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Studies on Nigerian cashew nut shell liquid: Greening-up extraction process, chemical composition and cost effectiveness

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ABSTRACT

Extractions of cashew nut shell liquid (CNSL) have always widely been carried out with non-environmentally friendly solvents. Hence, greener solvents are desired as alternative to currently used solvents. Herein, batch extractions of Nigerian CNSL with greener solvents: ethyl acetate and cyclohexane mixture in different ratios were investigated in hot and cold system and results compared with conventional solvent (petroleum ether). Compositional studies of the extracted CNSL and its isolated components were done with Fourier-Transformed Infrared (FTIR), Nuclear Magnetic Resonance (NMR) spectroscopy and Ultra High-Performance Liquid Chromatography-Mass Spectrometry (UHPLC-MS). Cost effectiveness analysis for the extraction solvents and methods was also investigated. It was revealed that ethyl acetate and ethyl acetate-cyclohexane mixture at cold and hot conditions recorded higher CNSL yields than previous reports even at a lower liquid-to-solid ratio. Chemical composition and component quantity extracted did not significantly change under hot or cold system. The present composition of the Nigerian CNSL contains unusually higher amount of anarcardic acid (79 %) and cardanol (14 %) than ever reported. Additionally, degree of unsaturation in the alkyl chain of the CNSL is in the order triene>monoene>diene in the anarcardic acid and cardanol components of the liquid. Cost effectiveness analysis at a kilogramme scale revealed that the order of greenness of extraction route based on solvent type, energy requirement and condition of extraction is ethyl acetate-solvent cold system> ethyl acetate-hot system> ethyl acetate-cyclohexane-system> cyclohexane system > pet. ether system.

1. Introduction

Insufficient management of abundant agricultural wastes poses a serious challenge in emerging nations like Nigeria. A significant quantity of agricultural debris, including corn cob, banana stem, and rice husk, is generated through incorrect disposal practices. Cashew nutshell is an additional waste generated from agro-based processes. The improper disposal of this material results in significant environmental degradation on a broad scale. Researchers have been utilizing agro-based wastes from many processes to generate additional useful products, including resin, chemicals, renewable energy, and various value-added chemicals [1–7]. This is in line with one of the key principles of green chemistry which advocates for a reduction in waste generation and utilization of wastes that are unavoidably generated from processes [8,9].

Cashew (*Anacardium occidentale L.)* is a prominent cash crop that is extensively planted across various regions of the globe, particularly in Asia and Africa, where it exhibits a substantial production rate [10]. The cashew tree produces cashew apple, which serves as the primary product of the tree and serves various purposes. The apple is consumed in its raw form in various regions across the globe, and it is also utilized for the production of several important commodities, including apple fruit beverages, jelly, jam, syrup, and juice [11]. Consumption of raw cashew apple and the processing of this fruit into a valuable product result in a significant quantity of cashew agro-based waste as shown in Fig. 1. The cashew nut is a product derived from the cashew tree. Cashew kernels, which are the raw nuts without shells, often times, undergo a roasting procedure to get the final kernel product. These kernels are known to be a valuable source of cashew nut shell liquid (CNSL). CNSL is composed of anarcardic acid (60–70 %), cardol (10–20 %) and cardanol (3–10 %) and 2-methyl cardol (2–5 %) and others in trace amount [12]. The

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chemical structures of these molecules are shown in Fig. 1.

CNSL can be extracted with organic solvents using a Soxhlet apparatus or with supercritical carbon dioxide [13], or with superheated water [14]. Anacardic acid contains an aromatic carboxylic acid functional group with varying levels of unsaturation in the C-15 chain and is a useful chemical in the synthesis of biobased polymers [15,16], dyes [17], nanoparticles [18], etc. Cardol contains an aromatic ring having two hydroxyl functional groups with varying levels of unsaturation in the C-15 chain and has been largely applied in the synthesis of biobased polymers [19,20], hydrogel [21], nanoparticles [22]. Cardanol also possesses one hydroxyl group on aromatic ring attached to a C-15 carbon chain with varying levels of unsaturation. Cardanol has been used widely for polymer synthesis [20], additives [23], nanoparticles [24] etc.

Based on extraction processing methods, there are two classifications of CNSL, namely natural CNSL and technical CNSL. Cardanol, after the anarcardic acid component had been decarboxylated, constitutes a substantial portion of technical CNSL. Conversely, anarcardic acid serves as the primary constituent of natural CNSL.

Extraction of CNSL via Soxhlet process is widely achieved with organic solvents such as petroleum ether and chloroform [25]. Such solvents as these, which continue to face future increasing regulatory constraints because of environmental, health, and safety concerns, should not be for extractions [26–28]. According to green chemistry principles, toxic solvents should be avoided or completely eliminated and replaced with innocuous (greener) ones. Based on GSK's solvent selection guide, ethyl acetate, ethanol and cyclohexane are greener solvents compared to petroleum ether, dichloromethane and chloroform from the standpoint of environmental impact, health, safety and life cycle assessment [29].

