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Research Article

GC-MS PROFILE, SYNTHESIS AND SPECTRAL CHARACTERIZATION OF FLAVONOID-METAL (CADMIUM, COBALT, COPPER, NICKEL) COMPLEXES OF *JATROPHA CURCUS* LEAVES

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ABSTRACT

Objective: The main aim of this research is to determine the optimum conditions required for the synthesis of metal-flavonoid complexes from leaves of *Jatropha curcus*.

Methods: Soxhlet extractor was used for the extraction. Phytochemical screening was carried out using the method described by Harborne. The phytochemical profile of the extract was determined using GC-MS. The flavonoid-metal complexes were synthesized using different transition metal salts and the methanolic plant leaves extract. The synthesis was carried out by varying the pH, metal ion and extract concentrations. The solubility of the flavonoid-metal complexes in different solvents was determined. The synthesized complexes were subjected to UV-visible and FTIR analysis.

Results: Methanol extract gave a yield of 4. 88%. Phytochemical screening revealed the presence of Flavonoids, steroids and alkaloids. The GC-MS analysis showed the presence of 14 compounds. Maximum dry weights of complexes formed between 600-700 mg were obtained at a concentration of 1000 ppm crude extract and for the metal ion concentrations, the optimum concentration observed for $Cd^{2+}$and Cu^{2+}complexes was 120 ppm while that of $Ni^{2+}$and Co^{2+}complexes was 140 ppm. Most suitable pH for copper-flavonoid was 8, for cobalt-and cadmium-flavonoid complexes was 9 and pH of 10 for nickel-flavonoid complexes. The FTIR results showed the formation of the complex due to the shift observed in the band assigned to C=O The UV/visible spectrum showed absorbance in the wavelength range of 250-480 nm.

Conclusion: Flavonoid-metal complexes were synthesized and their optimum conditions determine.

Keywords: GC-MS, Synthesis, FTIR, UV/VIS, Flavonoids, Metals, Complexes, *Jatropha curcus*, Leaves

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INTRODUCTION

Flavonoids are natural products that occur in plants. They are found in fruits, leaves, stems and roots. They possess the basic structure of diphenyl propane referred to as a C6-C3-C6 structure. The possession of a carbonyl and several hydroxy groups in the flavonoid structure gives it the ability to chelate metals [1]. Many flavonoid-metal complexes have been synthesized, characterized [2, 3] and their properties, composition, complex formation features, stability constants, etc. investigated [4, 5]. Flavonoids have been shown to possess health-promoting effects and have found use in pharmaceutical, nutraceutical, medicinal and cosmetic industries due to their biological properties such as antioxidant [6-8] anti-inflammatory [9], antimutagenic [10], antimicrobial [11], anti-carcinogenic [12]. They also inhibit enzymes such as xanthine oxidase, cyclooxygenase, lipoxygenase and phosphoinositide 3-kinase [13] but flavonoid-metal complexes exhibit greater effectiveness than the parent flavonoids [14, 15]. Studies on flavonoid-metal interactions in solution using potentiometric and spectroscopic measurements indicate that flavonoids exhibit varying degrees of deprotonation [16-19]. From spectroscopic measurement studies the coordination site of the flavonoids and their stoichiometric ratios in complex formation are obtained [20-22]. Several stoichiometric ratios of flavonoid/metal ion have been established for the synthesis of flavonoid-metal complexes and most of them are dependent on the pH of the reaction solution and the metal ion [23].

Jatropha curcus is a medicinal plant that grows well in Nigeria. It is also found in Central and South America, Southeast Asia and India. It is a member of the family of plants known as euphorbiaceae. In Nigeria, the leaves are used as antiseptic during child delivery and as tea against malaria fever. Other parts of the plant are used for the treatment of skin infections, healing of wounds, dropsy, rheumatism, diarrhea and dysentery.

The aim of this research is to examine the phytochemical profile of the methanol leaf extract, synthesize, characterize, and determine the effect of crude extract and metal ion concentrations, pH of the reaction solution and the setting time on the flavonoid-metal complexes formed so as to obtain the optimal conditions for the formation of flavonoid-metal complexes from the leaves of *Jatropha curcus*.

MATERIALS AND METHODS

Materials

All reagents used are of analytical grade and were utilized without further purification. Cadmium (II) acetate, cobalt (II) acetate, copper (II) acetate and nickel (II) acetate were obtained from BDH. Methanol, n-hexane, acetone and absolute ethanol were from merck.

Sample collection and preparation

The samples were collected from a traditional health practitioner's farm in Omu aran, Kwara State, Nigeria. Omu aran is located on longitude 5·0963 °E and latitude 8.1402 °N. It was taken to the Department of Pure and Applied Biology, Ladoke Akintola University of Technology, Ogbomoso, Oyo State, Nigeria where the sample was identified by Prof. A. T. J. Ogunkunle. A voucher specimen was deposited in their herbarium and specimen number of LHO 591 was attached to it. The plant leaves were dried under the prevailing atmospheric condition in the laboratory for three weeks. The dried leaves were pulverized into fine powder and stored in a clean container for further use.

