Geochemical, Physico-Chemical and Mineralogical Characterization of Clayey Soils Used Traditionally as Therapeutic and Cosmetic Ingredients in Edo State Nigeria

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ABSTRACT

Clayey soils used traditionally for therapeutic and cosmetic purposes in Edo state, Nigeria were studied and characterized for their Geochemical, Physico-chemical and Mineralogical properties. Five clayey soil samples were collected from selected communities-Uzalla, Aforwa and Ohordua within Edo state and standard laboratory methods were used to determine their colour, particle size distribution, pH, specific surface area (SSA) and cation exchange capacity (CEC). Atomic Absorption spectrometry (AAS) were used to characterized the major and minor elemental composition. X-ray Diffractometry (XRD) was used to identify the mineralogical component of the soils samples. Results show that the pH values range from 5.22 to 6.46. The CEC range from 30.8 to 25.6meq, The SSA values were between 0.5 and 2.4 m^2/g. From the colours of the samples, they are inferred to contain hematite and goethite which are present in many skin sunscreen and beauty products. Results of the AAS analysis show that major and minor elements range from 1.0 mg to the limit of delectability 0.0001mg/g. SiO_2 values range between 54.85 and 63.1wt%, whereas Al_2O_3 values range from 12.63 to 26.78%. Results of XRD analysis for mineralogical investigation reveal that the samples are dominantly composed of quartz, kaolinite, halloysite, illite, mica and feldspar.. Samples with the highest concentration of iron oxide showed also the highest UV protection ability.

Keywords: *Clayey soil; Therapeutic; Cosmetic and skin*

Introduction

Minerals have been used for therapeutic purposes since prehistoric times. Besides serving as either active ingredients or excipients in pharmaceutical preparations, minerals have other medical uses[Carretero, M.I., et al 2009] have also reviewed the use of minerals in the pharmaceutical industry as excipients and minerals with other medical purposes, in relation to their physical and physico-chemical properties. These Minerals serving as active ingredients (i.e., having therapeutic properties) may be administered either orally (by ingestion), or topically (by application in the body surface).

The use of clay minerals as active ingredients in pharmaceutical and cosmetic formulations is well documented [Carretero, M.I., 2002; Carretero, M.I.et al 2006; Droy-Lefaix, M.T.et al 2006; Viseras, C. et al 2007]. According to these authors, these clays are widely used for cleansing the skin, emulsification, and detoxification, adsorption of UV radiation, ion exchange with the skin and trans-dermal nutrient supplementation of elements such as calcium, iron, magnesium and potassium. These phyllosilicates minerals could be in any of these forms (smectite, palygorskite, sepiolite, kaolinite, talc, mica).

The therapeutic activity and cosmetic actions of these minerals is controlled by their physical and physico-chemical properties, chemical composition as well as the mineral type. For example, minerals u that is composed of non-toxic ions and capable of reacting with acids that can serve as antacids. They are also effective as anti-diarrhoeaics, osmotic oral laxatives, and mineral supplements. Those minerals with a high sorption capacity and a large specific surface area can also function as gastrointestinal and dermatological protectors, and anti- inflammatory and local anesthetics, Minerals with a high refraction index can be used as solar protectors. Those minerals with a high sorption capacity and a large specific surface area can function as creams, powders and emulsions.

Suitable consistency and appropriate viscosity are required for products to remain in contact with the application surface until the objective is achieved, hence, cosmetic products must therefore be smooth, adhesive and without grittiness [Viseras, C. et al 2007] they must be easy to handle and have pleasant sensation when applied to the skin [Veniale F, et al 2007]. These requirements are greatly influenced by the physical and the physico- chemical properties of the material such as the particle size. So therefore, the physico- chemistry of raw clays plays significant role in their cosmetic and therapeutic suitability.

The cosmetic capabilities of clays are being exploited by many beauty spas around the world. In these spas, the colour of the clays mostly determines their usage. Yellowish clay is used in some spas to prevent bacterial infection on the skin; reddish clays are used for cleansing the skin, and bluish clays against the development of acnes. Greenish coloured clays are applied to reduce the amount of oil on the skin; and black clays for general body nourishment. In many African communities, the traditional usage of clays for cosmetic purposes is a common practice [Mpuchane S, et al 2008].The Wodaabe men of Niger use different clays to beautify their faces during their annual Gerewol festival. The Himba of Namibia smear clays from head to toe to protect their skin from ultraviolet radiation [Nelda P.2004; Baeke V 2009] and the Maasai of Kenya as well as the Xhosas of South Africa smear clays on their bodies for skin cleansing purposes. This practice, which is based on indigenous knowledge has been going on for several years, and has been handed from one generation to another.

