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Ion Exchange Properties of Crosslinked and Carboxylated Peanut (*Arachis Hypogaea* L.) Testa Extract

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ABSTRACT*:* *After polymerization via polycondensation of catechin units in the acetone extract of peanut (arachis hypogaea L.) testa (PTE) using phosphorus oxychloride ($POCl_3$) as a crosslinking agent, $POCl_3$-crosslinked PTE (Crosslinked-PPTE) was functionalized by etherification (PC-PTE) using monochloroacetic acid (MCAA) in the presence of an alkali according to the method of Williamson ether synthesis. Subsequent to characterization by Fourier Transform Infrared spectroscopy (FTIR) as well as physical properties, Crosslinked-PPTE was assessed for cation exchange capacity (CEC) and pH at point of zero charge (Z_{PHC}) following demonstrated capacity to remove heavy metal ions in single and multi-elements aqueous solutions by Atomic Absorption Spectrometry (AAS) technique while functionalized (carboxymethylated) Crosslinked-PPTE (PC-PTE) was further characterized by degree of substitution (DS). FTIR absorption bands due to -C-O-P=O, -P=O, P-O-C- and R-O-P-OH stretching vibrations were seen at 1350/1250, 1244/1246, 997/993 cm^{-1} respectively. Asymmetric and symmetric stretching vibrations of the -C=O of a COOH, Ar-O-C- of an aromatic ether as well as -P-O-C - of an aromatic PO_4^{3-}, R-P=O of a -PO_4^{3-}, -R-O-P- and R-O-P-OH of a PO_4^{3-} ester created by crosslinked and carboxymethylated PTE respectively were seen at 1743, 1377, 1278, 1190, 1062 and 823 cm^{-1}. The results obtained showed that 0.6 was the DS of PC-PTE while 6.72 meq/g and 3.57 defined the CEC and pH $_{(zpc)}$ respectively of Crosslinked-PPTE. Quantitative removal of Fe^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} in laboratory simulated metal ion wastewater (LSW) to the levels of 84.4, 81.7, 76.5, 72.0 and 75.1% respectively was achieved using Crosslinked-PPTE resin in batch adsorption experiments in which the efficiency was found to depend significantly on the temperature and pH of the water as well as initial adsorbate concentration and contact time but partially on the amount of adsorbent used was observed to be independent of the speed of stirring of the wastewater. Stable, Matakana and fine powder crosslinked-PPTE which is insoluble in water and common laboratory solvents holds great potential in the purification of heavy metal ions polluted water and consequently a highly beneficial way to employ peanut testa for sustainable development.*

KEYWORDS: Peanut testa extract, catechins, Crosslinked-PPTE, etherified PC-PTE, degree of substitution, adsorption.

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MATERIALS AND METHODS

Equipment

The apparatus and equipment used in the study were mutually provided by The African Centre of Excellence, Centre for Oilfield Chemicals and The Department of Pure and Industrial Chemistry, University of Port Harcourt. Nigeria.

Reagents

The reagents and chemicals used for the experiments in this research were of analytical grade, sourced from Idex Scientific Supplies Company, Ltd, Aba, Nigeria and were used without further purification.

Preparation of Metal Ion Solutions

Collection/ Processing/ Extraction of Polyphenols from Peanut Testa

The collection of peanut testa (PT), its storage and processing as well as extraction of polyphenols (PTE) therein are reported in Uchechukwu *et al.* (2016).

Crosslinking of PTE (Crosslinked-PPTE) and Etherification of Crosslinked-PPTE (PC-PTE)

The methods for the crosslinking of PTE and preparation of Crosslinked-PPTE as well as the etherification of Crosslinked-PPTE to obtain PC-PTE have been described in Chukwu *et al*. (2018).

Characterization of the Resins

Characterization of Crosslinked-PPTE and PC-PTE according to physico-chemical properties and Fourier Transform Infra-Red (FTIR) Spectroscopy as well as the instrument and apparatus used, the techniques, varieties and operational ranges are described in Chukwu *et al*. (2018).

Resin Activation/ Adsorption Studies

The procedure for activation and the conversion of Crosslinked-PPTE to the H^+ form as well as the exchange of the latter with Fe^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} in synthetic metal ion wastewater (SMW) (adsorption) is described in Uchechukwu *et al.* (2021).

Ion Exchange Capacity (IEC)/ Point of Zero Charge (pH(pzc)) of Crosslinked-PPTE

The procedures for the determination of the number of exchangeable ions in Crosslinked-PPTE as well as the pH at zero-point charge (pH(zpc)) are described in Uchechukwu *et al.* (2021).

