

Physical and Chemical Evaluation of Geophagic and Cosmetic Clays from Southern and Western Nigeria: The Health Implications

Bisi-Johnson Mary Adejumoke¹, Oyelade Hamzat Adebayo², Adepelumi Adekunle Abraham³, Adewole Stephen Olarinde⁴

^{1,2}Departments of Microbiology, Obafemi Awolowo University, Ile-Ife, Nigeria

³Departments of Geophysics, Obafemi Awolowo University, Ile-Ife, Nigeria

⁴Departments of Anatomy and Cell Biology, Obafemi Awolowo University, Ile-Ife, Nigeria

(¹jumokade@yahoo.co.uk, ³adepelumi@gmail.com, ⁴sadewole@yahoo.com)

Abstract-The use of geophagic and cosmetic clays is a common practice in both rural and urban areas of Nigeria mostly due to tradition and medicinal reasons. There is a need to analyze the components of these clays purposely for their public health value and safety. This study determined the prevalence of use, the physical characteristics and chemical properties of geophagic and cosmetic clays to ascertain the impacts of their constituents. Structured questionnaire was used to collect data on mining, geophagic and cosmetic uses of the clays. Samples of clay were collected from mining and market sites and taken to the laboratory for analysis. Organic and moisture content estimation, colour determination, cation exchange capacity, exchangeable cations, pH, total elemental composition, heavy metal analysis, radiation estimation were done using standard methods.

The clay colour ranged from dark grey to white most samples being acidic at pH values between 2.7 and 5.3. The mean cation exchange capacity value was 19.20 ± 0.01 meq/100 g.). Some of the clay samples are rich in Fe with considerable amount of other elements such as K, Ni, Cu and Zn. Lead had high values above allowable limits of 0.06 ppm across all the samples. Gamma (γ) radiation was $2.64 \times 10^{-8} \pm 0.04$ mSv/hr, $\alpha+\beta+\gamma$ ($7.61 \times 10^{-8} \pm 0.03$ mSv/hr) and $\beta+\gamma$ ($-1.5 \times 10^{-8} \pm 0.1$ mSv/hr). The organic matter values were between 9.25% in Em and 17.15% in CCB. Moisture content was generally low in most samples with a wide range values below 0.71% in EG and 11.75% in CCB. The geophagic and cosmetic clays in this study could be sources of micronutrient supply; however, the clays could also cause health issues due to heavy metal contamination.

Keywords-Physico-chemical quality, heavy metals, geophagic, cosmetic clays

I. INTRODUCTION

Clay refers to a naturally occurring material composed mainly of fine grained minerals, which is generally plastic at appropriate water contents and will harden upon firing or drying [1]. The consumption of clay and other soil materials is

widely practiced in certain parts of the world and this practice is called Geophagia [2-4]. The act of deliberate eating of soil is also considered to be an unusual eating disorder, an outcome of poverty and famine but could also be observed in the absence of hunger and in both scenarios may be associated with mortality and morbidity [5]. Clay cakes and biscuits are consumed regularly in china and Haiti to alleviate hunger due to food scarcity [6]. Human geophagia is an ancient practice that has been sustained for thousands of years despite the associated health drawbacks. Geophagic individuals are known to consume 40-50 g/day [7-8]. More women than men are engaged in geophagic practice [9] and particularly pregnant and lactating women [10-11]. A number of reasons have been put forward for the habit of geophagy. It has cultural acceptability in so many societies though some deem it an abnormal practice. It has been reported as a physiologic response to a deficiency of iron or calcium in the body [10]. Cultural, psychological, medicinal and nutritional needs have been advanced to justify the practice [12-13].

The cosmetic capabilities of clays are being exploited by many beauty spas around the world. Traditionally, clay is mixed with water to form a gel or paste that can be applied externally for cosmetic purposes or skin protection [14]. Clays are widely used for cleansing the skin, emulsification, detoxification, adsorption, UV radiation protection, ion exchange with the skin, and trans-dermal nutrient supplementation of elements such as calcium, iron, magnesium and potassium [15]. Clays can also eliminate excess grease and toxins from skin thus preventing dermatological diseases such as boils, acnes, ulcers, abscess, and seborrhea [16]. The ability of clays to perform the various functions is influenced among others by their colour, particle size, specific surface area and cation exchange capacity (CEC) [15, 17]. Specific properties of clay minerals such as the nanometer size and thin platy or fibrous shapes, the negative electric charge, and high adsorption and absorption capacities probably justify the therapeutic uses [18]. Because of their small particle size, large specific surface area, and peculiar charge characteristics, clays and clay minerals have interesting surface properties. Clay minerals exhibit ion exchange behavior, as do zeolites, colloidal metal hydroxides, and natural organic matter [19].