In many communities in Edo state Nigeria, clayey soils have been observed to be topically rubbed on the body of children and adults for various reasons. Chief among this reasons, is the traditional usage for cosmetic and therapeutic applications, specifically for cleansing, sunscreen and body beautification in many of these communities. Studies have been conducted on the general usage of clays of Edo state clays [Vermeer DE,et al 1985; Eigbike CO. et al 2013] but the cosmetic application of clayey soils use traditionally in Edo state had not been investigated particularly with respect to their geochemical and mineralogical properties. This paper thus reports on the geochemical and mineralogical properties of clayey soils used traditionally for cosmetic purposes in Edo state Nigeria and their influences on cleansing, sunscreen, body beautification and external healing capability.

Materials and Methods

Study Location /Geology of the study area

The study areas are in three different communities, in Edo State, Nigeria, within coordinates N06°27' 06°80'67" and E005°43' - 006°21' (Figure 1).

5^0 30E $6^0$50 E

Figure 1: Map of Edo state showing the difference sample locations

Edo State is geologically characterized by rocks, whose ages range from Tertiary to Cretaceous [Reyment RA 1965].The geologic formations that underlie Edo State include; Benin, Ameki, Ogwashi-Asaba, Imo and Nsukka Formation and Ajali Sandstone. The study area thus is partly within both the Anambra and the Niger Delta basins. The clays within Uzalla-Benin and Ohordua-Ewatto, for example, belong to the Benin and Ogwashi-Asaba Formation respectively.

Field relationship suggests that, the clays within Auchi-Jattu belong to the Ajali Sandstone. The geological map of the sampling sites is shown in Figure 2.

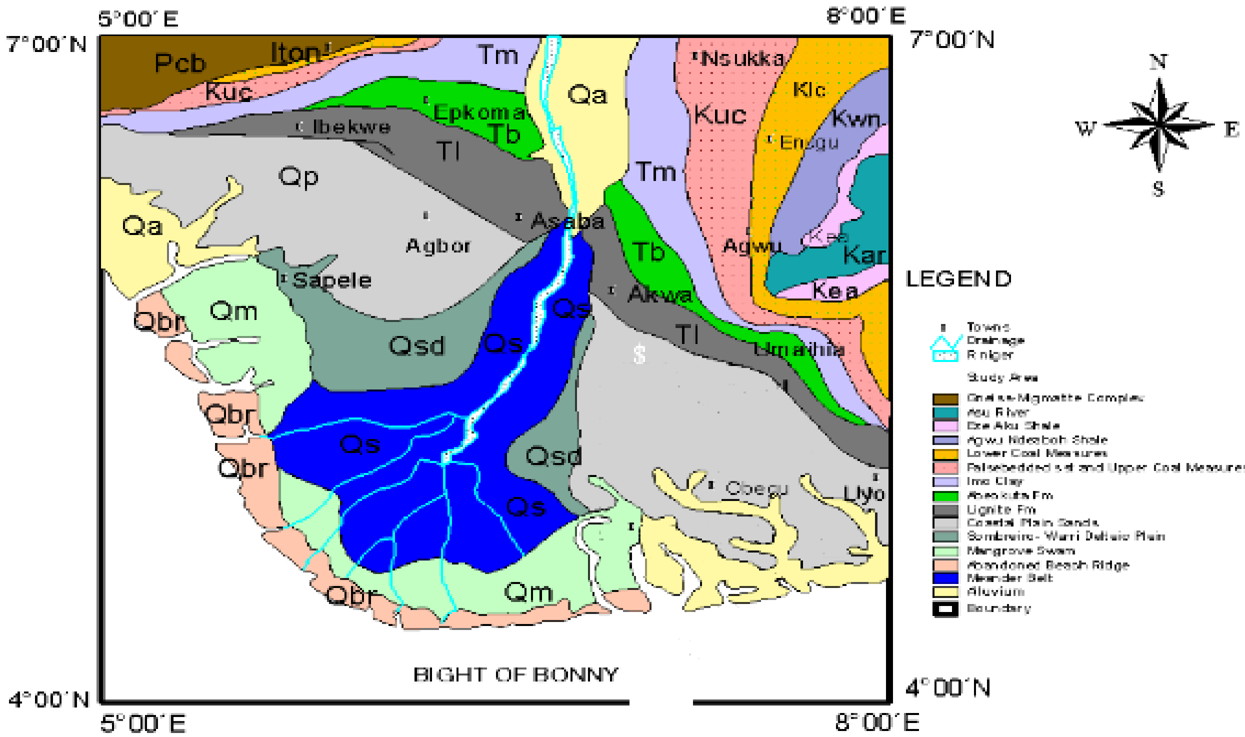

Figure 2: Geological map of Anambra and the Niger Delta basins

Collection of samples/interviews

Five clay samples were collected from three mining sites; Aforwa community in Auchi- Jattu (Edo North), Ohordua (Edo Central) and Uzalla-Benin (Edo South).