Degree of Substitution (DS) of Carboxymethyl Group in PC-PTE

The technique described by Kim and Lim (1999) was employed for the determination of the degree of substitution (DS) of carboxymethyl groups in PC-PTE resin. For this purpose, 3 g of PC-PTE, dispersed in 20 ml deionized (DI) H_2O and adjusted to pH 2.0 using 1 N HCl was stirred for 10 mins to transform the ionized carboxyl (COO^-) groups to the free acid form. By means of Whatman No. 41 filter paper, the dispersion was sieved, washed 3 times using 40 ml of DI H_2O and gelatinized in 40 ml of H_2O by boiling in a water bath for 30 mins. Free CH_3COO^- groups were thereafter titrated with standardized 0.1 N NaOH solution using Crosslinked-PPTE (before etherification or carboxymethylation) as blank. DS was at the end calculated in consistence with Rutenberg and Solarek (1984) equation and the experimental yield calculated as percent molar ratio of substituted (exchanged) carboxymethyl groups to added chloroacetic acid.

RESULTS AND DISCUSSION

Modification with $POCl_3$

The chemistry about the modification of PTE that yielded Crosslinked-PPTE and the proposed reaction schemes are described in Chukwu *et al*. (2018).

Etherification of Crosslinked-PPTE (PC-PTE)

Etherification of Crosslinked-PPTE took place via a two-step process in which Crosslinked-PPTE was first converted to the alkoxide by treatment with NaOH (alkalization) to obtain the alkali-Crosslinked-PPTE. The latter was subsequently reacted with monochloroacetic acid (MCAA) in the manner of the Williamson ether synthesis to attach carboxymethyl (CH_3COO^-) groups before finally neutralizing with aqueous MeOH. Although variations in the concentration of NaOH: 5%, 10%, 20%, 30%, 35% and 40% could be used to obtain the alkoxide complex in the preliminary step, 10% NaOH was used in the alkalization stage because it was the least strength that produced a solid Crosslinked-PPTE alkoxide complex. In line with the certification (Spychaj *et al.*, 2013) that the aqueous NaOH to be used in the preliminary alkalization reaction must be of suitable and acceptable strength to be able to generate active alcoholate group centres, explained as the sites for the characteristic nucleophilic substitution by MCAA (a process typified by producing carboxymethylated products with high DS values), Saputra *et al.* (2014) discovered that 10% aqueous NaOH against other concentrations yielded carboxymethylated products with the highest DS. The tentative scheme and pathway for the alkalization and carboxymethylation of Crosslinked-PPTE is published in Chukwu *et al*. (2018).

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FTIR Spectra of Crosslinked-PPTE and PC-PTE

The characteristic absorption bands found in the FTIR Spectroscopy of Crosslinked-PPTE and PC-PTE are tabulated and described in Uchechukwu *et al.* (2021) and Chukwu *et al*. (2018).

Other Physical Parameters

The results of the determination of the physical properties of Crosslinked-PPTE and PC-PTE are presented in Uchechukwu (2017).

Yield and DS of PC-PTE

The yield of the carboxymethylation reaction of Crosslinked-PPTE to form PC-PTE and the DS of this product are 17% and 0.056 respectively, with the latter property attributable to the observed solubility of PC-PTE resin in water. The outcome of Rahim *et al.* (2017) investigation of the influence of DS on the physicochemical properties of acetylated *arenga* starches revealed association between rising DS and decreased crystallinity (Colussi *et al.*, 2014) in the studied carb, consequently, the observed hydrophilicity and solubility of the acetylated native *arenga* starches. Subsequently, Otoni *et al.* (2018) found out that among other properties, DS significantly influenced the hydrophilicity of modified cellulose, so treated to enhance processability of the biomass into a film-forming material for food packaging.

Crosslinked-PPTE and PC-PTE in Metal Ion Adsorption

The amounts of the divalent metal ions: Fe^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} in single element LSW removed by Crosslinked-PPTE are reported in Uchechukwu *et al.* (2021). Characteristically rubbery, manganese-violet PC-PTE presented a unique appearance. Annadurai *et al.* (2000) listed physical as well as thermal and chemical stability as requirements for a biomass or its derivative to serve as an effective solid support for the duo purposes of immobilization and metal ion adsorption. Metal ion adsorption by tough and inelastic PC-PTE could not be accomplished because the resin solubilized in H_2O, thus lacked a basic requirement for a suitable water purifier. A review of the literature about resins and water purification showed that CH_3COO^- resins characterized by high DS values, ranging 0.5 and above are water soluble and have not been successfully employed to purify H_2O. For example, Heinze (2005) and Sancey *et al.* (2010) reported 90% binding of Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+} and Al^{3+} and complete removal of Cu^{2+} and Fe^{2+}as well as significant decreases in the concentration of Pb^{2+}, Cd^{2+} and Ni^{2+} in aqueous solutions and drop in the concentration of Zn^{2+} to a level below the permissible limit in the effluent of the Zindel Industry using the H^+ form of H_2O insoluble CMC and 1,4-butanediol diglycidylether crosslinked carboxymethyl starch with a DS value lower than 0.3 and 0.2 respectively. The usage of water-soluble resins for water purification will therefore create additional challenge of secondary pollution by impacting undesirable colour to the water and consequently requiring another purification step to eliminate the colour and ultimately, increasing the time and raising the financial cost and implication to obtain potable water for domestic use and sundry purposes.

