



ISSN 2278 – 0211 (Online)

Synthesis, Characterisation and Application of Phenol-Formaldehyde Resin Blended with Sulphonated *Terminalia Bellerica*, Roxb. Charcoal

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Abstract:

Phenol – Formaldehyde Resin (PFR) is the prepared base for cross linking agent for blending of Sulphonated *Terminalia bellerica*, Roxb., Charcoal (STBC). A few composite cation-exchangers were prepared by varying the amount of STBC (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 STBC in the blend. The thermodynamic equilibrium constants ($\ln K$) are calculated for $H^+ - Zn^{2+}$ ion exchanges on the resins having a various amount of STBC. Thermodynamic parameters are also computed and suitable explanations are given. The composites up to 30% (w/w) blending retains the essential properties of the original PFR, since the *Terminalia bellerica*, Roxb., is the low cost, freely available plant material. Therefore, the composites could be used as low cost ion-exchangers, when STBC partly replaces the original PFR up to 30% (w/w) blending without affecting the properties of PFR.

Key words: Phenol – formaldehyde Resin – Sulphonated *Terminalia bellerica*, Roxb. Charcoal – Cation Exchange Capacity – Composite resins – Ion Exchangers – Equilibrium constants – Thermodynamic properties

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 clinoptilolite, titanate nanoflowers and poly(Hydroxy ethyl methacrylate/Maleic 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 PhOH – HCHO type blended with sulphonated *Terminalia bellerica*, Roxb., charcoal (STBC) and estimate the column exchange capacity for some

selective metal ions, to study the selectivity coefficients of H^+ - Zn^{2+} ion exchanges and to find out the optimum conditions for using cationic resins for the separation of Zn^{2+} from aqueous solution.

2. Materials and methods

2.1. Chemicals

The raw/plant material used was *Terminalia bellerica*, Roxb. This is a plant material freely 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. 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

Terminalia bellerica, Roxb., (500g) was carbonised and sulphonated by con. sulphuric acid, washed to remove excess free acid and dried at $70^{\circ}C$ for 12 h. It was labeled as STBC.

Pure phenol – 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 PFR.

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 STBC in the blend / composites, respectively were labeled as TB1, TB2, TB3, TB4 and TB5. A separate sample of STBC was also subjected to the characterisation studies.

2.3. Characterisation of samples

Samples were ground and sieved into a size of 210 – 300 μm 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 was 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 was determined [22].

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 equilibrium constants (K_{eq}) of ion exchange reaction between metal ions (Zn^{2+}) and the PFR and its composites were obtained as per the literature method [23,24].

The FT-IR spectral data of pure resin (PFR), 10% (w/w) composite and pure sulphonated *Terminalia bellerica*, Roxb., charcoal (STBC) 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 phenol – formaldehyde resin (PFR) and 20% (w/w) composite resin by using TZSCH- Geratebau GmbH Thermal analysis.

3. Results and Discussion

The experimental and theoretical compositions of STBC in the composites

(TB1 – TB5) 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 PFR and its composites (TB1 – TB5) are more reliable and reproducible.

The relationship between the various amounts of para-formaldehyde in the resin and the CEC reveal that the higher values of CEC are shown by the resins prepared with 15 – 25% (w/w) para-formaldehyde. However, these percentages are less chemically stable than the resins that contain 35% (w/w) para - formaldehyde. The CEC values decreased with the increased para-formaldehyde content in the matrix. The optimum value of para-formaldehyde and phenol are found to be 10ml and 11.5 ml, respectively.

The data given in Table 1 show that the values are absolute density are decreased from pure resin to highest percentage of composite resin and then finally to pure STBC.

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 STBC 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 1 indicate that the swelling percentage decreases from PFR (85.56%) to STBC (45.06%). The value of average % of swelling decreased with increasing STBC content. The values of swelling percentage are found to be 89.03%, 75.07% and 69.54% respectively, for 10, 20 and 30% (w/w) of mixing of STBC compare with the parent resin, *viz.*, PFR. This indicates that up to 20% (w/w) STBC could be mixed with the PFR. The rigidity of the resin matrix was thus concluded from the swelling measurements. Therefore, these cationic resins with increasing STBC content showed lower swelling which revealed much lower

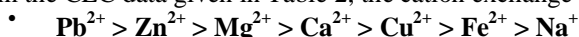
rigid shape, and the rigidity decreased with the increase in % of STBC. It indicates that, pure resin and composites are rigid with non-gel macro porous structure [19].

