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SYNTHESIS OF CO (II) AND ZN (II) COMPLEXES OF MODIFIED AND UNMODIFIED CASHEW NUT (*ANACARDIUM OCCIDENTALS L.*) SHELL LIQUID EXTRACT

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ABSTRACT

Cashew nut shell liquid (CNSL) extract obtained using soxhlet extraction method with acetone as solvent has been used in the synthesis of Co (II) and Zn (II) metal complexes. The CNSL gave a molecular peak ion of 298g/mol^{-1} on a GC-MS, an indication that cardanol was more prominent than anacardic acid in the obtained extract. Physicochemical parameters such as saponification value (50.30 mgKOH/g), moisture content (5.10), iodine value (241.00 mgKOH/g), ash content (1.30) and pH (6.31) were equally obtained. The metal complexes of Co (II) and Zn (II) prepared with unmodified (UMCNSL) and aniline modified CNSL (AMCNSL) were characterized using UV-visible, FTIR, melting point and electrical conductivity. Some characteristic FTIR bands were observed for AMCNSL, UMCNCL, AMCNSL-$ZnCl_2.H_2O$ (1612cm^{-1}) and AMCNSL-$CoCl_2.6H_2O$ (1612cm^{-1}). The presence of C=N were confirmed in the metal complex of AMCNSL-$ZnCl.H_2O$ and AMCNSL-$CoCl.6H_2O$ but were not present in the UMCNSL-$ZnCl.H_2O$ and UMCNSL-$CoCl.6H_2O$.

Keywords: Cashew nut shell liquid, Zn(II),Co(II), metal complexes, modified-CNSL, unmodified-CNSL.

INTRODUCTION

Coordination Chemistry is an interesting area in inorganic chemistry. Many coordination complexes have been synthesized over the years (Sakhare, 2015). Metal complexes have been intensively studied in recent years due to their great variation in biological activities (Prates, *et al*., 2018, Chukwu, *et al*., 2014). They are vital in pharmaceutical, agricultural and industrial chemistry (Kumar, *et al.*, 2009). Agro wastes extracts such as peanut skin and onion skin have demonstrated significant impact in coordination chemistry by forming good metal ligand complexes with several metals (Uchechukwu *et al*., 2016. Chukwu *et al*., 2017, Akaho *et al*., 2018).

CNSL is a dark brown liquid with a viscous nature found in the soft honey comb structure of the nut (Rwahwire, *et al.*, 2019). It is a seed vessel fluid of the cashew nut that contains phenolic compounds such as anacardic acid, cardanol and cardol as well as aliphatic side chains. There are two types of CNSL depending on the extraction method; Solvent extracted/Natural CNSL and Technical CNSL. Cold-extracted CNSL using low-boiling solvents is termed natural CNSL; it is composed of anacardic acid (60-65%), cardol (15-31%), cardanol (10-21%) and trace amounts of methyl-cardol. While Technical CNSL consist of

(60- 65%) cardanol, (15-20%) cardol (1-2%), anacardic acid, (0.3-10%) polymeric material and (1.2-4.1%) traces of 2-methylcardol (Remya, *et al*., 2016, Peungjitton, *et al*., 2009 and Victor-Oji *et al*., 2019).

CNSL has been used for the preparation of many products like plywood adhesive (Akaranta *et al*., 1996) for antifungal and antibacterial (Echendu, 1991) production. Furthermore, CNSL has been used as additives in the manufacture of cellophanes and plastics (Ajayi, 2008). Additionally, CNSL has been modified through the coupling reaction with aromatic diazonium salts and used in industrial applications (Akaho, *et al*., 2018).

Hence the use of cashew nut shells liquid (CNSL) an agro waste in the formation of metal complexes will be demonstrated in this study. Modifying the CNSL using aniline and using both modified CNSL and unmodified CNSL in the synthesis and characterization of Zn(II) and Co (II) metal complexes will also be explored.

EXPERIMENTAL

The reagents used in this research are of analytical grade and were used as obtained without further purification. They include: Aniline ($C_6H_5NH_2$) (loba Chemie) 99%, methanol (CH_3OH) (JHD China) 99.5%, sodium nitrite ($NaNO_2$) (JHD China) 99%, acetone (C_3H_6O) (lobachemie) 97%, sodium hydroxide (NaOH) (lobaChemie) 97%, hydrochloric acid (HCl) (BDH chemicals Limited) 36-38% specific gravity (1.18), distilled water (H_2O, Zinc (ll) chloride monohydrate ($ZnCl_2.H_2O$) (lobachemie), Cobalt (ll) chloride hexahydrate ($CoCl_2.6H_2O$) (Kermel China).