Interests in using greener solvents to extract CNSL are growing. A few studies have applied ethanol, ethyl acetate, and cyclohexane in the extraction of CNSL [30,31]. However, most of these solvents have only been applied individually in extraction under hot systems. A synergistic performance could be achieved leading to improved extraction of CNSL when solvents are combined. Therefore, this study investigates the use of ethyl acetate and cyclohexane as greener alternatives for the extraction of CNSL under both hot and cold conditions. It also compares the cost effectiveness of using the solvents against traditional solvents under both extraction conditions. Additionally, chemical composition of the resulting extracts obtained under both conditions were profiled with ultra high-performance liquid chromatography-mass spectrometry (UHPLC-MS) and subsequently characterized using Fourier-transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy.

2. Materials and methods

2.1. Chemicals and reagents

Petroleum ether (40–60 °C, Baker, 90 %) cyclohexane (Baker, 99.5 %), ethyl acetate (Baker, 99.5 %), hydrochloric acid (34.5 %), n-hexane (Baker, 97 %), Ammonium hydroxide (25 %), methanol (Baker, 99.8 %), celite, activated charcoal, 3-pentadecyl phenol (TCI, 92 %) and cardanol (Biosynth Carbosynth). All chemicals were of analytical grade and were used as received.

2.2. Cashew nut shell collection

Large quantity of cashew nut shell (CNS) waste was collected from Huxley Industrial Limited, Lagos – Sagamu Expressway, Ogun State, Nigeria.

2.3. Cashew nut pre-treatment

Collected shells were kept in clean bags, comminuted in a milling machine, stored in an air tight container and kept in a refrigerator. Prior to extraction, refrigerated sample was dried in an oven for 96 hours at 60°C.

2.4. Extraction of CNSL with cold extraction method

Milled CNS, 50 g, was submerged into 100 mL of solvent of choice in a cleaned brown 250 mL conical flask, sealed tight and left for 72 hours The extracted cashew nut shell liquid (CNSL) was filtered, and the residues were kept for further use. The process was repeated two more times after the first extraction process. Solvent mixtures in ratios 1:1 and 1:2 for ethyl acetate and cyclohexane respectively was also used for

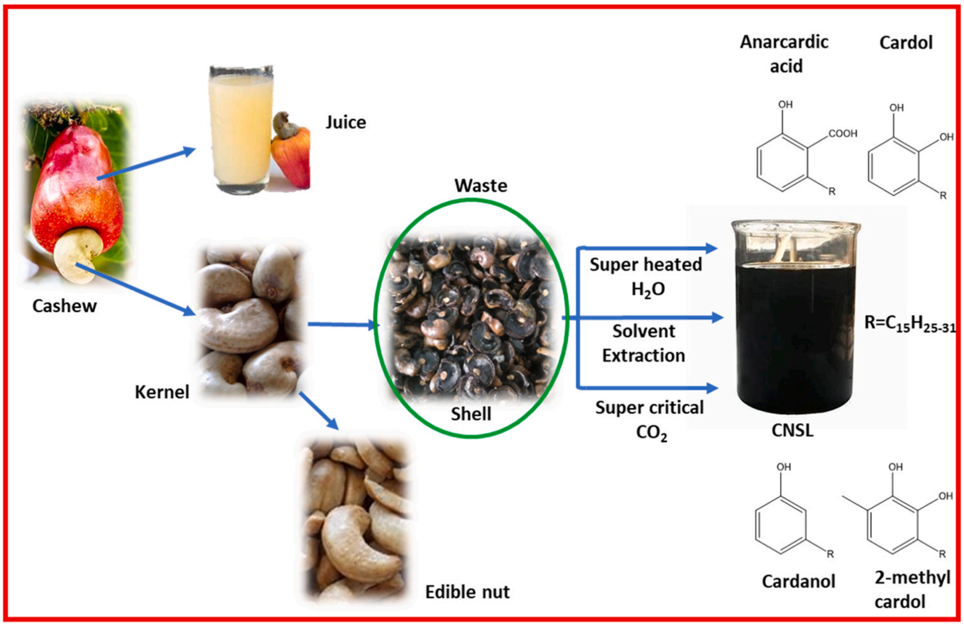

Fig. 1. Cashew shell originally obtained from cashew kernel, a waste from processed cashew nuts is a main source of CNSL via any of super heated water, solvent extraction and supercritical CO2 processes to yield anarcardic acid, cardol, cardanol and 2-methyl cardol.

extraction. Percentage yield of the oil recovered was calculated according to Eq. 1.