The values of attritional breaking (Table 1) increase with increase in STBC content (w/w) in the resins, representing the stability of the resin, which decreases from pure resin to STBC. Therefore, the mechanical stability is good upto 20 - 30% (w/w) substitution of STBC in pure resin. This observation also shows that, the capillaries of the resin may be occupied by the sulphonated carbon (STBC) particles [6-8].

The chemical stability of the samples in terms of its solubility in various solvents was determined. It reveals that PFR, composites and STBC 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 2 indicate that, the CEC values (for 0.1M solution of metal ions) decrease when the STBC % content (w/w) in PFR 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 2, 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 [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 Fig.1 conclude that, upto 30% (w/w) blending of STBC with PFR retains 75.43 – 94.66% of CEC for all metal ions, except Cu^{2+} ion. Hence, 30% (w/w) blending of STBC in PFR reduces the cost of original resin. It is observed that there is a continuous decrease in cation exchange capacity (CEC), as the percentage of STBC content in the blend increases. Hence, any chemical methods requiring ion exchangers of small ion exchange capacity, 30% (w/w) blended STBC –PFR resin could be used. STBC can be inexpensively prepared from the plant materials, *Terminalia bellerica*, Roxb., which is freely available in plenty, in India.

The percentage values of CEC of the blends for exchange of H^{+} ions with Na^{+} , Fe^{2+} , Cu^{2+} , Ca^{2+} , Mg^{2+} , Zn^{2+} and Pb^{2+} ions in 0.1M solution are about 60-65% for TB1 – TB5 and nearly 60% as compared to that of the pure commercial resin (SD's; CEC = 100%). This indicates that the composites can partially replace commercial IERs in making the ion exchangers for industrial applications.

The values of cation exchange capacity (CEC) increase with increase in the concentration of Ca^{2+} ions. The equilibrium load of Ca^{2+} ions in unit mass of resin linearly increases with increasing the initial concentration of Ca^{2+} ions in solution from 0.025M to 0.15M [28]. Linear plots were obtained (not shown). The values of slope, intercept and correlation coefficient are given in Table 3. Beyond 0.15M there is a leveling effect of the value of CEC (*i.e.*, a constant CEC value) is noticed for all the metal ions at high concentrations above 0.15M of CaCl_2 .

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 STBC. Upon treatment of resins with various organic solvents, the loss in CEC value was 1.4 - 3.5%.

The decrease in CEC value with boiling water was 0.9 – 4.4% according to the decreasing amount of STBC in the resin. Heating the resins for 10h at 100°C caused a loss in the CEC between 8.0 – 19.1%. 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 $<200\ \mu\text{m}$ are fine and $>500\ \mu\text{m}$ are coarse compared to a particle size of $300 - 500\ \mu\text{m}$ to cause very low ion exchange capacity. Hence, for the effective CEC, the bed size and particle size are to be maintained and the recommended particle size is $300 - 500\ \mu\text{m}$ (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 STBC (Fig.2). Most of the commercial IERs are in Na^{+} form and hence 40ml of 0.2M NaCl was used as a regenerant for every 2g of the resin.