Physicochemical parameters and characterization of unmodified CNSL and AMCNSL

The physicochemical parameters studied include: percentage yield, colour, saponification value, iodine value, moisture content and pH. These were obtained according to methods described elsewhere (Akinhanmi*et al*., 2008).

Sample Collection and pre-treatment

Cashew nut shells were collected from cashew plantation in Achi, Oji-River Local Government Area, Enugu State, Nigeria. The nuts were washed thoroughly with distilled water, dried for 7days, shelled and crushed; thereafter, they were introduced into the soxhlet extractor with acetone and extracted using the method described by Bharat et *al*., 2012.

Preparation of aniline diazonium salt

CNSL was modified with aniline using diazonium reaction in the preparation of the salt according to the method of Akaho *et al*., 2018 as described below.

Aniline ($1cm^3$) was dissolved in $45cm^3$ of distilled water in a $250cm^3$ beaker, $12cm^3$ of HCl was slowly added while stirring and in an ice-bath at $0\text{-}5^0C$. Five cubic centimetres of $NaNO_2$, (0.068g) was added drop wise to the mixture while stirring. The resulting solution in the beaker was further stirred for 3 minutes to obtain aniline diazonium salt.

Preparation of aniline modified cashew nut shell liquid AMCNSL

CNSL (2.98g) was weighed and dissolved into 10% (w/v) solution of sodium hydroxide. The resulting solution was stirred for 3 minutes and cooled in ice-bath

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at temperature of 0-5^{0}C. This gave us alkaline CNSL solution. Thereafter, aniline modified CNSL (AMCNSL) was prepared by adding aniline diazonium salt slowly to the alkaline CNSL at 0-5^{0}C, the solution mixture was stirred for 5 minutes. The resulting solution was further stirred for 10 minutes and allowed to stand for few minutes. The precipitate obtained was filtered, washed with some cold distilled water and dried under room temperature for 2 days.

Synthesis of Zn(ll) and Co(ll) metal complexes with unmodified CNSL.

The methods of (Akaho *et al*., 2018 and Chaudhary *et al*., 2017) were used with little adjustment. CNSL (1.4g) was dissolved in 10cm^3 of methanol in a 100ml beaker for 10 minutes. The colour of the solution was yellowish brown. Thereafter, $CoCl_2.6H_2O$ (1.9g) was quickly added and stirred on an electromagnetic stirrer for two hours; the colour of the resultant solution turned dark brown. After which, it was filtered and the filtrate evaporated at room temperature. The resulting coloured product was washed with ethanol and dried in a vacuum desiccator for 3-5 days.

Similarly, to another set of CNSL beaker dissolved in methane, (1.23g) of $ZnCl_2.H_2O$ was added quickly to the reaction mixture, the colour of the solution turned yellowish brown; it was stirred for 2 hours, filtered and evaporated at room temperature. The yellowish brown product was washed with methanol and dried in a vacuum desiccator for 3-5 days.

Synthesis of the modified metal complexes (Zn-AMCNSL and Co-AMCNSL)

To a 100ml beaker, AMCNSL extract (1.76g) was dissolved in 10cm^3 of methanol for 10minutes which gave a reddish brown solution. Thereafter, $CoCl_2.6H_2O$ (1.90g) was added quickly while stirring on an electromagnetic stirrer for two hours giving a brown solution. The solution was filtered and the filtrate evaporated at room temperature. The resulting dark brown product was washed with methanol and dried for 3-5days.

Similarly, to another beaker of AMCNSL extract (1.76g) dissolved in 10cm^3 of methanol, $ZnCl_2$. H_2O (1.23g) was added quickly and the colour of the solution turned light brown. It was stirred on an electromagnetic stirrer for 2 hours, filtered and the filtrate evaporated at room temperature. The resulting coloured product was washed with methanol and dried in a vacuum desiccator for 3-5 days.

Physicochemical parameters and characterization of unmodified CNSL and AMCNSL

The physicochemical parameters studied include: percentage yield, colour, saponification value, iodine value, moisture content and pH. These were obtained according to methods described elsewhere (Akinhanmi *et al*., 2008).