Unstructured in-depth individual interviews were conducted with the people of the communities both young and old, women, men and children. Interview sought information on the usage; the motives and the specific clay type use and for what purposes. It was evident that clays from these communities were mined for various purposes, we also found out that the Uzalla clays were majorly mined in large quantity and are sold to neighbouring towns and countries like Cameroon, Togo and Ghana. Pregnant and lactating women consume them as they believe it reduces vomiting and spitting/salivating and that it guarantees the quality and quantity of breast-milk etc.

Again, interview responses revealed that some women turned clays into pastes and rubbed regularly on their skins and those of their children. This practice, they noted, prevented infections and sweating, soften their skin and make them more beautiful.

Physico-chemical analyses

The samples were air-dried after collection, according to the methods of [Van Reeuwijk LP 2002]. Physio-chemical analyses were determined on all the samples. Colour determination was done by visually comparing the samples colour with those in the Munsell Soil Colour Charts 1992),

The particle size distribution and specific surface area of the geophagic soil samples were determined by the hydrometer method as described by [Van Reeuwijk LP 2002], The pH of the clayey soil samples was determined both in a 1:2.5 clayey soil-water suspension ratio according to the methods advanced by [Van Reeuwijk LP 2002], Electrical Conductivity (EC) of samples was measured on the saturated paste extract of each sample as described in the United States Soil Survey Laboratory Manual (1996). Water Retention Capacity (WRC) of the samples was determined using the methods advanced by Forster. The ammonium acetate method advanced by Tan (1996) was used to identify exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and H^{+}) in each sample; and their concentrations were obtained by use of a flame photometer (Model).

Geochemical analyses

To ascertain the major and minor elemental composition of the clayey soil use for both the cosmetics and therapeutic purpose, geochemical analyses were carried out on the samples using Atomic Absorption Spectrometry (210VEP AAS model), following the procedures developed by [Szántó Z, et al 1998]

Mineralogical analyses

Mineralogical composition the clays were determined at Iron and Steel institute in Kaduna via X-Ray powder Diffractometer equipped with Cu K radiation and a secondary graphite monochromator. Data were collected at 40kV and a current of 30mA in the range from 2 to 70^{o} 20 with speed of 3.4^{o} 20/min. Diffraction patterns were identified with the Expert High Score plus program and Rietveld method, a full-pattern fit method where the measured profile and a calculated profile are compared.

RESULTS AND DISCUSSION

Physico-chemical analyses

Colour of analysed therapeutic and cosmetic clayey soils

Results of the colour cosmetic clayey soils analysis show that the samples from the Ohordua are light gray to grayish colour, samples from Aforwa-Auchi) range from reddish brown to red, while those from Uzalla sample are white to grayish in colour.

Table 1: Colours of the samples from the different locations.

Sample No./Code Colour	Locations (site) of samples	Hue value and chroma of samples	Colour
UZ1 (fresh)	Uzalla-Benin	2.5Y/8/2	White
UZ2 (fresh)	Uzalla-Benin	5Y/7/2	Light-grey
AJ 3 (fresh)	Aforwa-Auchi	5YR/5/4	Reddish brown
UZ 4(smoked)	Uzalla-Benin	7.5YR/5/8	Strong brown
OH5 (fresh)	Ohordua	2.5Y/N6/0	Gray

The colour of the clayey soils may play a role in their sun screening abilities. Most of the clayey soils used for sunscreen had a hue of 2.5 YR corresponding to the colour of hematite (Fe_2O_3). This hue value may infer to the occurrence of hematite and goethite in the clayey soils. Both hematite and goethite are oxides of Fe, which are colour causing minerals in soils and are responsible for the reddish and yellowish colour [Carretero MI, 2010] reflected in the analysed soils hence their possible application for sunscreen. The ability of yellowish and reddish coloured clays to perform sun screening activity has been reported to be influenced by hematite and goethite which have low UV radiation transmission values due to their high refractive indices (nw=3.15 and nα=2.39, respectively) (mindat.org/min-1719.html). Sun screening by clays is also influenced by their small particle sizes [Juch RD, et al 1994]. Most of the clayey soils used for sunscreen had majority of their particle sizes in the 2 to 50 µm range. Given their small particle sizes, their specific surface area may provide a platform for the absorption or scattering of radiant energy [Juch RD,et al 1994]. and thereby reduce the intensity of UV radiation that reaches the skin.