The use of clays against poison, even mercury poisoning and the success of this treatment has been ascribed to the ion-exchange capacity of the clays [20]. While clay minerals have been used with favorable outcomes for centuries in pharmaceutical applications, technology, and dermo-pharmacy as excipients and as active substances, their use in medical applications does not come without possible side effects. Several important factors that contribute to mineral toxicity include (i) site of ingress to the body (inhalation, ingestion and absorption), (ii) duration of exposure to the particles, and (iii) particle size [21]. In addition, [22] showed that ions, specifically Li, Sr, B, I, Rb, Br, Ba, Na, Cl, Se and Ca, bound to pelotherapy clays were released from the mineral surface and penetrated human skin. Although the skin is the first line of defense for the immune system against external toxicant insults, percutaneous exposures can be a source of adverse health effects for some earth materials which can be readily absorbed directly through the skin, particularly those that are non-ionic or lipophilic, such as methyl mercury [23]. There has been increasing discussion in the biomedical literature regarding the potential for solid metallic or metal-bearing nanoparticles (particularly those used in personal care products) to be absorbed directly through the skin and therefore present a potential source of toxicity [23]. The objective of this study, therefore, was to assess the physical characteristics and chemical composition of geophagic and cosmetic clays to ascertain their possible impact on health.

II. METHODS

A. Clay Sample Collection, Preparation and Identification

First, Nine mined and market samples of clay were collected from four sites, a river bank in Ozanogogo village, Orhiowhon local government in Delta state; a river valley in Igbanke local government, Edo state; Warri Hausa market and Main Market in Warri South local government, Delta state and labeled thus: Atike Ela (AE), Calabash Chalk Brown (CCB), Calabash Chalk Igbanke (CCI), Calabash Chalk Oza (CCO), Eko Black (EB), Efun_(market) (EFm), Eko Grey (EG), Eko_(market) (Em), Nwanra (NW). The clay samples were air dried and ground to achieve a smooth consistency and sieved until no more filtrate was recovered. The colour of the clay samples were identified using the Munsell soil colour chart [24]. Color determination was done by visually comparing the samples with soil color values in the Munsell Soil Color Charts to obtain the hue, value and Chroma of the samples.

B. Moisture Content and Organic Matter Estimation

Clay samples were air dried at room temperature, ground and sieved. Tared tins were weighed and 10g of clay samples were weighed into the tared tins and placed in an oven at 110°C for 24 h. The tins and its contents were weighed after the completion of the experiment. The moisture content of the sample was calculated following the method of [25] Ekosse and Ngole (2012). Samples from the moisture content estimation transferred into porcelain dishes were placed in a furnace at a temperature of 660°C for 24h. The samples were cooled and weighed to find out the difference in weight after oxidation of organic matter.

C. Cation Exchange Capacity

Clay samples were air dried at room temperature, ground and sieved. Air dried sample of clay 2.5 ± 0.01 g was measured into a 50 mL centrifuge tube and 33 mL 1N Potassium Chloride was added, the tube was stoppered and shaken for 5 min. The tube was opened and centrifuged until the supernatant was clear. The supernatant was decanted and the process repeated 2 to 4 times. Then, 20 mL of 95% ethanol was added into the tube stoppered and shaken for 5 min, centrifugation was repeated and the clear supernatant was decanted. The sample was further washed with 20 mL portions 95% ethanol twice. Thirty three milliliter 1 M ammonium acetate was added and the mixture was shaken for another 5 min, opened and centrifuged. The clear supernatant was poured off into a 100 mL volumetric flask and the step was repeated twice. The flask was made up to 100mL with ammonium acetate and mixed well. The amounts of the exchanged cations including Ca, Mg, and K, were measured individually and calculated accordingly [26-27].

