Synthesis, Characterization, and Metal Adsorption Properties of Tannin–Phenol–Formaldehyde Resins Produced Using Tannin from Dried Fruit of *Terminalia chebula* (Aralu)

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ABSTRACT: In this study, tannin extracted from *Terminalia chebula* (Aralu) was used to produce tannin–phenol–formaldehyde resins. They were produced to obtain resins with different tannin to phenol ratio in an attempt to optimize the ion exchange capacities of resins produced. The resins made were sulfonated to improve their properties further. Bivalent cations, such as Zn^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, and Cu^{2+}, were used to estimate the adsorption properties of both unsulfonated and sulfonated resins. The glass transitions of representative resins were estimated using differential scanning calorimeter thermograms. Fourier transform infrared spectroscopic analysis was used to gauge changes on resins by sulfonation and adsorption of cations. The glass transition values of unsulfonated, sulfonated, and metal-adsorbed sulfonated resins showed a similar increasing trend with the increase of phenol content in the resin. The glass transition temperature values reach a plateau beyond the tannin/phenol ratio of 1 : 0.5, indicating the formation of large molar masses facilitating entanglements beyond that ratio. The phenol ratio of 1 : 0.5 has shown the highest adsorption capacity for all the metal ions used. The highest adsorption capacity was shown for sulfonated tannin–phenol–formaldehyde resin with the tannin/phenol ratio of 1 : 0.5 for Pb^{2+}, which is 0.610 meq/g. The adsorption equilibrium data obtained using the column technique were found fitting Freundlich isotherm. J Appl Polym Sci 115: 1081–1088, 2010

Key words: tannin of *Terminalia chebula*; synthesis; tannin–phenol–formaldehyde resins; sulfonation; adsorption; metal–polymer complex

INTRODUCTION

Tannin is an inexpensive material that can be extracted from various parts of a plant, such as wood, bark, fruits, and leaves, Tannin molecules have high affinity toward proteins, metal ions, and various other molecules because of the presence of multiple adjacent polyhydroxyphenyl groups in their chemical structure.[1,2] Use of tannin as a material in various fields, such as tanneries, wood adhesives, manufacture of inks, dyeing of textiles, flocculants for water treatment, corrosion inhibitor for steels, dispersants, antioxidants, medicine, and cosmetic, has been reported extensively.[3–7]

Being a material that has affinity toward various cations and anions, one of the interesting areas of research that has been reported is the use of tannin-based compounds as ion adsorbents. Although some tannin-based compounds that have been reported as adsorbent materials are of natural origin, there are some tannin-based compounds reported of synthetic origin. Adsorption mechanisms for adsorption of divalent metal ions onto various tannin-based resins have been reported. Tannins have excellent adsorption–desorption properties and the adsorption isotherms of the tannins could be described by the Freundlich model.[8–11]

Although tannin can adsorb ions, its high solubility in water found to be a constraint to use tannin as an adsorbent in applications such as ion exchange resins. This problem can be overcome by polymerizing it with formaldehyde to form polymers or copolymers.[8,9] However, Marutzky and Dix[12] have studied the ion exchange capacity of resins made of various types of plant-based tannins and have concluded that resins have lower cation exchange capacity. This is due to the presence of weak acidic character of the phenolic hydroxyl group attached to the tannin–formaldehyde resin.[8] Hence, the use of the modified tannin–formaldehyde resins to increase the ion exchange capacity has been reported in various studies. The

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sulfonation of tannin–-formaldehyde resins to increase the cation exchange capacity using various techniques has been one of the successfully used techniques.[8,12]

The tannin content of the bark of *Terminalia* family is high and reported to be in the range of 20–25% (w/w).[13] Aralu (*Terminalia chebula*) is an indigenous medicinal plant belongs to the genous *Terminalia*, family Combretaceae. It is native to the Asian countries such as Sri Lanka and India. It is a deciduous tree growing to 30 m tall, with a trunk that can be as large as 1 m in diameter. *Terminalia chebula* is one of the most promising sources of vegetable tannin in Sri Lanka. It grows in abundance in the dry zone of Sri Lanka where it occurs mainly as a remnant of the ancient ayurvedic herbarium located in that area. Nearly, an area of 10,000 acres of forest is dominated by this species. This dominance has been attributed to its fire resistance that ensures survival through the firing practiced during 'Chena' cultivation.[14] Although the use of dried fruit of Aralu is well known in the indigenous medicine of the region, the use of tannin obtained from *T. chebula* in the production of tannin–phenol–formaldehyde resins has not been reported. Hence, in this study, we report the synthesis, characterization, and metal adsorption properties of tannin–phenol–formaldehyde resins produced using tannin from dried fruit of *T. chebula* (Aralu).

