Nepal Journal of Biotechnology
Publisher: Biotechnology Society of Nepal ISSN (Online): 2467-9313
Journal Homepage: https://nepjb.com/index.php/NJB ISSN (Print): 2091-1130

Preparation and Characterization of Ink from *Hibiscus sabdariffa*, *Curcuma longa* and *Sorghum vulgare*

Idara U. Ntuen[1], Aniekan Effiong Akpakpan[2], Godwin Ndarake Enin[1], Iniobong Sylvester Enengedi[2], Emaime Jimmy Uwantta[2], Edet William Nsi[2], Itoro E. Udo[1], Edidiong Emmanuel Ikpe[2], Ukana Davies Akpabio[1]

[1]Department of Chemistry, University of Uyo, Uyo, Nigeria
[2]Department of Chemistry, Akwa Ibom State University, Ikot Akpaden, Nigeria

Received: 01 Nov 2024; Revised: 12 Nov 2024; Accepted: 17 Nov 2024; Published online: 31 Dec 2024

Abstract

Hibiscus sabdariffa (Roselle flower), *Curcuma longa* (Turmeric) and *Sorghum vulgare* (Guinea corn) are utilised in Nigeria for food and as natural colorants in home industries for dye and beverage production. The study investigates the formulation, characterization, and production of inks from these plant extracts using standard procedures. Inks were prepared from water-based and methanol-based extracts of Turmeric (WTE and MTE), Guinea corn stalk (WGE and MGE), and Roselle flower (WRE and MRE), with *Dacryodes edulis* exudate serving as a binder of eco-friendly, sustainable and cost-effective stamp pad ink. The raw materials were characterized according to standard procedures. Different ratios of the plant extracts were used to formulate the inks, with the optimal blend selected for stamp pad production. Characterization of the inks were conducted using Fourier Transform Infrared spectrometer (FTIR), Ultra violet/visible (UV/vis) spectrometer, viscometer and pH meter. Results indicated the presence of phytochemicals such as alkaloids, tannins, saponins and flavonoids. The inks exhibited viscosity ranging from 121.06 –313.86 $kgm^{-1}s^{-1}$, absorbance values from 0.010 – 2.578, and pH levels from 3.1- 6.5. FTIR analysis showed the inks contain chromophores and auxochromes including NO, C=C, C=O, C≡C, and -OH groups. Drying times for the formulated inks varied from 3 –11 minutes, compared to 1-3 minutes for the control ink, with methanol-based formulated inks (MbFI) drying faster than water-based formulated ink (WbFI). The produced stamp pad demonstrated good ink adhesion on paper.

Keywords: Turmeric, Guinea corn stalk, Roselle flower, phytochemicals, formulations, ink.

Corresponding author, email: enin.godwin@gmail.com, godwinenin@uniuyo.edu.ng

Introduction

Ink has long time been used for writing, drawing, and printing, and is made up of pigments or dyes mixed in a liquid medium. It has its roots in ancient cultures about five thousand years ago where carbon inks were used for writing on palm leaves before the invention of papers [1, 2]. As time has progressed, ink has undergone significant changes, resulting in a variety of types designed for different uses, ranging from fountain pens to contemporary printers. Today, ink is used for communication and artistic expression, influencing how we document and convey our thoughts [3]. The components of ink serve many purposes; the ink's carrier, colorants, and other additives affect the flow and thickness of the ink and its appearance after applying on material [4].

Organic inks are viewed as eco-friendly inks since they come from natural materials such as plant leaves, roots, flowers, fruits, and minerals. They address some issues associated with synthetic inks by being more cost-effective and simpler to produce, while also being non-toxic and safe. In contrast, synthetic inks can pose health risks, including headaches, skin irritation, and nervous system problems, primarily due to the solvents and pigments or dyes used to create their colours [5]. Nearly all the inks used in printings and writings are made from synthetic materials such as petrochemicals. These materials are hazardous to the health of the user since it contains toxic materials such as bromine, titanium, copper-zinc alloy, metallic gold and other transition metals that impact different colours, therefore, synthetic ink are pollutants when exposed to the environment since it is non-biodegradable [6, 7]. Additionally, materials used in the preparation of synthetic ink is expensive [7].

Most materials namely; leaves, flowers, stems, fruits and seeds are beautifully coloured and their extracts may be formulated into inks which are biodegradable, nontoxic, less expensive, safe in general applications and easy to process with readily available local materials. Research has been reported on the utilization of coloured plant pigments in the preparation of acid-based indicator [8, 9, 10] and in the formulation of ink [5, 11]. Research in Nursery/Primary schools have shown that some children inadvertently ingest ink while sucking their pens [12].

Currently, there is a growing interest in the used of organic materials of plant origin for the production of inks because most inks employed today for writing and printing are synthetic-based. Hence, for the benefit of society at large, it is necessary to produce inks free of health hazards or with minimal health implications by using locally available and non-toxic natural resources. In this study extracts from some locally available plant materials in Uyo metropolis, Nigeria, were used for the formulation of stamp pad inks to corroborate its usefulness. Plant extracts from locally available plant materials, such as Roselle (*Hibiscus sabdariffa*) flower, Turmeric (*Curcuma longa*), Guinea corn (*Sorghum vulgare*) stalk, and exudates, would be health wise safe ingredients for ink preparation instead of petrochemicals which are toxic in nature. Additionally, it is hoped that the use of locally available raw materials from plants for inks making should produce cheaper ink compared to the present synthetic ink.