$$\%\text{yield} = \frac{\textit{Mass of extracted oil}}{\textit{Mass of cashew nut shell}} \times 100 \tag{1}$$

2.5. Extraction of CNSL using hot extraction method

CNSL was extracted from milled cashew nut shell using a Soxhlet extractor apparatus. The apparatus was thoroughly cleaned and assembled, and 100 mL of the solvent was transferred into a round bottom flask. Fifty grams (50 g) of the milled CNS was weighed and moved into the fitted thimble part of the extractor. The solvent in the flask was heated up to boil to its boiling point, which then condensed and returned to the flask. The extraction process lasted 4 hours until sufficient CNSL was obtained. Simple distillation was used to recover the oil from the solvent. The process was carried out in triplicate after the first extraction process. Solvent mixtures in ratios 1:1 and 1:2 for ethyl acetate and cyclohexane respectively was also used for extraction. Percentage yield of recovered oil was calculated according to Eq. 1.

2.6. Decarboxylation of recovered CNSL

Recovered CNSL (RCNSL), 500 g, was transferred into a round bottomed flask and heated for 3 hours at a temperature of 200 °C. Thin layer chromatography (TLC) using a mixture of cyclohexane and methanol in a ratio of 1:3 (mobile phase) was used to monitor the progress of decarboxylation of CNSL. The R_f values were calculated for RCNSL and decarboxylated oil (DCNSL).

2.7. Isolation of cardanol and cardol from DCNSL

2.7.1. Cardanol isolation

100 g of DCNSL was dissolved in 320 mL methanol and 200 mL ammonium hydroxide (25 %), stirred for 3.5 hours. N-hexane (4 ×200 mL) was used to extract the resulting solution. 5 % HCl, 100 mL, was used to wash the organic layer, followed by 100 mL distilled water. 10 g activated charcoal was added to the organic layer and stirred for 10 mins. The solution was filtered in a column through 15 g of celite, and the filtrate dried over anhydrous sodium sulphate and concentrated using a rotary evaporator to obtain pure cardanol [32].

2.7.2. Cardol isolation

Cardol was extracted by further extracting the methanolic ammonia solution (aqueous layer) with an ethyl acetate-hexane mixture in a ratio of 4:1 (2 ×200 mL). The resulting organic layer was removed using 5 % HCl (100 mL), followed by 100 mL distilled water. The resulting solution was dried over anhydrous sodium sulphate and concentrated to yield pure cardol [32].

2.8. Fourier transform infrared spectroscopy (FT-IR)

FT-IR analysis was performed on a Bruker vertex 70 v spectrophotometer. Samples were placed on the diamond prism followed by 16 background scans with sample measurement taken from 400 cm^{-1} to 4000 cm^{-1}.

2.9. Nuclear magnetic resonance spectroscopy (^1H and ^{13}C NMR)

Proton and carbon-13 (^1H and ^{13}C) NMR spectra of samples were taken on a Bruker 400 (100 MHz for ^{13}C and 400 MHz for 1 H) in $CDCl_3$ solvent.

2.10. Ultra high performance liquid chromatography-mass spectrometry (UHPLC–MS)

Sample, 0.5 mg, was dissolved in 1 mL solution containing acetonitrile-water (80:20 %) + 0.1 % formic acid. The solution was filtered through 0.2 μm syringe filter into a 2 mL vial and then analysed. HPLC analysis was carried out on a Chromolith Performance RP-18e column (Merck, Darmstadt, Germany). Solvent A was 0.1 % formic acid in water, and solvent B was acetonitrile. Separation of sample was achieved with isocratic elution using solvent A/B) 40/60 at a flow rate of 0.5 mL min^{-1}. The UV detection (Hewelett-Packard 1100) was performed at a wavelength of 240 nm and detected with an electrospray mass spectrometer in positive or negative mode, using MS scan.

3. Results and discussion

3.1. Solvent extraction of CNSL

Percentage yields of CNSL, also referred to as RCNSL, produced by cold and hot extractions using different greener solvents and pet. ether at liquid to solid ratio of 2:1 are shown in Table 1. Results of the cold extraction revealed that ethyl acetate with a 27.92 % yield is distinctly the best alternative to any other solvent/mixture considered. Cyclohexane, a non-polar solvent, which is expected to interact better with the hydrophobic group of the CNSL components, yielded 13.88 % oil followed by pet. ether, also a non-polar solvent, with a yield of 11.31 %. On the other hand, mixtures of ethyl acetate and cyclohexane (1:1) and (1:2) yielded 20.38 % and 17.2 % respectively. A higher CNSL extraction with the 1:1 mixture is a clear demonstration of ethyl acetate's strong affinity for the components of CNSL. Overall, extraction yield with ethyl acetate is twice higher than with both cyclohexane and pet. ether. The unprecedented extraction performance of ethyl acetate over these solvents could suggest that extraction of CNSL was possibly determined mainly by the interaction and association of solvent with the polar functional group and not the hydrophobic group in the CNSL components under this reaction condition.