MATERIALS AND METHODS

Materials

The chemicals used in the study except tannin material were products of Merck Chemical (Turkey). Dried fruits of *Terminalia chebula* were collected from local sources in Sri Lanka.

Extraction of tannin

Aralu fruits were cleaned, air dried, and ground to powder form. The powdered samples were extracted initially in hexane (at 68°C for an hour) and then in petroleum ether (at 45°C for an hour) to remove the nonpolar compounds. Then, the dried fruits were extracted with 80% aqueous methanol at 70°C for 2 h. Subsequently, nontannin compounds of the extract were removed using hexane extraction at 68°C for an hour. Finally, the extracts were concentrated under reduced pressure using a rotary evaporator (Labrota 4000-efficient, Germany) and the resulting brown precipitates (tannins) were removed by filtration.

Determination of tannin content

Total polyphenolic content of the *T. chebula* extract was determined using the Folin-Ciocalteau micro method as described later.[15]

Gallic acid solutions containing concentrations 100, 50, 25, and 10 ppm were used as the standard. A 1.0 mL aliquot of the gallic acid solution was taken into a test tube. Then, 5.0 mL of Folin-Ciocalteau reagent was added to this solution and allowed to react for 6–8 min. Thereafter, 4.0 mL of sodium carbonate solution (7.5% (w/w)) was added and the content of the test tube was mixed well. The test tube was covered using an aluminum foil and kept at 30°C for 2 h. Then, absorbance measurements were done at 755 nm using UV spectrophotometer (Thermo Spectronic, England). A calibration curve was drawn using the data obtained. Then, the absorbance of the extracted tannin sample, which was used in the polymerization reactions, was measured using the same procedure. The amount of polyphenolic content of the extracted tannin was calculated using the calibration curve.

Preparation of resin matrix

A sample of dried Aralu polyphenolic extract (100 g) was dissolved in 50 mL of distilled water, and then 10 mL of methanol was mixed at room temperature. Concentrated solution of NaOH [(33% (w/w)] was used to maintain the pH of the reaction mixture at 10. To this mixture, 65 mL of formaldehyde aqueous solution [(37% (w/w)] was added dropwise at 40°C. The mixture was brought to 80°C and kept for an hour. The resultant mixture was neutralized using dilute HCl (1.0*M*). The resin produced was cooled and allowed to harden. The dry resin was finely ground and sieved through 30-mesh sieve to get uniform particle size. The sample was cured in an oven operating at 100°C for further cross-linking. Finally, the powdered resin was stored for further analysis in a desiccator.

A series of resins was prepared by incorporating varying amounts of phenol to substitute tannin. The resin matrix without phenol was labeled ART1P0 (A-Aralu, R-Resin, T-Tannin, and P-Phenol), whereas others were labeled ART1P0.05 through ART1P1.5 to indicate the increasing amount of phenol as given in Table II.

Sulfonation of the resins

The resin (10.1 g) was refluxed with 25 mL of H_2SO_4 [98% (w/w)] at 100°C for 6 h in a paraffin bath to obtain the sulfonated resin. The sulfonated resin was cooled and washed carefully with distilled water to remove residual free H_2SO_4. The resin was then washed with a NaCl solution to convert to its Na^+ forms. The Na^+ form of resin was washed and dried in an oven at 100°C for an hour. The dried resin was stored. The sulfonated resin matrix was also labeled with respect to each virgin resin as given in Table II.

TABLE I
Constituent of Dried Extract of Fruit of *Terminalia chebula* (Aralu)

Tannins	Nontannins	Insoluble part	Moisture
23.91%	68.26%	2.1%	5.73%

Determination of exchange capacity of the resins

The total exchange capacity of the resin is the total number of exchanging sites available per unit mass of resin. The total ion exchange capacity of resins prepared was obtained by titrating using a standardized solution of 0.1*M* NaOH in 1.0*M* NaCl and standard 0.1*M* HCl solution as titer.