A B C

Figure 1. Turmeric (A), Roselle flower (B) and Guinea corn stalk (C)

Materials and Methods

Sample Collection

Colourants, Exudate and Additive

Turmeric (*Curcuma longa*), roselle (*Hibiscus sabdariffa*) flower and guinea corn (*Sorghum vulgare*) stalk (**Figure 1**), were purchased from Akpan Andem market in Uyo, Uyo Local Government Area of Akwa Ibom State, Nigeria. Plant exudate used as natural binder was sourced randomly from local pear trees (*Dacryodes edulis*) at Nsit Ikpe, in Obot Akara Local Government Area of Akwa Ibom State. Many incisions were made on the bark of the trees and after some few minutes, the exudate oozed out of the tree. The fresh exudate was collected using a knife blade and stored in a container before used [13]. Honey was emulsifier and common salt, NaCl used as preservative were purchased from Akpan Ndem market in Uyo, Akwa Ibom State, Nigeria.

Sample Preparation

Roselle (*Hibiscus sabdariffa*) flower and guinea corn (*Sorghum vulgare*) plant stalks were chopped and washed with deionised water and oven dried at a temperature of 70°C for 24 hours. It was blended and stored in jars for pigment extraction. Turmeric (*Curcuma longa*) was washed with deionised water, ground into pulp and oven dried at the temperature of 70°C for 48 hours, and stored in dry jar for extraction [12].

Pigment Extraction

Crude plant extracts were prepared by Soxhlet extraction method [14]. The prepared powdered sample 20 g ground guinea corn plant stem, 30 g each of ground turmeric and roselle flower were uniformly packed into a thimble and extracted separately with 250 mL of water and methanol respectively for 1 hour. The extracts were stored in refrigerator at 4°C prior to use. The colour of water-based turmeric (*Curcuma longa*) extract (WTE), methanol-based turmeric (*Curcuma longa*) extract (MTE), water-based roselle (*Hibiscus sabdariffa*) flower extract (WRE), methanol-based roselle (*Hibiscus sabdariffa*) flower extract (MRE), water-based guinea corn (*Sorghum vulgare*) stalk extract (WGE) and methanol - based guinea corn (*Sorghum vulgare*) stalk extract (MGE) were noted and recorded.

Exudate Purification

The crude exudate (150 mL) was dissolved in 250 mL of acetone, filtered with funnel stoppered with cotton fibre and kept for 24 hours for the impurities to settle. The resulting mixture was decanted and 200 mL of pure exudate was obtained.

Phytochemical analysis

The confirmatory qualitative tests on the phytochemicals such as alkaloids, flavonoids, saponin. tannins anthraquinones, phenols, and carbohydrate were done according to standard procedures [15].

Ink Formulation and Preparation

The method of Agdew et al. (2023) was used with little modification [16]. During formulation, several trials were made by varying the quantity of binder and emulsifier from 0.6 – 1.4 mL, while the quantity of colourant was kept constant in order to determine the best formulation for the ink production. After many trials, the ratio of 6:1:1 for colourant, binder and emulsifier were the best formulation and this was adopted for the preparation of the inks.

Determination of physical parameters of the formulated ink

pH analysis was carried out using PHS-25 pH meter. The viscosities of the inks were determined with Ostwald single ball Viscometer. The drying time of the

formulated inks and commercial ink were observed by stamping the inks on the paper and recording their respective drying times.

Spectroscopic analysis

The UV/Vis and FT-IR analyses were conducted using the method of Kalaichelvi and Dhivya (2017) [17]. The UV/Vis analysis of the inks was done using Genesys-50 UV/Visible spectrophotometer. FT-IR Spectroscopic analysis to determine the infrared spectra of samples was recorded using Shimadzu FT-IR-990. These spectra revealed the functional groups present in the formulated inks.

Results

Extraction

The results of the aqueous and methanolic extraction of turmeric (*Curcuma longa*), roselle flower (*Hibiscus sabdariffa*) and guinea corn (*Sorghum vulgare*) showed the different colours exhibited by the extracts. The colours were yellow, red and maroon for turmeric, roselle flower and guinea corn stalk extract respectively (**Table 1**).

Qualitative Phytochemicals Analysis

Phytochemical screening of turmeric, roselle flower and guinea corn extracts indicated the presence of alkaloids, saponin, tannin, phenol, and carbohydrate. However, the presence of flavonoid was not detected in methanol-based turmeric extract and water crude extract of turmeric respectively. Anthraquinone was absent in the methanol and water-based extracts of guinea corn stalk (**Table 2**).

FTIR Spectroscopic analysis

The FTIR spectra of the formulated inks WTI, WRI, WGI, MTI, MRI, and MGI are reported in **Table 3-8**. The corresponding bands occurred at WTI (3295.0, 2926.0, 1636.3, 1513.3 and 1453.7), WRI (3306.1, 2922.2, 2542.0, 2113.41, 640.0, 1509.6 and 1423.8), WGI (3272.6, 202.09, 2105.9, 1636.3, and 1453.7) MTI (3339.7, 2944.6, 2840.2, 1640.0, 1509.6 and 1423.8), MRI (3306.1, 2948.3, 2840.2, 1640.0, 1449.9 and 408.9) and MGI (3306.1, 2948.3, 2836.5, 2109.7, 1509.6 and 1420.1) corresponding to different stretches such as OH stretch, C-H stretch, C=C stretch, N-O bend and C-H bend, C≡C, C=C vibration, N-H stretch, C-H bend (**Figure 2-6**). The IR spectrum of the purified *Dacryodes edulis* exudates sample is interpreted in **Table 12**. The frequencies show the presence of OH stretching vibration of alcohol group in the region of 3389.5cm^{-1}, =C-H stretch in the region of 3071.3cm^{-1}, C-H stretch in the region of 2922.2 cm^{-1} and 2870.1 cm^{-1}, C=O stretch in the region of1707.1cm^{-1}, C=C stretch in the region of 1640.0 cm^{-1} and C-H bend I the region 1453.7cm^{-1}.

Table 1. Extraction of turmeric, roselle flower and guinea corn stalk

Extract	Colour
WTE	yellow
MTE	yellow
WRE	Red
MRE	Red
WGE	Maroon
MGE	maroon

Water-based turmeric extract (WTE), water-based Roselle flower extract (WRE), water-based Guinea corn stalk extract (WGE), methanol-based Turmeric extract (MTE), methanol-based Roselle flower extract (MRE), methanol-based Guinea corn stalk extract (MGE).