D. Particle Size Distribution measurements of Clay Samples

Fifty one grams of each of the air dried samples which has been passed through a 2mm sieve were weighed into different conical flasks and transferred to a "milk shake" mix cup. Twenty five milliliter of 1.0N sodium hexametaphosphate was added along with 100mL of distilled water. The mixture was stirred and left to settle for 30 mins. Stirring was repeated for 15 min after which the suspension was transferred to a 1200 mL glass cylinder with hydrometer inserted and the volume was made up with distilled to 1130 mL. The hydrometer was later removed and the covered cylinder was inverted several times until all the soil was in suspension. The cylinder was left and the hydrometer reading noted. Lower soil hydrometer was placed immediately into suspension and the first reading was taken. The first reading measures the percentage of silt and clay in suspension. The second set of readings was taken when the suspension remained for 3 h [28-29].

E. Measurement of pH and Exchangeable Cations Analysis of Clay Samples

Fifty one grams of each of the air dried samples which has been passed Ten grams each of the clay samples (passed through 2 mm sieve) was weighed into two 50 mL beakers and 20 mL of distilled water was added to one beaker. Twenty milliliter of 0.01N CaCl₂ was added to the third beaker. The mixtures were allowed to stand for 30 mins, while stirring occasionally with a glass stirring rod. The pH value determination was done using digital hand held pH meter (pH10 WETP 500) which was inserted into the partially settled suspension [30]. Exchangeable cations determination involves the displacement of exchangeable cations with a concentrated solution of some cations and determining the concentration of the displaced cations in the displacing solution. The cation most often used for extracting exchangeable cation is NH₄⁺ usually as NH₄OAC. Ten grams of the sieved clay sample was weighed into a 250mL conical flask to which 100 mL of 1N NH₄OAC was added and shaken for 30mins. The suspension was filtered through Whatman No. 1 filter paper. The first 10 to 20mL that passed through were discarded and 25mL of filtrate for exchangeable cation determination was added to a

50mL conical flask. The concentrations of Ca, Mg, K and Na (ppm and meq/100g of sample) were determined using flame photometer [33].

F. Elemental and Heavy Metal Analysis of Clay Samples

Fifty one Clay samples were analyzed for elemental constituents using energy dispersive X-ray fluorescence spectrometer (ECLIPSE III, AMTEK INC. MA, USA) according to the method of [31]. The detection system for the measurements is a high performance X-ray detector (XR-100CR) with preamplifier and a cooler system which uses a thermoelectrically cooled Si-PIN photodiode as an X-ray detector. The resolution of the detector for the 5.9 keV peak of ^{55}Fe is 220 eV FWHM with 20 μs time constant for optional setting was used for measurements. The quantitative analysis of samples was carried out using the XRF-FP quantitative analysis software package. Ten grams of clay filtered through a 2 mm sieve was weighed into a 50mL beaker and 10mL of 0.1N HCl was measured added. The content of the beaker was shaken for 30 min and filtered. The filtrate was then analyzed using the Atomic Absorption spectrophotometer Model no AA500 [32].

G. Radiation Residue of Geophagic and Cosmetic Clays

Fifty one Radiation residue was measured using GAMMA-SCOUT^(TM) instrument. A cardboard box was selected as measurement site and the gamma (γ), gamma + beta ($\gamma+\beta$), gamma + beta + alpha ($\gamma+\beta+\alpha$) triplicate reading of the site was taken at 10 second interval. The readings were taken in $\mu\text{Sv/hr}$ and converted to mSv/hr [34].

III. RESULTS

A. Prevalence of Geophagic and Cosmetic Clays, Uses, Sourcing and Handling

Geophagic and cosmetic clay users cut across various professionals including both learned and unlearned individuals, and 4.9% of respondents consumed more than one serving of clay per day, 2.9% had more than 3 servings per day. A total of 78% of respondents do not treat the clay with heat prior to consumption. The proportion of respondents which use clay in cosmetic skin treatment, face treatment, treating skin infections and in wounds management are 20.6%, 10.8%, 22% and 3.9% respectively. A total of 91.7% of respondents dig to get the clay they use, 83.3% dug for wet clay, while only 8.3% look for dry clay. During processing, all the miners dry the clay

after moulding into cakes, 75.0% pound the clay while 8.3% grind the clay after mining (Table 1).

All eleven vendors of the clay materials attested to the fact that pregnant women and young girls were there most frequent customers for geophagic clay whereas cosmetic clays user included young men, young women and old women additionally. Pregnant women and young women made up 45.5% of the group, while young men and old women were 9.1% of most frequent customers for cosmetic clay. All the respondents handle their clay products with bare often unwashed hands.