Weighed quantities (ca. 5 g) of the Na^+ forms of sulfonated resins were filled into burette-type exchange columns. Exchange capacities of the resins prepared were studied using solutions of analytical-grade chlorides or sulfates of metal cations (0.01*M*). However, nitrate of Pb^{2+} was chosen as the Pb^{2+} solution because it is the most water-soluble lead compound [solubility: 52 g/100 mL (20°C)].

Initial pH was controlled by addition of 0.1*M* NaOH and the pH values should be maintained ranging from 6.5 to 7.0 to prevent the precipitation of cations as hydroxide.

The aqueous solutions of the salts (50 mL of 0.01*M*) were allowed to pass through the resin columns downward at the rate of 5 cm^3 min^{-1}. Cation content of both the effluents and influents was determined. In the case of bivalent cations, this was done by measuring the difference in concentrations between the influent and effluent. In addition, the estimation was confirmed ascertaining the cation content in the effluent obtained by washing down the ions "sorped "on the resin phase with 0.1*M* HCl. Bivalent ions, such as Zn^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, and Cu^{2+}, were determined complexometrically using 0.01*M* EDTA and Eriochrome black T as the indicator. Cu^{2+} was determined iodometrically.

Study on adsorption kinetics

A 1.0 g sample of the ART1P0.5SO_3H resin was suspended in distilled water for 12 h. Then, the resin was filled into a column of 11 mm in diameter and 215 mm in height. Then, 100 mL of Pb^{2+} solution of 750 mg dm^{-3} concentration with an initial pH of 6.5 was pumped into the column at the rate of 5 cm^3 min^{-1}. In 5 min interval, effluent (5 mL) was collected and filtered through Whatman GF/C filter paper, and the Pb^{2+} concentration in the filtrate was determined in triplicate by atomic absorption spectrophotometer (GBC 932 plus Avanta Ver 1.33 apparatus, Australia).

Spectral measurements

FTIR spectra of the resins prepared were recorded using a FTIR instrument (Thermo Nicolet, USA). Potassium bromide disks were prepared mixing 1 mg of dried and ground samples of resins with 200 mg of KBr (spectrometry grade) at 10,000 kg cm^{-2} pressure. The spectra were recorded by carrying out 100 scans at 4 cm^{-1} resolution.

Differential scanning calorimetry

Thermal analysis was carried out using a 2010 DSC V4.4 E differential scanning calorimeter (TA instrument, USA). Resin samples of 8–12 mg encapsulated in crimped aluminum pans were used, and the heat flow required to increase the temperature at 20°C min^{-1} heating rate was monitored with time under a dynamic nitrogen flow (5 L h^{-1}).

RESULTS AND DISCUSSION

The polyphenolic body content of the extract of dried Aralu fruit used in this study was 23.91% (Table I).

Table II gives the data on the amount of polyphenolic material and phenolic bodies (polyphenolic–phenol materials) used in the preparation of resin

TABLE II
Data of Materials Used and Resins Obtained

Label of synthesized resin matrix	Total polyphenolic content present in the starting material (%)	Dry weight of resins obtained (g)	Exchange capacity H^+/Na^+ (meq/g)	Label of sulfonated resin produced	Dry weight of the sulfonated resin produced (g)	Exchange capacity H^+/Na^+ (meq/g)
ART1P0	23.91	10.1	0.021	ART1P0 SO_3Na	8.31	0.083
ART1P0.05	25.11	30.31	0.040	ART1P0.05 SO_3Na	19.20	0.110
ART1P0.11	26.54	49.21	0.047	ART1P0.11 SO_3Na	34.34	0.234
ART1P0.22	29.17	49.31	0.087	ART1P0.22 SO_3Na	40.47	0.317
ART1P0.44	34.43	61.90	0.094	ART1P0.44 SO_3Na	46.87	0.436
ART1P0.5	35.87	69.12	0.219	ART1P0.5 SO_3Na	51.98	0.645
ART1P1.0	47.82	71.16	0.094	ART1P1.0 SO_3Na	48.61	0.412
ART1P1.5	59.78	78.39	0.096	ART1P1.5 SO_3Na	48.43	0.201