CONCLUSION

The study portrays Crosslinked-PPTE, obtained from peanut testa waste as a good metal ion adsorbent for removing Fe^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} in aqueous solutions and PC-PTE as otherwise. The results of the investigation shows that a modified peanut testa extract cation exchange resin, such as Crosslinked-PPTE could help to conserve the foreign exchange that is expended currently in procuring such resins. It also presents carboxymethylated peanut testa extract as a resin to prospect for its usefulness and utilization to the service, promotion and sustainability of mankind. The research supports the potential application of the techniques in the recovery of wastewater, thus mitigating the problem of water scarcity and waste disposal, development and turning of ideas and discoveries into useful products and novel materials for the use of man while protecting the beleaguered environment from undesirable heavy metal pollution.

REFERENCES

Annadurai, A., Babu, S. R., Mahesh, K. P. O. and Murugesan, T. (2000). Adsorption and biodegradation of phenol by chitosan-immobilized *Pseudomonas putida* (NICM 2174). *Bioprocess Engineering.* 2: 493-501.

Chukwu, U. J., Uchechukwu, T.O. and Akaranta, O. (2018). Synthesis of new cation exchanger resins from chemically modified peanut (*arachis hypogaea* L.) testa extract. *Journal of American Science*. 14: 69-75. http://www.jofamericanscience.org.

Colussi, R., Pinto, V. Z., Halal, S. L. M., Vanier, N. L., Villanova, F. A. and Silva, R. M. (2014). Structural, morphological and physicochemical properties of acetylated high, medium and low-amylose rice starches. *Carbohydrate Polymers*. 103: 405–413.

Heinze, T. (2005). Carboxymethyl ethers of cellulose and starch – A review. *Chemistry of Plant Raw Materials.* 3: 13–29.

Kim, B. S. and Lim, S.- T. (1999). Removal of heavy metal ions from water by cross-linked carboxymethyl corn starch. *Carbohydrate Polymers.* 39: 217–223.

Otoni, C. G., Lorevice, M. V., De Moura, M. R. and Mattoso, L. H. C. (2018). On the effects of hydroxyl substitution degree and molecular weight on mechanical and water barrier properties of hydroxypropyl methylcellulose films. *Carbohydrate Polymers*. 185: 105–111. https://doi.org/10.1016/j.carbpol.2018.01.016.

Rahim, A., Kadir, S. and Jusman, A. (2017). The influence degree of substitution on the physicochemical properties of acetylated *arenga* starches. *International Food Research Journal*. 24(1): 102-107.

Rutenberg, M. W. and Solarek, D. (1984). Starch derivatives: production and uses Ch. 10. In Whistler, R. L., BeMiller, J. N. and Paschall, E. F. (Eds.). *Starch Chemistry and Technology*. 2. New York: Academic Press.

Sancey, B., Trunfio, G., Charles, J., Minary, J., Gavoille, S., Badot, P. and Crini, G. (2010). Heavy metal removal from industrial effluents by sorption on cross-linked starch: Chemical study and impat on water toxicity. *Journal of Environmental Management.* xxx: 1-8.

Saputra, A. H., Qadhayna, L. and Pitaloka, A. B. (2014). Synthesis and characterization of carboxymethyl cellulose (CMC) from water-hyacinth using ethanol-isobutyl alcohol mixture as the solvents. *International Journal of Chemical Engineering and Applications.* 5(1): 36-40.

Uchechukwu, T. O. (2017). Cation exchange properties of chemically modified peanut testa (*arachis hypogaea* L.) extract for the treatment of wastewater. *Ph D. Thesis*. Department of Pure and Industrial Chemistry. University of Port Harcourt. https://www.scirp.org/(S(vtj3fa45qm1ean45wffcz5%205))/reference/referencespapers.aspx?referenceid=3132472.

Uchechukwu, T. O., Akaranta, O., Chukwu, U. J., Okike, N. E. and Abayeh, O. J. (2016). Binding of heavy metal ions in hydrocarbon produced water by phosphorus oxychloride modified peanut (*arachis hypogaea* L.) testa extract. *Journal of Chemical Society of Nigeria.* 41(2): 123- 129. https://journals.chemsociety.org.ng/index.php/jcsn/article/view/84.

Uchechukwu, T. O., Chukwu, U. J. and Akaranta, O. (2016). Competitive adsorption of metal ions on peanut testa (*arachis hypogaea* L.) extract using cation exchange resins. *Open Access Library Journal*. 8: e7575. https://doi.org/10.4236/oalib.1107575.