Gas chromatography-Mass spectrometer (GC-MS) Analysis

Gas chromatography-Mass spectrometer (GC-MS) analysis of the extract were done with finnigan 8000 series, interfaced using voyager electron impact-mass selection detector, on RTX-5ms column. One milligram (1mg) of the acetone extracted cashew nut shell liquid was dissolved in dichromethane (10 ml) and 1μL of the solution mixture injected into the GC- MS.

The temperature was set from 50 to 250^oC for 10 min and kept at 250^oC for 30 minutes.

RESULTS AND DISCUSSION

The results obtained for the physicochemical properties of the CNSL are presented in Table 1.0 and the results compared favourably with literature works of Akinhanmi *et al*., 2008. Table 2.0 presents the results for the physical characteristics of both the unmodified CNSL and AMCNSL alongside their cobalt and zinc metal complexes.

Table 1.0: Physicochemical Properties of Unmodified Cashew nut Shell liquid (UMCNSL)

S/N	Properties	UMCNSL	Akinhanmi *et al*
1	% Yield	52.07	-
2	Colour	Dark brown	Dark brown
3	Saponification Value(mgKOH/g)	50.30	47.60
4	Iodine Value(mgKOH/g)	241.00	235.00
5	Ash Content	1.60	1.30
6	Moisture Content	5.10	6.70
7	pH	6.31	-

Table2.0: Physical Characteristics of CNSL, AMCNSL and their metal complexes

Compound	Colour	Melting Point (ºC)	Electrical conductivity (μs/cm)	Soluble in	Insoluble in
CNSL	Dark Brown	_		Methanol and ethanol	H_2O
AMCNSL	Yellowish brown	84	0.90	Methanol and ethanol	H_2O
Zn- UMCNSL	Brown	102		Methanol and ethanol	H_2O
Co- UMCNSL	Reddish Brown	104		Methanol and ethanol	H_2O
Zn-AMCNSL	Reddish brown	115	0.65	Methanol and ethanol	H_2O
Co-AMCNSL	Dark brown	116	1.70	Methanol and ethanol	H_2O

From table 1.0, the colour of the CNSL obtained was dark brown similar to reports of Akinhanmi *et al*., 2008. The saponification value of 50.3 mg/KOH was obtained. This value is similar to works of Akinhanmi *et al*., 2008. Saponification value is simply a measure of the molecular weight of fatty acid present in oil. Saponification values above 200 mgKOH/g indicate the presence of fatty acids of low molecular weight, while values below 190 mgKOH/g are an indication that high molecular weight fatty acids are present. This low value indicates that the oil is a low molecular weight fatty acid and may not be suitable for making soap (Idah *et al*., 2014).

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Iodine value detects the measures of unsaturation in oils and also gives information about the drying properties, the type of drying oil and the extent of adulteration of that same oil. The iodine value of CNSL sample was found to be 241.0 mgKOH/g. This value is similar to works of Akinhanmi *et al*., 2008 (235 mgKOH/g). The oil is thus considered as a drying oil because any oil with iodine value greater than 100 mgKOH/g is a drying oil according to Idah *et al.,* 2014.

Obtained values for ash content and moisture content (1.60 and 5.10 respectively) were very much comparable to literature Akinhanmi *et al*., 2008. The ash content is low; hence, the oil cannot be useful as animal feed. However, the moisture content of 5.10 indicates that the oil can have longer shelf life (Idah *et al*., 2014).

Physical characteristics result of both UMCNSL and AMCNSL together with their cobalt and zinc metal complexes presented in table 2 shows that all products are soluble in methanol and ethanol but insoluble in water. Thus they are non-polar. The difference in melting point between AMCNSL and its metal complexes is an indication that complexation with the metal ions took place.

Figure 1, presents the GC-MS for the extracted CNSL. The spectrum shows molecular peak ion at M-Z ratio of 298g/mol^{-1} which is equal to the molecular weight of cardanol, this suggests the presence of cardanol in the extract rather than anacardic acid as expected.The presence of cardanol could be attributed to the decarboxylation of anacardic to cardanol during extraction or distillation processes.