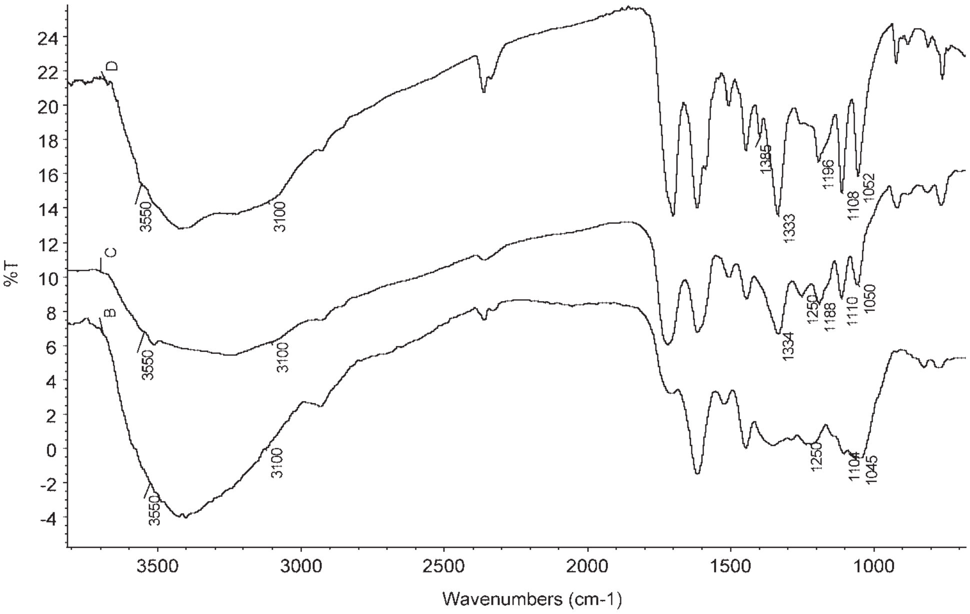

Figure 1 FTIR spectra of tannin–formaldehyde, phenol-modified, and its sulfonated resin. B: ART1P0, C: ART1P0.5, D: ART1P0.5SO_3H.

matrices and the corresponding amount of the sulfonated resins produced. It can be observed that the yield of sulfonated resin is always more than 60% (w/w) of the weight of original resin used in sulfonation. Hence, it can be treated as a reasonably good yield. Generally, the ion exchange capacity increases with the increase of the atomic number of the ion in the same charge because of the electric attraction between exchange groups and ions. Among the salts of metals with high atomic number, salts of Na^+ are available readily and inexpensively. Hence, all synthesized sulfonated resin matrices were converted to Na^+ form using NaCl. Further, it makes it easier to compare ion exchange capacities of resins with different polyphenolic contents. Further, Table II shows that the increase of phenol content beyond T1P0.5 significantly reduces the yield of the sulfonated resin and its ion exchange capacity with respect to Na^+.

As tannins are highly soluble in water, the solubility of tannin–phenol–formaldehyde resins was measured and found that the resins prepared do not dissolve in water. This indicates the formation of insoluble crosslinked structure.

The IR spectra of the tannin–formaldehyde resin (ART1P0), tannin–phenol–formaldehyde resins (ART1P0.5), and their sulfonated forms (ART1-P0.5SO3H) are depicted in Figure 1. In the spectrum of ART1P0, the presence of bands at 1045 and 1104 cm^{-1} that could be attributed to aromatic C—O bond stretching and to aliphatic C—O bond stretching, respectively, could be observed. The strong band at 1250 cm^{-1} is characteristic of C—O stretching of the cyclic ether. In the spectra of phenol-incorporated resins, the presence of a small band at 1188 cm^{-1} that is not present in the initial tannin–formaldehyde resin spectrum could indicate the formation of some other ether bonds that are different from the one in tannin extract. This new band could be explained by the ring-opening reaction proposed in the literature that could produce noncyclic ether bond via phenol group's present.[16] These evidences confirm the formation of tannin–formaldehyde and tannin–phenol–formaldehyde resins.

