Potentials of *Crescentia Cujete* Calabash Shell Ash (CCCSA) for Possible Pigmentation Ceramic Product Development

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Abstract
Ceramic materials are continually used for the production of traditional ceramics wares. Surface finishing of the wares had accordingly witnessed enrichments with either direct glaze (company) recipes or experimental treatments with oxides of different rock minerals. The search for more glaze effects derived from both organic and inorganic materials remains important to guaranteed esthetic surface qualities in ceramics product development. This paper investigates the chemical constituents of Crescentia Cujete Calabash. Shell Ash (CCCSA) in view of ceramic pigmentations. The approach to this investigation combines analysis of the sample (CCCSA) using X-ray Fluorescence (XRF) and the application of heat on the sample. The results of the mineralogical analysis of CCCSA indicated the presence of Silver (Ag_2O) in the composition having a value of up to 98.1%. Even more surprising, a blue-green colouration was observed when CCCSA was fired to 930^{O}C in an oxidizing atmosphere. CCCSA was further fired to a higher temperature (about 1100^{O}C) in a reduced atmosphere to observe its effect on the ceramic body. At this point, the results indicated good organic fusion in the use of the material as well as an obvious connection between the material and the fired clay body. In conclusion, the presence of colour, stability and the fusion of CCCSA at 930^{O}C and 1100^{O}C temperatures is seen as an indication of the potentials of CCCSA for possible low-temperature pigmentation in ceramic product development. It is recommended that further experimentation into in-glaze/on-glaze/over-glaze treatment, on-glaze enamel, stains and ceramic inks using CCCSA should be encouraged.

Keywords: Potentials, Crescentia Cujete, Ceramics, Pigmentation, Composition

Introduction

The abundance of solid minerals, particularly those of the ceramic family in Nigeria, should have projected the country as a major exporter of ceramic raw and refined materials. However, raw materials development is relaxed to the success of the ceramic sector of the nation's economic and industrial growth. This could be due to the lack of standard beneficiation of the raw material from individuals, entrepreneurs, and companies who wants to produce good quality ceramic products to create wealth, but none want to prepare the raw materials (Datiri, 2012). However, the reality is that the country imports 65 million tons of ceramic wares and glaze materials annually (David, 2015). Reports also indicate that Nigeria spends Ninety-three Billion Naira (₦93bn) annually on ceramic imports, and in the recent report Nigeria spends Three hundred and twenty-five point eight Billion Naira (₦325.8bn) on importation of ceramics yearly (Jeremiah, 2019); thus leading to a loss in foreign exchange earnings. This is a source of worry and bring to light the need for the development of local ceramic materials. Nevertheless, no study has been carried out on the use of *Crescentia Cujete* Calabash Shell Ash as a ceramic material in an attempt to salvage this situation.

This paper is therefore intended to fill this gap by investigating the potentials of *Crescentia Cujete* Calabash Shell Ash (CCCSA) for possible pigmentation in ceramic product development.

Review of Related Literature

Brief History of the use of Ash and colourant

The earliest examples of ash glazes were produced in the Middle East. The advances made by the Chinese on kiln technology resulted in the development of kilns that fire up to 1200^{0}C. Glaze produced in China within this period (Bronze Age) was an accidental reaction of the components of the wood ash and heat within the kiln chamber. Archaeological evidence found at the Shang site in ancient China revealed high-fired stoneware ceramics with hard, thin greenish wood ash glazes dated to the Bronze age (3500 years ago) (Wood, 1999).

Wood ash and clay glazes were used almost unchanged for a period of about 2000 years from 1000 BC – 1000 AD and include the well-known grey-green Yue wares. From the 10th century, AD limestone was used either with or instead of wood ash to provide calcium or lime (CaO) for glazes. The introduction of lime in glaze formulation led to a decline in the amount of wood ash used (Metcalfe, 2008).

However, in Britain, the use of ash glaze was credited to Bernard Leach in the early 20th century. While the practice of glaze in Nigeria was linked to the activities of a British potter Michael Cardew, who studied under Bernard Leach. Cardew travelled extensively and taught pottery around the world including Nigeria. The impact of pottery created by Cardew in Nigeria from 1950, resulted in the establishment of pottery centres and studios in many of our institutions of learning and towns across Nigeria, where wood ash glaze production was taught and produced.

