Synthesis and Characterization of Tannin Based Porous Cation Exchange Resins from *Cassia auriculata* (Ranawara)

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Abstract

Tannins are one of the most abundant compounds in the nature. Naturally tannins have ion exchanging capability. Conversely, tannins are highly water soluble compounds, thus natural tannins cannot be used as ion exchangers. In this study, tannins extracted from *Cassia auriculata* (Ranawara) were used to synthesise renewable tannin based porous cation exchange resin systems. Essentially, the applicability of these resin systems as an ion exchange resin were considered.

Identification of the Tannin was carried out by using ferric chloride test, nitrous acid test and acid butanol tests. Total polyphenolic content of *Cassia auriculata* was 13.30% (w/w) and it was calculated by using Folin-ciocalteau method. Tannin-Formaldehyde resin was prepared, and the ion exchange capacity was measured. Then the Tannin-Formaldehyde resin was sulfonated to increase the ion exchange capacity by refluxing with concentrated H_2SO_4. Then, the ion exchange capacity of the resin was further increased by introducing a porous structure using virgin coconut oil as the porogenic agent. Ion exchange capacity, solubility, Fourier transform infrared spectroscopy and scanning electron microscopy analysis were used to characterise the resin systems. The modified resin with high fraction of surfactant contains mostly open porous structures and it has the highest IEC (0.9550 meq/g) among the synthesized resin systems.

Keywords: *Cassia auriculata* (Ranawara), porous tannin-formaldehyde cation exchange resin, ion exchange capacity, FTIR, SEM

1. Introduction

The term tannin is a French word which derived from tannin (tanning substance) (Khanbabaee and van Ree, 2001) and it indicates a plant material which allows the conversion of mask into leather. Tannins are one of the most abundant compounds in the nature and which are second most abundant source of natural aromatic biomolecules after Lignin (Arbenz and Avérous, 2015).

Tannins are polyphenolic compounds (also known as plant polyphenols), showing characteristic phenolic reactions such as blue color formation with iron (III) chloride (Khanbabaee and van Ree, 2001). Usually, tannins can be found in different parts (such as root, bark, leaves, wood and galls) of plants in different composition. The composition and concentration of tannin vary with the species, age of the plant and the part of the plant. Usually, many of plants in Sri Lanka contains considerable amount of tannins.

Depending on their structure tannins can be classified into three classes, which are hydrolysable tannins, condensed tannins and complex tannins. Hydrolysable tannins are a blend of ellagic acid, gallic

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acid or digallic acid and polyols. Those can be separated into two families, which are Gallotannins and Ellagitannins. Usually, gallic acid and its derivatives are produced from the hydrolysis of Gallotannins. Likewise ellagic acid and its derivative are produced from the hydrolysis of Ellagitannins (Arbenz and Avérous, 2015). Hydrolysable tannins have very weak nucleophilicity due to the low concentration of the phenolic substances (Mitra, Banerjee, and Sarkar, 1991). Hydrolysable tannins can be hydrolyzed by using acids or bases. Condensed tannins are polymeric flavonoids which have 3 to 8 units of flavonoid oligomers (Arbenz and Avérous, 2015). They are derived from flavan-3,4-diol and flavan-3-ol. Usually these tannins cannot be hydrolyzed easily, because of the fact that the structure contains interflavan carbon bonds (Oo, 2008). Complex tannin is a mixture of condensed tannins and hydrolysable tannins, which means a mixture of flavan-3-ol units and ellagitannin units (Arbenz and Avérous, 2015). In the structure of complex tannins, a catechin unit is bound to a gallotannin or an ellagitannin unit through a glycosidic bond.

Cassia auriculata is a branched small plant which typically distributed even in less fertile soil in Sri Lanka (Meenupriya et al., 2014). Hence it becomes one of the best known tannin materials of Sri Lanka. The bark is of dark brown in color which contains relatively higher percentage of tannins (Theresa et al., 1968).

Naturally tannins have the ability to behave as ion exchangers. However, natural tannins cannot be used as ion exchanging materials as tannins are highly water soluble compounds (Balasooriya and Sotheeswaran, 1982). Hence, a water insoluble tannin based compound should be synthesized to use the tannins as ion exchange materials.

Condensed tannins (proanthocyanidins) are included in the bark of the *Cassia auriculata* and flavonoid units are the monomers of condensed tannins. When consider a flavonoid unit which has two aromatic rings. Predominantly, A-rings are resorcinolic, phloroglucinolic or pyrogallolic and B-rings are catecholic or pyrogallolic groups (Zhan and Zhao, 2003). Usually, A-ring is more reactive because of its higher nucleophilicity than the B ring. Furthermore, vicinal hydroxyl substituents merely cause ordinary activation in the B ring without any localization effects such as those found in A-ring (Özacar, Soykan, and Şengil, 2006). In the following structure (Figure 1) shows the structure of flavonoid unit in condensed tannins and its reactive sites.

If the A-ring;

- R_1=OH, R_2=H for phloroglucinolic
- R_1=H, R_2=H for resorcinolic
- R_1=H, R_2=OH for pyrogallolic

If the B-ring;

- R_3=H for catecholic
- R_3=OH for pyrogallolic

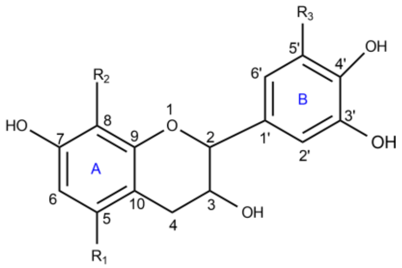

Figure 1. Structure of flavonoid unit.

Generally, tannins are reacted with formaldehyde to form an insoluble polymer, called tannin-formaldehyde resin. In order to discuss about the preparation of the tannin-formaldehyde resin, the reactivity of the tannins should be considered.

Tannins are phenolic compounds which react with formaldehyde in a same manner to the general reaction of formaldehyde with phenol. During the polymerization process methylene bridge linkages are formed at the reactive positions on the flavonoid molecules and the polymerization is occurred in between Formaldehyde and condensed tannins. Generally, active sites of the A-ring have higher affinity to form the methylene bridge linkages than the B-ring (Özacar et al., 2006). The free C8 or C6 positions are reacted with formaldehyde and form water insoluble tannins, due to the strong nucleophilic nature of A-ring.