A large-scale extraction of 1000 g CNS with 1200 mL pet. ether gave twice as much yield (24.5 %) as obtained when using 50 g CNS and 100 mL solvent with a 11.3 % yield as shown in Table 1. The reason for this higher yield even at a lower liquid to solid ratio (1.2:1) could be as a result of increased volume occupied by the solvent in the container leading to increased saturation of CNS fabrics.

Soxhlet extraction system did not witness much difference in CNSL yield, with ethyl acetate having a marginal 3.27 %, and 0.60 % over pet. ether and cyclohexane respectively. Expectedly CNSL yields under hot system are higher than at room temperature because of increased molecular interaction at elevated temperature resulting in improved extraction. Ethyl acetate: cyclohexane (1:1) mixture performed slightly higher (29.94 %) than when using only ethyl acetate (29.54 %). This could be as a result of synergistic interaction of both solvents with the

Table 1
Percentage yield of CNSL by cold and hot extraction methods.

Solvent	Yield of CNSL (%)	
	Cold*	Hot[a]
Ethyl acetate	27.92 ± 1.94	29.54 ± 1.30
Cyclohexane	13.88 ± 0.55	28.94 ± 0.71
Ethyl acetate: Cyclohexane (1:1)	20.38 ± 0.45	29.94 ± 0.41
Ethyl acetate: Cyclohexane (1:2)	17.20 ± 0.32	29.40 ± 0.38
Pet. Ether	11.31 ± 0.35	26.27 ± 0.31
Ethyl acetate	-	45.90[b]
Pet. Ether	24.50[c]	-

* Temperature (room), time (72 hours) and liquid to solid ratio (2:1)
[a] Temperature (60–80 °C), time (4 hours) and liquid to solid ratio (2:1)
[b] Temperature (80 °C), time (8 hours) and liquid to solid ratio (4:1)
[c] Large scale extraction of 1200 mL solvent to 1000 g nut shell (1.2:1)

CNSL components at elevated temperature.

When using a larger solvent to solid ratio, that is, 400 mL ethyl acetate in 100 g cashew nut, that is 4:1, yield almost doubled up to 45.9 %. This is because more CNS fabric is being exposed to extraction in the presence of higher volume of solvent.

CNSL yields from this study compared favourably higher than reported elsewhere for toluene (23.2 %), ethanol (8.3 %) and iso-octanol (26.94 %) [31,33]. Although oxygenated solvents such as methyl iso-butyl ketone and methyl ketone yielded 33.1 % and 30.5 % respectively at extraction at 60–100 °C, liquid to solid ratio (10:1) [31], these solvents are not environmentally friendly, except for ethanol. A recent study reported cyclohexane to have extracted CNSL 27.12 % at 50 ℃, 60 min and liquid to solid ratio of 5:1 in an optimised system [30]. Therefore, it is interesting to record a higher yield for ethyl acetate and ethyl acetate-cyclohexane mixture at cold and hot conditions than previously published reports even at a lower liquid to solid ratio.

3.2. Decarboxylation of RCNSL

Anarcadic acid, cardanol, cardol, and traces of 2-methyl cardol are the major constituents of RCNSL. Decarboxylation of RCNSL was carried out to remove anarcardic acid component from the oil. Decarboxylation was achieved by simply heating up RCNSL in a flask at 200 °C for 3 hour and progress monitored on a thin layer chromatography plate. Retention factors, R_f, 0.86 and 0.82 were calculated for the decarboxylated product (DCNSL) and RCNSL respectively. RCNSL contained a carboxylic acid group and thus expected to move slower on the plate due to a stronger affinity for silica than DCNSL which contains only hydroxyl groups, although the values are close.

3.3. Isolated cardanol and cardol from DCNSL

Quantitative yields were 61.2 % and 16.2 % for isolated cardanol and cardol respectively. Achieving equilibration between the methanolic ammonia solution (aqueous layer) and the organic layer was difficult, and this affected the purity of cardol isolated in the second stage.

3.4. Chemical compositional analysis of RCNSL, DCNSL, ICL and IC

3.4.1. FTIR analysis

FTIR spectra of recovered CNSL, decarboxylated CNSL and raw cashew nut shell waste is shown in Fig. 2a while Fig. 2b shows the spectra of isolated cardol and cardanol. Noticeable among all the spectra is the broad band covering from 3000 – 2000 cm^{-1} which signifies the presence of COOH functional group. The broad peaks at 3335/3334/3284 cm^{-1} are all indications of O-H stretching of phenol which is inherent in the structures of phenolic components of CNSL. Peaks at 3009 cm^{-1} indicate =C-H stretching of aromatic ring while the 2924/2854 cm^{-1} shows the C-H stretching vibration of the methylene group (symmetric and asymmetric group). It should be noted that the disappearance of peak at 1645/1605 cm^{-1} in the spectrum of decarboxylated CNSL indicated that no C═O stretching due to decarboxylation. 1590/1589 cm^{-1} is for C═C-C- aromatic ring. Peak at 1708 cm^{-1} noticed on isolated cardol spectrum may be due to residual solvent used.