Table 2. Phytochemical of turmeric, roselle flower and guinea corn stalk

Test	MGE	MRE	MTE	WRE	WGE	WTE	DEE
Alkaloids							
a. Tannic acid	+	+	+	+	+	+	+
b. Mayer's reagent	+	+	+	+	+	+	+
c. Harger's reagent	+	+	+	+	+	+	+
Flavonoids							
a. lead acetate	+	+	+	+	+	+	+
b. NaOH	+	+	–	+	–	+	+
c. $FeCl_3$	+	+	+	+	+	+	+
Saponins							
Frothing	+	+	+	+	+	+	+
Phenol							
a. $FeCl_3$	+	+	+	+	+	+	+
b. Lead acetate	+	+	+	+	+	+	+
Carbohydrate							
a. Iodine	+	+	+	+	+	+	+
b. Fehling solution	+	+	+	+	+	+	+
c. Molisch	+	+	+	+	+	+	+
Tannins							
a. $FeCl_3$	+	+	+	+	+	+	+
b. Lead acetate	+	+	+	+	+	+	+
Anthraquinones	–	+	+	+	–	–	–

Key: + = Present; – = absent.

UV/vis analysis

The UV absorbances of the formulated inks and that of the control (commercial ink) are presented in **Table 9**. The maximum wavelength (λ_{max}) of absorption of the formulated inks WTI, MTI, WRI, MRI, WGI, MGI and control (commercial ink) were 723.743, 578.768, 929.58, 1020.855, 987.831, 890.250 and 738.289 respectively. MTI had a lower λ_{max} (578.768) while MRI had a higher λ_{max} (1020.855) compared to the control (λ_{max}738.289). The absorbances of the formulated inks were: WTI (2.578), MTI (1.841), WRI (0.014), MRI (0.017), WGI (0.006), MGI (0.010) and while the absorbance of control was 0.015.

Table 3. FT-IR result of Commercial ink, water-based turmeric ink (WTI) and water-based turmeric extract (WTE) and DEE

Commercial ink (control)		WTI		WTE		DEE	
λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG
3291.2	O-H (stretch) Alcohol (H-bonded)	3295.0	O-H stretch	2851.4	O-H stretch, carboxylic acid	3389.5	O-H stretch, Alcohol
2109.7	C≡C, Terminal alkyne (monosubstituted)	2926.0	C-H stretch	2109.7	C≡C stretch, terminal alkyne (monosubstituted)	3071.3	=C-H stretch, methylene alkane (=CH_2)
1640.0	C=O (stretch), Carboxylic acid	1636.3	C=C stretch	1988.0	-NCS stretch, Isocyanate	2922.2	C-H stretch, methylene alkene
1461.1	C-H bend, Alkane	1513.3	N-O bend	1673.6	C=O (conjugated ketone)	2870.1	C-H stretch, Alkane
1349.3	C-H bend, Methyne (alkane)	1453.7	C-H bend	1548.1	C=O, Carboxylate (from carboxylic salt)	1707.1	C=O stretch, Carboxylic acid
		3242.8	O-H stretch	1509.6	N-O bend, Aromatic nitro compound	1640.0	C=C stretch, Alkene
		3104.9	=C-H stretch	1408.9	Vinyl (in- plane)	1453.7	C-H bend, methylene alkane
		2922.2	C-H stretch	–			

Water-based turmeric ink (WTI), water-based turmeric extract (WTE), Dacryodes edulis exudate (DEE), Functional group (FG).

Table 4. FT-IR result of Commercial ink, water-based Roselle flower ink (WRI) and water-based Roselle flower extract (WRE) and DEE

Commercial ink (control)		WRI		WRE		DEE	
λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG
3291.2	O-H (stretch) Alcohol (H-bonded)	3306.1	O-H stretch, (Alcohol)	3272.6	O-H stretch, Alcohol (H-bonded)	3389.5	O-H stretch, Alcohol
2109.7	C≡C, Terminal alkyne (monosubstituted)	2922.2	C-H stretch, (Alkane) (methylene)	2109.7	C≡C stretch, terminal alkyne (monosubstituted)	3071.3	=C-H stretch, methylene alkane (=CH_2)
1640.0	C=O (stretch), Carboxylic acid	1640.0	C=C, Alkene (asymmetric)			2922.2	C-H stretch, methylene alkene
1461.1	C-H bend, Alkane	1509.6	N-H stretch (1^o amine)			2870.1	C-H stretch, Alkane
1349.3	C-H bend, Methyne (alkane)	1423.8	C-H bend, (Vinyl group)			1707.1	C=O stretch, Carboxylic acid
						1640.0	C=C stretch, Alkene
						1453.7	C-H bend, methylene alkane

Water-based Roselle flower ink (WRI), water-based Roselle flower extract (WRE), Dacryodes edulis exudate (DEE), Functional group (FG)

Table 5. FTIR result of Commercial ink, water-based Guinea corn stalk ink (WGI) and water-based Guinea corn stalk extract (WGE) and DEE

Commercial ink (control)		WGI		WGE		DEE	
λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG
3291.2	O-H (stretch) Alcohol (H-bonded)	3272.6	O-H stretch, Alcohol	3268.9	O-H stretch, Alcohol (H-bonded)	3389.5	O-H stretch, Alcohol
2109.7	C≡C, Terminal alkyne (monosubstituted)	2202.9	C≡C stretch, Medial alkyne (disubstituted)	2113.4	C≡C stretch, terminal alkyne (monosubstituted)	3071.3	=C-H stretch, methylene alkane (=CH_2)
1640.0	C=O (stretch), Carboxylic acid	2105.9	C≡C stretch, Terminal alkyne (monosubstituted)	1636.3	C=C stretch, Alkene	2922.2	C-H stretch, methylene alkene
1461.1	C-H bend, Alkane	1636.3	C=C stretch Alkene			2870.1	C-H stretch, Alkane
1349.3	C-H bend, Methyne (alkane)	1453.7	C-H bend, Methylene (Alkane)			1707.1	C=O stretch, Carboxylic acid
						1640.0	C=C stretch, Alkene
						1453.7	C-H bend, methylene alkane