When the tannin-formaldehyde polymer is formed, ion exchange capacity (IEC) will defend on the surface area of the polymer formed. One way to increase the surface area of the resin is to a porous structure that can further increase the IEC of the resin. Generally, macro porous polymers have been prepared from using the High Internal Phase Emulsion (HIPE) polymerization method. In this research for the preparation of the HIPE structure Hexamine is used as the cross-linker which is important to lock the HIPE structure. Further, a tiny amount of the proper non-ionic surfactant is used, and which stabilizes the HIPE structure. After the removal of the internal phase a macro porous polymer is formed and which is called as polyHIPE (Wu et al., 2012).

In order to obtain a strong acidic cation exchange resin, more acidic groups have to be introduced to the tannin-formaldehyde resin. Sulfonic acid groups can be introduced by Sulfonating with concentrated H_2SO_4 (98% w/w) (Marutzky and Dix, 1982).

2. Materials and Methods

2.1 Preparation of plant material

Dark brown color bark layers of *Cassia auriculata* (Ranawara) were taken from local source around Panadura area, Sri Lanka. The bark layers were cleaned, cut into small pieces and allowed to air dry under partial sunlight for three weeks. Dried Ranawara barks were finely ground to reduce particle size.

2.2 Extraction of tannins from powdered bark sample

Extraction process was performed according to the procedure described in literature, by using the Soxhlet extraction method. Firstly, powdered bark sample was extracted using hexane at 68^{o} C for an hour to remove the non-polar impurities. Then, it was extracted using petroleum ether at 45^{o} C for an hour to remove most of non-polar compounds. Finally, the powdered bark sample was extracted using methanol [80% (V/V)] at 70^{o} C for two hours. Then, the methanol extract was concentrated using rotary evaporator under reduced pressure. The resulted concentrated tannin extract was further concentrated by heating under the water bath at 80^{o} C for two hours. Finally, it was kept in a desiccator for a week to obtain the solid form of tannins (Karunanayake and Arasaretnam, 2010).

2.3 Identification of tannin type

Ferric chloride test, nitrous acid test and acid butanol test were done to confirm the presence of polyphenolic compounds, ellagitannins and condensed tannins, respectively. Then the total polyphenolic content was determined by using the Folin-ciocalteau (FC) micro method.

2.4 Synthesis of Tannin-Formaldehyde (TFR) cation exchange resin

10 g of dried Ranawara extract was dissolved in 25 mL of 0.225 M NaOH solution at room temperature. Then 5 mL of methanol was added at same temperature. 3 mL of formaldehyde aqueous solution [37% (w/w)] was added to this mixture drop wise at 40^{o} C. The mixture was brought to 80^{o} C and kept for an hour. The resultant mixture was neutralised by using 1.0 M HCl. Then, the resin was cooled and allowed to harden. The sample was cured in an oven operating at 100^{o} C for an hour for further cross-linking and allowed to cool.

2.4 Sulfonation of Tannin-Formaldehyde cation exchange resin

About 5.0 g of tannin-formaldehyde cation exchange resin was refluxed with 25.00 cm^3 of H_2SO_4 [98% (w/w)] at 105^{o} C for 6 hours in a paraffin bath. The resultant mixture is the sulfonated tannin-formaldehyde resin (STFR) and it was allowed to cool, washed carefully with hot distilled water. Then it was filtered (suction filtration) to remove the residual free H_2SO_4. Then the resin was washed by using 250.00 mL of 1.0 M NaCl solution to convert it to Na^+ form. Then, the sample was dried in an oven operating at 100^{o} C for an hour and allowed to cool.

2.5 Preparation of porous cation exchange resin by using virgin coconut oil

Initially, 20 g of tannin was dissolved in 40 mL of distilled water. Then, about 0.7 g of pure Para toluene sulfonic acid (pTSA) was added. The latter made the pH of the solution be equal to 3 for all formulations. Then, the solution was stirred with a mechanical stirrer at 200 rpm over 20 min to obtain a homogenised reaction mixture. Then, Wettuam reagent, a non-ionic stabilizer, was added at a concentration of 1.0 wt.% or 3.0 wt.% with respect to the total weight of aqueous solution, and stirring was continued over 20 min. Then, virgin coconut oil (porogenic agent) was introduced dropwise at a rate of 45 drops min^{-1}, while the growing emulsion was being continuously stirred at 250 rpm. When 15 mL of virgin coconut oil was added, 4.47 g of hexamine (40 wt.% in water) was introduced into the emulsion. At this moment, the mixing speed was shortly increased to 600 rpm from 250 rpm for around 1.5 minutes and after 1.5 minutes, the mixing speed was again adjusted to 250 rpm. The increment of the mixing speed was done to improve dissolution of hexamine. After the addition of all the virgin coconut dropwise, the emulsion mixture was further stirred for 15 minutes. Then resultant homogeneous, brown colored viscous emulsion was covered with an Aluminium foil. Then, the polyHIPE was cured in an oven operating at 85^{o} C for 24 hours for further cross-linking. Then, the excess virgin coconut oil was removed. The polyHIPE was cut into smaller pieces and the remaining oil was completely removed by refluxing with acetone for 7 days. Finally, the light weight, brown colored product was kept in a desiccator for further analysis.

2.6 Determination of Ion Exchange Capacity (IEC) of the resins

The ion exchange capacity of the resin systems can be calculated by using titrimetric analysis method (Karunanayake and Arasaretnam, 2010). The solutions were used for the titration are standardized 0.1M NaOH solution as the titrant, 1.0 M NaCl solution and standard 0.1 M HCl solution as the titrand.

5.00 g of the resins were allowed to wet in distilled water for 30 minutes. Then the resins were packed in burette-type ion exchange columns using distilled water. Then all the neutral forms of the resins were converted to H^+ form by using 0.1 M HCl solution as influent. Then, the resin columns were washed with distilled water to remove excess $H^+_{(aq)}$ ions which were trapped in the column. The acidity of the eluate was checked with litmus papers and pH papers. After the eluate was approximately neutral, the 0.1 M NaCl solution was allowed to run through the columns as an influent at a rate of 5 $cm^3 min^{-1}$. The eluate was collected, and it was titrated with 0.1 M NaOH solution in the presence of phenolphthalein as the indicator. Finally, the IEC was calculated.

2.7 Scanning Electron Microscopic (SEM) analysis

All the resin systems were characterized by using SEM (Hitachi SU6600) under micrometer and Nano meter scales. Samples were sputtered with gold before obtaining images. Finally, the images were analyzed, and the pore diameters were calculated by using ImageJ (Version 1.60) software.