3.4.2. Proton and carbon-13 NMR analysis

Proton NMR spectroscopy results of RCNSL showed the anacardic acids, cardol and cardanol present an aromatic moiety with absorption bands at ~7.25–7.18 ppm, ~7.10–6.94 ppm, and ~6.56–6.51 ppm; the methine protons of the double bonds for the monoene, diene and triene absorb within ~6.25–4.75 ppm (Fig. 3a). The methylene proton on the alkyl chain attached to the aromatic ring absorb at ~2.8–2.6 ppm while other methylene protons and methyl protons (for monoene and diene) on the alkyl chain were absorbed at ~2.4–0.8 ppm. The broad peak at ~8.0–7.5 ppm could sometimes be due to COOH proton although this is not within the usual chemical shift range where it is found. COOH proton has been reported to absorb at ~7.8 ppm [34]. The DCNSL proton NMR spectrum showed similar chemical shifts except in the disappearance of the peak at ~8.0–7.5 ppm which could be said to have confirmed the decarboxylation as shown in Fig. 3b.

Carbon-13 NMR spectra showed that RCNSL had COOH carbon at 163.68 ppm which disappeared in DCNSL spectrum, confirming successful decarboxylation.

3.4.3. UHPLC–MS analysis

UHPLC analysis of standards namely: commercial 3-pentadecylphenol (Cardanol 15:0) and commercial cardanol alongside RCNSL, DCNSL, ICL and IC are presented in Fig. 4 and Table 2. Components were detected by MS in the positive $[M+H]^+$ or negative $[M-H]^+$ modes. Based on approximate peak area composition, commercial saturated cardanol sold as 3-pentadecyl phenol contained ~93 % cardanol 15:0 while commercial cardanol contained ~4 % cardol, ~70 % cardanol (triene), ~8 % cardanol (diene), ~15 % cardanol (monoene) and ~2 % cardanol (saturated) as shown in Fig. 4a and Table 2. Fig. 4a and Table 4 shows that RCNSL contain a mixture of (saturated **12**; monoene **3**, **7**, **11**; diene **2**, **6**, **10**; and triene **1**, **5**, **9** in the fifteen-carbon side chain) ~79 % anacardic acid, ~14 % cardanol, and ~6 % cardol. Results further revealed abundance according to level of unsaturation in this order: triene>diene>monoene in cardol, triene>monoene>diene in anarcardic acid and triene>monoene>diene>saturate in cardanol. This composition of cardol to anacardic acid to cardanol ratio is outside the range that has been mostly reported for CNSL extracted in the literature. Previous studies reported that CNSL obtained from solvent extraction is

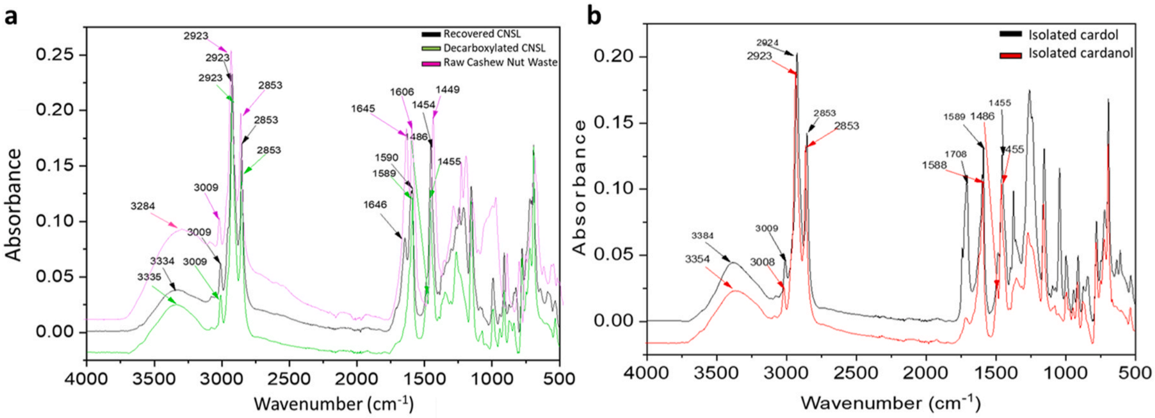

Fig. 2. FT – IR Spectra of (a) recovered CNSL, decarboxylated CNSL and raw cashew nut waste; (b) isolated cardol and cardanol.

