Synthesis of new cation exchanger resins from chemically modified peanut (Arachis hypogaea L.) testa extract

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Abstract: New resins based on crosslinking of peanut testa catechin units with phosphorus oxychloride have been synthesized from abundantly available but menace-causing peanut testa waste. The synthesized resins were converted to strong and weak cation exchangers by functionalizing with chlorosulphonic and monochloroacetic acid respectively. FTIR spectra of chemically modified peanut testa catechin resins showed a disappearance/reduction in the intensity of –OH band at 3400 cm-1 and the formation of new ones at 1325, 1345, 855, 1240 and 990 cm-1 showing the stretching vibrations of O=S=O, --SO3, R-- O--S--, -P=O and -P-O-R bands respectively. New bands around 1743 and 1190 cm-1 reveal the presence of –C==O and –C—O- groups respectively on carboxymethylated phosphorus oxychloride crosslinked peanut testa extract. Specific gravities of the cation exchange resins lie between 1.08 and 1.79 g/cm3. The resins were stable above 300°C, insoluble in common organic solvents: methanol and ethanol, water and solutions of pH< 9 but were soluble in alkaline solutions of pH ≥10. The point of zero charge (pHpzc) and cation exchange capacity (CEC) values ranged between 2.2- 4.2 and 0.62- 5.9 respectively.

Keywords: Peanut testa extract, catechin, crosslinking, functionalizing, Fourier transform infrared spectroscopy (FTIR).

1. Introduction

Peanut known variously as: the 'king' of oilseeds, 'wonder nut' and 'poor men's cashew nuts' is a low-priced cash crop and a rich source of many food nutrients. According to Thamaraikannan et al, (2008), Nigeria ranks 4th position among major peanut producing countries in the World. Peanut testa, derived from peanut processing operations is rich in phenolic compounds such as proanthocyanidins; caffeic, ferulic and coumaric acids, flavonoids: catechins and procyanidins as well as stilbene; resveratrol and is currently under-utilized a additives in functional foods and animal feeds (Hathorn and Sanders, 2012; Zhang et al., 2013; Holser, 2014). Yadav et al., (2014) reported a range of 15-80% for total phenolic compounds in peanut testa derived by roasting and blanching peanuts. It is estimated that 35–45 g of peanut skin is generated from every kilogram of shelled peanut kernel and that more than 0.74 million metric tonnes of peanut skins are produced annually worldwide as a by-product of the peanut processing industry (Sobolev and Cole, 2003). A large portion of these are discarded into the environment where they litter and cause many environmental pollution problems (Zhao et al., 2012; Sobolev and Cole, 2003).

For this reason, research has been going on in the area of finding use for largely abundant agricultural wastes especially of plant origin. Such wastes are rich in tannins and other polyphenolic substances. Among these researches, the use of plant wastes as adsorbents has received tremendous attention and conversion into ion exchange resins for the removal of contaminant ions in polluted water is a fascinating way to utilize and rid the environment of undesirable agricultural wastes such as peanut testa waste and its attendant problems.

Tannins extracted from most plants and vegetable sources are rich in catechins and contain multiple hydroxyl groups which exhibit high affinity for metal ions. For this reason, they can be used as alternative, effective and efficient adsorbents for the concentration and recovery of metal ions in solutions. Unfortunately, tannins cannot be used directly for water purification because they are soluble in and easily leached by water. To overcome this drawback, researchers immobilize tannins by converting to polymeric matrices such as synthetic and cellulosic substrates. In the immobilization process, phenolic moieties present in tannin are reacted with a chemical species: acid, base and organic dye or oxidizing, cross-linking or grafting agent and are converted to an insoluble matrix in a chemical modification process. Chemical modification enhances the ability of tannins to interact with metal ions by addition, removal or masking of groups.