The spectrum of sulfonated phenol-modified resin (ART1P0.5SO_3H) shows that the intensities of peaks at 1108 and 1196 cm^{-1} which can be attributed to S=O peak are broad and increased with sulfonation. These changes indicate the sulfonation of resins produced. In addition, it could be observed that the presence of a small peak at 1385 cm^{-1} could be due to S=O stretching for SO_3H group. Further, the change of peak that can be assigned to OH (3550–3100 cm^{-1}) from lower wave numbers (~3200 cm^{-1}) to higher (~3500 cm^{-1}) and the appearance of a shoulder (~3200 cm^{-1}) can be seen in the spectrum of the sulfonated sample (ART1P0.5SO_3H). The shoulder has a wave number closed to that of the OH peak of unsulfonated sample. This indicates that the presence of two different types of OH groups in the former. As the peak around 3500 cm^{-1} can be assigned to free OH, it can be concluded that the sulfonation has liberated some of the hydrogen-bonded OH groups. Further, it shows that the sulfonation has left some OH groups unaffected represented by the shoulder at ~3200 cm^{-1}. From these results, we conclude that the sulfonation in phenol-modified resins was successfully performed. This is the further evidence by the fact that the ion

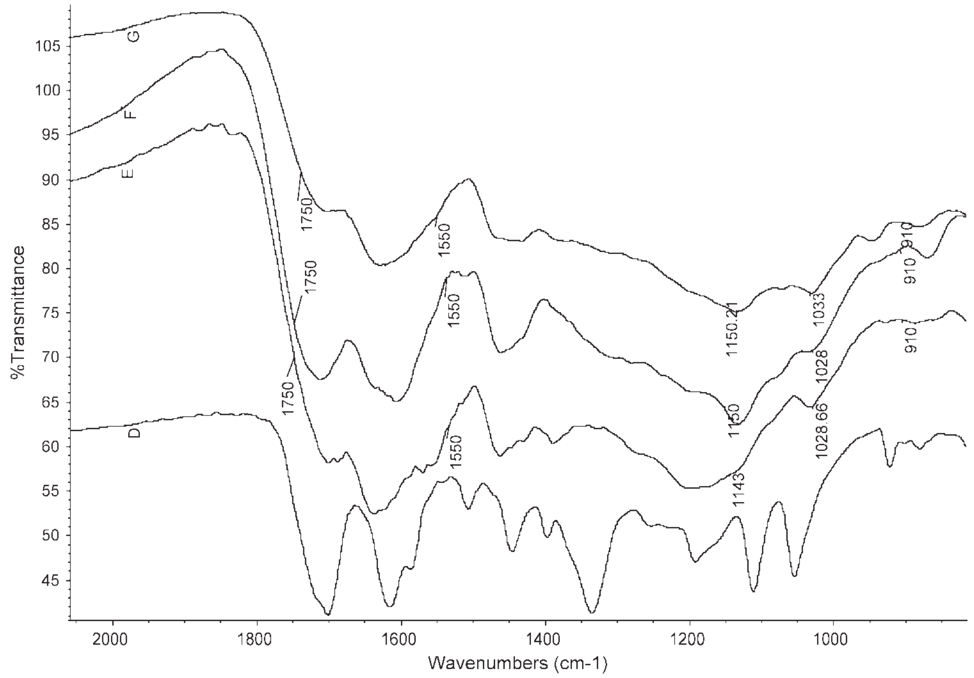

Figure 2 FTIR spectra of the ART1P0.5SO_3H resin and its metal complexed form. D: ART1P0.5SO_3H, E: ART1P0.5SO_3H resin with Ca^{2+} adsorbed, F: ART1P0.5SO_3H resin with Zn^{2+} adsorbed, G: ART1P0.5SO_3H resin with Pb^{2+} adsorbed.

exchange capacity of the resin made was also increased by sulfonation (Table II).