The thermodynamic equilibrium constants ($\ln K$) are given in Table 6 for the removal of Zn^{2+} ions using PFR and composites ($\text{R-SO}_3^{-}\text{H}^{+}$). It has been found that the equilibrium constant (K_{eq}) for the ion exchange reaction increased with the increase in temperature and decreased with the increase in the content of STBC (% w/w) in the resin. The standard values of thermodynamic parameters (ΔG° , ΔH° and ΔS°) were computed and also listed in Table 6. ΔG° values range from -403 to $-1033\ \text{J}\cdot\text{mol}^{-1}$ which indicate that the ion exchange reaction was spontaneous which is attributed due to the negative values of Gibbs free energy. The stability of system increased when Zn^{2+} ions bound with IERs. The ΔH° values range from $2366 - 9462\ \text{J}\cdot\text{mol}^{-1}$, which implied that the ion exchange reaction between the IERs and aqueous solution of Zn^{2+} was endothermic. Similarly, it was found that the ΔS° values range from $9.14 - 34.64\ \text{J}\ \text{mol}^{-1}\ \text{K}^{-1}$, which indicates the increased randomness or disorderliness from STBC to PFR. This may be due to higher amount of Zn^{2+} ions entering into the resin and therefore causing much more amount of H^{+} ions released into the solution. Hence, the

increased amount of H^+ ions in solution reflects the randomness (or) disorderliness *i.e.*, ΔS^0 values increases from PFR to STBC. Hence, PFR has higher CEC values and therefore has higher positive ΔS^0 value. The results are consistent with the earlier reports [10]. FT-IR studies are used to confirm the various stretching frequencies and to identify the ion exchangeable groups [29]. Fig.3a and b indicate the appearance of absorption band at $1039 - 1055 \text{ cm}^{-1}$ ($S = 0$ str.) $1163 - 1193 \text{ cm}^{-1}$ (SO_2 sym str) and $575 - 602 \text{ cm}^{-1}$ ($C - S$ str.) in pure resin (PFR), 10% composite resin and pure STBC confirm the presence of sulphonic acid group.

The appearance of broad absorption band at $3169 - 3409 \text{ cm}^{-1}$ (bonded $-OH$ str.) indicate the presence of phenolic and sulphonic $-OH$ group in the samples. The appearance of absorption band at $1611 - 1624 \text{ cm}^{-1}$ ($C-C$ str.) confirms the presence of aromatic ring in PFR, 10% blending of STBC in PFR and pure STBC. The absorption band at $1447 - 1471 \text{ cm}^{-1}$ ($-CH_2$ def.) confirms the presence of $-CH_2$ group in the samples. The weak absorption band at $888 - 902 \text{ cm}^{-1}$ ($-C-H$ def.) in the samples indicate that the phenols are tetra substituted.

Thermal gravimetric analysis (TGA) is used for rapidly assessing the thermal stability of various substances [30]. TGA curves shown in Figs.4a and b reveal that there is a very small (6%) loss in weight for both PFR and resin blended with 20% (*w/w*) STBC up to 80°C . This is due to the loss of moisture absorbed by the pure resin and resin blended with 20% (*w/w*) STBC. Between $50 - 190^\circ\text{C}$ there, is 20% weight loss in PFR and 16% loss in weight in resin blended with 20% (*w/w*) STBC. Up to 450°C , approximately 57% loss in weight in PFR and up to 530°C , approximately 52% weight loss in resin blended with 20% (*w/w*) STBC was observed.

Two exothermic peaks were obtained in PFR, approximately at 80°C and at 466°C , respectively (Fig.4a). At 80°C , the presence of broad peak was observed, due to the dehydration process of resin (PFR). A peak at 466°C , indicates, the chemical changes of pure resin, which reflect approximately 57% weight loss in PFR.

DTA curves of 20% (*w/w*) STBC (Fig.4b) show that, the same two exothermic peaks were obtained at 80°C and at 530°C , respectively. Again the first broad peak indicates the dehydration of 20% (*w/w*) STBC and second moderate sharp peak indicates the chemical changes of 20% (*w/w*) STBC.

From Figs. 4a and b it is concluded that, the limiting temperature for the safer use of PFR, and resin blended with 20% (*w/w*) STBC as ion exchangers was 80°C , since the resin degrade thermally after 80°C .

4. Conclusion

It is concluded from the present study that PFR sample could be blended with 30% (*w/w*) of STBC, without affecting its physico-chemical, thermal properties. Also the effect of particle size and the concentration effect of Ca^{2+} ions on CEC, its regeneration level by using NaCl, spectral properties and the CEC values of various metal ions of resins blended with 30% (*w/w*) STBC were very close to the original PFR resin. Equilibrium constant for the removal of Zn^{2+} ion and thermodynamic parameters reveal that the process is spontaneous, endothermic and occur within randomness. Hence, blending of PFR with STBC will definitely lower the cost of IER.