Extraction

500g of the pulverized plant leaves was soaked in n-hexane for 24 h and filtered using a Whatman12 filter paper. This process was repeated three times and the filtrate collected pooled together and concentrated using a rotary evaporator. The concentrated extract was evaporated to dryness and weight measured.

Phytochemical screening

The crude extracts were screened for the presence of phytochemicals using the method described by Harborne, 2000 [24]. The screened phytochemicals were flavonoids, steroids, alkaloids, saponins, terpenoids, tannins, phlorotannin, anthraquinone glycosides, cardiac glycosides, coumarin glycosides and cyanophoric glycosides.

Gas chromatography-mass spectrometry analysis

Agilent 7890A/5975C a GC-MSD instrument fitted with an Agilent 19091S-433HP-5MS capillary column with dimensions 30 m X 0.25 mm inner diameter and 0.25 µm phase thickness and a split (50:1) injection system was used for the analysis. The oven temperature was programmed from 100 °C to 300 °C at a rate of 4 °C/min. The initial temperature was held for 4 min. Helium was used as the carrier gas and had a flow rate of 1.5 ml/min and a running time of 49 min. 1.0 µl aliquot of the sample was injected automatically and analyzed in the full scan mode. The source temperature was 250 °C and was held isothermally for 10 min. The solvent delay was for 5 min and the electron ionization energy of 70 eV was employed. The separated compounds were identified based on their mass spectrum. The data obtained from the mass spectrum was matched with that of National Institute of Science and Technology (NIST), 2011 database incorporated within the computer system of the instrument.

Synthesis of metal-flavonoid complexes

A solution of different metal salts (nickel (II) acetate, Copper (II) acetate, Cadmium (II) acetate and Cobalt (II) acetate) (4.2×10^{-3} mole) was measured and 50 ml of distilled water added to it. Then 1.0 g of the extract was dissolved in 200 ml of methanol. The metal salt solution was gradually introduced into the solution of extract and stirred for an hour at room temperature. The complex formed gradually and was filtered in a vacuum system, washed with water and dried by lyophilization. The obtained solid was weighed and kept for further analysis. The concentration of the extract, metal salts and the pH of the reaction medium were varied so as to obtain the optimum conditions.

Solubility test for synthesized complexes

Each of the synthesized complexes was tested for solubility in the following solvents: water, methanol, ethanol, acetone, n-hexane, DMF and DMSO.

FTIR and uv/vis analyses of synthesized complexes

The FTIR spectroscopic analysis was carried out using KBr pellets on a Model 500 IR spectrophotometer, while the uv/visible spectroscopic analysis was performed on a Jenway 6405 model spectrophotometer with absolute ethanol as the solvent.

RESULTS

Table 1: Percentage yield of extracts

Extracts	% yield
n-hexane	1.46
methanol	4.88

Table 2: Phytochemical screening of extracts

Extracts	Flav	Ster	Sap	Alk	Tan	Ter	Anthr	Gly
Met	+	+	-	+	-	-	-	-
n-hex	-	-	-	-	-	+	-	+

Note: +-Present, --Absent, Flav–Flavonoids, Ster–Steroids, Sap–Saponins, Alk–Alkaloids, Tan–Tannins, Terpenoids, Anthraquinones, Gly-Glycosides

Table 3: GC-MS report on the methanol extract

Peak	Retention time	% Composition	Name of compound	Molecular weight	Molecular formula
1	24.976	5.50	2-methoxy-4-vinyl phenol	150	$C_9H_{10}O_2$
2	27.797	1.05	1-(3,6,6-trimethyl-1,6,7,7a-tetrahydrocyclopenta[c]pyran-1-y) ethanone	206	$C_{13}H_{18}O_2$
3	29.328	1.57	(Z)-2-methoxy-4-(1-propenyl) phenol	164	$C_{10}H_{12}O_2$
4	37.796	2.01	-	-	-
5	38.425	1.71	Hexadecanal	240	$C_{16}H_{32}O$
6	38.660	16.87	-	-	-
7	38.723	3.64	6,10,14-trimethyl-2-pentadecanone	388	$C_{28}H_{36}O$
8	38.888	2.76	3,7,11,15-tetramethyl-2-hexadecen-1-ol	296	$C_{20}H_{40}O$
9	39.053	8.86	-	-	-
10	39.415	1.01	Hexadecanoic acid, methyl ester	270	$C_{17}H_{34}O_2$
11	39.784	1.40	2-hexadecenoic acid, methyl ester	272	$C_{17}H_{32}O_2$
12	40.632	10.90	Phytol	296	$C_{20}H_{40}O$
13	40.986	2.10	-	-	-
14	43.743	11.36	Di-n-octylphthalate	328	$C_{24}H_{38}O_4$