2.8 Determination of solubility of resin systems

Exactly 0.500 g of a resin system was placed in 25 mL beakers. It was soaked in 5 mL of different solvents separately. Then, beakers were covered with Aluminum foils and allowed to stand for 1 week. Finally, the weight change was measured, and the solubility of the resin was checked.

3. Results and Discussion

3.1 Identification of tannins type

When ferric chloride was added, there was a formation of greenish gray colour. It implies the phenolic groups have reacted with the iron salts. However, ferric chloride test can be used to distinguished both condensed and hydrolysable tannins. Hydrolysable tannins form bluish gray color while the condensed tannins form greenish gray color. However, it was very difficult to observe a subtle distinction between these two colors (Falcão and Araújo, 2011). Nitrous acid test was carried out to confirm the presence of hydrolysable tannins. Generally, ellagitannins are reacted with nitrous acid. Initially the brownish orange color of the sample mixture was progressively turned in to bluish purple color. Acid butanol test was carried out to confirm the presence of condensed tannins. Initially the brownish orange color of the sample was turned in to crimson red color due to the formation of correspondent anthocyanidins via an oxidative depolymerisation reaction (Falcão and Araújo, 2011).

3.2 Synthesis of Tannin-Formaldehyde cation exchange resin

The final resole was brownish black colored solid material. While the extracted tannins are soluble in distilled water, the final resole did not dissolved. Hence, it indicates that the formation of water insoluble tannin-formaldehyde resin. General reaction mechanism for the formation of Tannin-Formaldehyde cation exchange resin is shown in Figure 2.

3.3 Sulfonation of Tannin-Formaldehyde cation exchange resin

When the tannin-formaldehyde resin was refluxed with H_2SO_4 [98% (w/w)] a heterocyclic ring opening was happened. At that point, an insertion of sulphonic acid group was occurred at the position 2 as given in the Figure 3. Hence, the brownish black color of the resin was turned into black color and the resin was also water insoluble. The IEC has been increased compared to the conventional TF resin due to the very reactive acidic character.

3.4 Preparation of porous resin by using virgin coconut oil

Virgin coconut oil was used as the porogenic agent, Wettum was used as the non-ionic emulsifier and Para toluene sulfonic acid was used as the catalyst. Similarly, Hexamine was used as the crosslinking agent instead of formaldehyde. In the acidic condition, hexamine releases the formaldehyde and NH_3 to the medium. Similarly, in alkaline conditions, hexamine releases the formaldehyde and trimethylamine to the medium (Figure 4).

The reaction between nucleophilic tannins and amino-methylene bases is very fast. Hence it prevents the reaction between tannins and formaldehyde. However, the reaction between tannins and amino-methylene leads to the formation of benzylamine bonds on the tannins molecules.

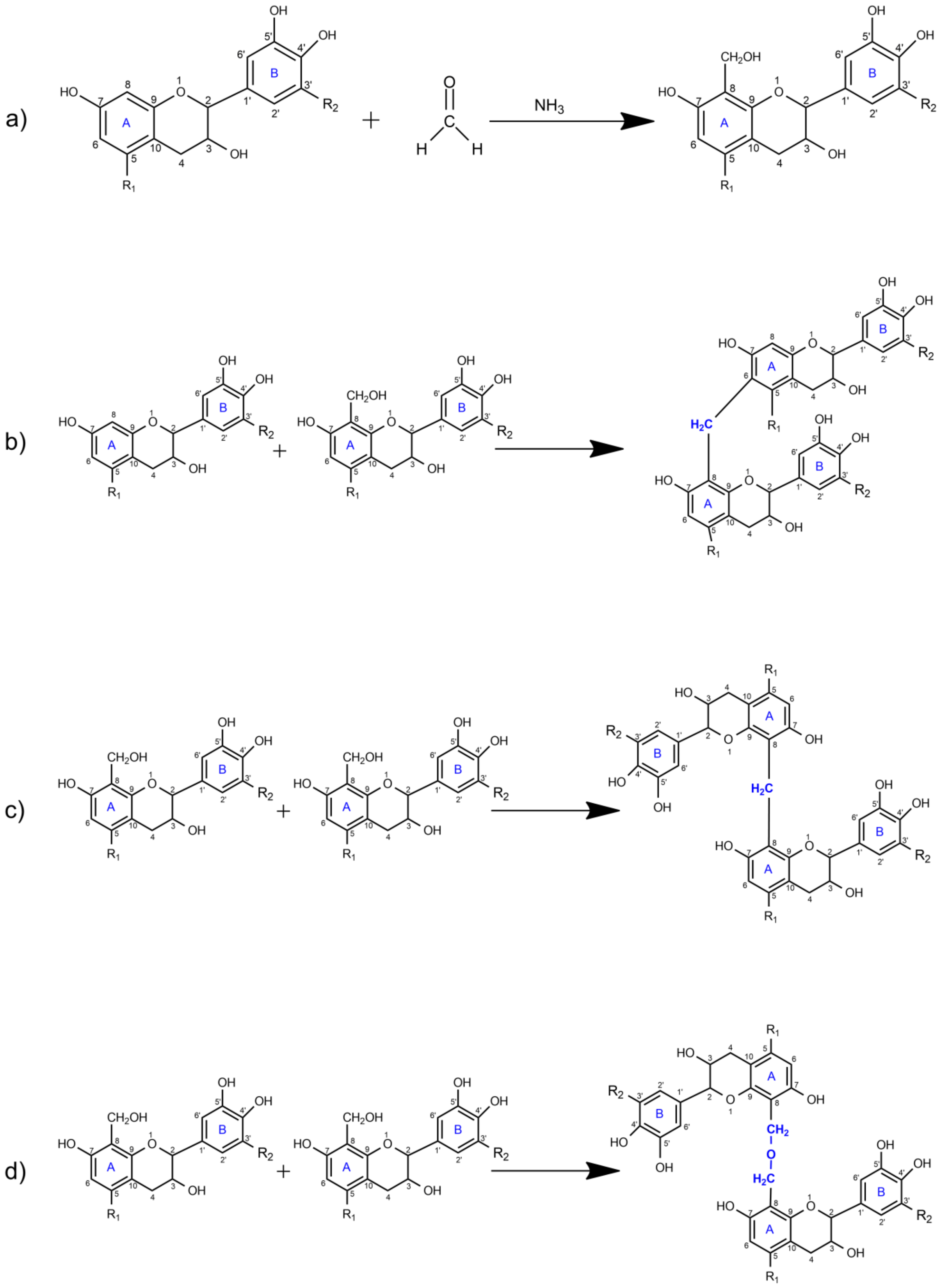

Figure 2. Reaction of condensed tannin with formaldehyde.