Sample	% of STBC in PFR	Density (g mL^{-1})		% of Gravimetric swelling	% of attritional breaking
		Wet	Dry		
PFR	0	2.011	2.066	85.56	8.00
TB1	10	1.926	1.929	76.17	10.89
TB2	20	1.901	1.854	64.23	11.00
TB3	30	1.768	1.783	59.50	11.89
TB4	40	1.506	1.663	52.15	15.00
TB5	50	1.371	1.556	46.01	17.65
STBC	100	1.235	1.322	45.06	22.77

Table 1: Physico chemical properties of PFR and its composites prepared from Sulphonated Terminalia bellerica, Roxb., Charcoal

Sample	% of STBC in PFR	Cation exchange capacity (m.mol g^{-1})						
		Na^+	Fe^{2+}	Cu^{2+}	Ca^{2+}	Mg^{2+}	Zn^{2+}	Pb^{2+}
PFR	0	0.822	1.624	1.835	1.644	1.816	1.779	1.840
TB1	10	0.798	1.350	1.555	1.565	1.732	1.714	1.726
TB2	20	0.754	1.300	1.415	1.505	1.636	1.702	1.678
TB3	30	0.726	1.225	1.305	1.446	1.535	1.684	1.600
TB4	40	0.711	1.150	1.160	1.351	1.369	1.428	1.488
TB5	50	0.594	0.950	1.005	1.131	1.256	1.208	1.422
STBC	100	0.038	0.675	0.770	0.512	0.559	0.643	0.655

Table 2: Cation exchange capacities of H^+ form of the IERs

Sample	Correlation Co-efficient	Slope	Intercept
PFR	0.988	0.700	0.0125
TB1	0.903	0.362	0.0248
TB2	0.902	0.347	0.0245
TB3	0.919	0.352	0.0216
TB4	0.961	0.301	0.0204
TB5	0.949	0.310	0.0154
STBC	0.937	0.178	0.0069

Table 3: Correlation analysis on the concentration of Ca^{2+} ion by PFR, Composites and STBC

Reagents	Cation Exchange Capacity (m.mol. g ⁻¹)					
	PFR	TB1	TB2	TB3	TB4	TB5
Original Capacity	1.816	1.732	1.636	1.535	1.369	1.256
0.2M NaOH boiled for 1 h	1.798	1.700	1.599	1.509	1.313	1.196
Benzene boiled for 1h	1.762	1.708	1.609	1.514	1.309	1.212
Boiling water for 1h	1.800	1.720	1.618	1.516	1.333	1.201
Thermal treatment in hot air oven at 100°C for 12h.	1.671	1.472	1.374	1.259	1.123	1.017

Table 4: Chemical and Thermal effect on CEC of PFR and its composites (by blending with STBC) Exchange with 0.1M Mg^{2+} ions at 303K

Sample	Particle Size μm	Cation exchange Capacity (m.mol g ⁻¹)			
		Na^+	Mg^{2+}	Ca^{2+}	Zn^{2+}
PFR	< 200	0.785	1.409	1.047	1.325
	200 – 300	0.822	1.816	1.644	1.779
	300 – 500	0.793	1.475	1.562	1.680
	> 500	0.780	1.350	1.432	1.651
TB2	< 200	0.689	1.033	1.257	1.513
	200 – 300	0.754	1.636	1.505	1.702
	300 – 500	0.737	1.183	1.483	1.542
	> 500	0.681	0.964	1.405	1.420

Table 5: Effect of particle size on cation exchange capacity of PFR and 20% (w/w) of STBC

Sample	ln K		- ΔG ⁰ (J.mol ⁻¹)	ΔH ⁰ (J.mol ⁻¹)	ΔS ⁰ (J.mol ⁻¹ K ⁻¹)
	303K	313K			
PFR	0.41	0.53	1033	9462	34.64
TB1	0.40	0.50	1008	7855	29.35
TB2	0.36	0.44	907	6308	23.81
TB3	0.30	0.37	756	5520	20.71
TB4	0.28	0.34	705	4731	17.94
TB5	0.24	0.29	605	3943	15.01
STBC	0.16	0.19	403	2366	9.14