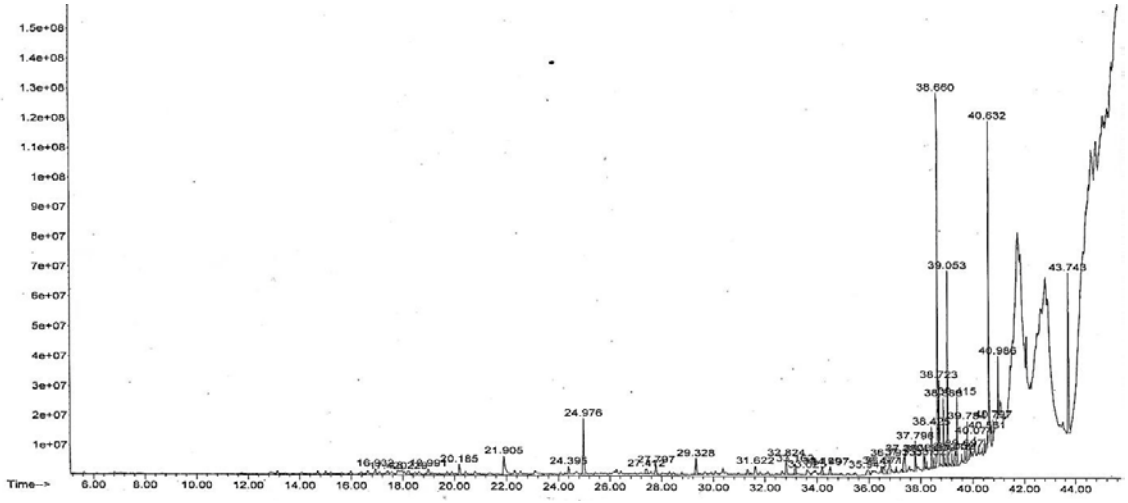

Fig. 1: Total ion chromatogram of the methanol extract

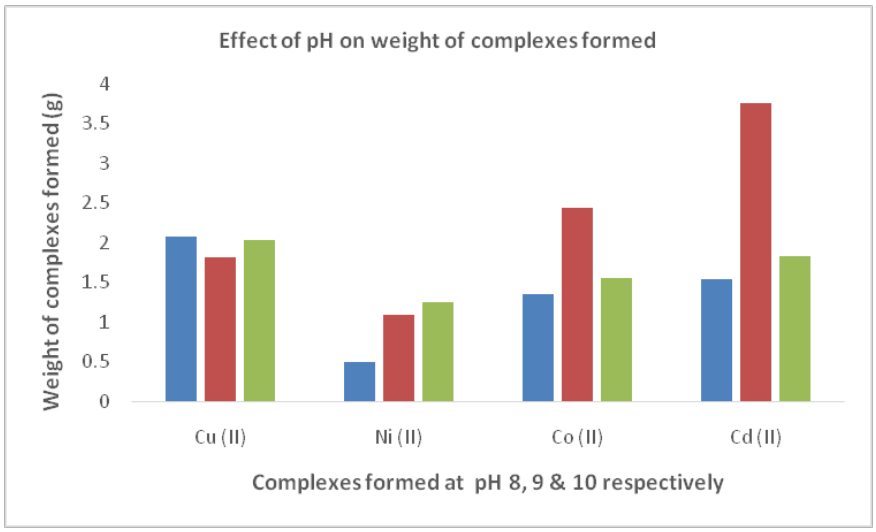

Fig. 2: Chart showing effect of pH on the complex formation (pH 8, 9 and 10 (from left to right). Data is expressed as the mean of three determinations

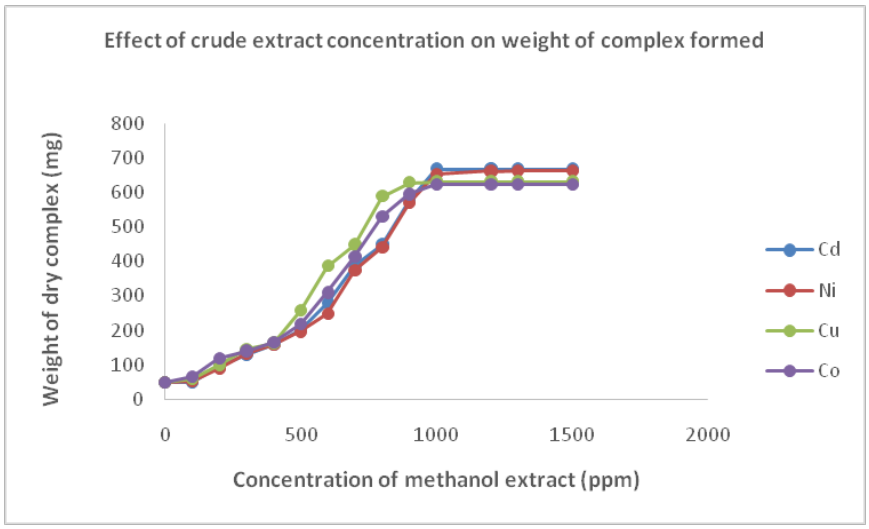

Fig. 3: Effect of crude extract concentration on the weight of complexes formed. Data is expressed as mean of three determinations

