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ORIGINAL ARTICLE

NOVEL STRONG AND WEAK KOLA NUT (*COLA- STERCULIACEAE)* TESTA CATION EXCHANGERS FOR THE REMEDIATION OF POLLUTED WATER

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ABSTRACT

Background: Freshly processed kola nut (*C. nitida and C. acuminate*) testa powder was separately modified with chlorosulphuric acid (CSA) and citric acid (CA). **Objectives:** After characterization by Fourier Transform Infra-Red (FTIR) Spectroscopy and according to other physical properties, the synthesized resins were evaluated for their capacity to remove the heavy metal ions of Pb^{2+} and Cu^{2+} in laboratory simulated aqueous solutions using the technique of Flame Atomic Absorption Spectrometry (FAAS). **Methods:** In addition to the FTIR absorption bands found in the 3400 cm^{-1} region of the electromagnetic spectra assigned to the –OH groups of unmodified testa which also showed in the spectra of the chemically modified products, new IR absorption bands were seen at 2750, 1720, 1340, 1325, 1160, 1047 and 850 cm^{-1} confirming the presence of –COOH, -C=O, $-SO_3H-$, O=S=O and –S-OH in the products. **Results:** The results which showed that chemically modified KT removed higher amounts of the pollutant metal ions than unmodified KT also indicated that both adsorbents demonstrated higher affinities for Pb^{2+} and consequently, a more favourable adsorption for it and its removal at nearly 80% than for Cu^{2+} at 70%. While CSMKT and CAMKT removed 8.14 and 6.97 ppm and 7.63 and 5.86 ppm respectively of Pb^{2+} and Cu^{2+}, 2.03 and 1.74 ppm of the metal ions were removed by KT from the polluted water samples containing 10 ppm of the individual metal ions. **Conclusions:** The ease of modification of KT and the effectiveness of the new chlorosulphonic acid modified kola-nut testa (CSMKT) and citric acid modified kola-nut testa (CAMKT) cation exchangers in decontaminating the polluted water samples suggest the usefulness of kola nut testa as a potential adsorbent for the remediation of heavy metal polluted water and other aqueous streams.

Keywords: Polyphenols, esterification, adsorption, heavy metals, domestic water, coronavirus,

1. INTRODUCTION

The importance of water can hardly be overemphasized as our planet, Earth would be a massive desert that is incapable of sustaining life without it [1]. As the basic necessity for the numerous and diverse organisms in the ecosystem, the cells and tissues of all lives, including plants, animals and humans consist of 50–80% water without which all would frazzle, sicken and ultimately die [2, 3]. In these organisms, water is the medium for biochemical reactions and cellular transportation, thus, threatening our general wellbeing in times of inadequate water supply.

Irregular rainfall and distribution of the Earth's water bodies, drought and depletion of natural water sources, groundwater contamination, boost in population, industrialization and urbanization as well as agriculture and dependence on a single source of supply have been captured as reasons for the increasing demand and shortage of water in many regions of the globe [3]. Despite its status as a common gift and the enshrining of the right to its sufficiency as a universal law in strategic international agreements [1, 4-5] acknowledged the current lack of clean drinking water by over 20% of the global populace, resulting to the high annual infant mortality [4]. For example, while a daily 130–150 and 300 litres of potable water is available for use per person in Europe and North America, majority of the people in Africa can hardly access 20 litres of water a day for their use. Akinola (2014) confirmed that residents of Ikeji and most Nigeria towns and settlements have no potable domestic water supply [6]-; a source and infrastructure that provide water to households and include stream, hand-dug well, borehole, rainwater collection system, pipe borne water supply among others. Potable water serves the households for drinking, cooking and cleaning of utensils, bathing, laundry, watering animals and irrigation as well as sanitation and hygiene purposes and commercial activities.

Enugu, the Coal City and headquarters of Eastern Nigeria lacks pipe borne water supply. While boreholes are a luxury that is only affordable by the rich, majority of the town dwellers depend on commercial water tanker operators or hand-dug wells for their domestic water supply. Reports of several scientific studies reveal that water from both sources are contaminated with heavy metals such as Fe, Cu, Pb, Ni, Cr, Mn and Zn [7-8] associated with coal formations that underlie the geology of the town [9-11] and are attributable for the high level of toxic heavy metals detected in the blood samples of the residents of the town [12].