B. Physical and Chemical Properties of Clays

Nine clay samples were obtained. Visual comparison of clay samples with known Munsell color standards yielded values based on known Chroma, value and hue values which were interpreted to give color representations. EB was dark grey, CCO pinkish white and CCI white. AE, cosmetic clay had no hue value. Table 1 shows the physical properties of the clay samples. Organic matter and moisture content estimation ranged from 9.25 % to 17.15% and 0.71 % to 11.75 % respectively. Eko Grey has the lowest moisture content of 0.71% and Em has the lowest organic matter content of 9.25% as shown in fig 1.

The lowest pH value was in Eko grey 3.8 (in H_2O) and 0.7 (in CaCl_2). EB has the lowest pH in both H_2O and CaCl_2 suspension with values of 2.8 and 2.7 respectively, while AE had the highest pH of 5.3 in H_2O and 5.1 in CaCl_2 respectively. While Eko (market) and Atike Ela had the highest pH of 5.3 in H_2O and 4.2 and 5.1 in CaCl_2 respectively (Table 1).

Iron (Fe) was the most abundant element in all the samples having highest value of 3.37 ppm in EB sample and lowest in the AE sample (1.24 ppm) while Copper was the least elemental content in all the samples with highest value of 0.034 ppm in EG and least value of 0.021 ppm in E_m as shown in Table 2. Heavy metals such as Cadmium, Lead, Iron, Copper, Zinc and Nickel were assayed for. Cadmium (1.14mg/l) was found only in EB and EG even as EB had the highest Fe content of 829.995 mg/l, followed by EG with 202.86 mg/l. All the samples had similar Pb content of 0.12mg/l except for EG with a value of 11.89 mg/l. (Table 2).

The radiation residues are as shown in fig 2 where CCI had the highest value for γ of 0.232 SeV. EB had the highest value of 0.214 SeV for $\alpha+\beta+\gamma$ and Nw 0.019 SeV for $\beta+\gamma$. CCB and CCO had negative values for all the radiological parameters as shown in fig 2.

TABLE I. Physicochemical Analysis of Clay

Sample	Source	Uses	Colour	CEC	pH		Exchangeable Cations (ppm)					Particle Size Distribution %		
					H ₂ O	CaCl ₂	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Sand	Silt	Clay
AE	Market	Cosmetic	-	15.84±0.0	5.3	5.1	0	37.2	315	7.005	0	4	38	58
CCB	Mined	Geophagic/Cosmetic	Pinkish white	14.39±0.01	5.1	4.3	20.5	23.3	0	4.126	20.5	2	24	74
CCI	Mined	Geophagic/Cosmetic	White	27.345±0.02	5.1	4.3	21.8	12.8	69.5	2.87	21.8	4	62	34
CCO	Mined	Geophagic	Pinkish white	19.445±0.00	5.2	4.4	27.9	11	0	7.027	27.9	4	82	14
EB	Mined	Geophagic	Dark Grey	22.31±0.01	2.8	2.7	11.4	5.8	0	1.463	11.4	12	78	10
EFm	Market	Geophagic/Cosmetic	Pinkish white	13.69±0.01	4.6	4.3	503	25.3	282	0.878	503	0	48	52
EG	Mined	Geophagic	Light grey	20.15±0.01	3.8	1.7	17.5	26.8	0	3.318	17.5	0	22	78
Em	Market	Geophagic	Light grey	23.75±0.01	4.9	4.2	26.6	37.8	0	13.328	26.6	24	12	64
NW	Mined	Geophagic	Pale yellow	15.85±0.01	5.1	1.7	28.4	39	0	3.043	28.4	18	26	56