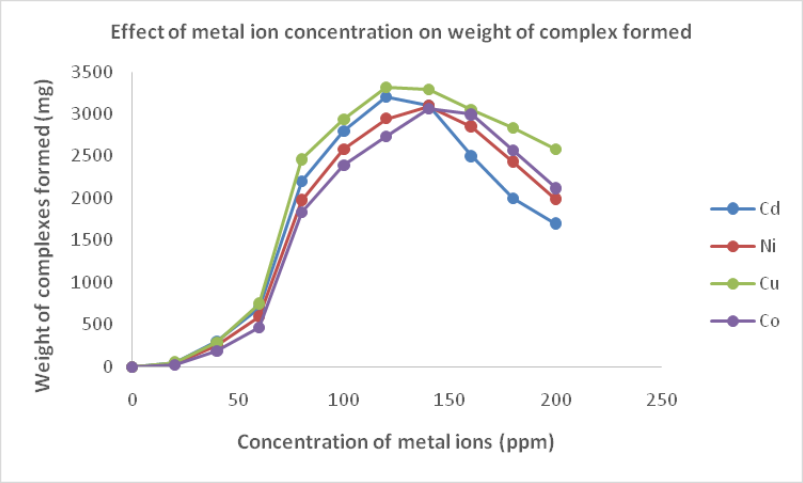

Fig. 4: Effect of heavy metal ion concentration on weight of complexes formed. Data is expressed as mean of three determinations

Table 4: UV/visible absorption data for methanol extract and complexes formed

Complexes	Absorption wavelength (nm)	
	Band I	Band II
Nickel (II)	250	424
Cobalt (II)	250	430
Cadmium (II)	250	356
Copper (II)	250	428

