Exhaustive valorization of cashew nut shell waste as a potential bioresource material

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In this paper, we report extraction of cashew nut shell liquid (CNSL) from cashew nut shell waste (CNSW) and further use of residues for generation of activated carbon for removal of heavy metals and methylene blue (MB). Solvent extraction yielded 24.6 ± 0.4%, 38.2 ± 0.4% and 40.1 ± 0.9% for petroleum ether, hexane and ethanol respectively. Phytochemical screening showed presence of alkaloids, carbohydrates, saponins, phenols, tannins, flavonoids, amino acids, terpenoids, proteins, steroids, glycosides and carboxylic acids. The CNSL had a pH of 3.2, viscosity (104.6 ± 1.8 mPa s), moisture (6.5%), ash (1.6 ± 0.1%), refractive index (1.52 ± 0.001), specific density (0.9561 ± 0.0002 g/cm³), acid value (118.7 ± 9.2 mg KOH/g), free fatty acid value (60.1 ± 4.7%), saponification number (138.1 ± 3.2 mg KOH/g) and iodine value (188.1 ± 2.3 mgI 2/100 g). The average percentage removal of Cu (II), Pb (II), Cd (II) and Zn (II) was 99.4 ± 0.5, 95.4 ± 1.5, 99.5 ± 0.1, 98.4 ± 0.1%, and removal efficiency of MB at 50, 150, 250 and 350 mg/L was 99.63, 97.66, 96.48 and 94.81%, respectively. Equilibrium data were best described by the Freundlich isotherm model. The maximum monolayer adsorption capacity was 12.1 mg/g. The adsorption kinetics conformed to pseudo-second-order model. ∆G° was negative and a ΔH° of +22.76 kJ/mol indicated that adsorption was endothermic. The ΔS° (+0.086 kJ/mol/K) showed that there was spontaneous interaction of the solution and adsorbate. These results show that CNSW is a potential bioresource for CNSL production for use in the paints, varnishes, surface coatings, agrochemicals and ethnomedicine industries. Residual shells can be exploited as fuels or converted to activated carbon for use as low-cost filters in water purification.

Abbreviations

AC  Activated carbon  
CIDP  Cashew Infrastructure Development Project  
CNS  Cashew nut shell  
CNS-AC  Cashew nut shell-activated carbon  
CNSL  Cashew nut shell liquid  
CNSW  Cashew nut shell waste  
DRGS  Directorate of Research and Graduate Studies  
FFA  Free fatty acid  
GRZ  Government of the Republic of Zambia  
MB  Methylene Blue  
MIN  Minutes  
NASREC  Natural and applied sciences research ethics committee  
RPM  Revolutions per minute  
SEM  Standard error of the mean  
UNZA  University of Zambia

The cashew tree (Anacardium occidentale) is a native of Brazil and the Lower Amazons. The major producing countries of cashew are Tanzania, India, Mozambique, Sri Lanka, Kenya, Madagascar, Thailand, Malaysia, Indonesia, Nigeria, Senegal, Malawi and Angola1. In Zambia, Cashew trees were first introduced in 1940s by the Portuguese traders in Western Province (then, Barotseland), an area characterized by Kalahari sandy soils that

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are relatively poor for most conventional crops. In order to diversify the economic base of the poor households in the Western Province, the Government of the Republic of Zambia (GRZ) promoted the planting and processing of cashew trees in the 1980s. However, the growth of the cashew industry was very slow due to low production and lack of marketing and processing facilities.

In 2015 Zambia acquired a loan from Africa Development Bank under the Cashew Infrastructure Development Project (CIDP) to boost cashew nut production, as well as increasing production in the province that has largely remained poor for a long time. In Zambia, cashew is grown mainly for its kernels while the shells are discarded in the environment as waste hence, contributing to the already existing waste management crisis in the country. However, unlike other solid wastes, the cashew nut shell (CNS) harbour’s a dark brown viscous oil called cashew nut shell liquid (CNSL), located in the soft honeycomb structure found between the inner and outer shell. Cashew nut shell liquid contributes approximately 30–35% to the total weight of shell and is by far the most important constitute of the shell. It is a cheap, abundantly available, and renewable raw material with diverse industrial applications and biological activities. Technical CNSL is obtained by heating natural CNSL at temperatures above 180–200 °C. During the heat process, the thermolabile anacardic acid decarboxylate and converts to cardanol, leading to high content of cardanol (60–65%) in technical CNSL. This form of CNSL has found wide industrial applications as raw material in friction linings, paints, varnishes, laminating, epoxy resins, foundry chemicals, plastic formulations and as antioxidant in biodiesel. The innumerable industrial applications of CNSL are based on the fact that it leads itself to polymerization by various means. Simple phenols from petrochemical feedstocks have restrictions hence, the range of products obtained from them are few. The current rise in the prices of petrochemical feedstocks as well as concerns of environmental pollution and depletion of natural reserves, puts CNSL at the center stage as the best sustainable alternative source of renewable energy.