Although, the deficiency of microelements impact negatively on metabolic processes in living organisms [13], heavy metal pollution in these organisms have been found to be responsible for systemic diseases and other health challenges encountered by humans [14-17]. Slaninova *et al.* (2014) and Jonge *et al.* (2009) listed impaired growth and development, reduced fish survival rates and extinction of specie as some of the consequences of heavy metal accumulation in fish and benthos [18, 19]. Besides the report of other research [20] about inhibition of the enzymatic breakdown of organic compounds to the soil, [21-22] found out that heavy metals toxicity in plants is responsible for poor nutrient intake and the consequential stunted growth and low fruits yield, chlorosis as well as poor stomatal activities and other metabolic disorders in plants. For these reasons, domestic water supplies from hand-dug wells and tanker operators is unwholesome and cannot be guaranteed to safeguard the residents of Enugu and other towns and communities across the globe who use it for handwashing and sanitation practices to prevent and curtail the spread of coronavirus, the pandemic currently ravaging Nigeria and endangering humanity across the world. Continued use of water from these sources will lead to accumulation of heavy metals in individuals, thus, increasing their vulnerability to covid-19 infection. Water from hand-dug wells and tanker operators need to be purified by removing toxic heavy metal ions in order to make it suitable for domestic use, disinfection and sanitization of medical facilities and public places.

Filtration, ozonization, carbon adsorption, co-precipitation, electrochemical deposition, clarification and membrane processing are among the treatment methods to remove pollutant heavy metal ions in water. Majority of the techniques are effective, but command little applications due to under performance in high metal ion concentration systems, often requiring high chemical consumption and long application cycles which ultimately render them unproductive and consequently, unpopular choices for metal ions removal [23-25] in favour of polymeric resins which eliminate pollutant heavy metal ions by binding and formation of stable resin-metal-ion complexes [26]. Ewansiha *et al.* (2013) suggested surface adsorption and ion exchange as popular and effective techniques for the processing and purification of water [27]. Corroborating, the finding of previous studies [28, 29] who confirmed the popularity of widely and industrially applied ion exchange technique which reportedly surpassed existing technologies in the purification of coal bed methane produced water. Effective removal and recovery of target metals without sludge generation were identified by other authors [30, 31] as highpoints of ion exchange against other metal ion removal techniques.

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An ion exchange material is an insoluble matrix holding loosely bound ions which can be replaced by other ions coexisting in its surroundings. In ion exchange chromatographic process, ions in solution are transferred to a solid matrix which, in turn releases ions of opposite charge but of the same polarity. During ion exchange, the hazardous ions being exchanged are reversibly removed from the wastewater (mobile phase) and transferred to the ion exchanger (stationary phase) in which there is no permanent structural change. Using the resin, purification of wastewater can be accomplished to such an extent that the water can be reused. Conventional ion-exchange resins, derived from petrochemical sources are prepared either by grafting anionic or cationic functional groups onto a synthetic copolymer of styrene and divinyl benzene (DVB) or implantation of same on a biological polymer such as cellulose [32]. Apart from the high cost, substrates of this nature do not decompose, thus are unsafe and are characterized by short life span as well as require pre-treatment procedures in order to use them.

The need to overcome the challenges of exorbitant petrochemical substrates and the necessity to preserve the ecosystem led to the search for effective, healthier and simpler methods to remediate heavy metal ions polluted water. Hubbe *et al.* (2011) identified transformation of agricultural wastes to eco-friendly substitutes for petrochemical substrate handles or support systems for ion exchange functional groups as the current area of scientific research [33]. These and the economic crisis of the 21st century inspired researchers to seek adsorbents from renewable materials of plant origin with capacity to accumulate heavy metal ions. Agricultural wastes such as peanut testa, sphagnum peat, sugarcane bagasse, orange and cassava peels as well as their mesocarps, spent tea leaves, tamarind fruit shell, coconut coir, cherry seed shell and rubber fruit pericarp have been developed and used to remove different heavy metal ions in aqueous systems due to the availability of polar constituents like the hydroxyl (-OH), amines (-NH_2), carboxyl (-COO) and thiol or sulfhydrl (-SH) groups in the plants' chemical structures [3, 7, 27, 30].

Water purification using these nauseating and huge lignocellulose wastes, estimated above 320, 000, 000, 000 Kg/year [34, 35] and 70% of the world's biomass in the natural state or as modified products premises on the interaction between the contaminant specie and the polar groups and possess the capacity to remove high levels of metal ions at favourable conditions. Moreover, the potential of agricultural wastes in remediating metal ions polluted aqueous systems show to improve by adaptation through the modification of the polar groups with suitable reagents. For example, previous studies carried out various chemical modifications of different agricultural wastes using diverse reagents and successfully employed the products to remove different metal ions in polluted water [36-42, 35].