Historically, potters made a glaze from feldspar, ash and whatever iron-rich clays were available locally. This usually meant brown pots, or occasionally another earth-tone colour. Then they began using metal oxides-like copper oxide, chrome oxide, manganese, iron oxides and blending them with opacifiers to create colours. There is a piece of historical evidence that coloured frits were used at least as early as 2600 BCE. Egyptian blue was a combination of silica, limestone, sodium, and copper oxides. This required a great deal of knowledge of glaze chemistry and firing to achieve the desired colours (Britt, 2021).

Permanent Markers

A marker can be classified as a permanent marker only if it adheres to most surfaces and/or is water-resistant. The pigment used, which gives the formulation a colour effect (colourants), determines how well a marking will resist fading and the combination of ingredients used in the formulation gives it permanent properties. All markers contain some basic ingredients that make up a marker. These ingredients dictate how they interact to deliver a reliable result. According to Andy (2018), a Permanent marker is composed of three elements: a colourant, a solvent, and a resin.

Colourant

The colourant is a pigment or dye that gives ink its specific colour. Whether black, blue, red, neon, pink, or any other hue, the colourant is what you see when you look at a line made by a permanent marker. The main difference between dye and pigment according to Andy (2018) is that dyes are water-soluble while pigments are generally insoluble in water or non-polar solvents unless the pigment is ground into very, very fine powder. Therefore, because of this property, pigments are usually the preferred colourant for markers, given their resistance to dissolution by humidity or other environmental agents.

Solvent

Solvent an important ingredient in the formulation of permanent markers. A solvent always differs in each type of marker while the other ingredient remains constant. Permanent markers use toluene and xylene in their solvent which gives the markers their ability to leave a long-lasting mark. Manufacturers use xylene as a solvent, but switched in the 1990s to less toxic alcohols like ethanol and isopropanol (Andy, 2018).

Resin
Resin is a glue-like polymer, it ensures that a colourant sticks to the surface once the solvent evaporates. If ink were just colourant and solvent, the colourant would turn to dust and fall off the surface as soon as the solvent dried or evaporated (Andy, 2018).

Types of Ceramic Colourants
Colourants used in pottery making are generally of two types, the simple metal oxides and carbonates. These cover the colour spectrum through the blending of two or more simple colourants or the use of stains used singly or in combinations. Recent developments in the production of stains have been very useful in simplifying colour blends to achieve a wide range of colour experimentation. Stains can be used in combination with simple oxides and carbonates. Generally, stains are more stable in their reactions with the glazes; they may be used in underglaze and over glaze as well as in glazes fired as high as cone 11 without being destroyed. Although, others tolerate firing only to the low temperatures, and some of this yield quite saturated colourations (Behrens, 1981). The cadmium sulfide, selenium reds are an example of these low-fired colourant stains. However, of the hundreds of colourants available from the various companies engaged in their manufacture, Behrens (1981) found some widely used colourants with desired effects as shown in Table 1.

Table 1: Summary of Some Commonly Used Ceramic Glaze Colourants

Oxide	Firing Conditions	% Use	Colour Effects
1. Chromium	Not reported	Since it dissolves poorly in most glazes, the addition of less than 1% tends to produce transparent greens, while larger amounts tend to produce a dispersed pigment green appearance.	Green colours, brown, coral reds or yellows, transparent greens, dispersed pigment green. A large amount of chromium green in the glaze may increase the viscosity, much as alumina does.
2. Cobalt	Cobalt oxide pigments are among the most stable under both oxidation and reduction conditions	Generally, in the range of from 0.5 to 2.0%.	Cobalt blue.
3. Copper (black, red, carbonate)	Either oxidation or reduction.	Copper pigments generally are added to the glaze in increments of 1 to 4%.	Turquoise blue in strongly alkaline glazes and gives green in more acid type of glaze. In reduction, copper reds are produced.
4. Gold		The amount of gold chloride needed to create such effects lies in the range of from 0.25 to 0.50%	In some low- temperature glazes, gold may produce rosy- colours.