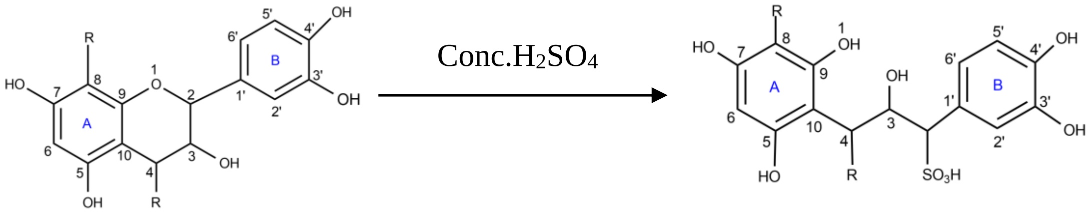

Figure 3. Sulfonation reaction of tannins.

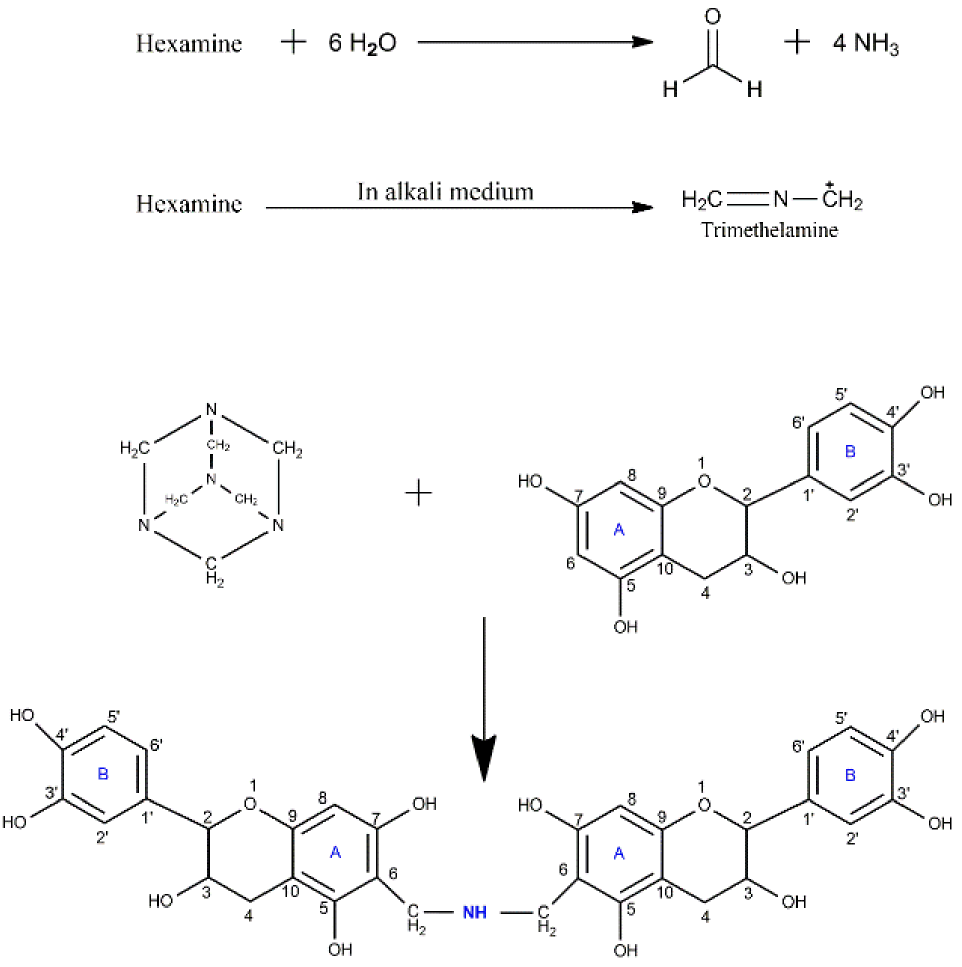

Figure 4. Possible reaction between hexamine and tannin.

When considering the physical structure of both modified resin with 3.0 w/w % of surfactant fraction (VMRH) and Modified resin with 1.0 w/w % of surfactant fraction (VMRL) the VMRH system had much porosity than the VMRL system. In the process of removing the remaining oil was done by refluxing with acetone for 7 days.

When the VMRH and VMRL systems were used as the ion exchange resins, it was difficult to pack those in burette type columns due to their light weight. It clearly indicated that the modified resin systems have low bulk density compared to the conventional tannin-formaldehyde resin. However, the mobile phase was passed properly through all the modified resin systems indicating that modified resin systems contain considerable amount of open cell structures.

The following figures are shown for the synthesis process of modified resin with high fraction of surfactant (3.0 w/w %).

Figure 5. Synthesized modified resin-After the heat treatment.

Figure 6. Synthesized modified resin-After the complete removal of oil.

3.5 Determination of ion exchange capacity (IEC) of resin systems

The IEC obtained for different resin systems shown in Table 1 and the highest ion exchange capacity obtained from VMRH system.

Table 1: IEC values for different resin systems.

Resins system	IEC [Na^+/H^+] (meq/g)		Average IEC [Na^+/H^+] (meq/g)
	Cycle 1	Cycle 2	
TFR	0.3600	0.3400	0.3500
STFR	0.5100	0.5000	0.5050
VMRL	0.6100	0.5900	0.6000
VMRH	0.9600	0.9500	0.9550

The TFR possessed the lowest IEC. This is due to the limited availability of the ion exchangeable sites and the weak acidic character of the phenolic hydroxyl groups. This IEC value can be increased by introducing sulfonic acid (SO_3^-) groups to the conventional TFR system. Although, the ion exchangeable sites are limited, introduction of sulfonic acid (SO_3^-) groups produced very reactive acids. Hence, the STFR system has a little higher IEC value than TFR system. Due to the branched complex structure of the tannin molecules the steric hindrance can be occurred limiting the number of available sites for the sulfonation resulting low IEC for both regular TFR and STFR (Mitra et al., 1991).

Considering the VMRL and VMRH porous resin systems the IEC depends on the pore volume of the of the resin structures. Furthermore, the IEC will be affected by the amount of the open cell structures. Secondary interconnected pore structures in open cell structures increase the pore volume. The increase of pore volume increases the surface area resulting a much higher number of ion exchange sites.