When IR spectra of metal ion-adsorbed ART1-P0.5SO_3H resins (Fig. 2) were compared with the IR spectrum of the ART1P0.5SO_3H resin, it could be observed that the peak assigned to methylol group (C—O) at 1150–910 cm^{-1} region in the spectra of metal ions adsorbed resins has been broadened further. The presence of a new peak around 1028–1034 cm^{-1} in the metal-adsorbed resins could be noticed. Significant changes to the peak present in the 1550–1750 cm^{-1} region which could be assigned to C=C stretching could be observed. This could be due to the effect of metal ion chelating on the double bonds present in the aromatic ring. It is interesting to note that the shoulder appeared around 1725 cm^{-1} has shown the lowest transmittance for the Pb^{2+}-adsorbed resin while showing the highest transmittance for the Zn^{2+}-adsorbed resin. It points toward an inverse proportionality to adsorption capacity (Table III). In addition, changes are observed at 1150–910 cm^{-1} region of which peaks present could be attributed to phenolic groups that participated in complexation or in ion exchange reactions in the spectra of ART1P0 and metal-adsorbed ART1-P0.5SO_3H resins indicating complexation or ion exchange reactions between the tannin resins and metal ions.

According to Table III, simple tannin–formaldehyde resin was found to possess ion exchange capacity, although of lower value. This is due to the presence of weak acidic character of the phenolic hydroxyl groups present in it. To produce a resin of better ion exchange capacity that could be used effectively in the neutral and acidic medium, the introduction of strong acid groups in the tannin–formaldehyde or modified tannin–phenol–formaldehyde resin (TPF resin) is needed. Sulfonation with concentrated H_2SO_4 (98% w/w) was carried out to obtain resins with increased ion exchange capacity and with high stability in neutral and acid medium.

As reflected in the results given in Table III, the exchange capacity of the resins made increases with the increase in the proportion of pure phenolic bodies in the resin matrix. It can also be noted that the exchange capacity falls off when the percentage of pure phenol in the resin matrix is increased beyond a certain limit. According to the literature,[17] tannin–formaldehyde resins formed would produce only a small number of crosslinks via methylene bridges because of the relatively rigid structure of tannin molecules. This could be a reason for very low ion exchange capacity shown by the sample ART1P0 that has no phenol in it. When phenol molecules were incorporated between tannin molecules and CH_2 bridges, the flexibility of the molecule improves. Moreover, tannin molecules separated by phenol units provide more sites for sulfonation in phenol as well as in tannin units of TPF resins due to the reduction of steric hindrances. However, further increase of phenol content, which may increase the molar mass more, would make molecules sufficiently long enough to make entanglements with

TABLE III
Ion Exchange Capacities of Unsulfonated and Sulfonated Resins for Five Bivalent Cations and Molar Ratio of —SO_3H Group to Adsorbed Metal Ion (Me^{2+})

	Ion exchange capacity (meq/g)				
Types of resins	H^+/Pb^{2+}	H^+/Ca^{2+}	H^+/Mg^{2+}	H^+/Cu^{2+}	H^+/Zn^{2+}
ART1P0	0.007	0.010	0.009	0.008	0.031
ART1P0SO_3Na	0.089 (1 : 1)[a]	0.090 (1 : 1)[a]	0.034 (5 : 2)[a]	0.062 (1 : 1)[a]	0.041 (2 : 1)[a]
ART1P0.05	0.052	0.031	0.013	0.012	0.014
ART1P0.05SO_3Na	0.103 (1 : 1)[a]	0.102 (1 : 1)[a]	0.074 (1 : 1)[a]	0.097 (1 : 1)[a]	0.089 (1 : 1)[a]
ART1P0.11	0.042	0.032	0.018	0.021	0.021
ART1P0.11SO_3Na	0.210 (1 : 1)[a]	0.201 (1 : 1)[a]	0.168 (1 : 1)[a]	0.197 (1 : 1)[a]	0.171 (1 : 1)[a]
ART1P0.22	0.089	0.072	0.029	0.050	0.047
ART1P0.22SO_3Na	0.312 (1 : 1)[a]	0.310 (1 : 1)[a]	0.199 (2 : 1)[a]	0.247 (3 : 2)[a]	0.210 (3 : 2)[a]
ART1P0.44	0.092	0.081	0.040	0.061	0.061
ART1P0.44SO_3Na	0.401 (1 : 1)[a]	0.371 (1 : 1)[a]	0.231 (2 : 1)[a]	0.312 (3 : 2)[a]	0.342 (1 : 1)[a]
ART1P0.5	0.210	0.176	0.114	0.151	0.140
ART1P0.5SO_3Na	0.610 (1 : 1)[a]	0.481 (3 : 2)[a]	0.331 (2 : 1)[a]	0.386 (2 : 1)[a]	0.392 (2 : 1)[a]
ART1P1.0	0.099	0.096	0.042	0.071	0.065
ART1P1.0SO_3Na	0.409 (1 : 1)[a]	0.391 (1 : 1)[a]	0.251 (2 : 1)[a]	0.340 (1 : 1)[a]	0.349 (1 : 1)[a]
ART1P1.5	0.098	0.019	0.009	0.011	0.010
ART1P1.5SO_3Na	0.210 (1 : 1)[a]	0.085 (5 : 2)[a]	0.061 (7 : 2)[a]	0.074 (3 : 1)[a]	0.065 (3 : 1)[a]