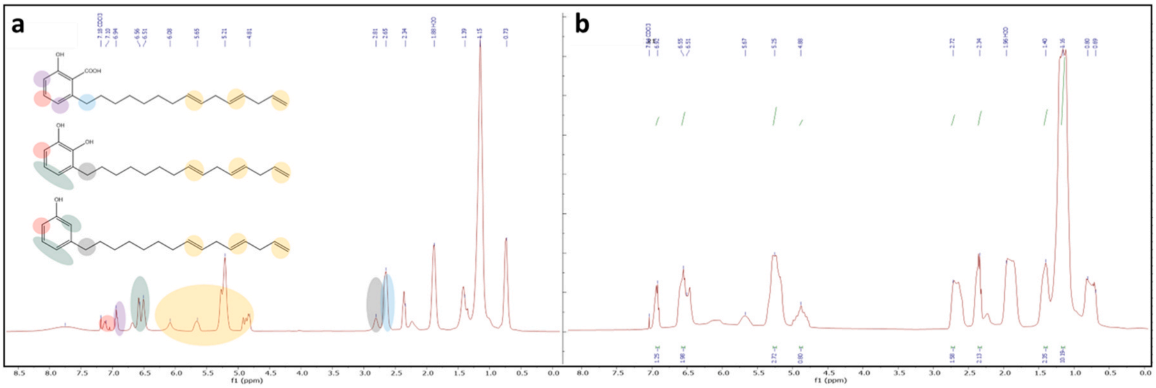

Fig. 3. Proton NMR spectrum for (a) Recovered CNSL and (b) Decarboxylated product of recovered CNSL.