Kola nut, the seed of the economically important fruit of the kola tree is a genius (*Cola*) of trees native to the tropical rain forests of Africa [43]. Over 300,000 tons of kola nut, shown in Figure 1 are produced annually across the West African countries of Nigeria, Gabon, Ghana and Ivory Coast as well as Brazil and the West Indian Islands out of which Nigeria accounts for nearly 88% of the total production [43-45]. Aside from its use as a masticatory and stimulant, large quantities of kola nut are harvested and processed for use in the industries to produce pharmaceuticals, beverages as well as confectionaries and flavorings [43, 45-46], generating tonnes of kola nut testa as waste. Hamzat et *al.,* (2007) used the potassium rich waste [48] to formulate feed for territorial snail (*archachatina marginata*) [47] but Fabunmi, et *al.,* (2019) found out that substitution of kola nut husk for maize in amounts that overaged 10% in poultry feed compromised the growth performance of boilers [49]. Consequently, kola nut testa is dumped carelessly to deface the landscape and rot to breed mosquitoes, therefore posing environmental problems [50]. It could be harnessed and utilized gainfully. Chukwu *et al*. (2017) reported a meagre increase in the equilibrium adsorption capacity of unmodified kola nut testa for Cu^{2+} in a simulated aqueous solution from 2.05 to 2.24 respectively using formaldehyde modified kola nut testa but the adsorption capacity for Fe^{2+} markedly dropped from 2.12 mg/g to 1.97 mg/g using the same adsorbents [51]. Okwunodulu and Eddy (2014) reported the effectiveness of mercaptoacetic acid treated *cola nitida* husk as a metal ion adsorbent for Cd^{2+}, Ni^{2+} and Pb^{2+} [52]. Interest in this research is stimulated by the need to explore additional methods of kola nut testa modification using other reagents and to further examine the potential of the fibre and polyphenol-rich [47] waste in water purification. The aim of the present study is to develop new strong and weak cation exchangers from kola nut testa.

2. MATERIALS AND METHODS

All the chemicals used in this work were of analytical grade, purchased from Bristol Scientific Nigeria, Lagos and were used without further purification.

2.1. SAMPLING

Testa of fresh and healthy kola nut seeds from both *C. nitida and C. acuminata* specie was gathered at a kola nut processing centre at Ajona, Mbu-Amon in Isi-Uzo Local Government Council of Enugu State. After identification by the Department of Applied Biology and Biotechnology of ESUT, testa was washed with deionized water (DI H_2O), air-dried for 2 weeks and further dried in the oven for 24 hrs at 60 ^oC. It was thereafter removed and allowed to cool down before milling to obtain 0.192-1.700 mm particle size. Processed kola nut testa, labelled KT was received in a clean dry glass laboratory container, the lid firmly secured and stored in the laboratory until it was ready for use.

Figure 1: Kola nut tree leaves, kola nut pod (with seeds inside their white testa. Source: Wikipedia) and dry testa.

2.2. PREPARATION OF TEST SOLUTIONS

2.2.1. Preparation of element primary solutions: Two primary stock solutions containing 10 ppm each of Cu^{2+} and Pb^{2+} was prepared by drawing 5 mL from a 1000 ppm stock solution of the respective metal ions in HNO_3 (Merck) into a 500 mL volumetric flask using a pipette and diluting to the volume of the flask with DI H_2O before mixing by inversion.

2.2.2. Preparation of calibration solutions: Calibration solutions were then prepared by serial dilution of the respective 10 ppm primary standards. For this purpose, aliquots of 10, 20, 25 and 50 mL respectively were drawn from the individual primary stock solutions (**2.2.1**) and delivered into separate 100 mL volumetric flasks. The solutions were then diluted to volume with DI H_2O and thoroughly mixed to obtain 1, 2, 2.5 and 5 ppm calibration solutions.

2.2.3. Preparation of the working solution: Each of the 10 ppm primary stock solutions prepared in **2.2.1** above served as adsorbate solution and was used to conduct the ion exchange/adsorption experiments for the particular metal ion. 5 mL of 10% HNO_3 was added to all the preparations before diluting to volume to prevent the precipitation of the metal ions out of the solutions.

2.3. SYNTHESIS OF KT RESINS

The conversion of KT into strong and weak cation exchange resins was achieved through the following procedures:

2.3.1 Modification with CSA: The transformation of KT to a strong cation exchanger by esterification with CSA was carried out by the procedure reported by Uchechukwu (2017) [3]. After stirring KT (25 g) in 250 mL of pyridine held in a 1 L three-neck flat bottom flask for 12 hrs at room temperature (RT), the flask was equipped with a thermometer, dropping funnel and a reflux condenser. Subsequently a freshly prepared mixture consisting of 25 mL of CSA in 120 mL of CH_2Cl_2 was introduced by drops through the dropping funnel within 1.5 hrs. When the flask was free of HCl fumes, the assembly was transferred to a heating paraffin oil bath and heated at reflux for 3 hrs at 90 ^oC with continued stirring on a Happybuy Magnetic Stirrer SH-2 HP heating plate. The oil bath was thereafter brought down, the flask disengaged and set to cool down. The content was poured into a 600 mL beaker containing 200 mL of ice H_2O, stirred thoroughly with a glass rod and rapidly filtered on a white band filter paper. The residue was repeatedly washed, first with DI H_2O until it was free from the smell of pyridine, 100 mL of 0.1 M HCl and DI H_2O again until the filtrate tested neutral to methyl red indicator. It was finally washed with CH_3OH (100 mL) and dried overnight in an oven at 65 ^oC to yield 57.68% of CSA- modified-KT (CSMKT).