[a] Molar ratio of —SO_3H group to adsorbed metal ion (Me^{2+}).

each other that could impart restrictions against sulfonation.[18]

Although, the glass transition of a polymer that contains high molar masses is a constant, it will decrease with the decrease of molar mass below a certain limit. Cowie has demonstrated the phenomena using eq. (1).[18]

$$T_g(\infty) = T_g + \frac{K}{M} = T_g + \frac{2\rho\theta N_A}{\alpha_f \overline{M}_n} \tag{1}$$

where $T_g(\infty)$, Θ, ρ, N_A, and α_f are the glass transition temperature of a polymer with very large molar mass, the free volume contribution for a chain end, the density of the polymer, the Avogadro's constant, and the free volume expansivity, respectively. According to eq. (1), it is clear that T_g of a polymer will increase with the increase of molar mass to reach $T_g(\infty)$. Three curves depicted in the Figure 3 show similar trends with the increase of phenol content in the resin which facilitate the increase of chain length of tannin–formaldehyde resin. Similarly, it can be observed that the T_g reaches toward maximum with the incorporation of phenol molecules beyond tannin to phenol ratio of 1 : 0.5 represented by ART1P0.5 resin. Hence, it could be assumed that the molecules start to make higher amount of entanglements restricting movements of molecules above the tannin to phenol ratio of 1 : 0.5.

The entanglements might have reduced the formation of sulfonated sites again reducing the adsorption capacity when the phenol content in the tannin–phenol–formaldehyde resin is high. This is further evidence by the fact that adsorption capacities of unsulfonated resins have shown a trend similar to that of their sulfonated counterparts (see Table II). This shows that metal ions have too faced restrictions imparted by entanglements formed by polymer molecules when trying to be adsorbed. This is further evidence from the data in the Table II where the yield of sulfonated materials reduces after passing through a maximum with the increase of phenol content.

In addition, according to Figure 3, it can be observed that a significant reduction of T_g with the sulfonation of the resins. An analogous observation has been made for sulfonated styrene-grafted FEP membrane systems by Gupta et al.[19] They have attributed the reduction of T_g to reduction in degree of rigidity or crosslinking of the resin matrix by both the dilution effect and the crystal defect imparted by sulfonation. As seen in the spectra of Figure 1, reduction of hydrogen-bonded OH groups could be

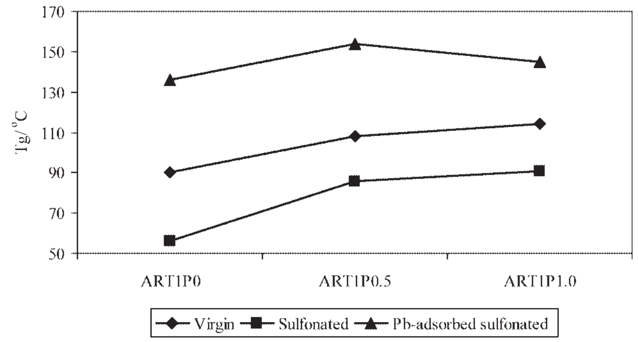

Figure 3 Glass transition temperatures (T_g) of virgin, sulfonated and resins obtained from the DSC thermograms.