Another major reason cosmetics application is for beauty apart from protection and healing and/or cleansing. Clays materials is topically applied to serve this purpose, hence the beautifying effect of the clayey soils could be influenced by their colour. White, red, yellow, gray and brown are common colours of several modern body beautifying cosmetic products such as face powders, lip glosses, nail polishes, blushers and eye shadows [Mpuchane S, et al 2008]. These colours, which occur as a result of the presence of colour causing clay and non clay minerals in soils, can cause radiance during application of the derived cosmetic mixture. The clayey soils had values ranging from 5 to 8, which are light shades that facilitate the painting of bright and colourful decorative patterns on the body.

Particle size distribution and texture of analysed therapeutic and cosmetic clayey soils

Textural analyses results show that the soil samples were texturally dominated by clay size particle with grain sizes ranging from 81.58-91.05% with some silt and very fine sand particles**.** The samples were classified into three textural classes namely: Silty clay loam, silt, sandy loam; with the majority of the samples identified as clay loam in texture.

The particle size distribution and texture of the clayey soils may influence their cleansing ability as the soil materials from all the locations were dominantly clay size (<20), the particle sizes were similar to those of clay mixtures used for cleansing in Thermal Centers, where 57 to 70% of the clay mixtures have particle sizes within the 2 to 20 µm diameter size range

Majority of the particle sizes in the clayey soils were < 50 µm in diameter that is mainly clayey; there was however a considerable amount of sand present in all the soils sample, Sand particles could cause problems when the derived cosmetic mixture is smeared on the skin, as sand particles are dominated by quartz (SiO2), which is a very hard mineral measuring 7 on the Mohr hardness scale [Ngole VM, et al 2010]. The outermost layer of the skin is relatively softer than quartz, and sand particles in the cosmetic clayey soils could damage the skin through bruising during application. Sand particles can therefore prevent the clayey soils from performing the body beautifying role for which they are used. Studies conducted by [Veniale F, et al 2007] indicate that cosmetic mixtures must be smooth, less gritty and non abrasive. Therefore, beneficiation of the cosmetic clayey soils through elimination of sand size particles prior to application on the skin is advised.

pH of analysed therapeutic and cosmetic clayey soils

The pH values of all the samples were generally lower than 7 indicating that they are acidic. The values of the pH (KCl) of all the samples were significantly higher than those of pH (H2O) indicating that the samples were all positively charged.

It has been noted that the pH of clayey soils used for cosmetic ingredients can influence their cleansing ability. According to [Schmid JM, et al 1995; Nash F, et al 2007], suitable skin cleansers must have pH similar to that of the skin or near neutral. Considering that the pH of healthy skin ranges between 4.5 to 5.5 [Korting HC, et al 1992] samples from the three locations (Aforwa, Ohordua and Uzalla) which recorded acidic and near neutral pH can be considered suitable for cleansing application as little chemical reaction is expected to occur when they are topically applied on the skin. An elevated pH > 9 can pose problems to the skin when used as cleansers. This is because highly alkaline cosmetic cleansers have high skin irritation potential and can cause damage to the lipid bilayer of the skin's stratum corneum, leading to dryness of the skin, itching and after wash tightness [Ananthapadmanabhan KP, et al 2004]. Frequent application of alkaline clayey soils for cleansing purposes is thus discouraged and moisturisation of the skin after the cleanser is washed off is advised.

The pH of these clayey soils samples from the study area, could also influence their abilities to beautify the skin. As majority of the clayey soils used by the local practitioners in the study area for body beautification were acidic and within the pH range of the skin, as well as near neutral. The acidic nature of the skin enables it to act as the body's first defense mechanism against bacteria by creating an unfavourable environment for bacterial growth However alkaline pH values which were much higher than the pH of the skin. Studies conducted on the skin's pH by [Korting HC, et al 1992] revealed that optimum growth for the bacteria *Propionibacterium acnes (P. acnes),* which causes acnes was found at pH 6.0 and 6.5; but the growth rate was found to be much lower at a pH of 5.5. This led to the conclusion that minor shifts in skin surface pH from its normal acid range towards alkaline values may be detrimental to the skin [Korting HC, et al 1992] such clayey soils may instead cause damage to the skin rather than beautifying it, even though this may depend on the frequency of application.

Cation exchange capacity (CEC) of analysed therapeutic and cosmetic clayey soils

The cation exchange capacities of the clayey soils from the different location were moderately high, within the range of 30.8 to 25.6meq/100g as compared to those reported by Abrahams and parsons.