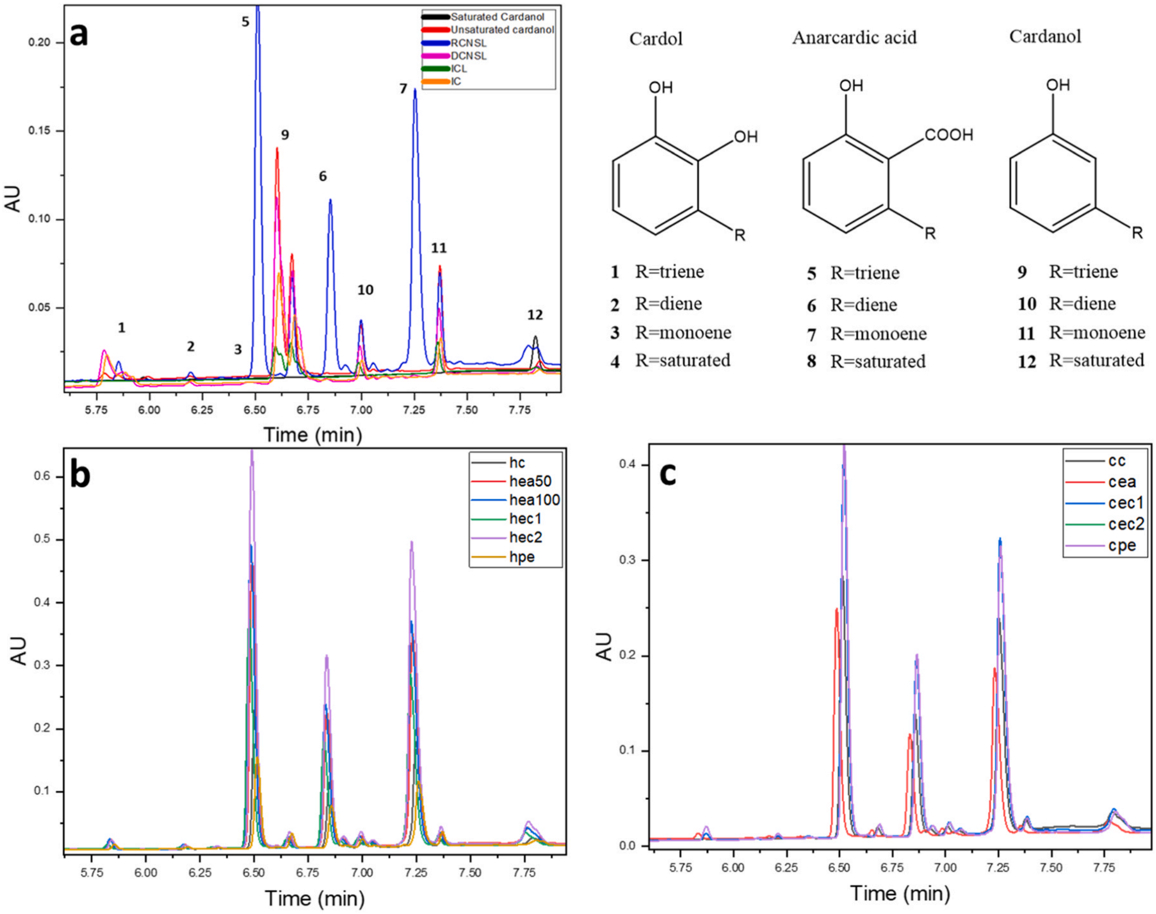

Fig. 4. UPHLC chromatograms of (a) Saturated cardanol, unsaturated cardanol, RCNSL, DCNSL, IC and ICL. (b) Chromatograms of extracts from using hot cyclohexane, hot ethyl acetate with 50 g residue, hot ethyl acetate with 100 g residue, hot ethyl acetate: cyclohexane (1:1), hot ethyl acetate:cyclohexane (1:2) and hot pet. Ether. (b) Chromatograms of extracts from using cold ethyl acetate, cold cyclohexane, cold ethyl acetate: cyclohexane mixture and cold pet. Ether.

usually composed of anacardic acid (60–65 %), cardanol (10–15 %), cardol (20 %) [35,36], noting particularly a higher level of cardol over cardanol. Additionally, the level of unsaturation in the phenolic alkyl chain is usually triene>diene>monoene contrary to what was obtained in the present study, although this is in line with what was obtained in the commercial cardanol purchased from Biosynth Carbosynth as stated earlier. Unfortunately, most studies that reported chemical composition of CNSL have mainly originated from India and Brazil [35,37,38]. Source of CNSL could be the only reasonable factor responsible for these variations. DCNSL contained ~84 % cardanol, ~15 % cardol and <1 % anarcardic acid as shown in Fig. 4a and Table 2. IC contained ~23 % cardol and ~77 % cardanol while ICL contained ~2 % cardol and ~98 % cardanol as shown in Table 2 respectively. The purity of ICL obtained in this study is higher than that of the commercial cardanol used. Elevated level of cardanol in IC suggests that the methanolic layer had a strong affinity for cardanol, hence it remained in the layer and largely contaminated the isolation of cardol in the next step.

Comparing the composition of CNSL from different solvent extracts in both hot and cold systems, a quick examination of the chromatograms (Fig. 4b and c) revealed that there was no significant difference in the chemical composition of the extract despite different extraction conditions.

Table 2
Chemical composition of saturated cardanol, commercial cardanol, RCNSL, DCNSL, ICL and IC as assigned based on detection by MS.

Sample Name	Retention time (min)	Area (%)	Molecular Weight (g/mol)	Detection Mode $[M+H]^+$ or $[M-H]^+$	Compound
Saturated cardanol (std)					
	5.971	7.16	-	-	-
	7.822	92.84	304.28	-	12
Commercial cardanol					
	5.787	1.63	314.22	315.24	1
	5.851	1.28	314.22	315.24	1
	5.991	0.49			1
	6.190	0.36	316.24	317.29	2
	6.602	45.13	298.23	299.22	9
	6.672	24.72	298.23	299.22	9
	6.757	0.23	-	-	-
	6.998	7.80	300.25	299.22	10
	7.055	0.26	300.25	299.22	10
	7.371	16.53	302.26	-	11
	7.848	1.56	304.26	-	12
RCNSL					
	5.856	0.49	314.22	315.27	1
	6.511	34.99	342.22	341.24	5
	6.673	6.82	298.23	299.28	9
	6.854	15.11	344.24	345.35	6
	7.000	2.52	300.25	299.22	10
	7.056	0.34	-	-	-
	7.196	0.33	320.27	319.27	4
	7.253	29.05	346.26	345.29	7
	7.371	5.70	302.26	-	11
	7.788	2.54	-	-	-
	7.828	1.67	304.28	-	12
DCNSL					
	5.786	10.10	314.22	315.27	1
	5.872	3.50	314.22	315.27	1
	5.903	1.39	314.22	315.27	1
	6.187	0.48	316.24	317.29	2
	6.470	0.62	342.22	341.24	5
	6.601	41.72	298.23	299.22	9
	6.674	26.94	298.23	299.22	9
	6.994	4.55	298.23	299.22	9
	7.367	9.28	302.26	-	11
	7.412	0.15	-	-	-
	7.832	1.26	304.28		12
IC					
	5.598	15.62	314.22	315.27	1
	5.692	6.32	314.22	315.17	1
	6.013	0.82	314.22	315.27	1
	6.443	39.22	298.23	299.22	9
	6.521	25.42	298.23	299.22	9
	6.686	0.11	298.23	299.22	9
	6.853	3.88	300.25	301.5	10
	7.242	7.54	302.26	-	11
	7.695	1.08	-	–	-
ICL					
	5.419	0.56	314.22	315.27	1
	5.699	1.00	314.22	315.17	1
	6.594	20.64	298.23	299.22	9
	6.618	13.30	298.23	299.22	9
	6.667	25.09	298.23	299.28	9
	6.696	9.74	298.23	299.22	9
	6.987	8.04	298.23	299.22	9
	7.045	0.39	300.25	301.5	10
	7.360	17.21	302.26	-	11
	7.824	1.82	304.28	-	12