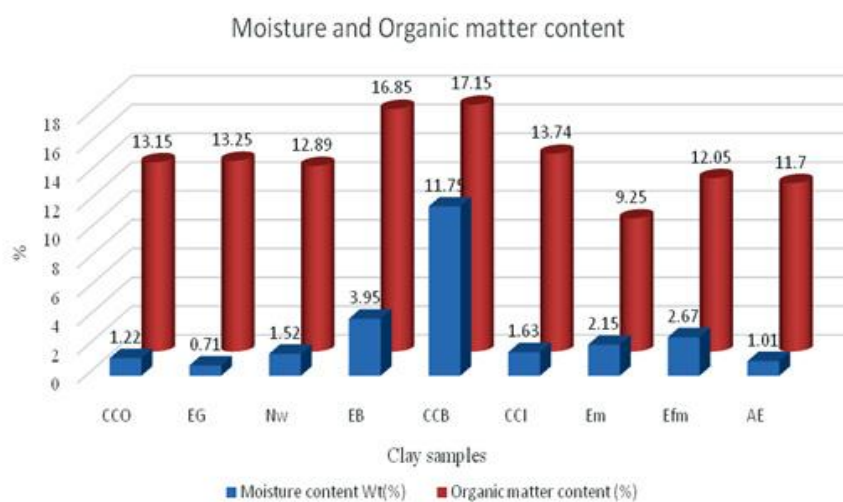


Figure 1. Organic Matter and Moisture Content Distribution in Clay Samples

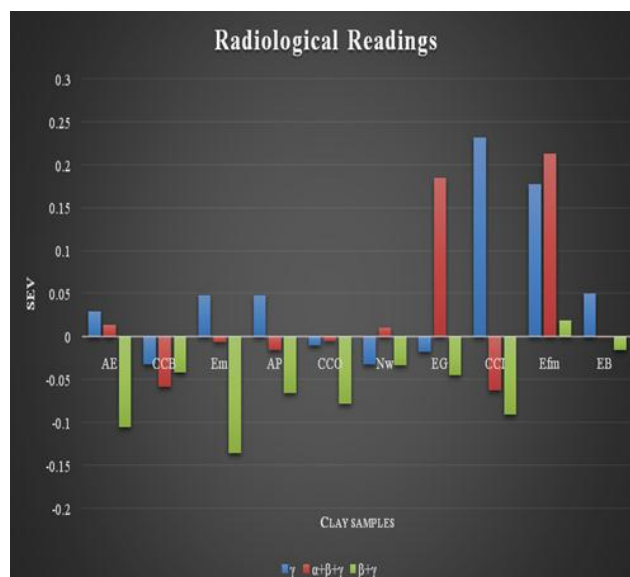


Figure 2. Radiological Residue

TABLE II. Total Elemental Composition and Heavy metal of Clay

Code	Elemental Composition of Clays (ppm)											Heavy metal analysis (ppm)			
	K	Ca	Ti	Mn	Fe	Ni	Cu	Zn	Sr	Zr	As	Cd	Pb	Ni	Zn
AE	0.18	0.05	0.74	0.14	1.24	0.11	0.033	0.10	0.25	0.45	0	0	0.12	2.94	0
CCB	0.22	0.04	1.1	0.22	1.94	0.12	0.029	0.12	0.25	0.83	0.07	0	0.12	215.15	178.35
CCI	0.2591	0.03	0.96	0.20	1.78	0.06	0.026	0.09	0.44	0.38	0.03	0	0.12	1.81	0
CCO	0.11	0.04	1.13	0.20	1.98	0.08	0.026	0.11	0.23	0.86	0.09	0	0.12	1.81	0.67
EB	0.22	0.02	1.01	0.27	3.37	0.24	0.031	0.07	0.25	0.76	0.06	1.14	0.12	0.68	43.24
Efm	0.17	0.04	1.01	0.28	1.80	0.07	0.022	0.09	0.18	0.65	0.07	0	0.12	5.2	1.98
EG	0.25	0.04	1.23	0.28	1.91	0.37	0.034	0.08	0.26	1.04	0.05	1.14	11.89	7.45	0
Em	0.24	0.03	0.62	0.45	2.33	0.09	0.021	0.11	0.13	0.36	0.02	0	0.12	2.94	0
Nw	0.25	0.03	0.92	0.26	2.30	0.10	0.025	0.09	0.24	0.53	0.06	0	0.12	5.2	0

IV. DISCUSSION.

The colors of geophagic clays in this study vary from dark grey, pale yellowish, pinkish white to white giving the consumers varying choices while the cosmetic clay were usually pink in colour. These results are contrary to the study of [29] who reported mostly brown clay. Mahaney *et al.* [35] reported that Chimpanzees of the Mahale Mountains consumed clays with color ranging from yellowish brown to bright brown and avoided soils of darker color due to the high organic content. Generally good soil conditions are associated with dark brown colors near the soil surface, which is associated with relatively high organic matter levels, good soil aggregation and high nutrient levels [36]. Cation exchange capacity values in this study were between 27.345 ± 0.02 meq/100g in CCI and 13.69 ± 0.01 meq/ 100g in E_m, an indication that they will be able to hold and release cations fairly well and thus become available for use in body processes. Clay with higher and lower CEC values may hinder release of cations and may not be able to hold on to cations. When the CEC of clayey soil is moderately high, it can influence exchange of ions from the clayey mixture to the skin and vice versa [22]. Matike *et al.* [15] recorded values between 0.5 meq/100g and 54 meq/100g, which was quite wider than the range recorded in this study.