5. Iron Oxide (red, black)	Red iron is finer in particle size and is more stable. It is the form used in oxidation firing. Black iron oxide is usually preferred for reduction firing.	Amount of 2 to 7% for oxidation firing. In reduction firing 0.5 to 2.0%. Addition of 10% iron-red results during cooling in oxidation firing.	Both oxides produced hues ranging from tan to brown in oxidation firing. In reduction firing, celadon colours may be obtained.
6. Manganese (oxide, carbonate)	Not reported	From 2 to 4% of this colourant may be used in the average glaze.	Browns in strongly alkaline glazes, purple hues may result.
7. Nickle (green, black)	Not reported	Nickel oxide is added to the glaze in the amount of about $1^{1}/_{4}$%; depending upon the composition of the glaze.	The colourant may produce greys, browns, greens, ice blues, and rosy reds.
8. Opacifiers (the prime opacifying agents are: tin, zircon, and titanium.	Not reported	Not reported	Tin will provide the whitest opaque in most glazes. While titanium tends to form warm colour titanates with lead and several other materials which may give a cream or yellow tinge to the glaze. After solution in the molten glaze, titanium may produce a segregated flock in the glaze while cooling.
9. Rutile	Not reported	An addition of 5% usually is adequate for opacifying with tin, the addition of 5% or more of titanium or rutile is sufficient to influence opacity and patterning of the glaze containing them.	An impure form of titanium reacts in much the same as does the pure form but tends to produce warm colours due to the iron impurity in the mineral.

Source: (Behrens, 1981)

Ceramic Stains

Each colour is not guaranteed on all bases, and being aware of these reference notes will help you achieve greater success. Ceramic stains are not meant for all firing conditions and are generally designed for neutral or oxidation firing atmosphere (although some may work in reduction atmospheres). Because ceramic stains contain colouring metal oxides along with other ceramic materials like opacifiers, silica, and alumina, adding them to such glaze bases can cause a glossy glaze surface to turn matte. Ceramic stains are generally added at 5-8% in a glaze and 15-25% in slips and bodies. At 8% most of the glazes are opaque and flat but if you add a small amount of stain (1-3%) it is possible to get transparent colours, including some very nice transparent celadon-coloured glazes, when fired in an electric kiln or similar neutral atmosphere (Britt, 2021).

Some Plants Species Identified to Have Been Used in Ash Glazes
In this review, Metcalfe (2008) listed out some plant's species identified to have been used in ash glazes, to increase our understanding of the use of organic glaze recipes. It was reported (see table 2) that the use of *Crescentia Cujete* Calabash Shell Ash as a ceramic glaze material has not been reported.

Table: 2 Plant species identified as having been used in ash glazes.

FAMILY	GENUS/SPECIES	COMMON NAME
Aceraceae	Acer pseudoplatanum	Sycamore
Betulaceae	Betula	Birch
Buxaceae	Buxus	Box
Compositae	Helianthus annus	Sunflower
Cruciferae	Brassica napus	Oilseed rape
Fagaceae	Fagus	Beech
Fagaceae	Quercus	Oak
Gramineae	Zea mays	Maize (com cob)
Gramineae	Oryza	Rice
Gramineae	Triticum	Wheat
Grossulariaceae	Ribes nigrum	Blackcurrant
Hippocastanaceae	Aesculus hippocastanum	Horse chestnut
Labiatae	Lavandula	Lavender
Leguminosae	Vicia faba	Field bean
Leguminosae	Trifolium repens	Clover
Leguminosae	Pisum sativum	Combining pea
Leguminosae	Phaseolus vulgaris	Navy bean
Leguminosae	Glycine max. vulgaris	Soya bean
Linaceae	Linum grandiflorum	Linseed
Oleaceae	Fagus	Ash
Onagraceae	Oenothera biennis	Evening primrose
Philadelphaceae	Philadelphus	Philadelphus
Polygonaceae	Fagopyrum esculentum	Buckwheat
Pteridiophyta	Pteridium aquilinum	Bracken
Rosaceae	Malus	Apple
Rosaceae	Crataegus	Hawthorn
Rosaceae	Prunus	Plum and cherry
Rosaceae	Pyrus communis	Pear
Salicaceae	Populus	Poplar
Salicaceae	Salix	Willow
Ulmaceae	Ulmus glabra	Elm
Vitaceae	Vitis vinifera	Vine

Source: Metcalfe, 2008).

Summary of Some Current Studies on the Production of Ceramic Pigments and Applications
Rosado, L., Vanperenage, J., Vandenabeele, P., Candeias, A., da Canceicao Lope, M., Tavares, D., Alfenim, R., Schiavon, N., & Mirao, J. **(**2017) carried out a multi-analytical study of ceramic pigments application in Iron Age decorated pottery from SW Iberia. In the study, pottery fragments, plates, Illite, and common clay minerals were sourced using Optical microscopy, XRD, XRF, EDXS, Raman spectroscopy techniques. The results suggested that hematite and pyrolusite are the main mineral

carriers of the Fe and Mn chromophore irons, responsible for the red and black colour, while Illite a common clay mineral is giving the white colour at 1000^{0}C.