Its advantages surpass those of other competing renewable bioresources such as vegetable and corn oils. Cashew nut shell liquid is non-edible hence, it does not put pressure on the food supply chain, and the fact that it is sourced from waste raw materials, it does not compete for production land. Other parts of the Anacardium occidentale plant have been exploited for their medicinal values. The fruit juice and the nut shell oil are both said to be folk remedies for cancerous ulcers, elephantiasis and warts. The oily substance from pericarp is used for cracks on the feet. Old leaves are applied to skin afflictions and burns. In Ghana, the bark and leaves are used for sore gums and toothache. Decoction of the astringent bark is suggested for severe diarrhea and thrush. In India, bark is used in herbal tea for asthma, cold and congestion and as an antidote for snake bites. Other uses of cashew nut shell liquid derivatives include anticancer and cardiovascular activity. In addition, residual shells after extraction of CNSL can be exploited as a source of fuel, or as gasifier feed stocks, or can be convert to bio-filters to remove heavy metals and organic pollutants from waste waters through adsorption processes. The nature of CNS would make synthesis of bio-filters very cheap and accessible to the locals. The increase in chemical industries, agricultural activities and abuse of water resources has contributed greatly to water contamination by heavy metals and organic compounds. The maximum permissible limit of cadmium, zinc, copper and lead in drinking water by World Health Organization are 0.003 mg/L, 3 mg/L, 2 mg/L and 0.01 mg/L respectively. Therefore, removal of these heavy metals from drinking water is a priority. In other studies, pharmaceutical products have been shown to have low biodegradability and hence find themselves in wastewater and surface waters. Other studies have shown potential of contamination of water and soil by agricultural chemicals such as pesticides. Conventional techniques for removal of waste from water includes; ion exchange process, chemical precipitation, membrane separation, ultra-filtration, chemical oxidation, reverse osmosis process and many others. These techniques are costly and requires high energy input. On the other hand, adsorption has a greater advantage because it is simple, safe and less costly. The main objective of this research was to extract CNSL, determine its phytochemical composition and physicochemical properties, as well as designing a low-cost adsorbent material from defatted shells which can be used to remove heavy metals and organic pollutants from water. Various literature cited gave this research room for adding baseline data for the Zambian grown cashew, as the family Anacardiaceae covers over 70 genera in which more than 600 species are distributed in tropical, sub-tropical and temperate regions in the world hence the plant cannot be easily generalized that Zambia has only one family or subspecies. Hence this paper seeks to evaluate the value of cashew nut shell waste for potential valorisation, wealth and employment creation under small scale enterprises.

Materials and methods

Materials. Concentrated sulfuric acid (H₂SO₄), hydrochloric acid (HCl) and nitric acid (HNO₃) (purchased from Hi-Media) were a kind donation by Medical Stores Limited (Ministry of Health, Zambia). Analytical grade Mercuric chloride (HgCl₂), sodium carbonate (Na₂CO₃), sodium nitrate (NaNO₃), metallic magnesium (Mg), lead acetate (C₂H₃O₂Pb), sodium hydroxide (NaOH) and methylene blue (C₁₄H₁₈CIN₃S) (BDH) were all supplied by the Department of Chemistry, University of Zambia.
Cadmium nitrate tetra-hydrate (Cd(NO₃)₂·4H₂O), Zinc nitrate hexa-hydrate (Zn(NO₃)₂·6H₂O), Copper (II) sulphate (CuSO₄·5H₂O), lead (II) nitrate (Pb(NO₃)₂), hexane (C₆H₁₂), ethanol (C₂H₅OH), petroleum ether (40–60 °C), chloroform (CHCl₃), acetic anhydride ((CH₃CO)₂O), methanol (CH₃OH), acetic acid (CH₃COOH), ninhydrin, potassium iodide (KI), potassium iodate (KIO₃), Sodium thiosulphate (Na₂S₂O₄), ferric chloride (FeCl₃), potassium sodium tartrate (KNaC₄H₄O₆·4H₂O), picric acid (C₆H₃N₃O₇), α-naphthol (C₁₀H₇OH), were purchased from Sigma Aldrich under Merck.