2.3.2. Modification with CA: KT was esterified by treatment with CA following the method of Marshall et al., (2006) with little modifications. For this purpose, a 12 g slurry of KT and 70 mL of 0.6 M CA in a 600 mL beaker was set to stand in an oven for an hour at 30 ^oC in order to let KT marinate the acid [53]. After drying the slurry overnight at 60 ^oC, the mixture was heated to 120 ^oC and maintained at this temperature for 2 hrs in a ventilated oven. At the end, the product, CA-modified-KT (CAMKT) was transferred to a 660 mL Porcelain Buchner funnel lined with a complementary size Whatman white band filter paper and liberally washed and filtered under suction with DI H_2O until it was free of CA. This was confirmed by the clarity of a suspension of CAMKT in 20 mL equi-volume solution of 0.1 M $Pb(NO_3)_2$ in H_2O. CAMKT was subsequently dried overnight in an oven at 60 °C and stored in an airtight bottle until it was used for adsorption studies. The yield of CAMKT was 97.54%.

2.4. Characterization

The modified products, CAMKT and CSMKT alongside the starting material, KT were tested for solubility in common solvents (H_2O, alcohol and dilute acid), specific gravity (Sp. g), melting point (M.P.) and inherent functional groups respectively by interfacing with the solvents, using a pycnometer, a model H305/0162 Gallenkamp melting point apparatus and an Agilent Technologies Cary 630 model FTIR Spectrophotometer operating within 4000 - 650 cm^{-1}. IR determination was carried out after thoroughly mixing 0.1 g of sample with nujol and all the measurements took place at RT.

2.5. Ion exchange and adsorption studies

Prior to use for the individual batch adsorption experiments, CAMKT, CSMKT and KT were activated by saturating overnight in dilute HNO_3, filtering and washing to neutrality before drying in the oven for 4 hrs at 60 ^oC to obtain the hydrogen ion (H^+) forms. Thereafter, 5 g of each acid activated adsorbent was suspended in 100 mL of the respective 10 ppm element solutions (**2.2.3**) which served as the working solutions) held in separate 250 mL Erlenmeyer flasks. The procedure was repeated in two other stands which served as duplicates. The pH of the test samples was adjusted to 6 ± 0.05 or 7 ± 0.05 respectively using a Combiotech OMEGA PHH 222 pH meter before adding the adsorbent. The flasks were placed on a Wiggens WH620 multistirrer digital magnetic stirrer and stirred at 150 rpm (revolutions per minute) for an hr at RT. At the end of the process, the flasks were brought down and the suspensions rapidly filtered on a Whatman No. 2^V folded filter paper. Using HNO_3-acidified DI H_2O as the calibration blank, the concentration (ppm) of Cu and Pb in the filtrates expressed as Cu^{2+} and Pb^{2+} was determined by means of Agilent F240AA Atomic Absorption Spectrophotometer operating with air: acetylene flame system and the amount of the metal ions removed from the water samples by CAMKT, CSMKT and KT at equilibrium, *Qe* was calculated using the formula**:**

$$\boldsymbol{Qe} = \left[\left(\frac{\boldsymbol{C_o - C_e}}{\boldsymbol{W}}\right)\right] \boldsymbol{x\ V}$$

Where: Co (ppm) is the initial concentration of the metal ion in the water; Ce is the concentration at equilibrium while *V* and *W* respectively are the volume of the water and the weight of the adsorbent (g) used in the experiment. The average of two values was reported in their percentages. A 4 ppm quality control standard for each metal ion prepared by diluting 40 mL of the respective 10 ppm primary standards (**2.2.1**) to volume in separate 100 mL standard flasks was tested along with the samples before and after the determinations to verify the performance of the spectrophotometer.

3. RESULTS

3.1. Physical properties

The results of the characterization of KT, CAMKT and CSMKT according to physical properties are tabulated in Table 1.