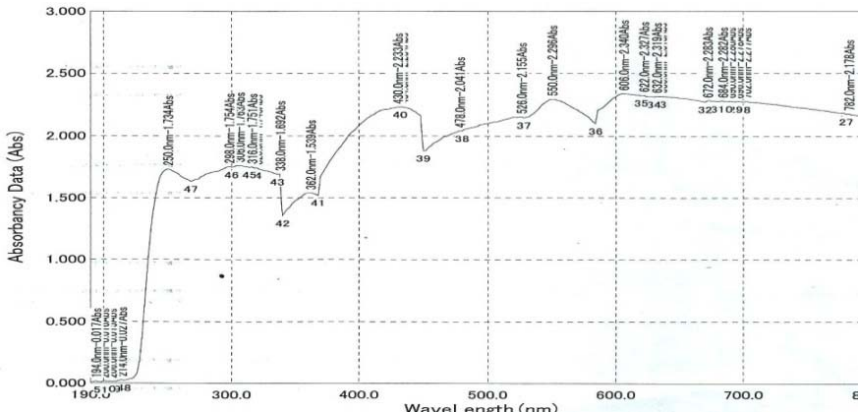

Fig. 5: UV spectrum of the Co (II) complexes

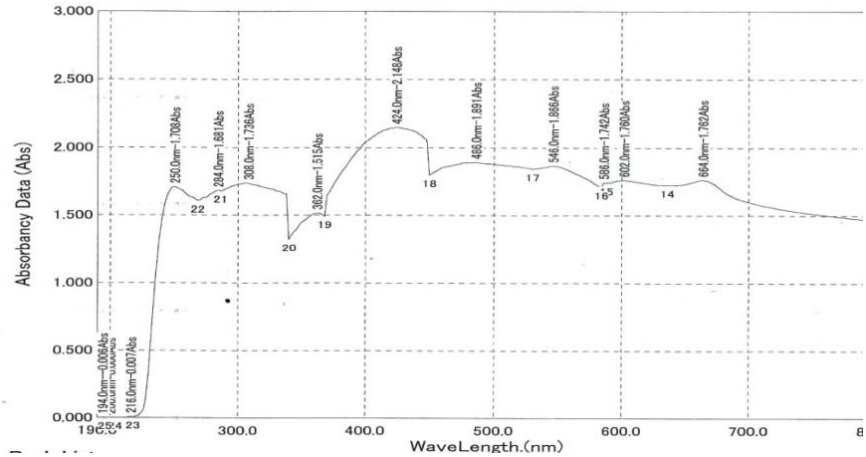

Fig. 6: UV-vis spectrum of the Ni (II) complex

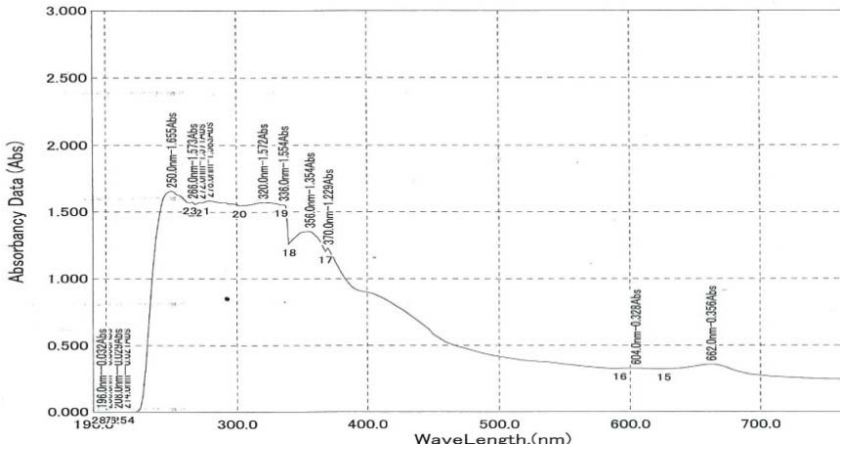

Fig. 7: UV-vis spectrum of the CD (II) complex

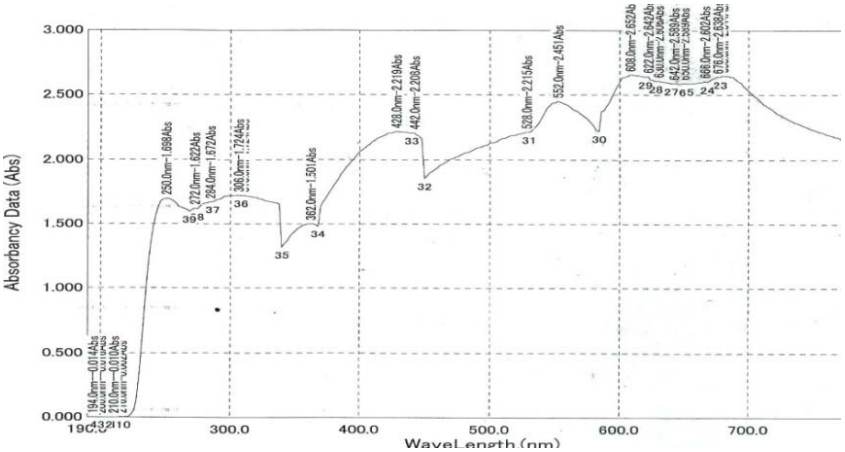

Fig. 8: UV-vis spectrum of Cu (II) complex

Table 5: FTIR absorption peaks for the methanol extract and the complexes formed

Absorption peaks (cm^{-1})					Assignments
Ni^{2+}complex	Co^{2+}complex	Cd^{2+}complex	Cu^{2+}complex	Methanol extract	
654	627	630	843		M-O
1099	1154	1150	1111	1101	C-O Str
			1329	1263	=C-COO Str
1462	1435	1462		1474	C=C (aromatic) Str
1579			1505	1511	C=C,C=O Str
		1659	1644	1693	Ar-C=O Str
1718	1718			1752	C=O Str
2583	2531	2523	2506	2548	-COOH Str
3241	3234	3270	3239	3247	OH Str