Clays with high CEC have been reported to ensure cleansing through absorption of toxins, bacteria and unwanted substances from the skin during topical application [Szántó Z, et al 1998; López Galindo, A. et al 2007]. The high volume % of clay size particles in the analysed clayey soils can justify the moderate to high CEC of the soil samples from the three locations, whose absorption capacity could be high. High CEC of the clayey soils can therefore influence exchange of ions from the clayey mixture to the skin and vice versa [Tateo F,et al

2009]. The exchange of ions between the clay mixture and the skin can enable absorption of unwanted substances from the skin by the clay; hence ensuring skin cleansing action. The smearing of clay on the skin can induce perspiration, which forms a medium through which ions are exchanged from the skin [Carretero MI,2010] and the result is a refreshing effect on the skin. It is important to state that excessive high CEC allows the retention of ions in the clays materials that may potentially be harmful to health [Quintela A, et al 2012].

Specific surface area of analysed therapeutic and cosmetic clayey soils

Specific surface area of the samples ranged from 0.55 m^2/g for Uzalla sample to 2.4 m^2/g for sample Ohordua, the Specific surface area of the Aforwa clays sample was 1.31 m^2/g and while the Uzalla roast has 0.96 m^2/g.

Water Retention Capacity of analysed therapeutic and cosmetic clayey soils (WRC)

Water retention capacity is also known as the porosity of the soil; it is ability of soil to hold or retain water. The clays soil samples differ in terms of their WRC. Those with high clay content tend to have higher WRC compared to those with high sand content.

Table2: Results of some Physico-chemical parameters analyses

Parameter	Units	UzallaBenin (Raw)	Uzalla-Benin (Smoked)	Aforwa-Auchi	Ohordua
pH H_2O		5.27	5.67	5.22	5.53
pHKCl		6.38	6.47	6.05	5.98
Sand	%	4.97	5.36	4.86	0.61
Silt	%	9.67	8.99	13.56	8.34
Clay	%	85.36	85.65	81.58	91.05
Porosity	%	30.39	30.23	25.45	40.38
CEC	Meq/100 g	27.8	30.8	28.6	25.6
Specific Surface Area	m^2/g	0.55	0.96	1.31	2.40

Geochemical Analyses

Below are the Bulk elemental oxides chemical composition of both major and trace elements analyses of the clays soil sample from the different locations in order to geochemically characterized the soil and know what it composition is and the relevant of the elemental composition with respect to its active ingredients in therapeutic and cosmetics purpose.

Table 3: Bulk elemental oxides chemical composition of both major and trace elements analyses of the clays soil sample from the different locations.

Parameter	Units	Uzalla-Benin (Raw)	Uzalla-Benin (Smoked)	Aforwa-Auchi	Ohordua
Na_2O		1.37	1.02	1.54	1.30

K_2O		0.44	2.97	6.05	5.98
MgO	%	0.19	0.64	0.83	0.42
CaO	%	0.35	0.11	0.23	0.33
Al_2O_3	%	23.62	12.63	26.78	22.44
P_2O_5	%	0.13	0.13	1.11	0.12
SiO	%	63.1	61.98	56.37	59.95
Fe_2O_3	%	2.31	1.75	3.14	2.19
MnO	%	0.04	0.04	0.04	0.04
ZnO	%	0.85	0.63	1.22	0.81
CuO	%	0.03	0.02	ND	0.03
PbO	%	0.01	ND	0.01	0.12
Cr_2O_3	%	ND	ND	ND	ND
Ti_2O	%	4.41	4.50	5.00	4.56

The sun protection ability is influenced greatly by the concentration of Fe_2O_3 in them. TiO_2 and ZnO also play a role in offering UV protection ability. It has been stated and proved that UV protection ability is closely related to the presence of iron containing minerals. For example, hematite (Fe_2O_3) contains Fe^{3+} bonded to O^{2-}, where the electron configuration of Fe^{3+} is characterized by an empty orbital (4s), so that inner electrons can absorb the energy and move from the 3d orbital to the 4s orbital with a higher energy level. TiO_2 particles (Specifically Ti^{4+}ions) have the same UV absorption mechanism. The octahedral sheet in the structure of clay minerals also can contain Fe^{3+} ions that have an electron configuration with an empty orbital, and thus it should theoretically absorb photons. This assumption was shown experimentally by [Serpone N.et al 2007] where the absorption intensity in the UV-C range was directly correlated to structural octahedral contents of Fe^{3+} in smectite clays.