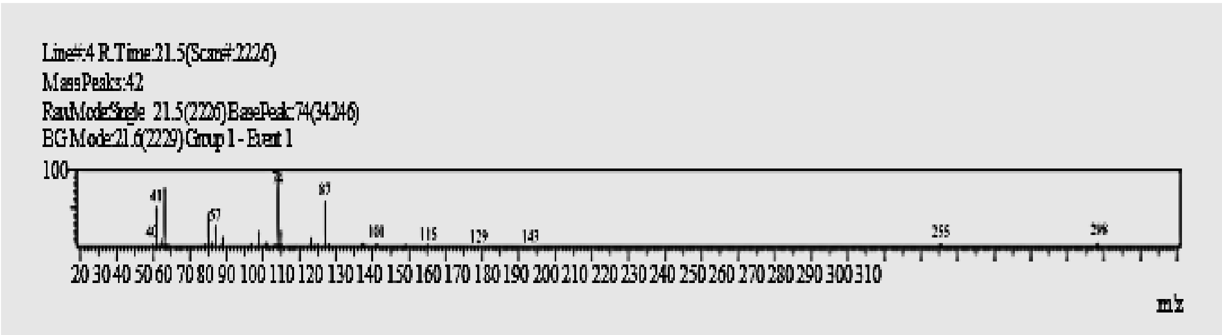
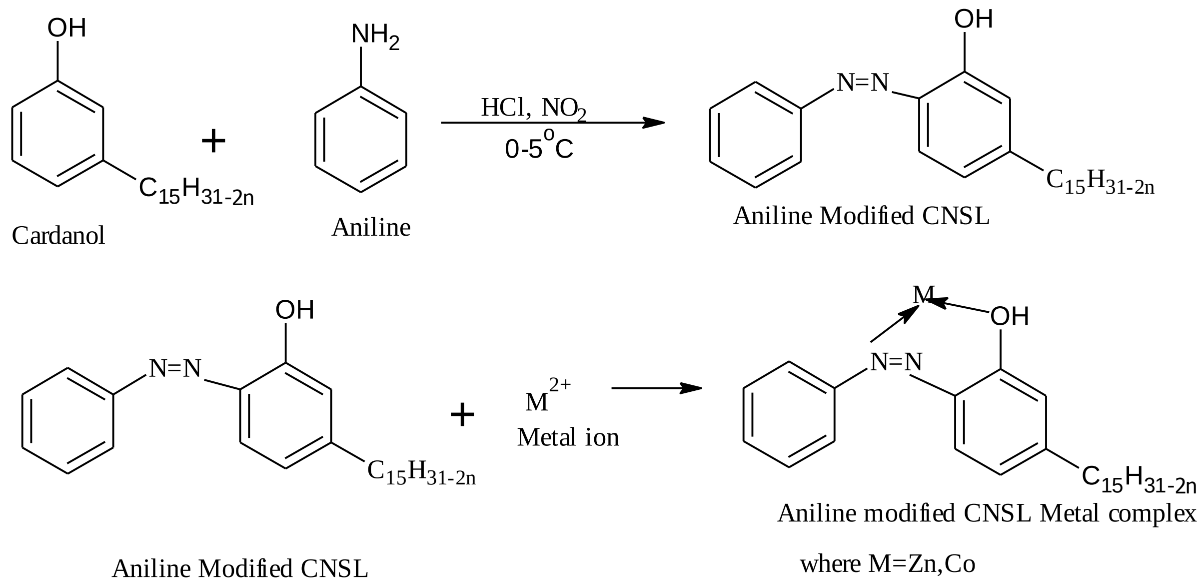


Figure 1:Mass spectrum (MS) result of cashew nut shell liquid

Scheme 1 represents the proposed reaction pathway for the formation of aniline modified cashew nut shell liquid metal complexes.



Scheme 1: Proposed scheme for the AMCNSL metal complex.

Plates 1 and 2 present the Scanning Electron Microscopy (SEM) of both the UMCNSL and AMCNSL respectively. The different morphologies observed are an indication that both products are entirely different.