**Methods.**

**Sample preparation.** Pre-processed (roasted) CNS were collected from small-scale cashew nut processors in Mongu District of the Western Province of Zambia. Upon their arrival in the laboratory, the shells were washed several times with tap water and twice with enough distilled water to remove all the dirty, contaminants and debris. After washing, the shells were air-dried under the shade for 7 days. Once dry, the shells were ground to homogeneity using a Thomas-Model-4-Wiley-Mill fitted with a 2 mm sieve, placed in airtight bags and stored in a refrigerator at 4 °C to avoid biological and chemical degradation of the constituents.

**Extraction of cashew nut shell liquid.** The extraction of CNSL from CNSW was carried out by using a soxhlet extractor system as described by 6,39. Briefly, 20.00 g of ground CNSW was put into a clean 33 × 100 mm cellulose thimble (Whatman) and extracted with a particular solvent for 8 h. After several cycles of extraction, the soxhlet apparatus was disassembled and the remaining solvent in the extracting chamber was added to the other extract in round bottomed flask, and evaporated under mild conditions with a Buchi Rotavapor until a constant oily mass remained.

**Phytochemical screening.** Twenty grams of ground CNS were exhaustively extracted under cold conditions in 200 mL acetone, ethanol and hexane respectively for 72 h with interval shaking in the dark. The organic solvents were recovered under mild pressure with a Buchi Rotavapor. The effect of solvent on phytochemical is presented in Table 1. The water extract was warmed at 60 °C for 10 min and left to stand for a total of 24 h with interval shaking. Phytochemical analysis for alkaloids, flavonoids, glycosides, phenols, saponins, steroids, tannins and terpenoids was done according to Refs.40–45 and for amino acids, carbohydrates, carboxylic acids and proteins46 with minor modifications. All reagents used in this process were prepared fresh before use.

**Physicochemical characterization of cashew nut shell liquid.** Methods by Refs.1,11,47 with minor modifications were followed for characterization of the CNSL extracted from the roasted CNS. Moisture content was determined by heating 2.0 g of sample to a constant weight in a crucible placed in a Memmert oven (Memmert GmbH + Co. KG) maintained at 105 °C for 3.5 h. The crucible was cooled in the desiccator and reweighed, the mass change in the sample was recorded. Ash was determined by incinerating 1.0 g sample in a Carbolite muffle furnace (HTF ELP4, Bamford, Sheffield UK) maintained at 550 °C for 5 h using sintered glass crucibles. Specific gravity was determined using a standard pycnometer bottle with a stopper. The 25 mL bottle was filled with distilled water and the CNSL respectively and weighed independently. The acid and free fatty acid values were determined using the methods of Refs.48–50. The saponification number and iodine values were determined by the method of Ref.51. Refractive index at 20 °C was determined using Bellingham Stanley Abbe refractometer. Viscosity was determined by the Oswald viscometer using distilled water as a reference at 24 °C. The pH was determined with a calibrated pH meter (Grison base 20).

**Preparation of activated carbon adsorbent.** The defatted cashew nut shells were pre-heated at 110 °C for 2 h using a Carbolite AAF 11/7 Furnace at a heating rate of 10 °C/min. Chemical activation with 50 wt% sulphuric acid was carried out using an impregnation method. The impregnation ratio of sulphuric acid to the raw materials was 2: 1. Thus, 60 g of the pre-heated precursors were soaked in 86 mL of 50 wt% sulphuric acid for 24 h.

| Phytochemical compounds | Aqueous | Ethanol | Acetone | Hexane |
|-------------------------|---------|---------|---------|--------|
| Carbohydrates           | ++      | +       | +       | +      |
| Proteins                | −       | +       | +       | ++     |
| Amino acids             | ++      | −       | −       | +      |
| Phenols/tannins         | ++      | +++     | +++     | +++    |
| Alkaloids               | −       | +       | +       | +      |
| Saponins                | +       | ++      | ++      | ++     |
| Flavonoids              | ++      | ++      | ++      | ++     |
| Steroids                | +       | +       | +       | +      |
| Terpenoids              | −       | +       | +       | +      |
| Glycosides              | −       | −       | −       | +      |
| Carboxylic acid         | +       | +       | +       | +      |

Table 1. Phytochemical Screening results for CNSW extracted with different solvents. Table Shows the phytochemicals present in various solvent types. Hexane was chosen as a solvent of choice due to extraction of all tested secondary metabolites.
After soaking, the precursor was dried in an oven at 110 °C. The dried precursors were carbonized in the same furnace as before at 400 °C for 3 h at a heating rate of 10 °C/min. The carbonized material was cooled to room temperature and washed several times with hot distilled water until the pH was neutral. The cooled activated carbon was then dried in an oven for 4 h, ground and sieved using a 0.5 mm sieve and stored in air-tight bottles until use.