Several studies have been carried out to introduce different chemical functional groups onto agricultural wastes constituents in order to improve their capacity as metal ion adsorbents for water purification and other purposes. Some of these agricultural wastes include: maize straw, (Guo et al., 2015), sugarcane bagasse, (Olowoyo and Orherhe, 2014), orange mesocarp extract (Iyekekpolor, 2013), palm branches (Shouman et al., 2013), tamarind kernel powder (Singh and Kumawat, 2012), sugar beet pulp (Arslanoglu and Tumen, 2012), groundnut Shell (Idris et al., 2012), cassava mesocarp (Akaranta and Agiri, 2010), groundnut hulls (Qaiser et al., 2009; Okieimen et al., 1991), wood pulp (Nada et al., 2009), banana stem cellulose fibre (Anggraeni et al., 2008), orange mesocarp (Ogali et al., 2008), aspen wood (McSweeny et al., 2006) and soya bean straw (Zhu et al., 2008).

There are studies about the use of groundnut shell (GS) (untreated, carbonized and chemically modified) to remove dyes, organics and metal ions from aqueous solutions. Haldhar et al., (2014), Prabha and Udayashankara (2014) along with Ajmal et al. (2006) reported the use of unmodified GS to remove As3+, Pb2+ and Ni2+ ions respectively from contaminated water. Wilson et al., (2006) developed activated carbon from peanut shells which they used in removing Cd2+, Cu2+, Pb2+, Ni2+ and Zn2+ ions; use of mercapto acetic modified peanut hulls by Ding et al. (2014) to remove Hg2+ ions from aqueous solutions and the adsorptive recovery of heavy metals using H3PO4 treated peanut hulls by Ugwekar and Lakhawat (2012).

The current research seeks to extract and transform catechin rich peanut testa extract into cation exchange resins. Peanut testa, extract and the newly formed cation exchange resins would be characterized according to

specific gravity (Sp.g), melting point (MP), solubility, point of zero charge (pH$_{(PZC)}$), infra-red spectroscopy (FTIR) and cation exchange capacity (CEC).

2. Material and Methods
Sampling
The freshly baked peanut testa wastes were collected from a commercial point in Alakahia, near Port Harcourt, Rivers State Nigeria. The peanut testa was thoroughly washed with deionized water (DI H$_2$O) to remove soluble salt particles and air-dried for one week. It was further dried in the oven at 110°C for 2 h to remove adhering moisture. Thereafter, it was ground in a mill to 250 µm particle size and stored in a polyethylene bag under laboratory conditions until it was ready for use. This was labeled peanut testa (PT).

Reagents
Acetone, hexane, (POCl3), pyridine, chlorosulphonic acid (ClSO$_3$H), methylene chloride (CH$_2$Cl$_2$) HCl, methyl red indicator, monochloroacetic acid (MCAA), NaOH, methanol (CH$_3$OH), Acetic acid (AcOH) and every other chemicals used in this work were of analytical grade, purchased from Idex Scientific and used without further purification.

Extraction of catechin from peanut testa (PTE)
Peanut testa catechin (figure 1) was extracted from 2810 g of PT using acetone by means of soxhlet extraction. After recovering the acetone by distillation using a water bath, the concentrated extract was washed with hexane and cold DI H$_2$O to strip adhering oil and acetone respectively before drying in the air. The yield of extract was 43.58%. It was ground to a fine powder in a laboratory mortar and labelled peanut testa extract (PTE).
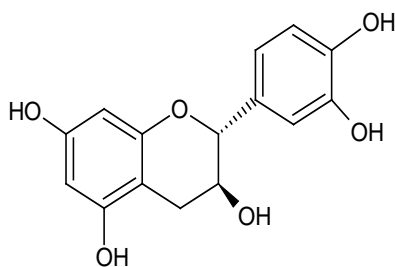

Fig. 1: Structure of Catechin

Synthesis of crosslinked–PTE (PPTE)
The procedure described by Anggraeni et al. (2008) was adopted for the crosslinking of PTE but with some modifications. PTE (25 g) was stirred for 12 h at room temperature (RT) in 250 mL of pyridine held in a 1-L three-neck flat bottom flask. The flask was equipped with a thermometer, dropping funnel as well as a reflux condenser and the whole assembly was placed in a fume hood. Thereafter, a freshly prepared solution containing 5 mL of POCl$_3$ mixed with 25 mL of CH$_2$Cl$_2$ was introduced in a drop-wise manner via the dropping