Table 6: Thermodynamic equilibrium constant (in terms of lnK), at 303K, 313K and Standard Gibbs Free energy, Enthalpy and Entropy of H⁺ / Zn²⁺ ion exchanges on various IERs at 303K

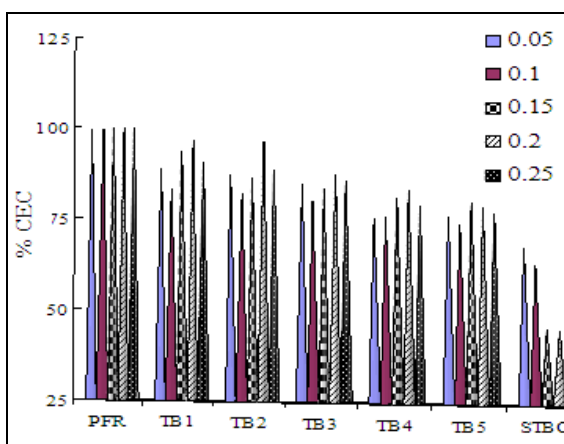
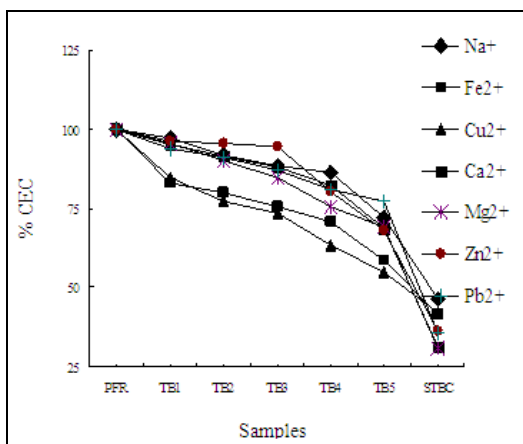


Figure 1: Cation Exchange Capacities of H⁺ form of IERs, for Various Metal Ions Relative to PFR
 Figure 2: Regeneration level for PFR, its Composites and STBC by using NaCl after exchange with Mg²⁺ ions

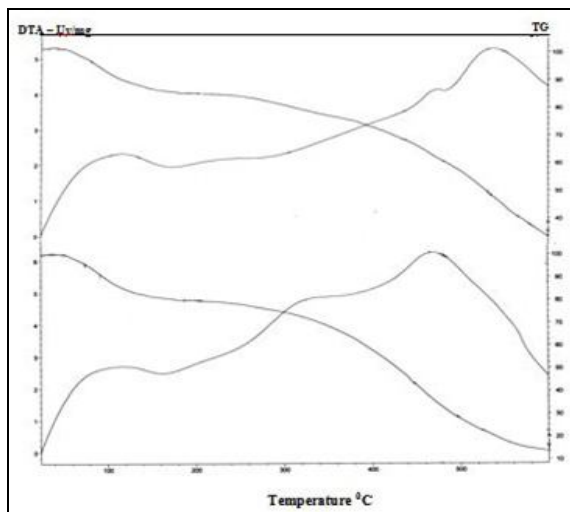
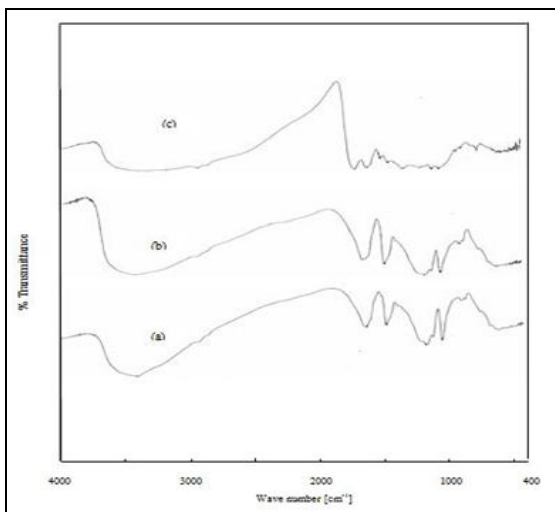