Patricia, M.; Cavalcante, T.; Dondi, M.; Guarini, G.; Barros, F. M.; & Benvindo da luz, A. (2017) had a study on the ceramic application of mica titania Pearlescent pigments in Brazil and Italy, where commercial pigment, gold, and silver lustre were used through XRD, FTIR, SEM, XRF, and PSD methods. The results indicated that Titania mica pigments are stable into glossy coatings up to 900^{0}C-1200^{0}C, being any deterioration of their optical properties due to anatase to-rutile and muscovite-to-feldspar transformations occurring at higher temperatures or after a long firing time. Pigment type with a gold shine is particularly suitable for third fire decoration of ceramic tile, involving low temperature and fast-firing schedule where it can replace expensive metal lusters.
In Turkey, Alasoy, A.; Can, E.; Sahin, O. (2017), conducted a study on the processing of ceramic pigment for higher temperature applications. They sourced their materials from black pigment and oxide Cr2O3, MnO and CuO. In the study, XRD, XRF was used for the analysis. The results indicated refractory pigment, which displays chemical stability at high-temperature application (1100^{0}C-1200^{0}C).

In Italy, Dondi, M.; Blosi, D.; Gardini, C.; & Zanelli, *(*2021) made experimentation on ceramic pigments for digital decoration inks. In this experiment organo-metallic complexes, micronized pigment, colloidal metal, nano-pigment and reactive sol precursors for in-situ synthesis. Five routes adopted in this study include soluble salt, micronized pigment, colloidal metal, nano-pigments, and precursors for synthesis in-situ. The main challenges for ink manufacturers are stability. The technological solutions to improve the colour performance are the Physico-chemical properties of inks, which affects the stability over time are turning critical with the increasing diffusion of digital decoration. From this standpoint, technologies that can control colloidal suspensions and design hybrid organic composites are rapidly gaining interest and application potentials.

In Nigeria, a study made by Fatile, B. O.; Lamidi, Y. D.; Ogundare, T. S.; & Sanya, O. T. (2018) involved the use of silica sand, metallic oxides, gum Arabic, and other fluxing materials for the production of enamel stains from Igbokoda silica sand. The materials used passed through the process of drying, milling, mixing, fritting at 1200^{0}C, grinding, mixing, screen printing and reheating at 680^{0}C. The results confirmed that colours of the composition -A- came out on the wares with brilliant colours than that of composition –B- that is matte in colour.

Methodology

This chapter presents material and methods, experimental procedures, data analysis, validation of results, and conclusion.

Crescentia Cujete Calabash Tree

Crescentia Cujete is an evergreen tree composed of long, spreading branches which create moderate shade beneath the tree. There is the emergence of large round fruit, with a smooth, hard shell, which hung directly beneath the branches of the tree (see Plate I). The fruit takes about six to seven months to ripen and eventually falls to the ground.

Plate I: Crescentia Cujete Calabash Tree
Source: Research Photograph Sheikh (2017)

Processing Crescentia Cujete Calabash Shell Ash (CCCSA)
The thin hard shell of the calabash makes it unusual in the family of Bignoniaceae; and brings forth the suspicion about the hard, Calabash-like might be useful in ceramics when transform into ash. Here, lighter was used to ignite the dried calabash in order to start the fire (see Plate II).

Plate II: Burning Crescentia Cujete Calabash Shell
Source: Research Photograph, Sheikh (2019)

In order to convert CCCSA into ash, the CCCSA collected from the tree was burnt. Before the burning, the CCCSA was heaped on a clean ground so that it will not contaminate with other impurities. Lighter was used to ignite and start the fire in an open air. With this controlled burning of CCCSA, it was possible to achieved complete conbustion as much as possible (see Plate III). The CCCSA took three hours due to the quantity to complete burning and allowed to cool after twenty four hours, which was then ready for sieving (see Plate IV).


Plate III: Burning CCCSA
Source: Research Photograph, Sheikh (2019)


Plate IV: CCCSA ready for sieving
Source: Research Photograph, Sheikh (2019)

The burnt CCCSA was grinded into finer particle sizes and sieved through 40-mesh sieve to convert it into powdered form (see Plate V). It was observed that CCCSA attracts moisture (Hygroscopic) from the surrounding atmosphere therefore, grinding and sieving has to be done under very dry atmospheric condition.