3.6 Fourier Transfer Infrared (FTIR) spectroscopic analysis

IR spectra of the Ranawara bark sample and its tannin extract were studied for characterisation (Figure 7). The broad absorption band in the range of 3,400-3,100 cm^{-1} of the IR spectrum is corresponded to O-H stretching vibration, a sharp band at 1,607 cm^{-1} can be assigned to the C=O stretching vibration. The 2,850-3,000 cm^{-1} absorption bands can be assigned to C-H stretching vibrations of aromatic, aliphatic hydrocarbon. The bands at 1,509 cm^{-1} and 1,450 cm^{-1} can be due to the aromatic skeletal vibrations representing C=C stretching (Khanbabaee and van Ree, 2001). Moderate bands at 1,338, 1,232 and 1,110-1,025 cm^{-1} regions are corresponded to O-H bending and symmetrical as well as asymmetrical C-O-C stretching vibrations (Gurung et al., 2012). The intensities of IR bands of extracted tannin (ET) are stronger than dried bark sample. That indicates tannin extracted from bark has a much higher concentration of aromatic compounds than dried bark sample (Karunanayake and Arasaretnam, 2010). Hence, the extraction process used is a better method for obtain the tannins from Ranawara bark.

Figure 8 shows a comparison of FTIR spectra of TFR and STFR. The strong broad peaks can be observed at 1,149 cm^{-1} and 1,148 cm^{-1} in TFR and STFR, which are attributed to dimethylene ether linkages. The two absorption bands at 840 cm^{-1} to 730 cm^{-1} correspond to the deformation vibration of the C-H bonds in benzene ring. However, this C-H bonds do not contribute to any chemical reaction during the resin formation.

Compared to the spectra of extracted tannin (ET) sample, a reduction of the peak intensity can be observed in TFR and STFR systems, due to the shrinkage of the volume during the polymerization process. The intensity of the C=C stretching band at 1,500-1,400 cm^{-1} was clearly decreased in both TFR and STFR spectra compared to the spectra of extracted tannin sample. This reduction of the band intensities indicates that a crosslinking reactions might have happened with the aromatic ring (Sumathirathne and Karunanayake, 2017). In the FTIR spectra of Sulfonated Tannin-Formaldehyde resin (STFR), a new intense peak is appeared at 1,194 cm^{-1} which can be attributed to S=O sulfoxide bond (Karunanayake and Arasaretnam, 2010). This is a clear indication that the Tannin-Formaldehyde resin has been successfully sulfonated.

The spectra in Figure 9 were recorded in the range of 650 cm^{-1} to 3,990 cm^{-1} and they are corresponding for VMRL and VMRH systems which are almost similar in basic features with minor changes. In the comparison of modified resin systems with the Sulfonated Tannin-Formaldehyde resin (Figure 8), the spectra of modified resin systems are shown the widespread –OH strong peak with a relatively small shoulder in the range of 3,500-3,200 cm^{-1}. Small peaks around 2,920 cm^{-1} in spectra can be assigned to C-H and $–CH_2$ stretching vibrations of methylene and methyl groups of side chains and aromatic methoxyl groups in the modified resin systems (Chupin et al., 2013). Those absorption bands are clearly weaker than those of the spectra in the tannin extract (Figure 7).

Usually the peak assign to C-O-C aliphatic ether bond of both the TF and STF resin systems was around 1,140 cm^{-1}. However, in this study the corresponding peaks in modified resin systems were shifted to the lower side and which are around 1,090 cm^{-1} and also their peak intensity has been decreased. The peaks which at lower than 900 cm^{-1} region are attributed to aromatic CH stretching (Chupin et al., 2013). There were new peaks arose around 1,225 cm^{-1}, which are attributed to the C-N stretching bonds (Pena et al., 2009). Considering the above FTIR spectra, it can be assumed that all three modified resin systems contain two types of linkages. The typical methylene ($–CH_2–$) linkages which are formed by aliphatic ether bonds and the amine ($–CH_2\text{-}NH\text{-}CH_2–$) linkages (Moubarik et al., 2010; Sumathirathne and Karunanayake, 2017).

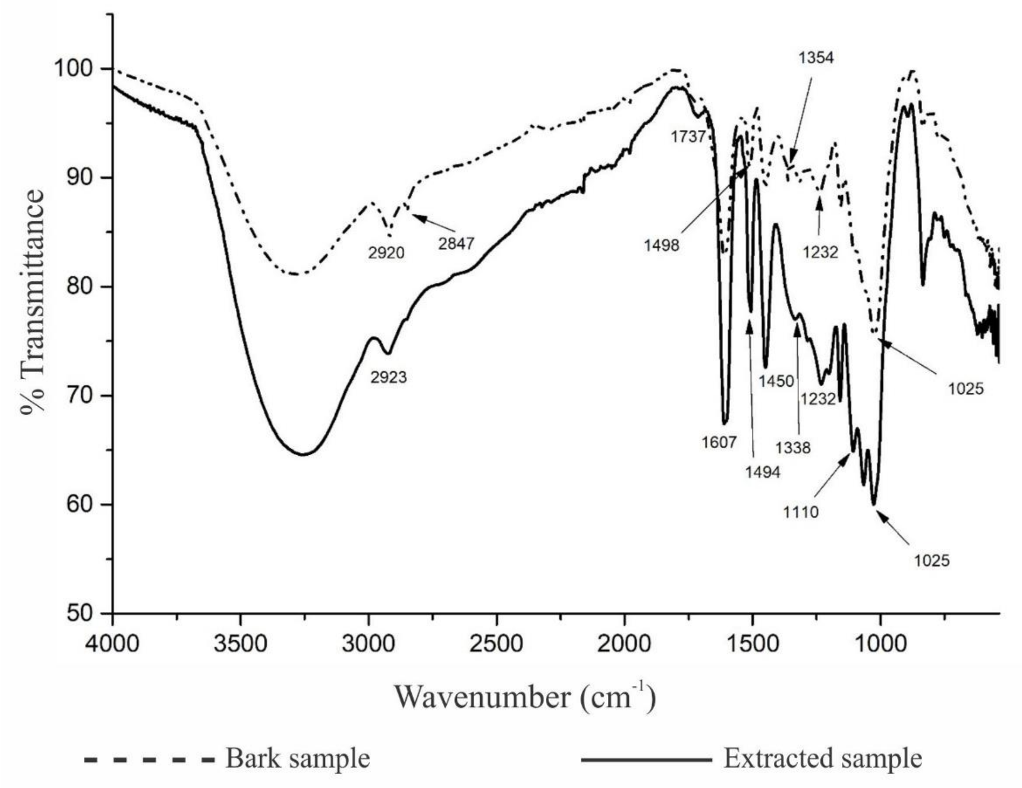

Figure 7. FTIR Spectra of bark sample and extracted taninns.