**Analysis of heavy metals and methylene blue (MB).** Heavy metal concentrations were measured on a PerkinElmer Analyst 400 Atomic absorption spectrophotometer and a Shimadzu UV-2600 spectrometer was used to determine the concentration of Methylene blue standard before and after adsorption.

**Adsorption experiments.** Adsorption percentage (%) and the amount of adsorbate per unit mass of activated carbon ($q_e$) was calculated using Eqs. (1) and (2).

\[
\% \text{ Adsorption} = \left( \frac{C_o - C_e}{C_o} \right) \times 100,  
\]

\[
q_e = \frac{(C_o - C_e) \times V}{m},  
\]

where; $C_o$ is the initial concentration of adsorbate (mg/L), $C_e$ is the final concentration of adsorbate after adsorption (mg/L), $q_e$ is the amount of adsorbate adsorbed at equilibrium (mg/g), $m$ is the mass of activated carbon used (g) and V is the volume of adsorbate solution used (mL).

**Adsorption isotherm models.** Three commonly models used to fit adsorption experiment results are the Langmuir, Freundlich and Temkin adsorption isotherm models.

**The Langmuir isotherm model.** The isotherm assumes that the monolayer adsorption process happens between the adsorbate and homogenous surface of the adsorbent. The binding sites have the same affinity for adsorption. The linear equation is given below:

\[
\frac{C_e}{q_e} = \frac{1}{K_Lq_{max}} + \frac{C_e}{q_{max}},  
\]

where; $q_e$ is the metal ions adsorbed (mg/g) at equilibrium, $C_e$ is the equilibrium concentration (mg/L), $q_{max}$ is the monolayer adsorption capacity (mg/g) and $K_L$ is the Langmuir adsorption constant which is related to the energy of adsorption and is a measure of the metal ions affinity to the adsorption sites. If the magnitude of $K_L$ is large, the interaction of the adsorbent with the adsorbate molecules will be more while a smaller value indicates a weak interaction. The Langmuir parameters $q_{max}$ and $K_L$ were calculated from the slope ($1/q_{max}$) and intercept ($1/q_{max}K_L$) of the plot of $C_e/q_e$ versus $C_e$. An important characteristic of the Langmuir isotherm can be expressed in terms of the dimensionless equilibrium parameter or the separation factor, $R_L$, which is defined as;

\[
R_L = \frac{1}{1 + K_L C_o},  
\]

where; $K_L$ is the Langmuir adsorption constant and $C_o$ is the initial metal ion concentration. The value of the separation factor gives an indication of the shape of the isotherm and the nature of the adsorption process. The values of the $R_L$ between 0 and 1 indicates favourable adsorption, unfavourable adsorption occurs when $R_L$ is greater than 1 and adsorption is linear when $R_L$ is equal to 1.

**The Freundlich isotherm model.** The Freundlich isotherm model is an empirical model that explains that adsorption occurs on an unevenly distributed or heterogeneous surface of the adsorbent. The adsorbent surface has different affinity and energy for adsorption. Stronger binding sites are occupied first and then the binding strength decreases with the rise in the degree of site occupation. It is represented by the equation below;

\[
\log q_e = \frac{1}{n} \log C_e + \log K_F,  
\]

where; $q_e$ is the metal ions adsorbed at equilibrium (mg/g), $C_e$ is the equilibrium concentration (mg/L), and $K_F$ is the Freundlich constant and $n$ is the adsorption intensity. The value of $n$ indicates the degree of non-linearity between metal ions concentration and its adsorption in the following manner; if $n$ is equal to 1 ($n = 1$) then adsorption is linear, adsorption becomes a favourable physical process when $n$ is greater than 1 ($n > 1$) and when $n$ is less than 1 ($n < 1$) then adsorption is a chemical process. From the slope $(1/n)$ and intercept $(\log K_F)$ of the plot of $\log q_e$ versus $\log C_e$, the constant $K_F$ and $n$ can be calculated.

**Temkin isotherm model.** The Temkin isotherm model considers the effect of indirect adsorbate-adsorbent interaction on the adsorption process. It is based on the assumption that the heat of adsorption of all the molecules in a layer decreases linearly due to increase in surface coverage of the adsorbent. The decrease in heat of adsorption is linear rather than logarithmic, as implied in the Freundlich isotherm. Further, the adsorption is characterized by uniform distribution of binding energies, up to a maximum binding energy. The Temkin isotherm model is represented by the following equation:

\[
C_e q_e = 1 K_L q_{max} + C_e q_{max},  
\]