Plate V: CCCSA ready for sieving---Powdered through 40-mesh sieve
Source: Research Photograph, Sheikh (2019)

Experimental Procedures

The samples sourced from CCCSA, were analyzed using X-ray Fluorescence (XRF).
The chemical constituents of CCCSA were subjected to XRF analysis to identify the oxides (mineral content) present in CCCSA. The mineralogical analysis was done using x-ray Fluorescence (XRF) at the National Steel Raw Material Exploration Agency (NSRMEA) Kaduna, Kaduna State, Nigeria.

Method of Preparation and conduct of Analysis.

A certain amount of prepared ash was sieved, first through a kitchen sieve, then through a 40- mesh sieve, before sampling, mixing well at each stage of the process. A small amount of the prepared ash was compressed to form a smooth disc 15mm in diameter and approximately 3mm thick, which is then scanned by the SEM. A beam of electrons strikes the sample, and then secondary electrons are emitted to reveal the characteristics of the element that has been hit. The emitted electron beam output is analyzed by the XRF facility of the microscope, to register the presence of certain elements and quantify the relative amount of each one. It is very important to note, that this tiny sample of ash is homogenous and representative of the ash supply as a whole. The Mineralogical analysis of CCCSA indicated the presence of Ag_2O, Cs_2O, Ce_2O, Tb_4O_7, and HfO_2. The oxides obtained from the analysis are presented in Table 3.

Table 3: Oxides Contained in CCCSA

S/N	Oxides	Physical Characteristics
1	Silver (Ag_2O)	Lusterous, white metallic element; with atomic number 47, weight 107.87, melting point 962^{O}C.
2	Cesium (Cs_2O)	Soft, gold-coloured, highly reactive alkali metal with atomic number 55, melting point 28.4^{O}C.
3	Cerium (Ce_2O)	Very soft, ductile, silvery-white metal that tarnishes when exposed to air; atomic number 58, melting point 799^{O}C.

4	Terbium (Tb_4O_7)	Metallic chemical element; a soft, silvery-white, rare-earth metal that is malleable and ductile. Has an atomic number of 65, melting point 1360^{O}C.
5	Hafnium (HfO_2)	Lusterous, silvery-grey tetravalent transition metal with atomic number 72, melting point 2200^{O}C.

Source: https://www.lenntech.com.elements (2021)

Application of Heat on the Sample (CCCSA)

Blue-green colouration was observed when CCCSA has fired alone in a reduced atmosphere to 800^{O}C as shown on Plate VI.

Plate VI: CCCSA fired to 800^{O}C at reduction atmosphere
Source: Research Photograph, Sheikh (2019)

The blue-green colouration changes to grey-white when CCCSA was cooled and exposed to an atmospheric temperature for 24hrs as shown on Plate VII.

Plate VII: Colour Changes to Grey white when exposed to the atmosphere for 24hrs
Source: Research Photograph, Sheikh (2019)

Nonetheless, when the same CCCSA was fired to 930^{0}C in an oxidizing atmosphere colour was observed as shown on Plate VIII.

Plate VIII: Blue Green Colouration fired to 930^{0}C
Source: Research Photograph, Sheikh (2019)

This suggests that, at above 900^{0}C, CCCSA colour is stable. The presence of colour on the CCCSA is also an indication of the potential of CCCSA as a colourant for Ceramic pigmentation. Compared with other ash materials such as rice husk ash (RHA) (arrow), which showed no colouration when fired to the same temperature (930^{0}C) with CCCSA as shown on Plate IX.

Plate IX: Inset: the colour of the rice husk did not change when fired to 930^{0}C
Source: Research Photograph, Sheikh (2019)

Stability and Fusion of CCCSA at Earthenware Temperature

At this temperature, the material displays chemical stability at high-temperature applications. Similarly, a good organic fusion in the use of the material was observed as well as an obvious connection between the material and the fired clay body. Furthermore, the blue-green colouration survived high temperatures in a reduced atmosphere (see Plate X).

Plate X: CCCSA fired in a reduced atmosphere to 1100 ^{0}C
Source: Research Photograph, Sheikh (2019)

RESULTS

The result of the chemical constituents of *Crescentia Cujete* Calabash Ash was determined by the analysis of the mineral contents of *Crescentia Cujete* Calabash Ash. The values obtained from the analysis are presented in Table 4 and in the line graph see Table 5.