3.4.4. Cost effectiveness analysis of extraction process with solvents

One of the challenges with embracing greener solutions is the high operational cost that industries incur leading to high market price of products. Hence, it is necessary to investigate the cost effectiveness of using the solvents in large scale extraction of CNSL. According to Merck chemicals, the market price of analytical grade ethyl acetate, cyclohexane and pet. ether is as listed in Table 3. By extrapolating from the yields obtained following conditions applied in Table 1 for cold and hot systems at a liquid-to-solid ratio 2:1, the cost of extracting 1 kg of CNSL was calculated. Results, presented in Table 3, showed that it will cost £201.30 to extract 1 kg of CNSL with ethyl acetate in cold system which is as twice less than the cost when using either cyclohexane or pet. ether. Ethyl acetate-cyclohexane mixture is next in line, requiring £291.20 to extract 1 kg CNSL. However, it will cost between £190.20 and £215.90 for all the solvents to extract 1 kg of CNSL under a hot system.

Additionally, the extraction process was ranked in increasing greenness based on three parameters: (i) the nature of solvent, (ii) conditions of extraction and (iii) cost implications as outlined in Table 3 footnote. A maximum scorable point of 2 was awarded for greenness of solvent used, 2 for those requiring no extra heating and 2 for those costing less than £200.00 to extract 1 kg. Obviously, the ethyl acetate-only solvent route is the most desirable in terms of greenness. As shown in Table 3, the ethyl acetate systems are the greenest routes ranking 5. Apparently, the ethyl acetate-cyclohexane hot system is the next ranked 4.5 despite energy cost that will be added. Following next in ranking is the ethyl acetate-cyclohexane cold systems, 3.5 and then the cyclohexane hot and cold systems, 3. The pet. ether system comes last and ranked 2 essentially because of their loss of green credential.

4. Conclusion

Ethyl acetate and cyclohexane and their mixture are greener solutions for extraction purposes when compared to other commonly used counterparts such as petroleum ether and chloroform. In this study, ethyl acetate, cyclohexane and their mixture were used to extract CNSL from cashew nut shell waste of Nigeria origin under different conditions. It was demonstrated that the solvent either as an individual or a mixture extracted higher amount of cashew nut shell liquid under hot and cold systems than when using petroleum ether. Specifically, ethyl acetate was found to yield twice CNSL as much as obtained in other solvents. Both ethyl acetate and cyclohexane and their mixture gave the highest CNSL yield when compared with other common and oxygenated solvents ever reported. Findings revealed that the cashew nut shell liquid is composed of anarcardic acid, cardanol and cardol. The anacardic acid content of this liquid is higher than the range usually reported for the acid in any CNSL, this being attributed possibly to the origin of the cashew. Overall, the use of ethyl acetate solvent will find ready and speedy application in the industry as this study reveals that it is the most cost effective and greenest route to extract CNSL.

CRediT authorship contribution statement

Michael Olusegun Alaka: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Data curation. **Joseph Kolawole Ogunjobi:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Methodology, Formal analysis, Conceptualization. **Olugbenga Oludayo Oluwasina:** Writing – review & editing, Supervision, Methodology. **Labunmi Lajide:** Writing – review & editing, Supervision, Project administration, Methodology.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Michael Alaka reports financial support was provided by Tertiary Education Trust Fund. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 3
Cost effectiveness and greenness ranking of solvents used for large scale extraction of CNSL under cold and hot conditions.

Solvent		Cold		Hot	
	Cost/L (£)	Cost to produce 1 kg CNSL (£)	Greenness$^{\Omega}$ ranking	Cost to produce 1 kg CNSL (£)	Greenness$^{\Omega}$ ranking
Ethyl acetate	56.20[39]	201.30	5	190.20	5
Cyclohexane	62.50[40]	450.20	3	215.90	3
Ethyl acetate: Cyclohexane (1:1)	59.35	291.20	3.5	198.20	4.5
Pet. Ether	52.60[41]	464.60	2	200.30	2

$^{\Omega}$ Scoring Indices: **Nature of solvent:** 2 point for ethyl acetate, 1.5 point for ethyl acetate-cyclohexane mix., 1 point for cyclohexane and 0 point for pet. ether. **Condition of extraction**: 2 point for cold system and 1 point for hot system. **Cost of extraction**: 2 point for $<$ £200, 1 point for £200–250 and 0 point for $>$ £250.

Data Availability

No data was used for the research described in the article.

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