Water-based Guinea corn stalk ink (WGI) and water-based Guinea corn stalk extract (WGE), Dacryodes edulis exudate (DEE), Functional group (FG)

Table 6. FTIR result of methanol-based Turmeric ink (MTI) and methanol-based Turmeric extract (MTE) and DEE

Commercial ink (control)		MTI		MTE		DEE	
λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG
3291.2	O-H (stretch) Alcohol (H-bonded)	3339.7	O-H stretch, alcohol	3324.8	O-H stretch, alcohol (H)	3389.5	O-H stretch, Alcohol
2109.7	C≡C, Terminal alkyne (monosubstituted)	2944.6	C-H stretch, alkane	2944.6	C-H stretch, alkane	3071.3	=C-H stretch, methylene alkane (=CH_2)
1640.0	C=O (stretch), Carboxylic acid	2840.2	C-H stretch, aldehyde	2832.8	C-H stretch, aldehyde	2922.2	C-H stretch, methylene alkene
1461.1	C-H bend, Alkane	1640.0	C=C stretch, alkene	2035.1	C≡C stretch, terminal alkyne	2870.1	C-H stretch, Alkane
1349.3	C-H bend, methyne (alkane)	1513.3	N-O bend, aromatic nitro	1654.9	C=C stretch, alkene	1707.1	C=O stretch, Carboxylic acid
		1449.9	C-H bend, methylene (alkene)	1449.9	C-H bend, methylene H	1640.0	C=C stretch, Alkene
				1408.9	C-H bend, vinyl	1453.7	C-H bend, methylene alkane

Methanol-based Turmeric ink (MTI) and methanol-based Turmeric extract (MTE), *Dacryodes edulis* exudate (DEE), Functional group (FG)

Table 7. FTIR result of methanol-based Roselle flower ink (MRI) and methanol-based Roselle flower extract (MRE) and DEE

Commercial ink (control)		MRI		MRE		DEE	
λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG
3291.2	O-H (stretch) Alcohol (H-bonded)	3306.1	O-H stretch, alcohol	3391.9	O-H stretch, alcohol (H)	3389.5	O-H stretch, Alcohol
2109.7	C≡C, Terminal alkyne (monosubstituted)	2948.3	C-H stretch, alkane	2955.8	C-H stretch, methylene (asymmetric/symmetric)	3071.3	=C-H stretch, methylene alkane (=CH_2)
1640.0	C=O (stretch), Carboxylic acid	2840.2	C-H stretch, aldehyde	2922.2	C-H stretch, methylene	2922.2	C-H stretch, methylene alkene
1461.1	C-H bend, Alkane	1640.0	C=C stretch, alkene	2109.7	C≡C stretch, terminal alkyne	2870.1	C-H stretch, Alkane
1349.3	C-H bend, methyne (alkane)	1449.9	C-H stretch, methylene (alkene)	1714.6	C=O stretch, carboxylic acid (H)	1707.1	C=O stretch, Carboxylic acid
		1408.9	C-H bend, vinyl (in-plane)	1651.2	C=C stretch, alkene	1640.0	C=C stretch, Alkene
				1513.3	N-O stretch, N of aromatic	1453.7	C-H bend, methylene alkane
				1461.1	C-H bend		

Methanol-based Roselle flower ink (MRI) and methanol-based Roselle flower extract (MRE), Dacryodes edulis exudate (DEE), Functional group (FG)

Table 8. FTIR result of methanol-based Guinea corn stalk ink (MGI) and methanol-based Guinea corn stalk extract (MGE) and DEE

Commercial ink (control)		MGI		MGE		DEE	
λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG	λ (cm^{-1})	FG
3291.2	O-H (stretch) Alcohol (H-bonded)	3306.1	O-H stretch, alcohol	3306.1	O-H stretch, alcohol (H)	3389.5	O-H stretch, Alcohol
2109.7	C≡C, Terminal alkyne (monosubstituted)	2948.3	C-H stretch, alkane	2944.6	C-H stretch, alkane	3071.3	=C-H stretch, methylene alkane (=CH_2)
1640.0	C=O (stretch), Carboxylic acid	1509.6	N-O bend, aromatic nitro compound	1654.9	C=C stretch, alkene	2922.2	C-H stretch, methylene alkene
1461.1	C-H bend, Alkane	1420.1	C-H stretch, (Vinyl H)	1449.9	C-H bend, methylene alkane	2870.1	C-H stretch, Alkane
1349.3	C-H bend, methyne (alkane)			1420.1	C-H bend, vinyl (in plane)	1707.1	C=O stretch, Carboxylic acid
						1640.0	C=C stretch, Alkene
						1453.7	C-H bend, methylene alkane

Methanol-based Guinea corn stalk ink (MGI) and methanol-based Guinea corn stalk extract (MGE), *Dacryodes edulis* exudate (DEE), Functional group (FG)

Table 9. UV Absorbance of the formulated Inks

Extract	Absorbance	λ_{max}	ink	Absorbance	λ_{max}
–	–	–	Ctrl	0.015	738.289
MGE	0.007	554.861	MGI	0.010	890.250
WGE	0.003	587.092	WGI	0.006	987.831
WRE	0.011	562.502	WRI	0.014	929.580
MRE	0.013	551.235	MRI	0.017	1020.855
WTE	0.081	415.346	WTI	2.578	723.743
MTE	0.086	425.181	MTI	1.841	578.768

Ctrl (control), Water-based turmeric ink (WTI) and water-based turmeric extract (WTE), water-based Roselle flower ink (WRI) and water-based Roselle flower extract (WRE), water-based Guinea corn stalk ink (WGI) and water-based Guinea corn stalk extract (WGE), methanol-based Turmeric ink (MTI) and methanol-based Turmeric extract (MTE), methanol-based Roselle flower ink (MRI) and methanol-based Roselle flower extract (MRE), methanol-based Guinea corn stalk ink (MGI) and methanol-based Guinea corn stalk extract (MGE).

