: FT-IR of RFR pure SAMC and 30% condensate

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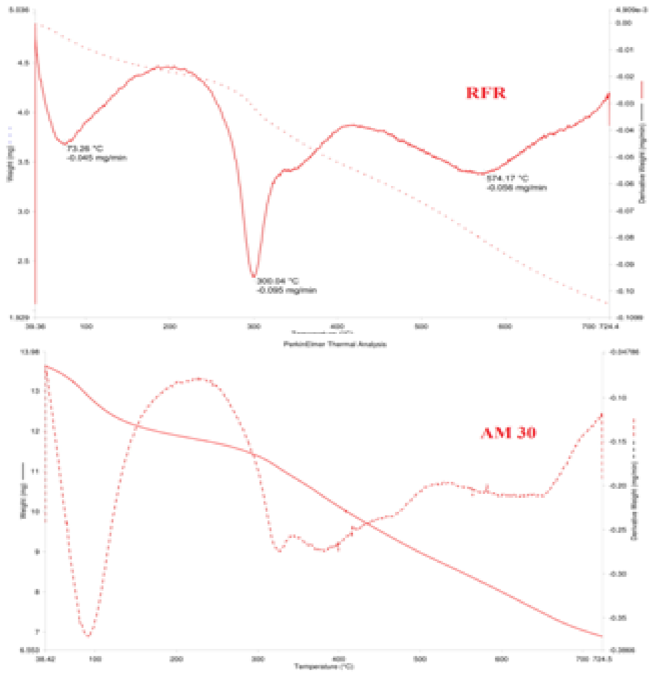

Fig 3: TGA and DTA curves of RFR and AM30

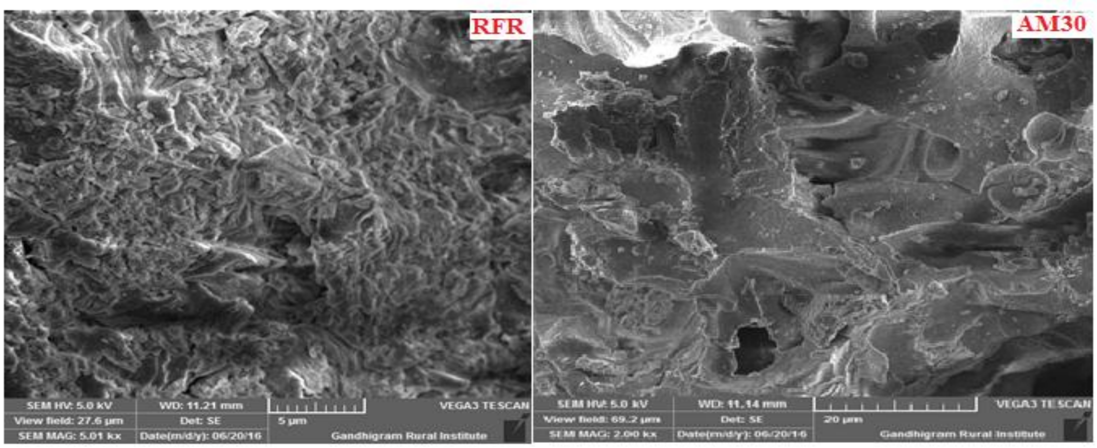

Fig 4: SEM images of RFR and AM30