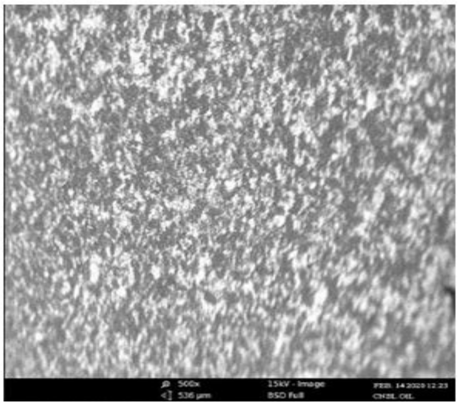


Plate 1: SEM of unmodified cashew nut shell liquid (UMCNSL)

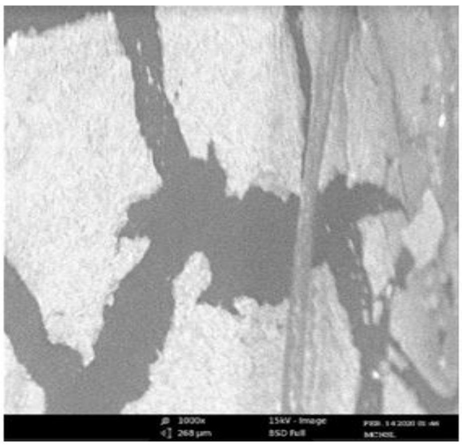


Plate 2: SEM of aniline modified cashew nut shell liquid (AMCNSL)

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Figures 2 to 7 presents the FTIR spectrum for AMCNSL, UMCNSL, UMCNSL-Zn complex, AMCNSL-Zn complex, UMCNSL-Co complex and AMCNSL-Co complex respectively.