Table 10. Variation of the quantity of exudate in the ink formulations

Plant extract (Pigment) (6 mL)	Exudate (mL)	Emulsifier (mL)	Observation
WTE	0.6	1	Extremely non-homogeneous, spread
	0.8	1	Moderately non homogeneous, spread
	1.0	1	Homogeneous, non-spread
	1.2	1	Slightly super saturated
	1.4	1	Supersaturated
MTE	0.6	1	Extremely non-homogeneous, spread
	0.8	1	Moderately non homogeneous, spread
	1.0	1	Homogeneous, non-spread
	1.2	1	Slightly super saturated
	1.4	1	Supersaturated
WRE	0.6	1	Extremely non-homogeneous, spread
	0.8	1	Moderately non homogeneous and spread
	1.0	1	Homogeneous, non-spread
	1.2	1	Slightly super saturated
	1.4	1	Supersaturated
MRE	0.6	1	Extremely non-homogeneous, spread
	0.8	1	Moderately non homogeneous, spread
	1.0	1	Homogeneous, non-spread
	1.2	1	Slightly super saturated
	1.4	1	Supersaturated
WGE	0.6	1	Extremely non-homogeneous, spread
	0.8	1	Moderately non homogeneous, spread
	1.0	1	Homogeneous, non-spread
	1.2	1	Slightly super saturated
	1.4	1	Supersaturated
MGE	0.6	1	Extremely non-homogeneous, spread
	0.8	1	Moderately non homogeneous, spread
	1.0	1	Homogeneous, non-spread
	1.2	1	Slightly super saturated
	1.4	1	Supersaturated

Table 11. Variation of the quantity of emulsifier

Pigment (6 mL)	Exudate (mL)	Emulsifier (mL)	Observation
	1	0.6	Moderately homogeneous, less spread
WTE	1	1.0	Homogeneous, non-spread
	1	1.4	Non-homogeneous, Spread extremely
	1	0.6	Moderately homogeneous, less spread
MTE	1	1.0	Homogeneous, non-spread
	1	1.4	Non-homogeneous, Spread extremely
	1	0.6	Moderately homogeneous, less spread
WRE	1	1.0	Homogeneous, non-spread
	1	1.4	Non-homogeneous, Spread extremely

MRE	1	0.6	Moderately homogeneous, less spread
	1	1.0	Homogeneous, non-spread
	1	1.4	Non-homogeneous, Spread extremely
WGE	1	0.6	Moderately homogeneous, less spread
	1	1.0	Homogeneous, non-spread
	1	1.4	Non-homogeneous, Spread extremely
MGE	1	0.6	Moderately homogeneous, less spread
	1	1.0	Homogeneous, non-spread
	1	1.4	Non-homogeneous, Spread extremely

Table12. Drying time of inks

Ink	Drying Time (sec.)	Observed Colour
Ctrl	1-3	Blue
MGI	3-5	Maroon
WGI	7-8	Maroon
WRI	7-9	Red
MRI	3-5	Red
WTI	7-11	Yellow
MTI	4-6	Yellow

Table 13. Viscosity and pH of ink Compositions

Ink Composition	Viscosity ($Kgm^{-1}s^{-1}$)	pH
Honey	10^1	4
Methanol	$5.43x10^{-1}$	-
Water	$1.01x10^2$	7
Exudate	$204x10^3$	5.1