where; $C_e$ is the equilibrium concentration (mg/L) and $q_{max}$ is the maximum adsorption capacity. The parameters $K_L$ and $q_{max}$ can be calculated from the slope $(1/q_{max})$ and intercept $(1/q_{max}K_L)$ of the plot of $C_e/q_e$ versus $C_e$. The value of $R_L$ between 0 and 1 indicates favourable adsorption, unfavourable adsorption occurs when $R_L$ is greater than 1 and adsorption is linear when $R_L$ is equal to 1.
where; $K_T$ is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy, $b$ is related to the adsorption heat, $R$ is the universal gas constant (8.314 J/K/mol) and $T$ is the temperature at 298 K. The constants $K_T$ and $b$ can be calculated from the slope $(RT/b)$ and intercept $(RT\ln K_T/b)$ of the plot of $q_e$ versus $\ln (C_e)$.

**Ethics approval and consent to participate.** Ethical approval and waiver was obtained from the Natural and Applied Sciences Research Ethics Committee (NASREC) of the University of Zambia (UNZA) under the project REF. NO. NASREC: 2019-AUG-009.

**Results and discussion**

Cashew nut shell liquid was extracted from CNSW with different organic solvents using a soxhlet extractor system. The percent yields are represented in Fig. 1. Extraction methods involving organic solvents under mild conditions have been reported to preserve the natural composition of CNSL. The quality and percent yields of extracted CNSL varied among the organic solvents. The hight yield was recorded from ethanol (40.1 ± 0.9%) followed by hexane (38.2 ± 0.4%) and petroleum ether (24.6 ± 0.4%) respectively. Although, ethanol recorded the highest yield, the quality of CNSL it extracted was poor, as it extracted more of undesirable polar coloured compounds from the shell. Even during the carbonization process, ethanol defatted shells produced toxic fumes, which led to a conclusion that it did not completely remove CNSL from the shell. Phytochemical analysis of the aqueous, ethanol, acetone, and hexane extracts of CNSW (Table 1) revealed the presence of phenols, tannins, flavonoids, saponins, steroids, terpenoids, glycosides, carboxylic acids, carbohydrates, proteins and amino acids. Various extracts from CNSW have been reported to have antimicrobial, antifungal, insecticidal (Acero, 2018) and antioxidant properties. Phyto-compounds such as saponins have been reported to have anticancer and anticholesterol activity. Flavonoids and other polyphenolic acids show antioxidant, anti-inflammatory, anti-diabetic and antineoplastic activities. Alkaloids are natural antitumor and analgesic agents. Steroids and terpenoids have anti-tumor, neuroprotection, antihypertensive, antimicrobial and insecticidal properties. Glycosides are better known for their physiological effect on the cardiovascular system, with cardiac glycosides being the drug of choice for treating congestive heart failure. Thus, the presence of these essential phyto-compounds in CNSW extracts signifies the importance of this wasted raw material.

The physico-chemical properties of CNSL are presented in Table 2, and were all determined using hexane extracted CNSL, because the quality and yield were better than the ethanolic and petroleum ether extracted-CNSLs respectively. The extracted CNSL was a reddish-brown viscous oil with a pH value of 3.2, probably due to a high concentration of anacardic acid and other phenolic compounds. The moisture and ash content of the CNSW biomass expressed in percentages were 6.5% and 1.6 ± 0.1% respectively. These values were in line with 6.7% and 1.3% reported by Ref. 1. The specific gravity, and refractive index values were 0.9561 ± 0.0002 (g/cm$^3$) and 1.52 ± 0.001 respectively. These values were higher than 0.9118 (g/cm$^3$) and 1.4325 reported by Ref. 1, but lower than 1.686 and 0.9999 (g/cm$^3$) reported by Refs. 1,69 respectively.