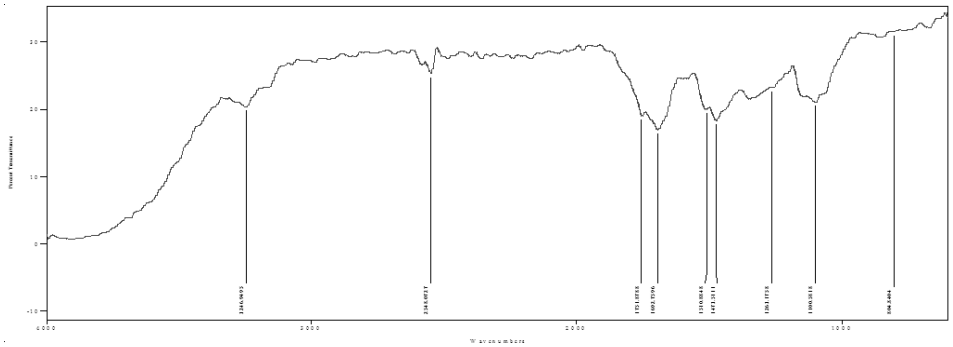

Fig. 9: FTIR of the methanol extract

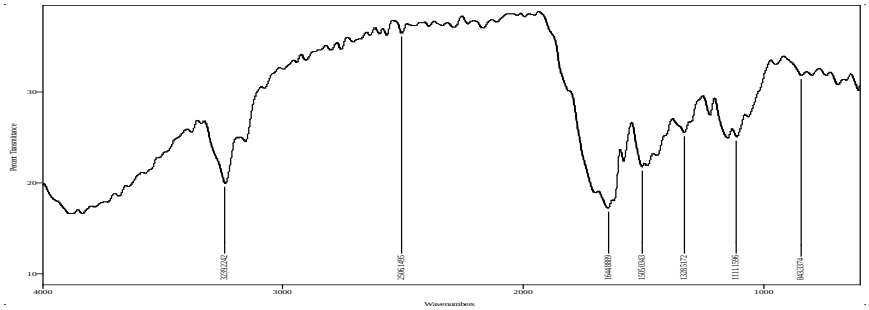

Fig. 10: FTIR of the copper (II) complex

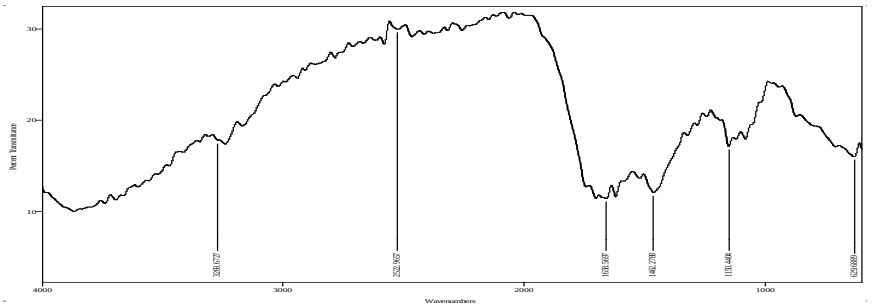

Fig. 11: FTIR of the cadmium (II) complex

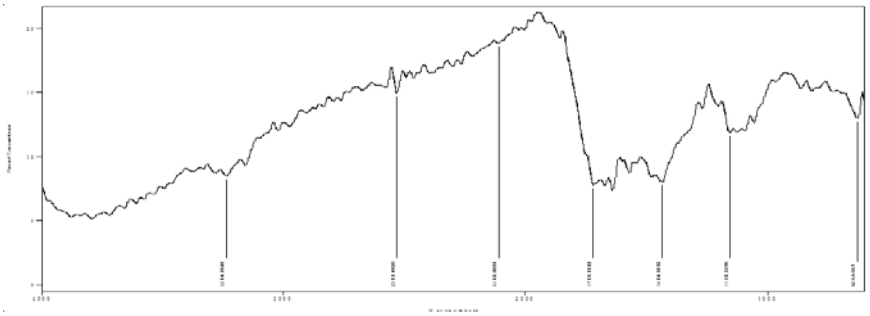

Fig. 12: FTIR of the cobalt (II) complex

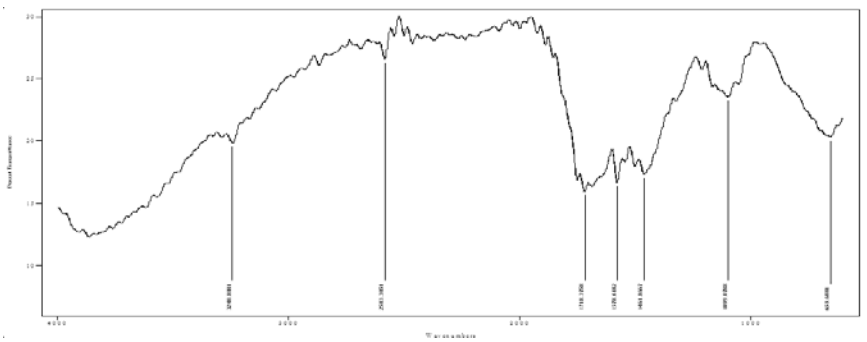

Fig. 13: FTIR of the nickel (II) complex

Table 5: Solubility of synthesized complexes

Complexes	Solvents	Solubility
Ni (II)	Water	Insoluble
	Ethanol (absolute)	Soluble
	Methanol	Slightly soluble
	Acetone	Soluble
	Chloroform	Soluble
	Dimethylformamide	Soluble

	DMSO	Soluble
Co (II)	Water	Insoluble
	Ethanol	Soluble
	Methanol	Slightly soluble
	Acetone	Soluble
	Chloroform	Soluble
	Dimethylformamide	Soluble
	DMSO	Soluble
Cu (II)	Water	Insoluble
	Ethanol	Soluble
	Methanol	Slightly soluble
	Acetone	Soluble
	Chloroform	Soluble
	Dimethylformamide	Soluble
	DMSO	Soluble
Cd (II)	Water	Insoluble
	Ethanol	Soluble
	Methanol	Slightly soluble
	Acetone	Soluble
	Chloroform	Soluble
	Dimethylformamide	Soluble
	DMSO	Soluble