The range of values obtained for pH were between 5.3 and 3.8 for dilutions in distilled water and 5.3 and 2.7 for dilutions in CaCl₂ which were mostly acidic. The values of the pH (CaCl₂) of all samples were lower than those of pH (H₂O) indicating that the samples were mostly negatively charged [37-38]. These results are in agreement with the study of [37] which had all its samples in the acidic range and varied to values recorded in the study of [15] which had pH range of 4.53 to 9.57. In a low pH environment, the abundant protons saturate metal binding sites in the solution, maximizing the concentration of soluble metal ions. Consequently, metal ions become more bioavailable, and possibly more toxic, as the pH of a solution decreases [39].

Soil organic matter affects soil chemical properties, through its charge and diverse functional groups which can be involved in the retention of elements such as cations or substances, such as pesticides. The organic matter values recorded in this study were between 7.18% in CCB and 20.7% in EB. The result

agrees with the report of [40] with organic matter content between 8.98% and 16.5% but at variance with [29] where values range from 2.61% to 11.26%. Organic matter tends to influence many characteristics of soil namely color, cation exchange capacity, pH, aggregate stability and microorganisms in soils. The higher the organic matter the higher the CEC, and the higher the microbial numbers. Moisture content of samples had a wide range values with most of the samples having low moisture content below $4 \pm 0.01\%$ while CCB had $11.75 \pm 0.01\%$ this contrasted with the work of [41] and [42].

Iron (Fe) was the highest element in all the samples followed by Titanium (Ti) while Copper (Cu) was the least abundant. EB had the highest Fe content 3.37 wt% while AE had the least Fe concentration 1.24 wt%. EG had the highest concentration of K (0.25 wt%) and the least concentration of K was in CCO (0.11 wt%). This study contrasted with the work of [43] Saat *et al.* (2009) who had values for K in the range of 0.45 – 3.39 wt%. Ni, Cu, Zn and As were also of considerable amounts in this study. The analysis also showed the presence of As in all the samples except the Atike Ela samples. The sample with the highest As content was CCO with 0.089 wt% which is well above the limits set by [44]. The sample with the lowest As content was E_m with 0.024 wt% which was below the [44] allowable limits of 0.05 wt%. Fe is an essential nutrient necessary for oxygen metabolism and mitochondrial function and exhibits a functional importance as a trace metal in the normal growth and functional maturation of the skin [45] hence iron-rich clay might serve a good source of mitigating iron-deficiency particularly in pregnant women but this is subject to its bioavailability. However, Fe overload results in iron toxicity, mainly due to the formation of hydroxyl radicals that strongly react with all kinds of biomolecules, of which DNA damage is the most deleterious consequences [46]. Zinc is generally considered to be non-toxic [47] though Zinc in excess has significant toxicity against bacteria [20]. It is of importance in physiological processes particularly spermatogenesis.

Radiological residues are all below the allowable limits of 1mSv/Y^{-1} and thus do not pose any health concern. CCI, Eb and Nw had the highest value for γ , $\alpha+\beta+\gamma$ and $\beta+\gamma$ respectively whereas CCB and CCO had zero value in all the radiological parameters. Naturally occurring radioactive

materials (NORM) are always present in our environment. This is due to the presence of thorium, uranium series and their decay products in our world and also to the radioactive potassium isotope [48]. Clay mineral, due to its high specific area and ion exchange capability, possess a great adsorptive capacity which can cause the accumulation of trace elements such as radionuclides [49].

IV. CONCLUSIONS

The clay materials in this study are rich in Fe which may be of positive impact to the users but some also contain some heavy metals at levels beyond acceptable limits of some regulatory bodies. The practice of geophagia and application of clay cosmetics has to be done with caution.

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