funnel over a 30 min period. When the set-up was clear of HCl fumes, it was transferred to a heating paraffin oil-bath and made to heat at 90°C for 3 h while still stirring. At the end, the set up was taken out, allowed to cool down and the content was poured into a 600-mL beaker containing 200 mL of ice water. It was stirred with a glass rod and filtered on a white band filter paper. The residue was washed repeatedly with DI H$_2$O until it was pyridine free. It was washed with 100 mL of 0.1 M HCl and again with DI H$_2$O until the filtrate was neutral to methyl red indicator. Finally, it was washed with 100 mL of CH3OH and dried at 65°C overnight. The yield was 63.01% of a fine nut-brown powder and labelled PPTE. This procedure is illustrated in Scheme 1.
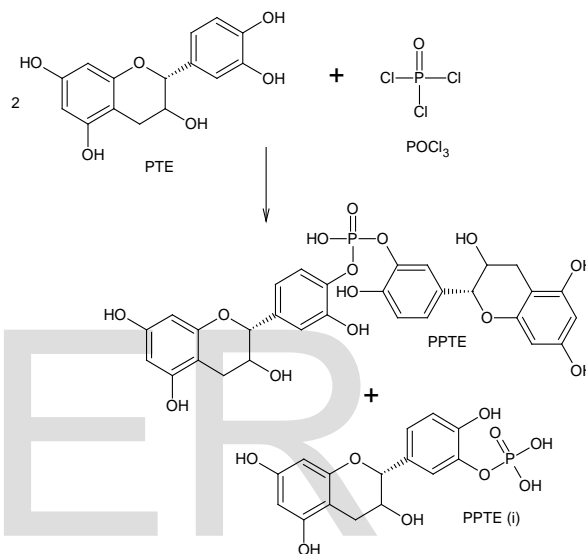
Scheme 1: Synthesis of PPTE and PPTE (i)

Phosphorylation of PTE (PPTE(I))
Synthesis of PPTE with phosphate groups at the end was accomplished through the procedure described above except that PTE (25 g) was stirred in 200 mL of pyridine and reacted with 25 mL of POCl$_3$ in 75 mL of CH$_2$Cl$_2$. The yield obtained was 50.37% of a signal red powder resin. Scheme 1 illustrates this procedure.
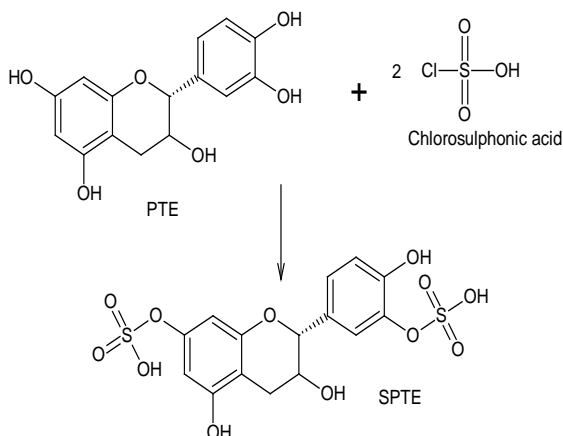
Sulphonation of PTE (SPTE)
The phenolic groups of PTE catechins were esterified with ClSO$_3$H to form the sulphonated product following the procedure for the phosphorylation above but with some modifications. In this case, the PTE (25 g) was stirred in 250 mL of pyridine and reacted with 10 ml of ClSO$_3$H in 50 mL of CH$_2$Cl$_2$ rather than POCl$_3$. The yield was 57.68% of a quarry red clay powder and labelled SPTE. Scheme 2 illustrates this procedure.
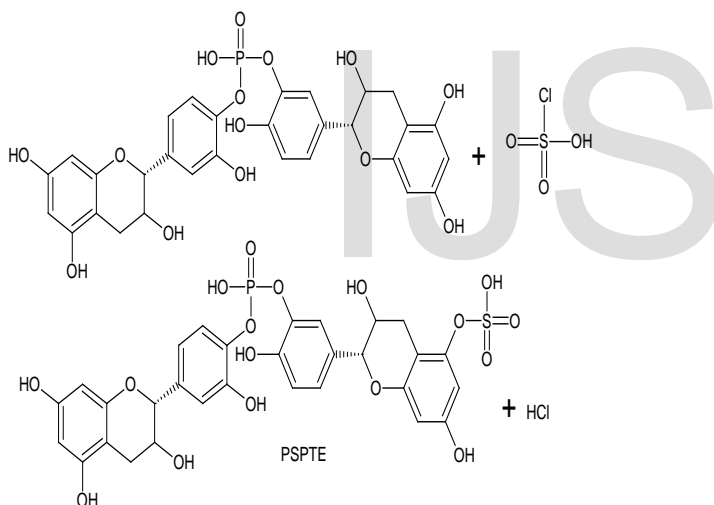
Functionalizing of PPTE by sulphonation (PSPTE)
In order to simultaneously crosslink PTE with POCl$_3$ and functionalize with ClSO$_3$H, the combined methods