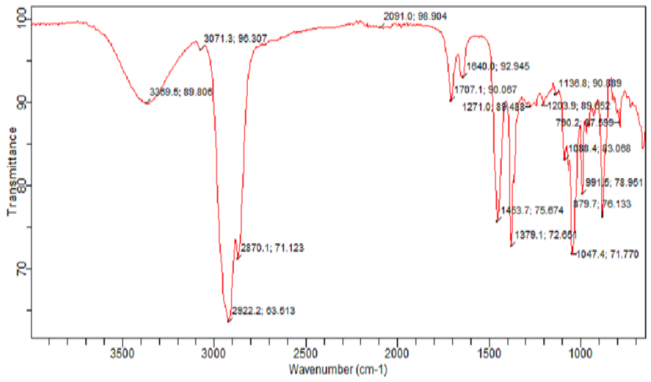

Figure 2. IR Spectrum of purified *Dacryodes edulis* exudate A

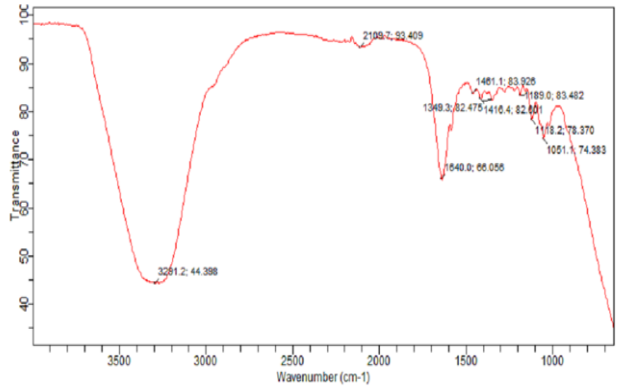

Figure 3. IR spectrum of commercial ink

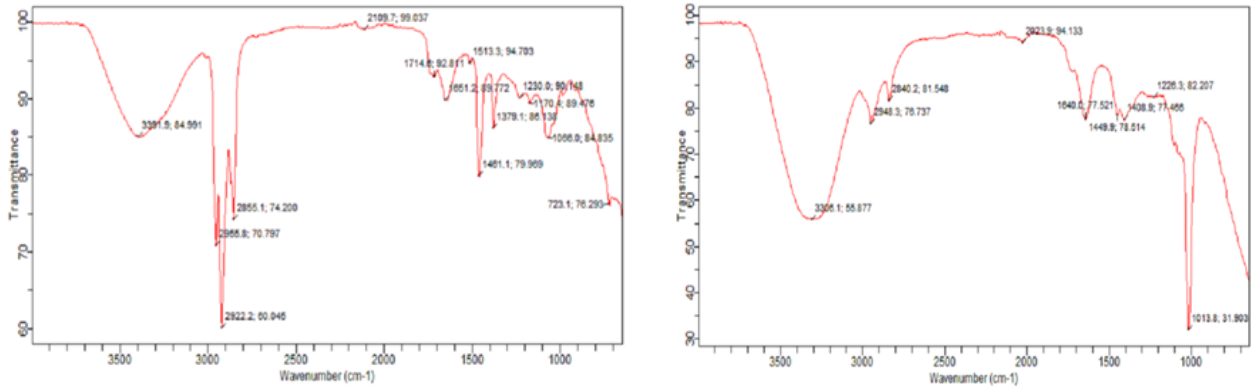

Figure 4. IR spectrum of water-based turmeric extract, and water-based turmeric ink,

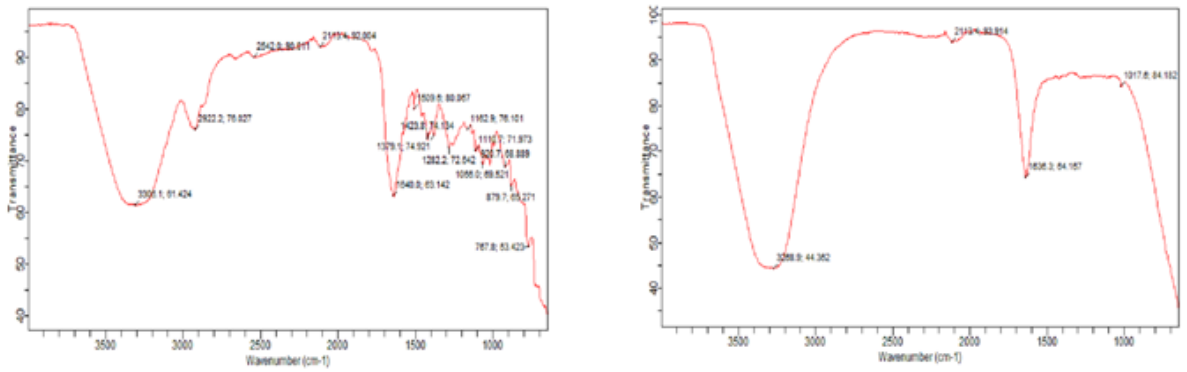

Figure 5. IR spectrum of methanol-based Roselle flower extract and methanol-based Roselle flower ink.

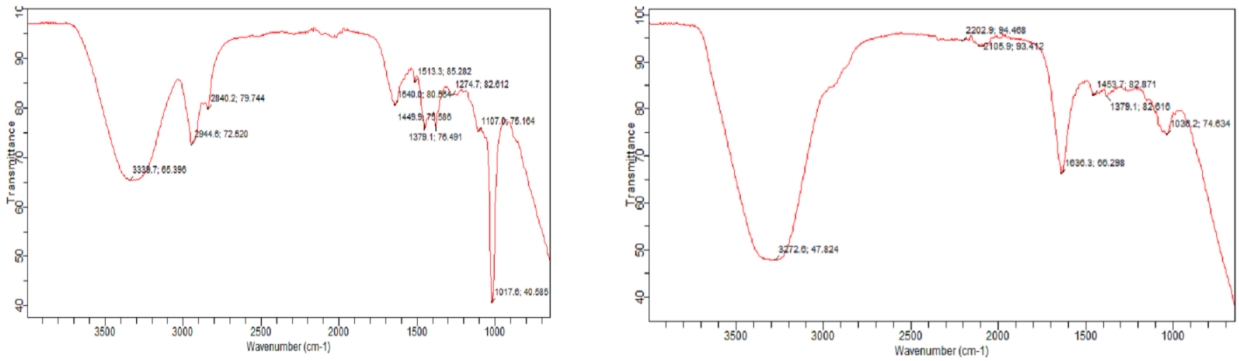

Figure 6. IR spectrum of water-based guinea corn stalk extract and water-based guinea corn stalk ink