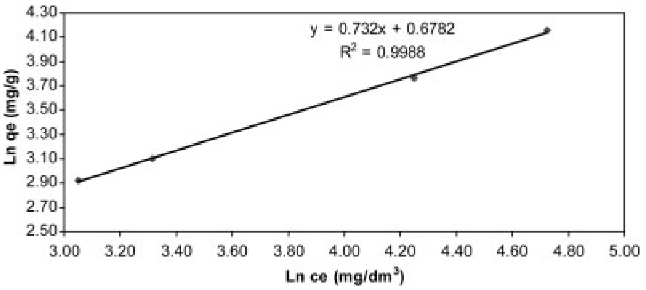

Figure 4 Freundlich's adsorption isotherms of ART1-P0.5SO$_3$H resin to Pb^{2+} (303 K, pH = 6.5).

an indication of reduction of intermolecular interaction imparted due to the sulfonation of tannin–phenol–formaldehyde resins. However, higher values of T_g are observed for metal-adsorbed (Pb^{2+}) sulfonated resins, albeit the trend shown is similar to those of unsulfonated and sulfonated resins increasing their thermal stability. Similarly, a twofold increase of T_g value has been reported when a synthetic formaldehyde-based resin was chelated with a bivalent metal ion by Samal et al.[20]

As the final part of this study, the kinetics of adsorption of Pb^{2+} ions to sulfonated tannin–phenol–formaldehyde molecule as an adsorbent was studied using column adsorption technique. The Pb^{2+} ion was used as it shows the highest adsorption capacity among other bivalent metal ions used in this study. The data obtained were applied in Langmuir and Freundlich equations to evaluate adsorption behavior of Pb^{2+}.

The Freundlich equation could be given as in eq. (2)

$$\ln(\mathrm{qe}) = \frac{1}{n}\ln(\mathrm{ce}) + \ln(k) \qquad (2)$$

where qe and ce are the amount of Pb^{2+} ions adsorbed (mg/g) and bulk concentration of Pb^{2+} ions (mg/dm^3) at equilibrium, respectively, and k and $1/n$ are the Freundlich constants referring to adsorption capacity and intensity of adsorption, respectively. It was found that the plot ln(qe) vs. ln(ce) is linear showing that the adsorption data comply with the classical Freundlich equation (2) ($R^2 = 0.9988$) much better than the Langmuir equation ($R^2 = 0.9420$) for the studied system at 303 K (Fig. 4). In addition, $1/n$ and k are found to be 0.73 and 1.97, respectively. In general, the value of $1/n$ is less than unity, indicating that the surface of the adsorbent is heterogeneous in nature.[21]

It could be observed that the Freundlich constants for the adsorption of Pb^{2+} on sulfonated tannin–phenol–formaldehyde resin produced using tannin from dried fruit of *T. chebula* were slightly higher than those of adsorption of Pb^{2+} on *Pinus pinaster bark* ($1/n = 0.27$, $k = 1.44$) reported in the literature.[22] This difference could probably be related to their molecular structures as bark of a tree contains various other molecules beside tannin molecules.

CONCLUSIONS

Tannin obtained from dried fruit of *T. chebula* could be used to produce formaldehyde-based resins with ion exchange capacity. The flexibility and the ion exchange capacity of the resin produced can be increased by the incorporation of phenol molecules to the resin to make tannin–phenol–formaldehyde resins. Ion exchange capacities of the resins produced could be further improved by sulfonation using concentrated H$_2$SO$_4$. The resin formation and sulfonation were confirmed by IR spectral data. The adsorption of cations such as Zn^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, and Cu^{2+} to resins developed was confirmed with IR spectral data. The maximum adsorption capacity is shown by the resin produced using the tannin/phenol ratio of 1 : 0.5. The glass transition temperature values reach a plateau beyond the tannin/phenol ratio of 1 : 0.5, indicating the formation of large molar masses facilitating entanglements beyond that ratio. This could be observed for unsulfonated, sulfonated, and Pb-adsorbed resins. Highest adsorption capacities of 0.210 and 0.610 meq/g are shown for unsulfonated and sulfonated resins, respectively, for Pb^{2+} ion. Further, the adsorption of Pb^{2+} ions on the sulfonated tannin–phenol–formaldehyde molecule follows the Freundlich adsorption isotherm. It can be concluded that tannin–phenol–formaldehyde resins produced using tannin extracted from Aralu could be used in applications such as removing heavy metal ions from water effectively.

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