described by Eid et al. (2007) and Anggraeni et al. (2008) was modified and adopted. PTE (25 g) stirred in 250 mL of pyridine was first reacted with 3 ml of $POCl_3$ in 10 mL of CH_2Cl_2 and then with 2 mL of $ClSO_3H$ in 10 mL of CH_2Cl_2. The yield was 55.48% of an auburn colour powder resin and labelled PSPTE. This procedure is illustrated in Scheme 3.


Scheme 2: Sulphonation of PTE (SPTE)

Scheme 3: Functionalizing of PPTE by sulphonation (PSPTE)

Etherification of PPTE (PCPTE)

After crosslinking with $POCl_3$, PPTE was carboxymethylated with (MCAA) by a combined procedure described by Blomstedt et al. (2007) and Latif et al. (2007) with some modifications. PTE (5 g) was stirred to homogeneity in 120 mL of isopropyl alcohol (IPA) contained in a 1-L Erlenmeyer flask. After 15 min, 20 mL of 40% NaOH solution was added by means of a dropping funnel over a 30 min period and the mixture was allowed to stir for 12 h at room temperature. Thereafter, 6 g of MCAA dissolved in 10 mL of DI H_2O was added drop-wisely over another 3 0 min. Subsequently, the flask was covered with a watch glass and transferred to a water bath where it was heated to and maintained at 60°C for 3.5 hr. At the end, the flask was taken out of the bath and left to cool down, 40 mL of

70% CH_3OH was added and it was left again to stand for 12 h. Later, 2.5 mL of 90% AcOH was added drop-wisely until the pH of the mixture became 6-8 at which point a solid separated at the base of the beaker. It was filtered and washed first with 150 mL of 70% CH_3OH and then with 250 mL of 90% CH_3OH before drying at room temperature. The yield was 37.56% of a rubbery manganese-violet product labelled PCPTE. Scheme 4 is the illustration of this procedure.
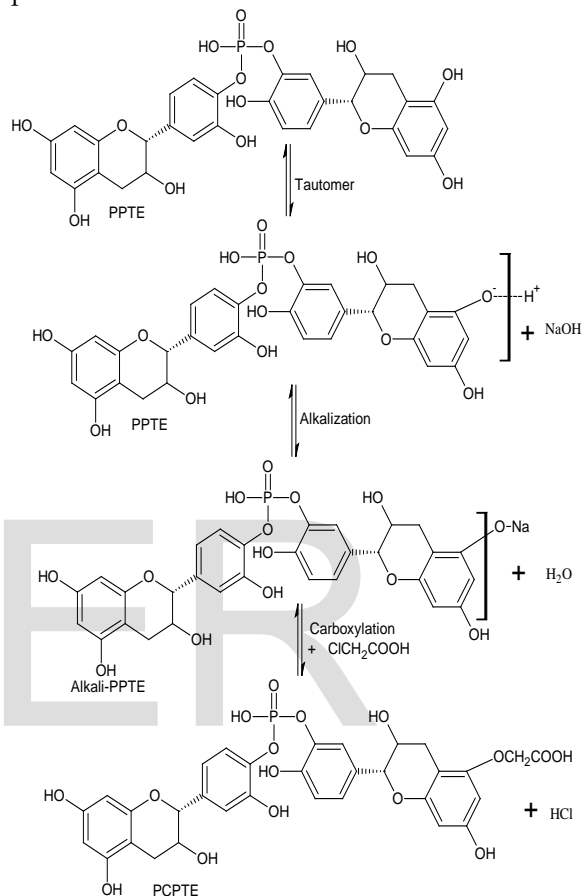
Scheme 4: Etherification of PPTE: (PCPTE)