The viscosity of CNSL in this work was 104.6 ± 1.8 mPa s. This value was lower than 160 mPa s and 410 mPa s reported by (Mohammed) and (Rodrigues et al.). The standard viscosity range for CNSL at 25 °C is 150–600 mPa s. The reason for low viscosity in this work could be that the shells were roasted under uncontrolled conditions by the local cashew nut farmers during processing. However, CNSL with low viscosity presents an advantage, as it can be blended with diesel to form biodiesel for heavy engines. Biodiesels with high viscosity
values are characterised with poor fuel atomization, larger droplet size and spray jet penetration, leading to inefficient mixing of fuel and air in the combustion chambers\(^1\). The acid and free fatty acid values were 118.7 ± 9.2 (mg KOH/g) and 60.1 ± 4.7% respectively. The acid value in this work was higher than most literature values 12.1, 15.5, and 112 (mg KOH/g) reported by Ref.\(^1\),\(^71\),\(^75\), but lower than 141 mg KOH/g reported by Ref.\(^70\). A high acid value suggests that CNSL cannot be consumed by humans or directly applied on acid sensitive surfaces to avoid corrosion. Ingestion of oils with high acid value leads to human gastrointestinal discomfort, diarrhea and liver damage\(^76\),\(^77\). Cashew nut shell liquid with high acid value is first neutralized with alkaline bases before it is applied in paints, vanishes and others surface coating agents\(^70\). The saponification number and iodine values for this work were 138.1 ± 3.2 (mg KOH/g) and 188.1 ± 2.3 (g I\(_2\)/100 g) respectively. The obtained saponification number was lower than 161 mg KOH/g reported by\(^7\). Saponification number depend on the amount of fatty acids present in a fat or oil sample. The higher the number, the higher the amount of fatty acids and vice versa. It is also used to determine the average molecular weight of fatty acid chains in fats/or oils\(^74\). Fats/or oils with long fatty acids have low saponification values because they have fewer carboxylic group per unit mass of fat/oil, as compared to short chain fatty acids. Fatty acids with longer chains make good surfactants. Their surfactants have excellent detergent properties and they do not irritate the skin\(^78\). Iodine value indicates the unsaturation of fats/or oils\(^74\). The value 188.1 ± 2.3 (g I\(_2\)/100 g) obtained in this work was in line with and 177.7 (mg I\(_2\)/100 g) reported by\(^7\). The higher the iodine value, the more unsaturated the fat/or oil sample is. Highly unsaturated oils or fats are good for paints and surface coating materials, as they dry faster and their conjugated double bonds help to slowdown the oxidation process of painted objects\(^1\). The difference in the composition and physicochemical properties of CNSL in this work and other literature sources may be due to variation in the species, climate and geography where cashew was grown as well as the operating conditions employed during analysis\(^79\).

Batch adsorption of heavy metals (copper, lead, cadmium and zinc) onto CNS-AC. The cashew nut shell activated carbon (CNS-AC) was used to remove heavy metals (lead, cadmium, copper and zinc) from synthetic aqueous solutions. The batch adsorption was carried out at conditions of 1 g adsorbent dosage, 0.002 to 3 mg/L initial metal concentration, 30 mL of adsorbate solution, pH of 6.98, 30 min contact time and agitation speed of 250 rpm. The average percentage removal of Cu (II), Pb (II), Cd (II) and Zn (II) is shown in Table 3.

Batch adsorption of MB onto CNS-AC. Some of the factors that affects adsorption such as pH, temperature, contact time and concentration were considered in this study.

### Table 2. Physicochemical properties of CNSL from Mongu waste cashew nut shell. Table shows the physicochemical properties of the cashew nut shell liquid extracted from roasted shells which were obtained from Mongu District of the Western Province of Zambia. Results were expressed as percent means ± SEM and milligram KOH, g I\(_2\) and viscosity was in mPa s respectively.

| Physicochemical properties | This study | Literature value |
|---------------------------|------------|-----------------|
| Colour                    | Dark Brown | Dark Brown (Idah et al.\(^7\)) |
| Odour                     | Choke      | Choke (Idah et al.\(^7\)) |
| Nature                    | Viscous liquid | Viscous liquid (Akinhanmi et al.\(^1\)) |
| Moisture (%)              | 6.50       | 6.7 (Akinhanmi et al.\(^1\)) |
| Ash (%)                   | 1.6 ± 0.1  | 1.3 (Akinhanmi et al.\(^1\)) |
| Specific Gravity (30 °C)  | 0.9561 ± 0.0002 | 0.9995 (Mohammed\(^69\)) |
| Refractive Index (20 °C)  | 1.52 ± 0.001 | 1.686 (Akinhanmi et al.\(^1\)) |
| Viscosity (mPa s , 24 °C) | 104.6 ± 1.8 | 150–600 (Rodrigues et al.\(^11\)) |
| Acid Value (mg KOH/g)      | 118.7 ± 9.2 | 141 and 112 (Achi and Myina\(^70\); Mahanwar and Kale\(^71\)) |
| Free Fatty Acid (%)       | 60.1 ± 4.7  | 58 (Akinhanmi et al.\(^1\)) |
| Saponification (mg KOH/g) | 138.1 ± 3.2 | 161 (Achi and Myina\(^70\)) |
| Iodine Value (g I\(_2\)/100 g) | 188.1 ± 2.3 | 177.7 (Achi and Myina\(^70\)) |
| pH                        | 3.2        | 3.0 (Achi and Myina\(^70\)) |

### Table 3. Percentage removal of heavy metals by CNS-AC. Table Shows the percentage heavy metal removal by 1 g activated carbon at room temperature and pressure.