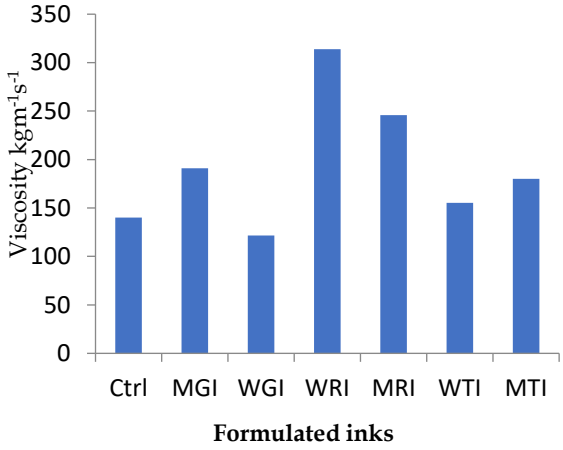

Figure 7. Viscosity of Inks

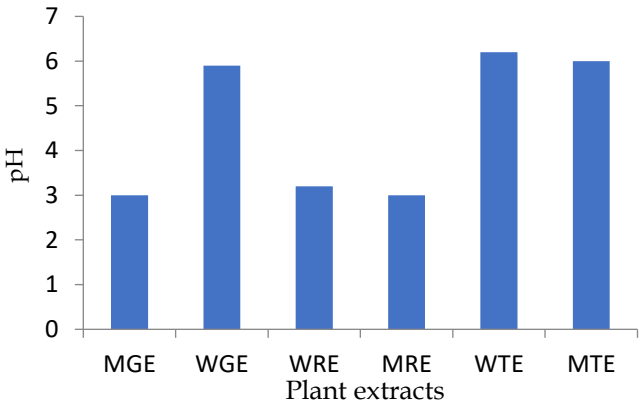

Figure 8. pH analysis of plant extracts

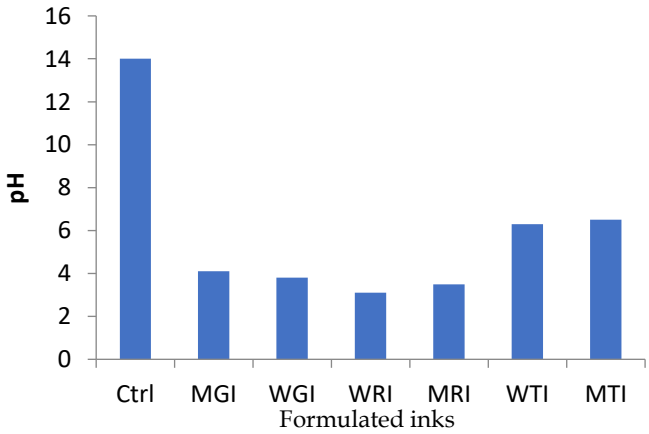

Figure 9. pH of the formulated ink

Ink Formulation and Preparation

The results of ink formulation and preparation by varying the quantity of exudate and/or emulsifier in the ink formulations is shown (**Table 10 & 11**). Different ratios for emulsifier or exudate with extract such as 0.4:1, 0.6:1, 0.8:1, 1.2:1 and 1.4:1 and vice versa of emulsifier to exudate with respective extracts (6 mL) also afforded inks of different natures. The resultant inks were; Water-based Turmeric ink (WTI), methanol-based Turmeric ink (MTI), water-based Roselle flower ink (WRI), methanol-based Roselle flower ink (MRI), water-based Guinea corn stalk ink (WGI) and methanol-based Guinea corn stalk ink (MGI)

Determination of Drying Time of Ink

Results of drying times of formulated inks is presented in **Table 14**. The formulated inks showed the following drying time: MGE (3-5s), WGI (7-8s), WRI (7-9s), MRI (3-5s), WTI (7-11s) and MTI (4-6s) compared to the control (1-3s). Generally, the Table revealed that methanol based formulated inks dry faster compared to the water-based formulated inks.

Determination of Viscosities

The viscosities of the formulated inks ranged from 121.06 $kgm^{-1}s^{-1}$ to 313.86 $kgm^{-1}s^{-1}$. WRI (313.86 $kgm^{-1}s^{-1}$) had the highest viscosity followed by MRI (246 $kgm^{-1}s^{-1}$). WGI (121.06 $kgm^{-1}s^{-1}$) had the lowest viscosity when compared to the control (140.10 $kgm^{-1}s^{-1}$), **Figure 7**. The viscosity of methanol, water and exudate used in this study were; 5.43 × 10^{-1} $kgm^{-1}s^{-1}$, 1.01 × 10^{2} $kgm^{-1}s^{-1}$ and 204 × 10^{3} $kgm^{-1}s^{-1}$ respectively (**Table 13**).

pH analysis

The pH of the extracts is illustrated in **Figure 9**. The results showed that WTE has the highest pH (6.5) of all the plant extracts. MGE and MRE have the lowest pH of 3.0. The pH value of WRE was 3.2. From the results obtained, it was observed that all the extracts were acidic in nature.

Discussion

Extraction of the plant samples afforded yellow-, red- and maroon-coloured extracts. Turmeric, Roselle flower, and Guinea corn stalk were chosen for this research because they were pigmented. Turmeric has yellow pigments which contain 3-15% polyphenols in turmeric rhizomes with curcumin as principal compound [18]. Curcumin, also known as diferuloyl methane or 1,6-heptadiene-3,5-dione-1,7-bis(4-hydroxy-3-methoxyphenyl) -(1E,6E) is a yellow-orange powder with a molecular weight of 368.37 g/mol [19]. The most dominant anthocyanins of roselle petals and guinea corn stalk are delphinidin-3-sambubioside and cyanidin-3-sambubioside. The intriguing red and maroon colours of these extracts were corroborated to the presence of these compounds [20]. The extracts: MGE, WGE, WRE, MRE, and MTE were coloured and soluble in methanol and water except WTE which was partially soluble in water as they formed supernatant when left on standing.

The presence of alkaloids, saponin, tannin, phenol, and carbohydrate in all the plant extracts further buttress the nutritional functions that could be derived from these plants [21]. Anthraquinone was not present in MGE and WGE respectively. Tannins were conspicuously present in all the extracts. Wudig and Woller (1989) [22] reported that tannins were employed as a caustic agent for cationic dyes in the dyeing industry, as well as in the manufacture of inks such as iron gall ink. Tannins are also used as mordant to mitigate the environmental hazard caused by metallic mordant or metallic salt [23].