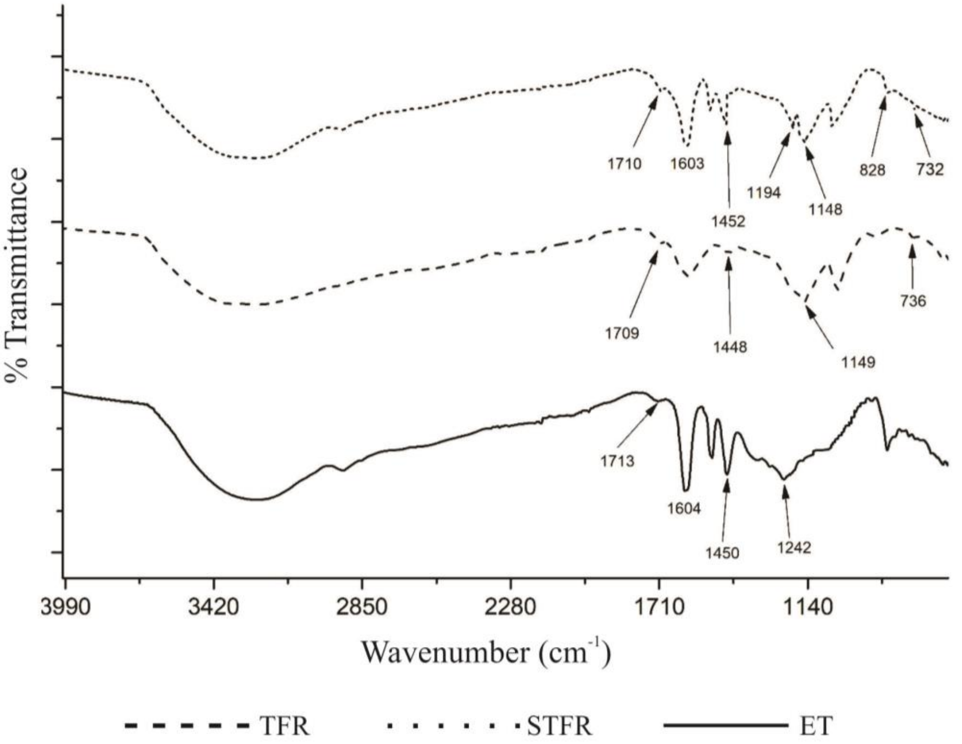

Figure 8. FTIR Spectra of tannin-formaldehyde resin, sulfonated tannin-formaldehyde resin and tannin extract.

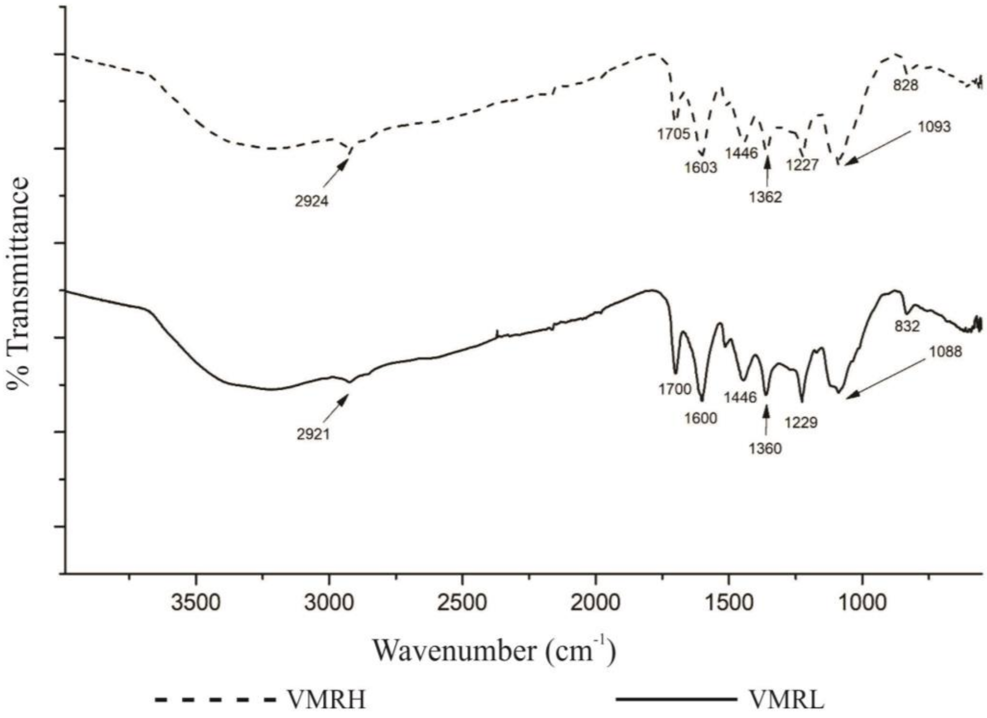

Figure 9. FTIR spectra of VMRL and VMRH systems.

3.7 Scanning Electron Microscopic (SEM) image analysis

Scanning electron microscopy (SEM) is used to demonstrate the pore architecture of the porous resin systems. The main reasons for use SEM analysis to illustrate the open cell structure in the polyHIPE structures formed and obtain the pore diameter distribution of the resin systems.

The following figures are shown the SEM images of TFR, VMRL and VMRH respectively. As usual, it is very hard to observe any porous structures in the SEM images of TFR (Figure 10). However, some heterogeneities can be observed in the structure and that is due to the low condensed and high condensed zones of polymerized resin matrix. However, TFR system has the lowest surface area. Hence TFR system should have the lowest IEC among the resin systems (Zhang and Cooper, 2005).