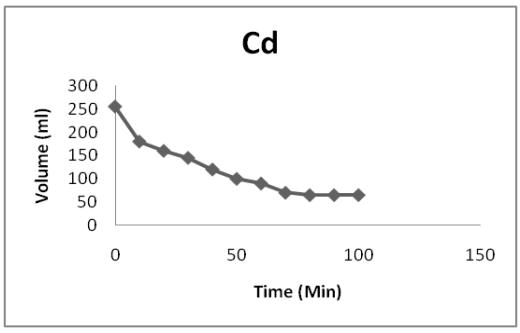

Fig. 14: Setting time for Cd (II) complex formation

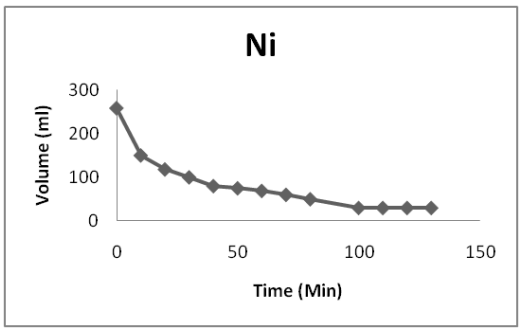

Fig. 15: Setting time for Ni (II) complex formation

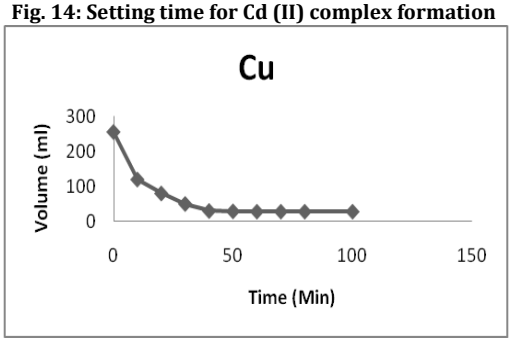

Fig. 16: Setting time for Cu (II) complex formation

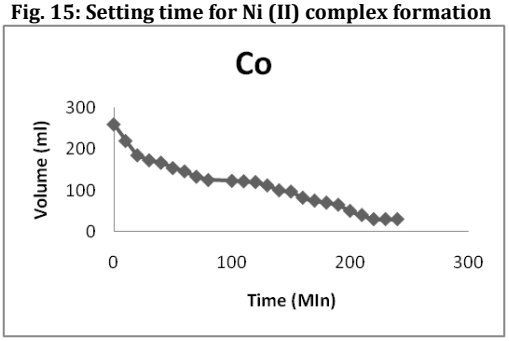

Fig. 17: Setting time for Co (II) complex formation

DISCUSSION

In most phytochemical studies, it is important to determine the weight of the extract so as to be able to obtain the percentage yield of the phytochemical sort for that is present in the plant. In this study, the percentage yield of the crude extracts of the plant leaves are presented in table 1. The percentage yield of the methanol extract is quite reasonable to contain a large quantity of polar compounds. Determination of the type or class of phytochemical is important since it serves as a preliminary step in the identification of a particular plant chemical. The phytochemical screening of the crude extracts of the plant leaves revealed the presence of flavonoids, steroids and alkaloids, while saponins, tannins, terpenoids, anthraquinones and glycosides were absent in the methanolic extracts. In the n-hexane extract only terpenoids and glycosides were present (table 2). The presence of flavonoid in the methanol extract led to our using the methanol extract for complexation with heavy metal ions. In the last decades, profiling of secondary metabolites has been made easier due to the establishment of GC-MS as a key technological tool for this process. In this study GC-MS was used to separate and identify phytochemicals that are present in the plant leaves. The GC-MS analysis of the methanol extract revealed the presence of 14 compounds while 10 were identified (table 3). The identified compounds were phenolics, fatty acid esters, alcohols and carbonyls. The total ion chromatogram is shown in fig. 1. The first compound to elute was 2-methoxyphenol with the retention time of 24.98 min while the last to elute was di-n-octyl phthalate with retention time of 43.74 min. the compound with retention time 38.66 min which was not identified had the highest composition of 16.87% followed by di-n-octyl phthalate 11.36% and phytol 10.9%. The effect of pH on the weight of complexes formed was examined as presented in fig. 2. The pH of the complex forming solution was varied between 5 and 12. It was noted that no complex was formed from pH of 5-7. But from pH of 8-10 appreciable quantity of complex was formed. The pH of 8 and 10 was the best for the