Figure 3: FT-IR Spectra of (a) PFR, (b) 10 % (W/W) STBC in composite and (c) Pure STBC
 Figure 4: Thermal Studies of (a) PFR, (b) 20% (W/W) STBC in Composite

4. References

1. Bolto. B.A and Pawlowsk L., Waste Water Treatment by Ion-exchange, Oxford & IBH Publ. Co., New Delhi, 1987.
2. Sharma N.L.N., Joseph Mary and Padma Vasudevan. Res.Ind., 21, (1976) 173
3. Padma Vasudevan and Sarma. N.L.N. J.Appl. Poly.Sci., 23, (1979) 1443
4. Mohan Rao. G.J. and Pillai, S.C. J. Indian Inst .Sci., 36A, (1954) 70
5. Shahha and Batna. S.L. J. Appl. Chem. Lond., 8, (1953) 335
6. Dheiveesan. T., and Krishnamoorthy. S. J. Indian Chem.Soc.,65, (1988) 731
7. Kathiresapandian. D. and Krishnamoorthy. S. Indian. J. Technol.,29, (1991) 487
8. Mariamichel. A. and Krishnamoorthy. S. Asian J. Chem., 9(1), (1997) 136
9. Kannan .N. Seenivasan R.K., and Mayilmurugan. R. Indian J. Chem. Technol., 10,(2003) 623
10. Metwally M.S., Metwally. N.E and Samy. T.M. J. Appl. Poly. Sci., 52, (1994) 61
11. Kannan. N. Murugavel. S., Seenivasan R.K., and Rengasamy. G. Indian J. Env. Prot., 23 (12), (2003), pp. 1367 – 1376
12. Kannan. N.and Seenivasan. R.K. J. Appl. Poly. Sci. 101,4104
13. Kannan. N.and Seenivasan .R.K. J. Ion Exch.,16, 164 (2005)
14. Kannan.N.and Seenivasan .R.K. Desalivation.,216, 77 (2006)
15. Fong Lo. S, Wang. S.Y, Tsai. M.J and.Lin. L.D, Chemical Engg. Res. and Design, 90(9), 1397, (2012).
16. Jovanovic. M, Rajic. N and Obradovic. B. J. Haz.Mat., 233, 57, (2012).
17. Huang J., Cao Y., Liu Z. and.Deng Z, Chem.Engg. J., 80(15), 75, (2012).
18. Wu. N and Zale, Chem.Engg. J. 215, 894, (2013).
19. Natarajan. M and Krishnamoorthy. S. Res. Ind., 38, (1993) 278
20. Bassett. G.H, Jeffery.J, Mendham. J and Denney. R.C, Vogel's Text Book of Quantitative Chemical Analysis, 5th Edn. Longman Group Ltd., London, 1989.
21. Ramachandran. S and. Krishnamoorthy.S, Indian J. Technol., 22, (1984) 355
22. Chandrasekaran. M.B and Krishnamoorthy. S, J. Indian Chem. Soc., 64, (1987)134
23. Son.W.K, Kim. S.H and Park. S.G, Bull.Korean Chem...Soc., 22 (1), (2001) 53
24. Dimov. D.K, Petrova.E.B, Panayotov. I.M and Tsvetanov. Ch.B, Macromolecules, 21, (1990) 2733
25. Kunin.R, Ion Exchange Resin, Wiley, Newyork and London, 2nd Edition, (1958)
26. Mattson.S, Ann. Agric. Coll., Sweden, 10, (1942) 56
27. Bonner.O., Easterling.G, Weit.D and Holland.V, J.Am.Chem.Soc., 77,(1955)
28. Kim.Y.K and Lee.K.J, J.Nucl. Sci. Tech., 38 (9), (2001) 785
29. Zagorodni.A.A, Kotova.D.L and. Selemenev.V.F, Reac. Func. Poly. 53, (2002)
30. Anderson.H.C, SPETrans., 1, (1962) 202