Characterization

The synthesized resins were characterized according to the following properties: solubility in common solvents (H_2O, alcohols, dilute acids) was determined by adding 0.1 g of a crushed sample to 5 ml of the testing solvent in a test-tube and swirling at intervals, Specific gravity (Sp.g) was determined by the pycnometer method. Melting Point (MP) was determined by means of a Gallenkamp melting point apparatus (Model: 66600-004). The functional groups present in PT, PTE, PPTE, PPTE (I), SPTE, PSPTE and PCPTE were characterized by FTIR (Fourier Transform Infrared spectroscopy). IR measurements were determined within the range of 400–4000 cm^{-1} using a ThermoFischer spectrometer, model 10 while nujol was used to prepare the samples prior to analyses.

The pH at the point of zero charge (pH_{PZC}) was determined following the solid addition method (Vieira et al., 2014) while the Cation Exchange Capacity (CEC) of PT,

PTE and resins was determined by the standard column method. Precisely, 300 mL of 0.5 M solution of Na$_2$SO$_4$ was run through a column packed with 1 g slurry of dilute HNO$_3$ activated resin and 25 mL of DI H$_2$O. The eluent was received in an Erlenmeyer flask and titrated to phenolphthalein endpoint using standard NaOH.

3. Results and Discussion
Infrared spectroscopy

PTE was crosslinked with POCl$_3$ and then functionalized by either esterification with chlorosulphonic acid or etherification with MCAA. The characteristic absorption bands in FTIR spectra of PT, PTE and the synthesized derivatives are tabulated in Table 1. Infra-red spectra of PT and PTE show intense stretching vibrations at 3423 and 3431 cm^{-1}. The bands are characterized by smooth tongues which were both strong and broad in appearance. Stretching vibration bands in the region of 3400cm^{-1} are typical of –OH group of alcohols-: R-OH and phenols-: Ph-OH and may probably come from the five –OH groups located on catechin molecules of PT and PTE. The bending vibration bands which occurred between 1330 – 1430 cm^{-1} and 650 –

770 cm^{-1} respectively are as a result of the in- and -out of plane bending movements of polyphenolic –OH groups.

Two peaks show as doublets at 2926cm^{-1} and 2854cm^{-1}. Doublets in this region come from stretching vibration of Sp^3 carbon (-C-H) of an akyl group which may probably be due to the –C-H bonds on the saturated part of the middle ring of peanut catechin molecule.

Similar peaks appear at 1629 and 1528 cm^{-1} and are characteristics of stretching vibration bands of –C=C- in a ring. They present as doublets because of incomplete conjugation in the middle ring of PTE catechin, otherwise, the bands would have shown as triplets. The stretching vibrations by these compounds are likely to come from –C=C- bonds of the side rings of PT and PTE catechins IR bending vibration band at 1442 cm^{-1} is the characteristic absorption frequency of Sp^3 hybridized carbon and is due to the –C-H of the partially saturated ether bearing middle ring of the catechin units. C-O-C stretching vibrations of large cyclic ethers are responsible for IR peaks which occur between 1140 – 1070 cm^{-1} (Meyer, 2000). Commonly called the alkoxy group, the band may emanate from -C-O- of this ether bearing middle ring.

Table 1: IR absorption bands of PT, PTE and PTE synthesized resins.