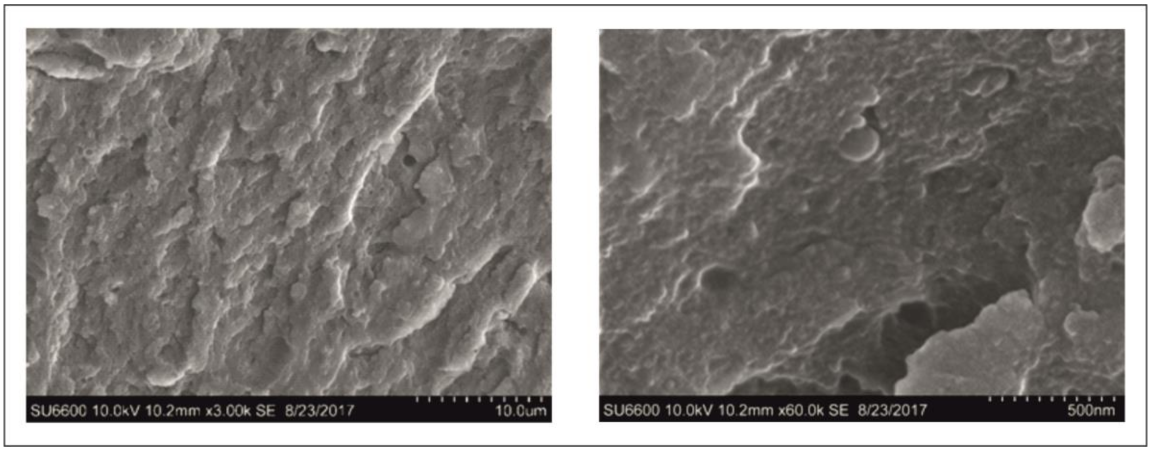

Figure 10. SEM images TFR in µm and nm scale.

When considering SEM images of the VMRL (Figure 11) system, it contains higher amount of closed cell structures and small amount of open cell structures. Due to the small amount of open porous structures, the pore volume is slightly increased. Therefore, the surface area is little bit higher than the TFR system. Hence the IEC of the VMRL system should be slightly higher than the TFR system. This result is further justified by considering the experimental IEC values (Table 1) (H. Zhang and Cooper, 2005).

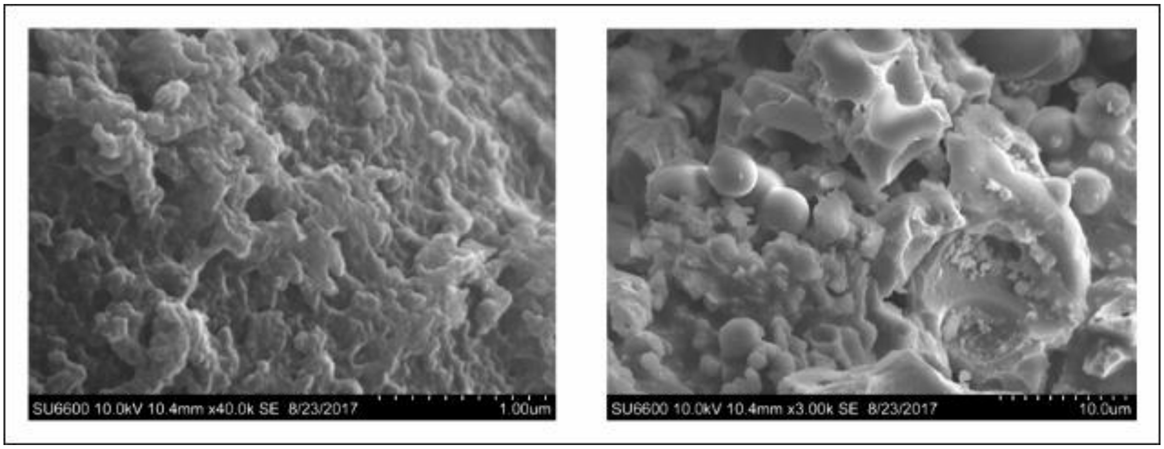

Figure 11. SEM images VMRL in µm scale.

According to the SEM images of VMRH system (Figure 12), the system contains much higher amount of porous structures and most of them are open cell structures. Also, few cracks can be seen with some heterogeneities. Hence, the pore volume of these resin systems is much higher. According to the literature, PolyHIPE materials generally have much higher pore volume (about 10 cm^3g^{-1}) (H. Zhang and Cooper, 2005). Therefore, the surface area is getting higher due to the higher pore volume resulting increase in ion exchange sites. Hence, the IEC should be much higher than the TFR and VMRL systems.

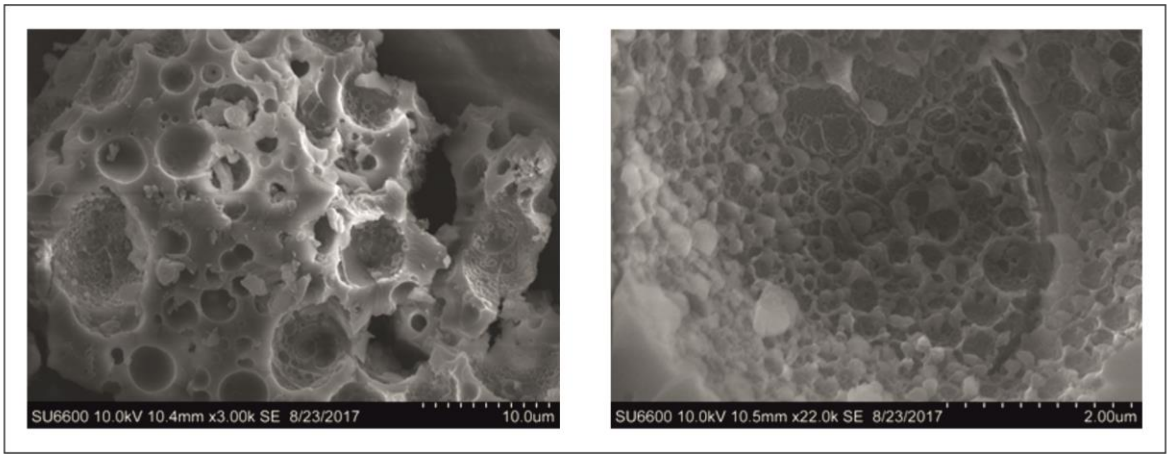

Figure 12. SEM images VMRH in µm scale.

When considering the SEM images of both VMRL and VMRH systems (Figure 11 and 12 respectively), there was a substantial difference in the both porous structures. VMRL system contains less amount of porous structures and most of them are closed cell structures. However, the VMRH system contains much higher amount of porous structures and the most of them are open cell structures. This is due to the effect of the concentration difference in the emulsifier. The only difference in the preparation of both resin system is the concentration of the emulsifier (i.e. VMRL system was made with 1.0 w/w % of the emulsifier while the VMRH system was made with of 3.0 w/w %).