formation of Cu^{2+} and Ni^{2+}-flavonoid complexes, respectively while pH 9 was most suitable for Co^{2+} and Cd^{2+} flavonoid complexes. Above the pH of 10 no complex was formed. The maximum yield of the prepared complexes occurred between pH of 8 and 10. This shows that pH has an important role in complex formation and the optimum pH necessary for complexation is dependent on the metal ion and type of flavonoid present in the plant leaves. Complexes were not formed at pH lower than 8 because the flavonoids which are polybasic in nature were predominantly present in their undissociated form. Deprotonation of flavonoids occur at high pH values resulting in the formation of more complex species. In the investigation of the effect of metal ion and crude extract concentrations on the dry weight of metal-flavonoid complexes formed at the optimal pH, it was noted that the quantity of the dry complexes formed was directly proportional to the concentrations of the crude extracts and metal ions in the first part of the curves as shown in fig. 3 and 4, respectively. The maximum dry weights of complexes formed between 600-700 mg were obtained at a concentration 1000 ppm crude extract and after that, no further increase was observed. For the metal ion concentrations, the optimum concentration observed for Cd^{2+} and Cu^{2+}complexes was 120 ppm while that of Ni^{2+} and Co^{2+}complexes was 140 ppm. Above these concentrations a drop in the weight of the complexes formed was observed.

Several analytical tools are used in the characterization of complexes and uv/visible absorption spectroscopy is used here as a tool for the characterization of the complexes formed. The absorption data is presented in table 4 and the spectra in fig. 5-8. Due to the presence of unsaturation in flavonoids, they undergo $\pi \rightarrow \pi^*$ transitions , thereby displaying absorption bands in the uv/vis region [25]. Flavonoids exhibit two bands in the uv/vis region: band I at 320-385 nm and band II at 240-280 nm. Band I is attributed to the cinnamoyl moiety while band II is for the benzoyl moiety. The three possible chelatogenic groups in flavonoids that can interact with metal ions are 3′,4′-dihydroxy group on the B-ring, 5-hydroxy on A-ring or 3-hydroxy and the 4-carbonyl group on the C-ring; but the chelating properties of flavonoids is attributed to the presence of 3-or 5-hydroxypyran-4-one instead of the O-hydroxy groups on the B-ring. Some researchers [26-29] noted that the major site for metal chelation in flavonoids is the benzoyl moiety. According to Cornard and Merlin, 2001 [30] the binding site in flavonoid-metal chelation are the-hydroxy chromone and the O-hydroxy groups, which are strongly dependent on the medium and pH. In metal chelation, a bathochromic shift is observed in both bands [31]; but where a red shift is observed in one band rather than the other; it signifies that the chelation occurred in that particular ring [32, 33]. This red shift is as a result of increased conjugation when the flavonoid-metal complex is formed, producing a new ring.

Another characterization tool is FTIR. This tool is used to identify functional groups and can also indicate the coordination site of the metal ion. It can indicate whether complexation has taken place in that when the coordination of the metal ion is with a hydroxy group of the flavonoid there will be disappearance of the characteristic broad peak υOH at 3600-3200 cm^{-1} although it can be masked by the presence of several other hydroxy groups; but if the coordination is with the carbonyl group, an increase in the bond length will occur and this can be observed in the decrease in the frequency of the C=O peak. In this research, the functional groups OH, C=O, C-C, C-O and aromatic were identified. The FTIR data is presented in table 5 and the spectra in fig. 9-13. The broad peak υOH at 3600-3200 cm^{-1} disappeared, confirming the formation of a flavonoid complex. A decrease in the frequency of the C=O peak was also observed. Supplementary bands at 654, 627, 630 and 843 cm^{-1} are for the metal-oxygen bond (M-O) for Ni, Co, Cd and Cu (II) flavonoid complexes [34].

Setting time for the formation of the complex was investigated by measuring the volume of precipitate formed with the time required for the flocks of the complex to separate and precipitate completely from the solution. The results for the four different complexes are presented in fig. 5-8. It took Cd, Ni, Cu, Co complexes 70, 100, 40 and 200 min, respectively for the complex particulates to decrease to a final minimal setting value.

CONCLUSION

The phytochemical screening of the plant leaves extracts showed the presence of flavonoids, steroids, alkaloids, terpenoids and glycosides. In this study heavy metal-flavonoid complexes were synthesized. The spectroscopic characterization of the complexes showed that the hydroxy and carbonyl groups of the flavonoids were involved in the coordination. The optimal conditions such as pH, setting time of complex particulates, concentrations of metal ions and crude extract for the syntheses of the complexes were determined. Further work is ongoing to determine various biological and pharmacological activities of the synthesized complexes.

DATA AVAILABILITY

Not applicable

FUNDING

Nil

AUTHORS CONTRIBUTIONS

The research work was designed, coordinated and the write-up edited by Edewor, T. I; Literature review was carried out by Mmuo A. I, Sample collection, preparation and extraction were done by Amuda M. O while the synthesis and analyses were performed by Bankole T. A, Ogunjimi D. V.

CONFLICTS OF INTERESTS

There is none with regards to this article.

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