Table 1: Physicochemical Properties of KT, CAMKT and CSMKT

Sample Identity	Sp.g (g/mL)	M.P	H_2O solubility	Solvent solubility	Ethanol
KT	0.57	> 300 °C	Partial	Partial	Partial
CAMKT	1.11	Decomposed above 100 °C	Insoluble	Insoluble	Insoluble
CSMKT	1.63	> 300 °C	Insoluble	Insoluble	Insoluble

3.2. FTIR of KT and modified products

Table 2 outlines the absorption bands found in the FTIR spectra of KT, CAMKT and CSMKT.

Table 2: Characteristics Bands in the FTIR Spectra of PT and PTE

Frequency (cm^{-1})	Origin/Type of Vibration	Functional Group Assignment
3400/3350 /3270	Stretching vibration of -O-H group in aromatic Ph-OH	Thought to come from -O-H of KT polyphenols
3070/1590 /1480 823/668	Asymmetric and symmetric –C-H stretches in aromatics and substituted aromatics	Probably from the Sp carbons in these units’
2980/2930 /2870	Asymmetric and symmetric –CH_2 stretches in alkanes	Supposedly from the Sp^3 carbons in the saturated parts of the polyphenol units
1142	C-H bend of a saturated cyclic ether	Ascribed to a partially saturated cyclic ether in KT polyphenol units
1160/1034	–C-O-C- stretch of a cyclic ether	Purported to be a constituent of KT polyphenol units
1100	Broad; –C-O- stretch	-Same-
1740	In the spectra of CAMKT; -C=O stretch of an ester	Ascribed to new chemical groups and bonds created during esterification of KT with CA
1285	-C-O- stretch of an ester	Ascribed to new chemical groups and bonds created during esterification with CA
1340/1164	In the spectra of CSMKT Symmetrical and unsymmetrical stretches of aryl O=S-	Ascribed to sulphone bonds created during functionalization of KT with CSA
1040/1342 -1415 /1054	Stretch movements of O=S=O; $^{-}HSO_3$, SO_4^{2-} and S-O-H	Ascribed to sulphone, sulphonic acid, organic sulphate and sulphoxide bonds created during functionalization of KT with CSA

3.3. Ion exchange and adsorption studies

Figure 2 shows the amounts of Cu^{2+} and Pb^{2+} removed by KT, CSMKT and CAMKT from individual water samples containing 10 ppm of the respective metal ions.

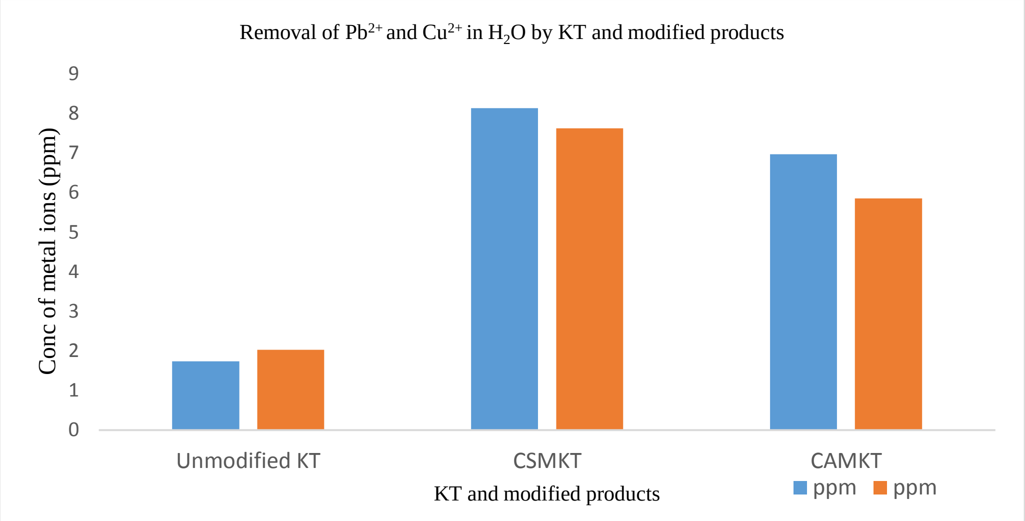
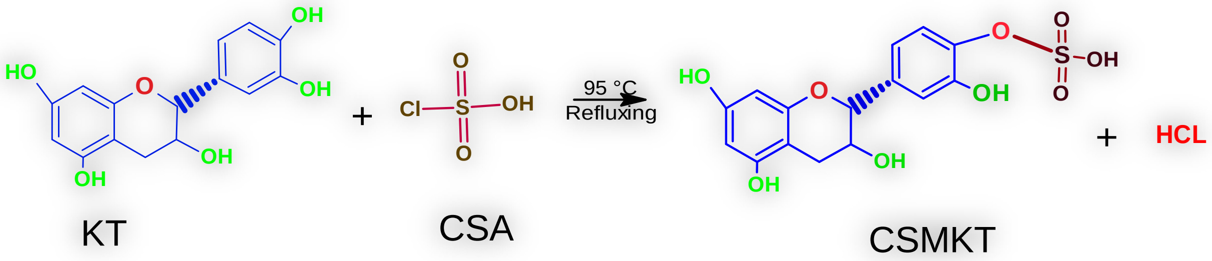


Figure 2: Amounts of Cu^{2+} and Pb^{2+} in H_2O removed by KT and the modified products.