In the Figure 13, it is shown that the structure of voids and windows by using the SEM image of VMRH system. The large cells are known as voids which need to be in open cell structure. Also voids composed with embedded small cells known as windows. The interconnected pore structures are formed via these windows (Wu et al., 2012).

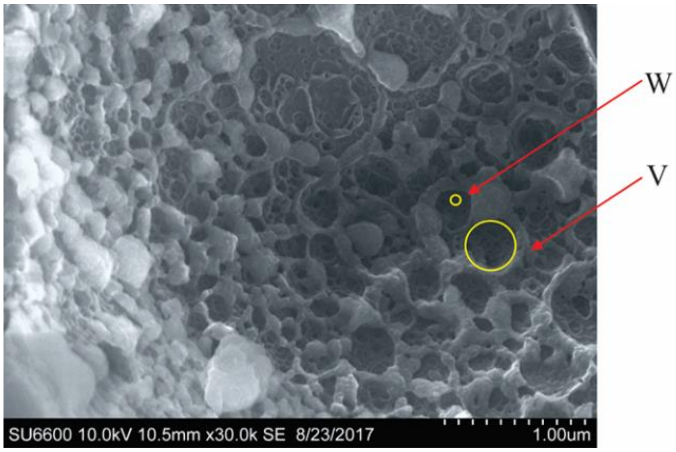

Figure 13. SEM image VMRH in µm scale (V-Void and W-Window).

Further, the extensive analysis of VMRH system was done through SEM images and the distribution of pore diameter was analyzed.

Figure 14 shows the pore diameter distribution histogram. Obviously, VMRH resin contains both meso-pores and macro-pores with size ranging in between 20-400 nm. Most of the pores are distributed around 40-100 nm range.

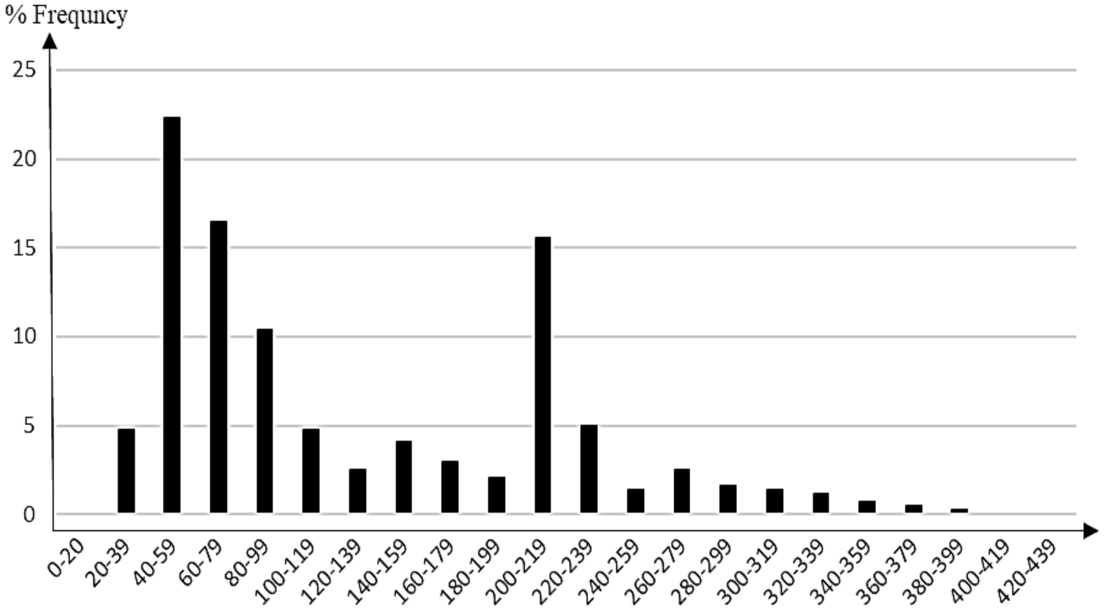

Figure 14. Pore diameter distribution.

Further, the second highest number of pores are distributed around 200-240 nm range. This observation clearly indicates that the VHRM system has bi-disperse pore diameter distribution. Hence, it can be said that an interconnected secondary pore structures have been produced (M. Zhang and Sun, 2001).

3.8 Dissolution properties

There was a light brownish colour in the final conc.H_2SO_4 solvent and it implies the VMRH system is somewhat unstable in the conc.H_2SO_4 medium. There was no substantial colour change observed in all the other solvent systems.

According to the results calculated in Table 3.4 the VMRH system was reasonably stable in most acidic and neutral mediums except conc.H_2SO_4 medium.

Table 2: Weight changes of the VMRH system samples in different solvents.

Solvent	Initial weight (g)	Final weight (g)	Weight change (g)
Water	0.500	0.487	0.013
Methanol	0.500	0.479	0.021
Acetone	0.500	0.482	0.018
Conc. HCl	0.500	0.452	0.048
Conc. H_2SO_4	0.500	0.307	0.193

4. Conclusion

In this work, it was proved that the tannin extracted from *Cassia auriculata* (Ranawara) can be used to synthesize cation exchange resin systems with considerable ion exchange capacity. Ferric chloride test, Nitrous acid test and Acid butanol test were confirmed the presence of the tannins in Ranawara bark. According to Folin-ciocalteau method dried Ranawara bark contains 13.30% (w/w) of tannins.

The ion exchange capacity of the conventional tannin-fomaldehyde resin (0.3500 meq/g) can be slightly increased by converting to Sulfonated tannin-fomaldehyde resin (0.5050 meq/g). Sulfonation was successfully done by refluxing the tannin-fomaldehyde resin with conc. H_2SO_4 and the final product was confirmed by FTIR analysis.

In addition, to further increase the ion exchange capacity, the synthesis of tannin based porous cation exchange resin was successfully carried out by using the virgin coconut oil as the porogenic agent. The average ion exchange capacity of VMRL system was 0.6000 meq/g and the average IEC of VMRH system was 0.9550 meq/g. This is due to the increment of the surface area of the ion exchangeable sites via the formation of the porous structures. Higher amount of emulsifier was required to synthesize an open cell porous cation exchange resin system by stabilizing the large interfacial area of the polyHIPE and forming the interconnected secondary pores. Furthermore, the stability of the VMRH system was tested in different solvents and it is reasonably stable in most acidic and neutral mediums except in conc. H_2SO_4 medium.

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