The commercial sunscreens containing TiO_2 and ZnO showed more intensive UV protection abilities in all UV-B and in the beginning of UV-A range, therefore they also have much higher SPF values – 15, 30 and 50. Pastes and creams containing TiO_2 and ZnO for application as sunscreens tends to be white on the skin, which is unacceptable for cosmetic use, therefore occasionally iron oxide pigments are added to improve the appearance of the product [Wagner, J.C.,et al 1998]. Because most of the clays from Aforwa and Uzalla are brown, they can be used as pigment in sunscreens of tonal creams. At the same time the addition of clay fraction would increase the sun protecting factor (SPF) of the product, thereby decreasing the necessary amount of synthetic UV filters to obtain certain SPF value.

Mineralogical Analyses

From the XRD analyses, series of minerals were identified from all of the five samples collected from the different locations; the primary minerals are quartz, (SiO_2), Feldspar (orthoclase and Albite) $KAlSi_3O_8$ and $NaAlSi_3O_8$ respectively, mica (possibly muscovite), $KAlSiO_3O_8$ several secondary minerals were also available but the most dominant groups were the kaolinite, Al_2SiO_5 $(OH)_4$; Illite, $K,H_3OAl_2Si_3AlO_{10}$; montmorllonitic, CaO_2 (Al, Mg) $2Si_4O_{10}(OH)2.4H_2O$. Other important clay mineral that was identified is Halloysite $Al_2Si_2O_5$ (OH) 4.2H2O. Diagnostic peaks for the identification of the minerals together with the International Centre for Diffraction Data (ICDD) reference numbers and the crystals system, d-values, peak intensity of the minerals are presented from figure 3-5.

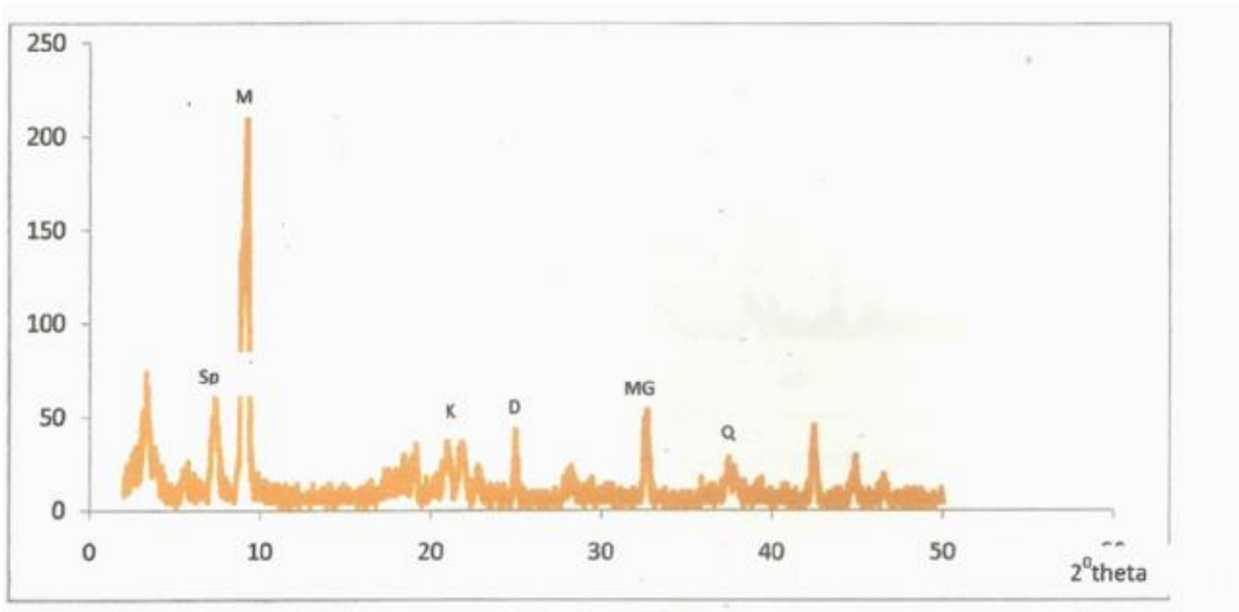

Figure 3**:** Representative diffractogram of Aforwa- Auchi samples of the geophagic clayey with the identified minerals:Q=Quartz,M=Muscovite,K=Kaolinite,Mg=Magnesite,Sp= sepolite,D=Dickite