4. DISCUSSION

4.1. Modification with CSA

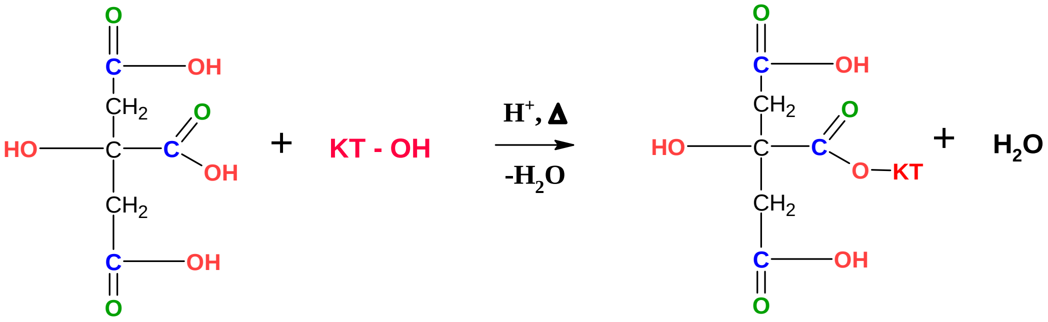
Modification of KT by functionalization was accomplished by direct sulphonation using CSA. The procedure involved a one-step condensation process in which CSA donated the active sulphonic acid ($^{-}HSO_3$) group to the acceptor -OH group of KT polyphenol units to create a sulphur ether (C-O-S-) bond. The synthetic process can be shown in Scheme 1 as follows:



Scheme 1: Synthetic scheme for the conversion of KT to CSMKT.

4.2. Modification with CA

Transformation of KT to CAMKT was achieved via the esterification of one of the weak carboxylic acid (-COOH) groups of CA by an –OH group of a KT polyphenol according to Fischer-Speier esterification reaction. The reaction, which was catalyzed by H^+ from CA involved the thermochemical condensation of CA imbibed KT polyphenols and proceeded by simultaneous conversion of the CA to the anhydride and the formation of an ester linkage between the later and a unit –OH group of the KT polyphenol through crosslinking to produce H_2O as a byproduct. This is shown in synthetic Scheme 2 as illustrated by [54]. In addition to the unreacted –OH groups of KT polyphenols, the product, CAMKT is capable of producing two additional negatively charged groups from the ionization of the free –COOH groups of CA, thus increasing the overall polarity of its solution and enhancing its metal ion adsorption at favourable pH.



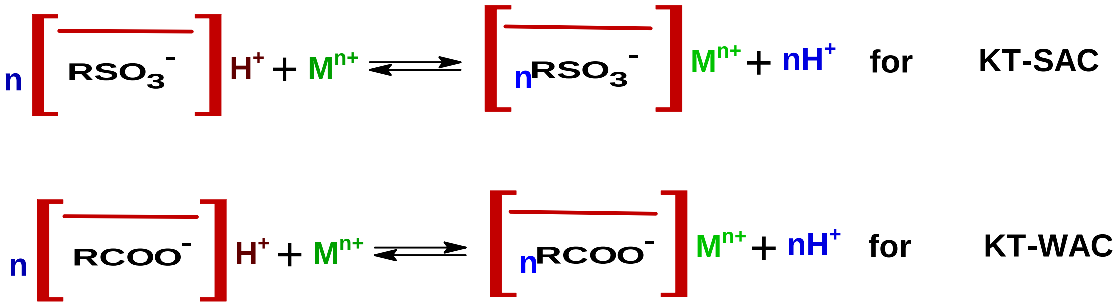
Scheme 2: Esterification of tricarboxylic acids of CA by OH groups of KT polyphenols