Sample	OH^{1st}	CH^{1st}	-C=C	CH^{2nd}	OH^{2nd}	C-H	C-O-C	COOH	C-OP^{1st}	C-OP^{2nd}	R-O-P-	C-O-
PT/ PTE	3423/343 1	2962/292	1629/152 8	1142	1377	823/668	1160/ 1034	-	-	-	-	-
PPTE	3447	2925	1636	1167	1395	75	1154	-	1350/ 1246	997	993	
PPTE (I)	3398	2918	1670	1172	1437	87	1156	-	1240	995	990	
PSPTE	3421	2924	1617	1127	1457	87	1112	-	1244	975	877	1375
PCPTE	3412	2921	1627	1155	1438	82	1190	1743	1271/1377	1062	864	-
SPTE	3447	2853	1624	1146	1457	-	1120	-	-	-	-	1375/1325/12

Finally, there are bands at 823 and 668 cm^{-1} arising from the –C-H stretching vibrations of an aromatic compound. Substituted aromatics also absorb IR radiation in this region. Hence the observed bands may be a result of contributions from the benzene rings (1 and 3) of the catechin and the ortho and para substitutions on them.

New bands are seen in the spectra of PPTE, SU-PTE, PS-PTE and PC-PTE. The intensity of the OH bands between 3423 and 3431 cm^{-1} showed detectable changes due to modification by POCl$_3$. For instance, there is a broadening and shifting of the OH absorption band with a significant decrease in absorption intensity in the modified products. The intensities of the OH stretching vibration were 5.37 and 8.49 in the unmodified PTE whereas they decreased to 2.36 and 5.39 respectively as a result of modification with POCl$_3$.

Moreover, the relative intensities of the –OH band of the stretching vibration around 3400 cm^{-1}, the bending vibration around 1400 cm^{-1}, the in and out-of-plane vibration brands in the neighbourhood of 700 cm^{-1} as well as the bending vibration band of the ring–C-OH at 1328 cm^{-1} shifted to the left due to the incorporated PO$_4^{3-}$. New large intensity bands at 1244 and 1246 cm^{-1} appeared because of phosphorylation and they are due to stretching vibration of

the newly formed aromatic Ar-O–P-O- bond on the new product. This is buttressed by the observed strong stretching vibration bands at 1350 and 1300 cm^{-1}. These bands are typical of an aromatic phosphate compound Ar-O-P=O. Furthermore, new bands seen between 997 – 993 cm-1 represent the stretching vibration of a phosphate ester; -P-O$_2$R. It is remarkable to observe that there are no IR peaks or bands at 1244, 1246, 997 or 993 cm^{-1} in any of the spectra of the starting material PT or its extract, PTE.

New bands which appeared in the spectra of SPTE include those at 1325, 1375, 1280, 1120, 1050 and 880 cm^{-1}. They are characteristic asymmetric stretching vibrations of a sulfone (O=S=O), group, asymmetric stretching vibration of a sulphonic (-SO$_3$H) acid group, strong stretching vibration of a -S-O$_2$R ester, symmetric stretching vibration of O=S=O, stretching vibration of O=S and a symmetrical stretch of a -S- O$_2$R ester.

The intensity of the –OH band at the 3400 cm^{-1} region of SPTE which is 3.3 is lower than that of PTE and PPTE (I) which were 3.7 and 4.2 respectively. PPTE showed an -OH absorption band which is broader than PPTE (I) and may be as a result of increase electronegativity around the newly formed bonds in the larger molecule. Nada et al. (2009) reported a higher relative absorbance for –OH

group in $POCl_3$ crosslinked wood pulp than in the phosphorylated one. They attributed the observation to the presence of strong support sites in the molecule of the crosslinked product and stated that the strength of the support site improved as a result of contact between wood pulp and $POCl_3$. On the other hand, the intensities of the –P=O and -P-O-R stretching vibration bands around 1240 and –990 cm^{-1} respectively in the PPTE (I) are lower than those in the PPTE. The intensities of the - P=O and –P-O-R bands are 4.6 and 3.9 and 3.0 and 2.8 for PPTE and PPTE (I) respectively. Modification of PTE by sulphonation seemed to be more effective than by phosphorylation. Apart from the comparative strengths of the oxidizing agents: $ClSO_3H$ and $POCl_3$ respectively, employed for the purposes, the intensities of the –P=O absorption band at 1240 cm^{-1} (4.6) is lower than that of –S=O at 1050 cm^{-1} (4.9) Moreover, the intensity of the strongest absorption band of –(SO_3H) at 1375 cm^{-1} (4.9) is larger than that of the strongest -P=O band at 1240 cm^{-1} (4.6). This means that more –(SO_3H) groups than PO_4^{3-} groups are substituted for –OH groups of the catechin molecule.