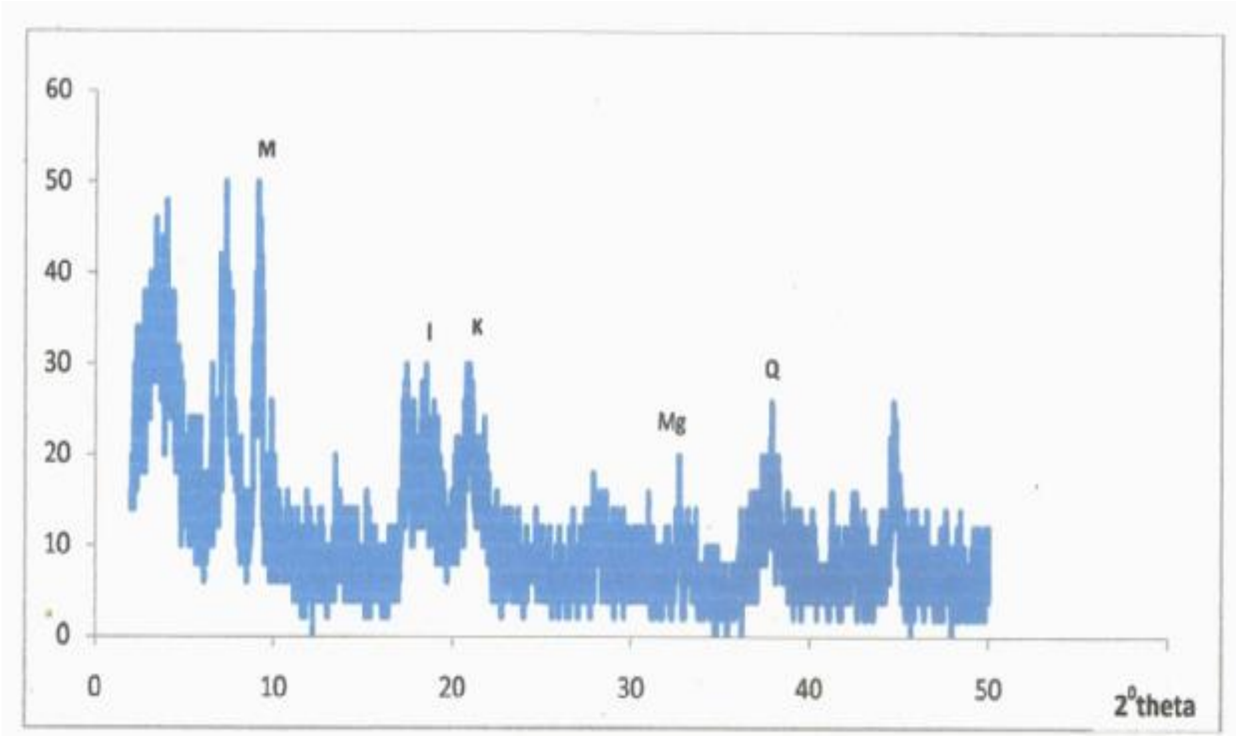

Figure 4**:** Representative diffractogram of Uzalla samples of the geophagic clayey with the identified minerals:Q= Quartz,M=Muscovite,I=Ilite,K= Kaolinite,Mg=Magnesite