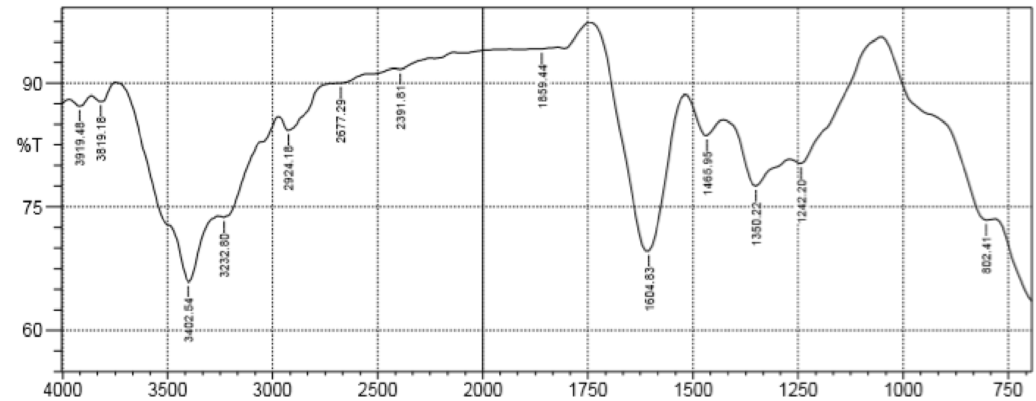

Figure 2: Infrared Spectrum of AMCNSL

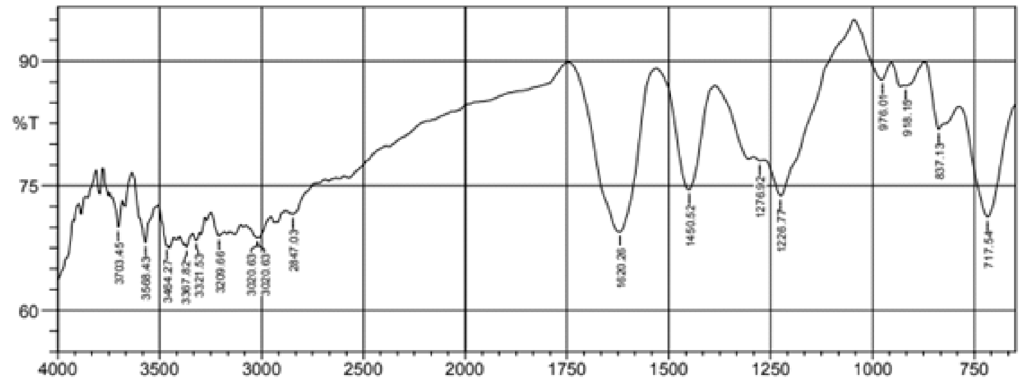

Figure 3: Infrared spectrum of UMCNSL

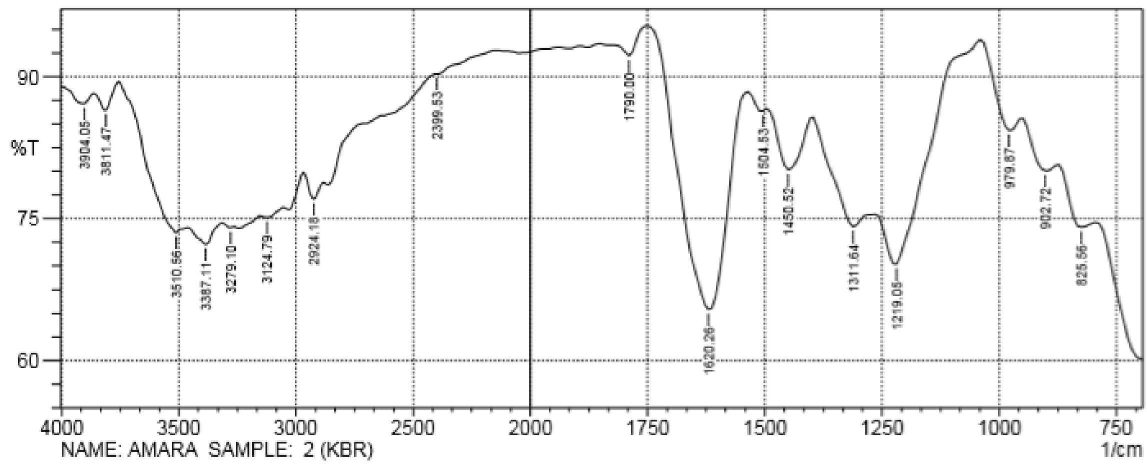

Figure 4: Infrared Spectrum of UMCNSL-Zn complex

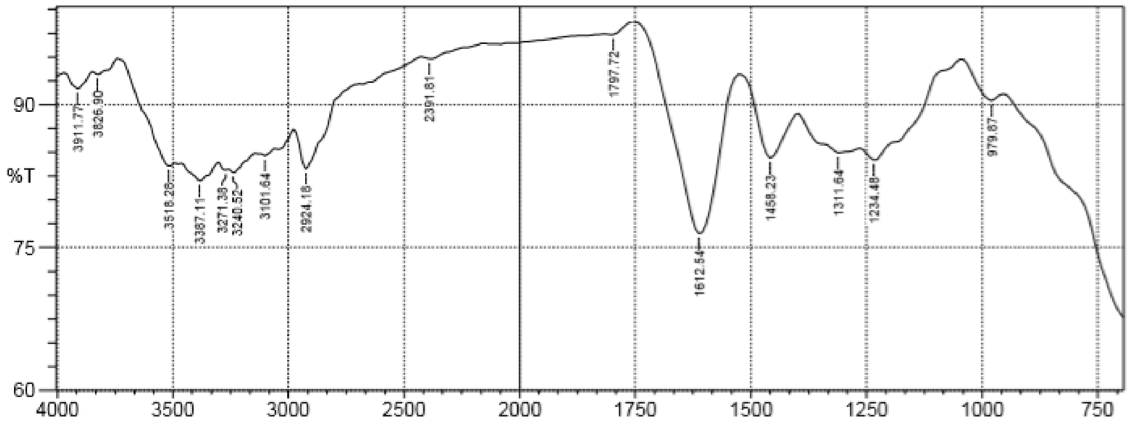

Figure 5: Infrared spectrum of AMCNSL-Zn complex

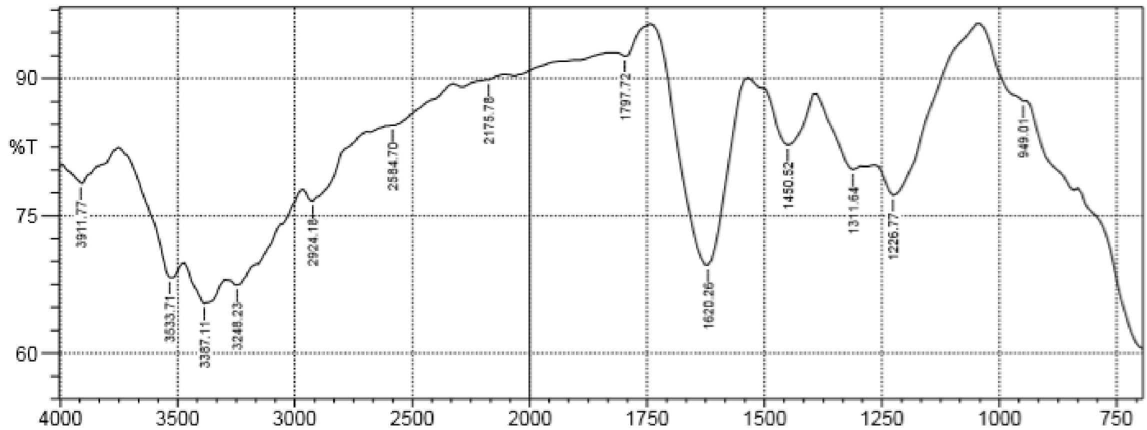

Figure 6:Infrared spectrum of UMCNSL-Co complex

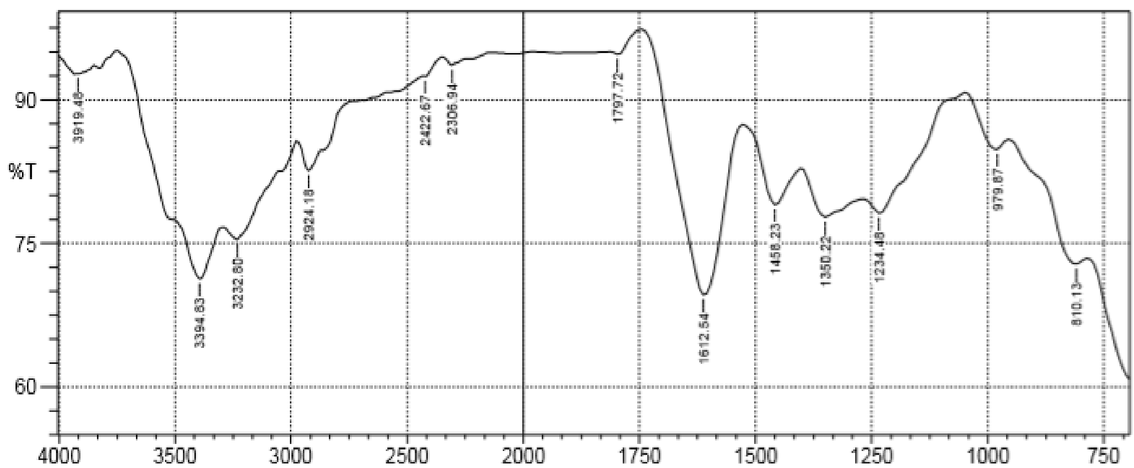

Figure 7: Infrared Spectrum of AMCNSL-Co complex

Within the area of 61.25 and 77.5 (2700-4000cm^{-1}) in fig 3 FTIR spectrum of CNSL shows some traces of impurities which were not observed in fig 2 of the FTIR of AMCNSL, 1620cm^{-1} C=C, 1465cm^{-1} C-H, 1226cm^{-1} and 717cm^{-1} were also observed for C-O and for benzene derivatives

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respectively. The appearance of 1604.83cm^{-1} and 3402cm^{-1} confirmed of the presence N-H (amine) in the AMCNSL, O-H bending 1350cm^{-1} (phenol) were also observed that is not seen on the UMCNSL.

In figures 4 and 5, the IR spectrum exhibited the value of 1612ccm^{-1}and 1234cm^{-1} (C=N) and (C-H) 1458cm^{-1} for the modified CNSL of $ZnCl_2.H_2O$ metal complex in figure 6, it was not observed in the unmodified CNSL of $ZnCl_2.H_2O$.

In figures 6 and 7 the appearance of 1612cm^{-1}and 1234cm^{-1}confirmed the presence C=N in the metal complex of $CoCl_2.6H_2O$ in figure 7, however this was absent in the unmodified CNSL of $CoCl.6H_2O$ in figure 6. FTIR shows that N=C are present in the metal complexes of the aniline modified cashew nut shell liquid.

CONCLUSION

Cashew nut liquid (CNSL) was extracted and modified with aniline through diazotization coupling reaction to obtain liquid AMCSNL which had cardanol as a major constituent. The metal complexes of zinc and cobalt were also prepared using obtained modified and unmodified cashew nut extract. Results of GC-MS, FTIR and SEM results were used to propose the structure of modified cashew nut extract and the metal complexes prepared from it.

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