| Adsorbent | % Adsorption |
|-----------|--------------|
|            | Cu          | Pb          | Cd          | Zn          |
| CNS       | 99.4 ± 0.5  | 95.4 ± 1.5  | 99.4 ± 0.2  | 99.5 ± 0.1  |

Effect of solution pH on MB adsorption onto CNS-AC. The influence of initial pH value of the solution on the adsorption process of MB onto CNS-AC was carried out at 50 mg/L initial MB concentration, 298 K temperature
The adsorption efficiency increases from 94.8 to 99.1% for an increase in pH from 2 to 11 (Fig. 2). The near sigmoidal adsorption pattern under different pH units agrees with other studies done on adsorbates for methylene blue removal from aqueous solutions. The adsorption of MB was highly favoured under basic compared to acidic conditions with the highest removal percentage of 99.1 at pH 10. Uptake of MB by CNS-AC was constant at pH 10 and 11 as shown in Fig. 2. The low adsorption efficiency of MB in acidic media could be attributed to high competition for adsorption sites between the excess hydrogen ions (H+ ions) in the solution and the cation groups on MB.

The relationship between adsorption of MB and contact time was investigated to establish the rate of MB removal. Figure 3 shows the plot of removal percentage versus contact time for different MB concentrations ranging from 50 to 350 mg/L. The adsorption of MB increased with the increase in contact time until equilibrium was reached in about 120, 150, 210 and 250 min for an MB concentration of 50, 150, 250 and 350 mg/L respectively. Also, the percentage removal decreased from 99 to 93.74% for an increase in initial MB concentration from 50 to 350 mg/L. The reason for this behaviour can be attributed to the fact that, there are more active adsorption sites on the surface of the adsorbent compared to the total MB molecules in solution at lower concentrations, thus, more molecules interacts with the adsorbent and are removed from the solution.

Adsorption isotherms. Analysis of isotherm models is significant in modelling and designing of the adsorption process as they show the distribution of the adsorbate molecules between the liquid phase and the solid phase when an equilibrium state is reached. In this study, Langmuir, Freundlich and Temkin isotherm models were considered. The isotherm constants and regression coefficients (R²) calculated from adsorption experiments are...
Table 4. Values of Langmuir, Freundlich and Temkin isotherm constants for adsorption of MB onto CNS-AC. The adsorption process was investigated at different temperatures (298, 308, 318 and 328 K) and MB concentrations of 50, 150, 250 and 350 mg/L. Increasing the temperature from 298 to 328 K as shown in Fig. 7 increased the adsorption efficiency of MB for all the concentrations from 94.81 (350 mg/L) to 99.63 (50 mg/L). Thus, increase in temperature increases the thermal motion, chemical potential and solubility of MB molecules, thereby, enhancing the efficiency of MB for all the concentrations from 94.81 (350 mg/L) to 99.63 (50 mg/L). Therefore, adsorption process was investigated. The Gibbs free energy change (ΔG°) was calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_C,$$

$$K_C = \frac{q_e}{C_e},$$

The enthalpy change (ΔH°) and entropy change (ΔS°) change was determined from the equation below:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ,$$

where; T is the absolute temperature (K), R is the universal gas constant (8.314 J/mol/K), ΔG° (kJ/mol) is the Gibbs free energy change, ΔH° (kJ/mol) is the enthalpy change and ΔS° (kJ/mol/K) is the entropy change. The
values of ∆S° and ∆H° (Table 6) are obtained from the slope and intercept of the plot of lnK versus 1/T (K⁻¹) and are shown in Fig. 8.

The negative values obtained for Gibbs free energy (∆G°) indicates the feasibility and spontaneity of the adsorption process. The positive value (22.76 kJ/mol) of enthalpy change (∆H°) indicates that the adsorption of MB by CNS-AC at different temperatures was endothermic. The value of the entropy change (ΔS°) was 0.086 kJ/mol/K implying that the randomness of solid/solution interface during adsorption process increased. These results were consistent with studies done by Ref.54.

Conclusion
In this paper, we analyzed the potential use of cashew nut shell regarded as a waste in Zambia and indeed in many countries growing cashew. Solvent extraction and synthesis of activated carbon experiments were done to evaluate the potential value of cashew nut as a source of both chemical feedstock and activated carbon for use as a low cost filtration system matrix. Best yields of CNSL were achieved by hexane (38.2 ± 0.4%). Physicochemical results showed that CNSL has high potential as an intermediate in the synthesis of paints, varnishes, dyeing-stuff, binders, lubricants, nanotechnology73 and the presence of bioactive compounds such as alkaloids, steroids,
Figure 5. Pseudo-first-order kinetics of MB adsorption on CNS-AC at different initial MB concentration, pH 10, S/L = 33.33 g/L and T = 298 K.