4.3. FTIR spectra of PT and PTE

Table 2 shows that in addition to the broad bands at 3400; 3350; 3270, the three discrete peaks at 3070; 1590; 1480 as well as the several distinct peaks at 2980; 2930; 2870 and the lone band at the 1142 cm^{-1} in the IR region of the electromagnetic spectrum corresponding to the –OH stretch of the aromatic phenolic groups, asymmetric and symmetric –C-H stretches of the Sp carbons in the aromatic parts of the polyphenol units as well as the asymmetric and symmetric -CH$_2$ stretches of the Sp^3 carbons in the saturated parts of the polyphenol units and the –C-H bending movement of a cyclic ether in the starting material, KT, which also showed in the spectra of the products, CAMKT and CSMKT exhibited one or another additional bands between 1800 and 900 cm^{-1} according to the reagent with which the modification was carried out. Two IR absorption bands at 1629 and 1528 cm^{-1} are ascribed to Sp^2 carbons in the side rings of the polyphenol units and whereas the –C-O-C- stretch of a cyclic ether demonstrated IR absorption at 1160/1034, a broad band due to the –C-O- stretch showed at 1100, while the bands at 823/668 cm^{-1} are thought to be due to –C-H stretches in these units. The single absorption bands at 1740 and 1285 cm^{-1} respectively found in the spectra of the CA-modified- KT are ascribed to the -C=O and -C-O- stretches of the ester product, CAMKT. Two strong bands which showed at 1340 and 1164 cm^{-1} in the spectra of the CSA-modified-KT are ascribed to the symmetrical and unsymmetrical stretches of the aryl sulphone (O=S-) bond created as a result of the functionalization of KT polyphenol with CSA to form CSMKT. Other bands present in the IR spectra of CSMKT include those at 1040, 1342, 1415 and 1054 cm^{-1} assigned to various stretches of O=S=O, $^{-}$HSO$_3$, organic sulphates (SO$_4^{2-}$) and sulphoxide (–S-O-H) groups.

4.4. Ion exchange and adsorption studies

It can be seen from the result shown in in Figure 2 that the modified products removed more of the metal ions than KT in all the water samples. This is due to the presence of the new chemical groups: -HSO$_3^-$ and –COOH added to the biochemical structure of KT during the modification. Hamzat *et al.* (2007) reported abundant presence of polyphenols in KT which in addition to accreditation to the removal of pollutant heavy metal ions [47, 7, 55-57], yield to successful modification with diverse chemicals and techniques and resulting to enhanced metal ion uptake from varieties of aqueous systems [58, 41, 35]. Modification with CSA and CA improved the overall polarity of the polyphenols in the chemical structure of KT biomass by the addition of carboxylic (-COOH) and sulphonic acid (HSO$_3^-$) groups. The processes of sulphonation and acetylation respectively imparted anionic character to the CSMKT and CAMKT molecules and aided the attraction and consequent binding of the positively charged metal ions in the solutions. Thus, the functional groups, HSO$_3^-$ and HCOO$^-$ attached to the KT backbone (support, handle or immobile resin phase) transformed them to KT-strong acid cation exchanger (KT-HSO$_3^-$ H$^+$ or KT-SAC) and KT-weak acid cation exchanger (KT-COO-H$^+$ or KT-WAC) with the charged sulphonic and carboxyl groups respectively acting as the exchange sites. The ion exchange reactions (metal ion exchange) for the ionized forms of KT cation exchange resins can be illustrated in Scheme 3:

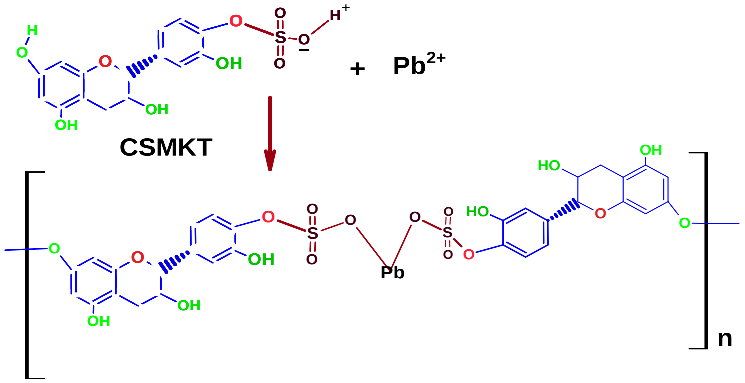


Scheme 3: Ion exchange reactions for the ionized KT cation exchange resins

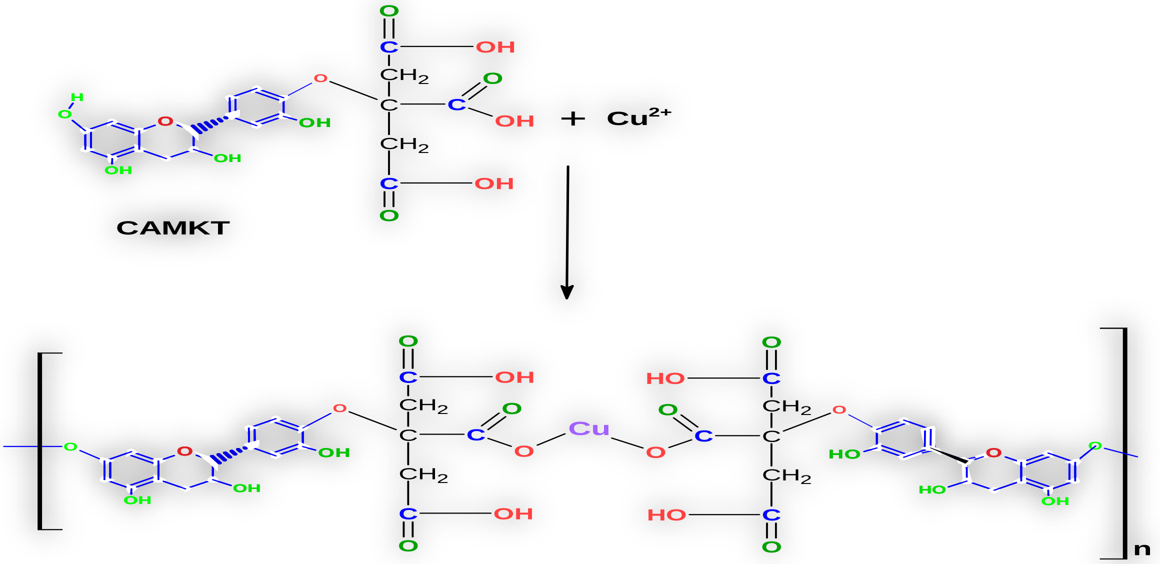
Where the overbar refers to the immobile resin phase, H$^+$ is the isolated proton, hydrogen ion or pre-saturant ion associated with the resin before exchange, M^{n+} is the metal ion or counterion in the solution being exchanged out of solution and *n* is the charge on the counterion.

The results showed that KT-SAC removed more of both Pb^{2+} and Cu^{2+} in the water samples than KT-WAC. This can be explained in terms of the extent of the ionization or dissociation of the functional groups on the resins. Strong acid cation exchanger (SAC) resins, characterized by low pKas (<0), such as HSO$_3^-$ are easily dissociated, demonstrate little affinity for the H$^+$ and give it up readily at any pH in exchange for another cation in the solution. On the other hand, a WAC resin, characterized by high pKa values (4–5) are only partially ionized and will not readily give up its H$^+$ except at pH greater than 7. Below pH 7, the affinity of WAC resins for H$^+$ is great, therefore, will not release it for exchange with another cation. This is the reason why the pH of the working solution which was treated with CAMKT was adjusted to 7 ± 0.05 prior to the introduction of the resin. It therefore means that CSMKT completely dissociated into KTSO$_3^-$ and H$^+$ in the test medium, completely released its H$^+$ and exchanged them readily with the surrounding Pb^{2+} and Cu^{2+} in the polluted water sample. Whereas 8.14 and 7.63 of Pb^{2+} and Cu^{2+} respectively were removed by CSMKT, 6.97 and 5.86 ppm of both metals ions were removed by CAMKT. The proportions of both metal ions removed by CSMKT were higher than those removed by CAMKT because the later clung to its H^+, hindering its mobility and limited its chances to exchange with the metal ions in the water samples.

The results also showed that both resins (CSMKT and CAMKT) removed more Pb^{2+} than Cu^{2+} from the water samples. The selectivity of an ion exchange resin reveals the relative preference of such a resin toward different types of ions in a solution and depends on the charges and sizes of the ions under consideration when their concentration in that solution is uniform. In a process involving strong or weak exchange sites on ion exchange resins of comparable degree of cross-linking and permeability, ions of smaller hydrated diameter, hence higher polarizability show to bind more strongly to the resin and are preferably exchanged in solution than those of relatively larger hydrated diameter if they are of similar charges. For example, 0.8, 0.6, 0.5 and 0.45 nm respectively are the hydrated diameters of Mg^{2+}, Cu^{2+}, Hg^{2+} and Pb^{2+}, therefore, the preference for and order of selectivity of the divalent ions in an ion exchange process is as follows: $Pb^{2+} > Hg^{2+} > Cu^{2+} > Mg^{2+}$. This is suggested as the reason for the higher adsorption and removal of Pb^{2+} than Cu^{2+} in the polluted water samples by both CSMKT and CAMKT. The reactions for the exchange of the metal ions by the resins are suggested in Schemes 4 and 5 viz:



Scheme 4: Exchange of Pb^{2+} in water with CSMKT.



Scheme 5: Exchange of Cu^{2+} in water with CAMKT.

5. CONCLUSION

In this study, kola nut testa, a nauseating waste that is taunted and trampled on has been converted to a value-added product and used to purify water. The results portray it as plausible way to ecosystem sustainability.

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