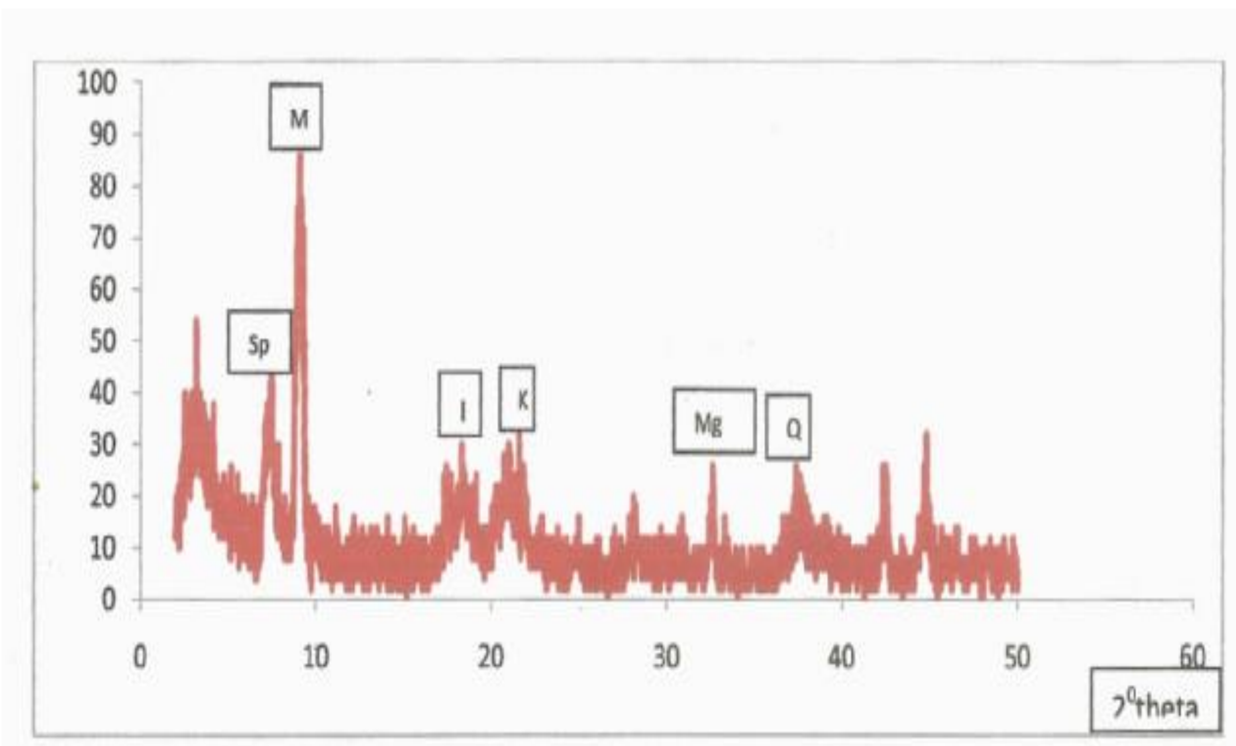

Figure 5**:** Representative diffractogram of Ohordua samples of the geophagic clayey with the identified minerals: Q= Quartz, M=Muscovite, K= Kaolinite, Mg=Magnesite,Sp= sepolite, I=Illite

From the XRD results it shows that the clays from the various study location contain quartz as it dominate minerals followed by feldspar and mica as the primary minerals, kaolinite, Illite, sepolite, and other were also in abundance as secondary minerals. These minerals with a high sorption capacity and a large specific surface area can function as creams, powders and emulsions, these minerals can adhere to skin to form a film, which provides (mechanical) protection against external physical and chemical agents. By taking up skin exudations and creating a surface for evaporation, such minerals also have a refreshing action. In addition, they exert a soft antiseptic action by producing a water-poor medium that is unfavourable to bacterial growth. Indeed, some of these minerals (e.g., kaolinite, talc, and smectites) are good sorbents of dissolved or suspended substances (greases, toxins), bacteria and viruses.

Therapeutic actions may be enhanced by using minerals with adsorbent and heat retention properties of which kaolinite is the most common. It is topically applied as a poultice to reduce inflammation and alleviate pain. Hot poultices are used, because the heat is also a therapeutic agent. Opaque minerals with a high sorption capacity are used in cosmetic formulations as creams, powders, emulsions in order to give opacity, remove shine, and cover blemishes. Besides adhering to skin and forming a protective film, these minerals can take up grease and toxins. Palygorskite and sepiolite (in liquid preparations) together with kaolinite, smectites, and talc are the principal minerals used for this purpose.

On the other hand, micas have long been used in eye shades and lipsticks for their high reflectance and iridescence. More recently, muscovite mica are added to moisturizing creams in order to produce a luminous effect on skin. The mineralogical composition of these clays from Edo state all have these minerals in there, though their concentration is not very certain.

CONCLUSION

This paper has examined the Geochemical, Physico-chemical and Mineralogical properties of therapeutic and cosmetic clayey soils from selected communities within Edo state Nigeria Based on the results obtained, the colours of the analysed clayey soils infer the presence of hematite which is present in several modern sunscreen products. Due to high CEC values of some of the samples, ion exchange from the skin to the clayey mixture, as well as release of ions unto the skin can occur during application, and thereby facilitate skin cleansing and refreshing. The acidic and near neutral nature of majority of the clayey soil samples may limit the chemical reactions that could occur between the skin and the clayey mixture during application; and the acid balance of the skin may remain intact. The cosmetic ability of clays however, is not only influenced by their physicochemical properties. Other specific mineralogical and chemical properties also play vital roles in the cosmetic and therapeutic capabilities of clays. Among the clay minerals, are the smectite group minerals enjoys wide applications in the pharmaceutical industry because of their high swelling and retention capability, and cation exchange capacity. Kaolinite, sepiolite, and palygorskite are also used in pharmaceutical and cosmetic products.

Future developments would include purification (e.g., elimination of potentially harmful trace elements), laboratory synthesis of selected minerals, delamination of clay minerals, It is therefore recommended that furthers studies be conducted on the identified samples to obtain in-depth understanding of cosmetic properties and capabilities of the identified clayey samples.

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