Figure 6. Pseudo-second-order kinetics of MB adsorption on CNS-AC at different initial MB concentrations, pH 10, S/L = 33.33 g/L and T = 298 K.

Table 5. Pseudo-first-order and pseudo-second-order kinetic models for the adsorption of methylene blue (MB) onto CNS activated carbon. Table shows the pseudo-first-order and pseudo-second-order kinetic models for the adsorption of methylene blue (MB) onto CNS activated carbon. The data best fits the pseudo-second order with a correlation coefficient of 0.9997, 0.9998 and 0.9995 at 150, 250 and 350 mg/g initial concentration. The values of $q_e$ cal and $q_e$ exp were correlated for the pseudo-second order kinetics model.

| Kinetic parameters       | Initial concentration (mg/L) |
|-------------------------|------------------------------|
|                         | 50  | 150 | 250 | 350 |
| $q_e$, exp (mg/g)       | 1.485 | 4.378 | 7.212 | 9.843 |
| Pseudo-first-order kinetics |
| $R^2$                   | 0.9969 | 0.927 | 0.9829 | 0.9448 |
| $q_e$, cal (mg/g)       | 0.149 | 0.846 | 1.193 | 1.149 |
| $k_1$                   | 0.032 | 0.026 | 0.018 | 0.012 |
| Pseudo-second-order kinetics |
| $R^2$                   | 0.9923 | 0.9997 | 0.9998 | 0.9995 |
| $q_e$, cal (mg/g)       | 1.278 | 4.456 | 7.321 | 9.921 |
| $k_2$                   | 0.074 | 0.066 | 0.031 | 0.026 |
terpenoids, polyphenols, saponins and glycosides indicates that CNSW can be a cheap source for pharmaceutical compounds. The iodine (188.1 ± 2.3 gI₂/100 g) and saponification (138.1 ± 3.2 mg KOH/g) values indicated that CNSL was a drying oil making it suitable for resins, surface coating materials and soap making respectively. The adsorption of heavy metals and MB onto CNS-AC has been studied. The average percentage removal of Cu (II), Pb (II), Cd (II) and Zn (II) was 99.4, 95.4, 99.5, 98.4%, and the removal efficiency of MB at 50, 150, 250 and 350 mg/L was 99.63, 97.66, 96.48 and 94.81, respectively. The study showed that increasing the initial pH, temperature and contact time increased the adsorption of MB onto CNS-AC and a decrease in initial MB concentration increased percentage removal of MB. Equilibrium data were fitted to Langmuir, Freundlich and Temkin isotherms models and the equilibrium data were best described by the Freundlich isotherm model. The maximum monolayer adsorption capacity was 12.1 mg/g. The kinetics of the adsorption process conformed to pseudo-second-order model and the negative value of the Gibbs free energy (ΔG°) and positive value of enthalpy change (ΔH°) indicates that the adsorption process was endothermic and spontaneous. This paper therefore

| Temperature (K) | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (kJ/mol/K) | R² |
|-----------------|-------------|-------------|---------------|----|
| 298             | −2.94       | 22.76       | 0.086         | 0.908 |
| 308             | −3.80       |             |               |     |
| 318             | −4.66       |             |               |     |
| 328             | −5.52       |             |               |     |

Table 6. Thermodynamic parameters for MB adsorption on CNS-AC. Table shows the thermodynamic parameters for MB adsorption on activated carbon prepared from waste defatted cashew nut shell.

Figure 7. Effect of temperature on percentage MB removal by CNS-AC (adsorbent dosage S/L = 33.33 g/L, pH 10 and contact time = 120 min). Plots were generated in Graphpad Prism 9.1.0 version. Values were expressed as means ± SEM (https://www.graphpad.com/).

Figure 8. Plot for the thermodynamic parameters on the adsorption of MB by CNS-AC, 50 mg/L MB concentration and 33.33 mg/L adsorbate.
provided useful information that cashew nut shell can be used as a source for CNS-AC, a suitable adsorbent for removal of heavy metals and organic soluble matter from water as modeled by Cd, Cu, Pb, Zn and methylene blue dye removal respectively. The waste shells on one hand are also as a source of cardanol, cardol and other phenolic compounds useful in the chemical industry.

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Author contributions
J.N., secured funding, designed and supervised the research. K.Z and G.K., C.S. and I.M. carried out sample collection and physicochemical experiments. J.N., wrote the manuscript. J.N., K.Z and G.K. analyzed the data, reviewed and edited the manuscript. All authors read and approved the manuscript.

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Competing interests
The authors declare no competing interests.

Additional information
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