The extracts were subjected to UV/Visible spectrophotometric analysis in the range of 190-1150 nm, the wavelengths of absorption of the extracts and their corresponding absorbances were revealed. Maximum absorbance peaks (λ_{max}) were detected at 569.346, 576.181, 562.502, 551.235, 587.092 and 554.861 for WTE, MTE, WRE, MRE, WGE and MGE respectively. The λ_{max} value for WRE, MRE, WGE and MGE did not match with those corresponding to anthocyanins like petunidin (λ_{max} = 543), malvidin (λ_{max} = 542) or (λ_{max} = 546). This fact suggests a bathochromic effect (a shift towards longer wavelength) probably caused by co-pigmentation mechanism. A phenomenon typical of anthocyanins intermolecular association within flavonoids like tannins and catechins acting like co-pigment as reported by several authors [24, 25, 26]. It was observed that increase in caffeic concentration shifted the λ_{max} to a higher value and also increased the possibility of hypsochromic effects in anthocyanins at pH value between 3.0 and 4.0 [25, 26]. We also notice that λ_{max} value for WTE (415 nm) and MTE (425 nm) were within the vicinity of that of curcumin (λ_{max} = 420 nm) [27], a situation which suggested a possible shift such as hypsochromic and bathochromic respectively. This deviation may be due certain factors like removal of conjugation, change in medium or addition of auxochromes [28].

The UV/Vis absorbances of the formulated inks and that of the control (commercial ink) are presented in

Table 9. The maximum wavelength (λ_{max}) of absorption of the formulated inks WTI, MTI, WRI, MRI, WGI, MGI and the control were 723.743, 578.768, 929.58, 1020.855, 987.831, 890.250 and 738.289 respectively. It was observed that MTI showed lower λ_{max} (578.768) while MRI showed a higher λ_{max} (1020.855) compared to the control with λ_{max} (738.289). Comparing the λ_{max} of the formulated inks to their respective extracts, it was observed a markable shift in wavelength (λ_{max}) of the extracts towards longer wavelength, a bathochromic shift of respective formulated inks. This may be due to the addition of auxochrome (Israel, 2009). WTI had the highest intensity when stamped on paper compared to commercial ink. This may be due to the presence of auxochrome which enhances attachment to the substrate and may also increase the intensity of the colour of chromophore [28, 29].

The pH of extracts are illustrated in **Figure 2**. The Figure shows that WTE has the highest pH of 6.2 while MGE and MRE have the lowest pH of 3.0. WRE has pH of 3.2. From the results obtained, the extracts were acidic in nature. The pH of the formulated inks and control (commercial ink) were presented in **Figure 3**. This reveals that all the pH of formulated inks MGI (4.1), WGI (3.8), WRI (3.1), MRI (3.5), WTI (6.2) and MTI (6.5) were acidic compared to the control with the pH of 14.0. We suggest that the additives may not have remarkable influence or alter the pH during the chemical reaction that produced the ink.

The FTIR spectrum has proven to be a valuable tool in identifying functional groups of organic compounds. The FTIR spectra have exhibited the presence of many functional groups for WTE, MTE, MRE, and MGE; characteristic bands were occurring at 2922.2 cm^{-1}, 2944.6 cm^{-1}/2832.8cm^{-1},2955.8 cm^{-1}/2922.2 cm^{-1}, 2944.6/2832.82cm^{-1} and 2922.2/2870.1 cm^{-1}respectively. This corresponds to the C-H stretching of methylene, alkenes, aldehydes, asymmetric methylene and methylene alkene in aliphatic compounds. WTE, WRE, MTE, MRE and MGE showed no absorption between 2220-2260 cm^{-1}which indicates the absence of the cyanide groups in all the extracts, meaning that all extracts do not contain the cyanogenic toxic group. The FT-IR spectra also revealed the presence of chromophoric groups in WTE (C=O, N-O), WRE (C=C), WGE (C=C), MTE (C=C), MRE (C=O, C=C, N-O) and MGE (C=C) indicating that the extracts could be colour carriers. The presence of O-H group was dominant, this group serves as auxochrome and confer colour to the substrate and also increases the intensity of chromophore [28, 29]. The absorption bands of WTI (C=C, N-O), WRI (C=C), MTI (C=C, N-O), WGI (C=C), MRI (C=C, N-O), and MGI (N-O) indicate the presence of chromophores in the inks (**Figure 2-6**). The presence of -OH in all the inks could probably enhance fastness of ink to substrate and also increases the intensity of the colour [28, 30].

The viscosities of the formulated inks were analyzed as illustrated in **Figure 7**, WRI (313.86 $kgm^{-1}s^{-1}$) had the highest viscosity while WGI (121.06 $kgm^{-1}s^{-1}$) had the lowest viscosity compared to the control (140.10 $kgm^{-1}s^{-1}$). The increase in viscosity of the formulated inks may be influenced by the viscosity of the *Dacryodes edulis* exudate and the densities of the solvents (water and methanol) used for the extraction of the dyes. Viscosity influences the rheology of inks. MGI, WRI, MRI, WTI and MTI have higher viscosities compared to WGI, we suggest that highly viscous inks may delay flow rate of formulated inks. The drying times of the formulated inks was monitored (**Table 12**). The formulated inks show the following drying time MGE (3-5s), WGI (7-8s), WRI (7-9s), MRI (3-5s), WTI (7-11s) and MTI (4-6s) compared to the control (1-3s). Generally, it was revealed that methanol-based formulated inks dry faster than water-based inks. The observed longer drying times for the prepared inks may be due to the influence of the binder and the density of the solvents used for the extraction of the dyes [31]. The best formulated inks were in the ratio of 6:1:1 (extract: exudate: honey). Most properties of the formulated inks compared well with commercial ink except for the pH value which, indicates that the formulated inks were acidic, this resulted in spreading and causing see-through on printed paper highlights the need for more research to modify the properties of inks formulated from local materials.

Conclusion

The findings of this study revealed that locally available plants, like Turmeric (*Curcuma longa*), Roselle (*Hibiscus sabdariffa*) and Guinea corn (*Sorghum vulgare*) exhibited ink-forming properties which can be linked to their phytochemical and physicochemical properties. Additionally, inks formulated from methanolic extracts were found to be of superior quality compared to water-based ink.

Conflict of Interest

The authors have no conflict of interest to declare

Funding

The authors declared that no financial support has been received from any organization that may have an interest in the submitted work.

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