Nearly all the IR absorption bands present in both PPTE and SPTE were present in PSPTE. The bands include: the –P=O stretching vibration at 1244 cm^{-1}, the –P-O-R stretching vibration at 975 and 877 cm^{-1}, the –S=O asymmetric stretching vibration at 1281 cm^{-1} and the asymmetric stretching vibrations of O=S=O variously at 1190, 1112 and 1375 cm^{-1} –P=O and –P-O-R groups were incorporated into PTE during crosslinking with $POCl_3$ while S=O and O=S=O were introduced during functionalizing with $ClSO_3H$ after the crosslinking step.

In addition to IR absorption bands due to the –P=O introduced during crosslinking, new absorption bands were seen at 1743, 1278 and 1190 cm^{-1} in the IR spectra of PCPTE. The bands resulted from the stretching vibration of the carbonyl (-C=O) of the COOH, Ar-O-C and the --C–O groups of the ether respectively formed during the carboxymethylation of Crosslinked-PPTE to form PCPTE.

Other physical parameters

The results of the physical parameters for all the resins synthesized are presented on Table 2. The results of the parameters were compared with that of a commercial resin Bio-Rex 70. The specific gravity for the commercial resin, Bio-Rex 70 was 0.7 and is lower than the specific gravity of all the synthesized resins. The average Sp.g of the synthesized resins was 1.61. Apart from PTE, all the synthesized resins are stable beyond 300°C while Bio- Rex 70 melted above 100°C. The MP of PCPTE could not be determined because its rubbery appearance would not allow it to be fed into the capillary tube for MP determination. Based on experimental data and calculations, the cation exchange capacities of the synthesized resins were: 4.76, 5.90, 5.53 and 4.71 meq/g for PPTE (I), PPTE, PSPTE and SPTE respectively. For comparison, the cation exchange capacity of Bio-Rex 70 is 10.2 meq/g.

The $pH_{(PZC)}$ values of the resins were determined and found to lie between 3.8 and 5.4. The pH(PZC) decreased as a result of the introduction of acidic groups. Vieira et al., 2014 stated that sorption of positively charged species is favoured only when pH>pHpzc. This means that the PTE cation exchange resins synthesized in this study would be effective in removing metal ions over a wide pH range. Cation exchange capacity and pH(PZC) for PCPTE were not determined because the resin was soluble in water, hence, cannot be used in water purification since it would impart colour to the water.

Table 2: Physico-chemical parameters for PT, PTE, PTE resins and Bio-Rex 70.

S/No.	Resin	Yield %	Sp.g (g/L)	M.P (°C)	CEC (Meq/g)	pHpzc
1	PT	N/	1.17	> 300	0.62	6.97
2	PTE	43.58	1.33	170	0.58	7.01
3	PPTE (I)	50.37	1.08	> 300	5.62	3.63
4	PPTE	63.01	1.32	> 300	6.71	3.57
5	SPTE	57.68	1.79	>300	5.19	4.13
6	PSPTE	55.48	1.29	> 300	9.52	2.32
7	PCPTE	37.56	2.1	-	N/	N/
8	Bio-Rex 70	NA	0.7	>100	10.2	2.02

N/A = Not Applicable Sp.g = specific gravity, MP = Melting point, CEC= Cation Exchange capacity.

Conclusion

The observation of Fourier infrared spectra absorption bands originating from –P=O, =S=O, -P-OH and –P-C- OR showed that crosslinking and functionalizing of peanut testa extract with phosphorus oxychloride and chlorosulphonic acid/ monochloroacetic acid were successful. The study shows that the use of peanut testa in the preparation of cation exchange resins minimizes waste generation and is a very useful way to recycle the waste material, protect and enhance the environment for sustainable development.

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