Table 4: Percentage concentration of oxides contained in CCCSA

Oxide	% Concentration
Ag_2O	98.1
Cs_2O	0.64
CeO_2	0.58
Tb_4O_7	0.47
HfO_2	0.22

Source: Research Table, Sheikh (2019)

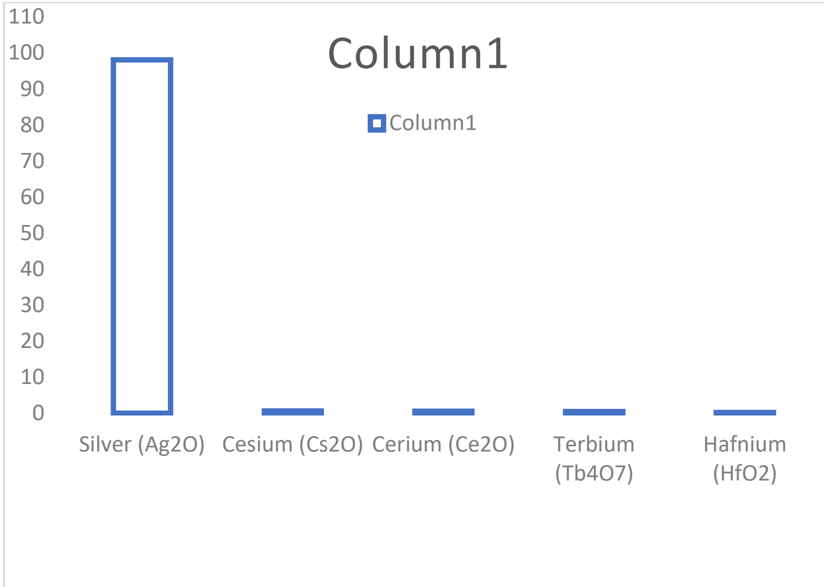

Table 5: Line Graph Showing Percentage concentration of oxides contained in CCCSA
Source: Research Graph, Sheikh (2019)

DISCUSSION OF RESULTS

Results obtained from the experiment conducted was discussed below.

Mineral content of *Crescentia Cujete* Calabash Ash (CCCSA)

Mineralogical analysis of CCCSA indicated the presence of Ag_2O, Cs_2O, Ce_2O, Tb_4O_7, and HfO_2. However, the significance is the percentage composition of Ag_2O, which has a value of up to 98.1%. Although the presence of Ag_2O in CCCSA is at variance with some studies conducted using ashes derived from wood, maize cob ash, rice husk ash, eucalyptus leaves ash (Birkhimer, 2006; Metcalfe, 2008; Ajala, 2009; Isa, 2018) where the major constituent of the ash is potassium (K) and sodium (Na). However, the researcher considers that silver (Ag_2O) which has a melting point of 962^{o}C (http:/lenntech.com/period/element, 2021) in agreement with the stability and fusion of CCCA at 930^{o}C and 1100^{o}C is an indication of the potentials of CCCSA for possible low-temperature pigmentation in ceramic product development.

Colour Changes

A blue-green colouration was observed when CCCSA was fired alone in a reduced atmosphere to 800^{o}C as shown on Plate I. The blue-green colouration changes to grey-white when CCCSA was cooled and exposed to an atmospheric temperature for 24hrs as shown on Plate II. Nonetheless, when the same CCCSA was fired to 930^{o}C in the oxidizing atmosphere no colour changes were observed as shown on Plate III. This suggests that, at above 900^{o}C, CCCSA colour is stable.

The presence of colour on the CCCSA is also an indication of the potential of CCCSA as a possible colourant for ceramic pigmentation. Compared with other ash materials such as rice husk ash (RHA) which showed no colouration when fired to the same temperature (930^{o}C) with CCCSA as shown on plate IV.

Conclusion

Given the over-dependence of Nigeria on the importation of foreign ceramics materials; the researcher considers that the successful development of ceramic colourants using *Crescentia Cujete* Calabash Shell Ash will not only reduce over-dependence on foreign ceramics materials but will also increase the spectrum of organic research thereby increasing local content development. It is important to note that the presence of colour, stability and the fusion of CCCSA at 930^{O}C and 1100^{O}C temperatures is an indication of the potentials of CCCSA for possible low-temperature pigmentation in ceramic product development.

Recommendation

It is recommended that further experimentation into in-glaze/on-glaze/over-glaze treatment, on-glaze enamel, stains and ceramic inks using CCCSA, and other organic materials should be encouraged.

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