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Characterization of Buriram volcanic clay for use in cosmetics

Pattaranun Thuadaij[1] ⬤ **, Sakesit Duangkham**[2] **and Thanyapan Hobanthad**[1]

1   Division of Chemistry, Faculty of Science, Buriram Rajabhat University, Buriram, 31000, Thailand
2   Division of Public Health, Faculty of Science, Buriram Rajabhat University, Buriram, 31000, Thailand

E-mail: pattaranun.ta@bru.ac.th and pattaranun.thad@gmail.com

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Abstract

This research aims to analyze volcanic clays from four different Buriram sources before and after decontamination to compare their cosmetic grades, as these clays are used as cosmetic ingredients. The volcanic clays were characterized both before and after decontamination using various techniques, namely, x-ray diffraction (XRD), flame atomic absorption spectrophotometry (F-AAS), x-ray fluorescence (XRF), thermogravimetric analysis (TGA), and the Brunauer–Emmett–Teller method. Further, the pH levels were measured using electrical conductivity measurements. Physicochemical characterization was performed by determining the percentage of organic matter and cation exchange capacity. The decontaminated clay showed the lowest percentage of organic matter and a high cation exchange capacity. After the removal of contaminants, the clay exhibited an amorphous structure. In addition, the analyses before and after contaminant removal revealed a decrease in the content of lead, nickel, selenium and copper, which were the heavy metals prohibited in cosmetics. The primary components were SiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O, MgO, TiO_2, and MnO_2 considering the component for cosmetics. Microbiological tests revealed an absence of *Escherichia coli*, fecal coliforms, and total coliforms. These characteristics theoretically indicate that the samples are suitable for use in cosmetics. Moreover, Buriram volcanic clays show low levels of contaminants and can be used as cosmetic ingredients.

1. Introduction

Clay minerals are usually found in natural rock and soil containing quartz, feldspars, carbonate, sulfates, ferric oxide, aluminum, and phases of amorphous materials that have high specific surface areas and levels of humic substances [1–3]. Cosmetic clays are used owing to their mineralogical and chemical compositions [4–6]; therefore, clays are characterized by their compositions and mineralogical and chemical-physical characteristics [3, 7, 8]. In the field of cosmetics, clays are used as an important ingredient, and are often the main mineral component, which must have a high specific surface area and superior cation exchange capacity. Clays with these properties are selected for use in cosmetics [4, 8, 9]. Clay minerals, which are suitable as cosmetic ingredients contain silicon, aluminum, iron, magnesium, zinc, calcium, potassium, and titanium. These metals have importance in cosmetic applications, and are expected to fulfil their roles in the form of several elements associated with the skin. A previous study has reported that iron may function as an antibacterial and a cell regeneration catalyst and silicon may improve skin tissue reconstruction and provide hydration and relaxing effects. Zinc and magnesium provide a feeling of refreshment [10]. Calcium and potassium help with exchange and tissue refreshment. Titanium is another mineral that may be useful in cosmetics because it can reflect harmful UV radiation [6]. However, clays can contain toxic metals or trace elements, such as arsenic, cadmium, cobalt, lead, nickel, selenium, copper, tellurium and antimony that are prohibited for cosmetics use [7]. The presence of such toxic constituents is the reason for testing clays prior to its use in cosmetics products. Several studies have been conducted to propose methods for the decontamination of clay, including drying at approximately 160 °C for 1 h or more and exposure to gamma radiation between 5 and 15 kGy. $_{60}$Co has been commonly used for gamma irradiation, and clay decontamination using 70% ethanol, and calcination at 550 °C
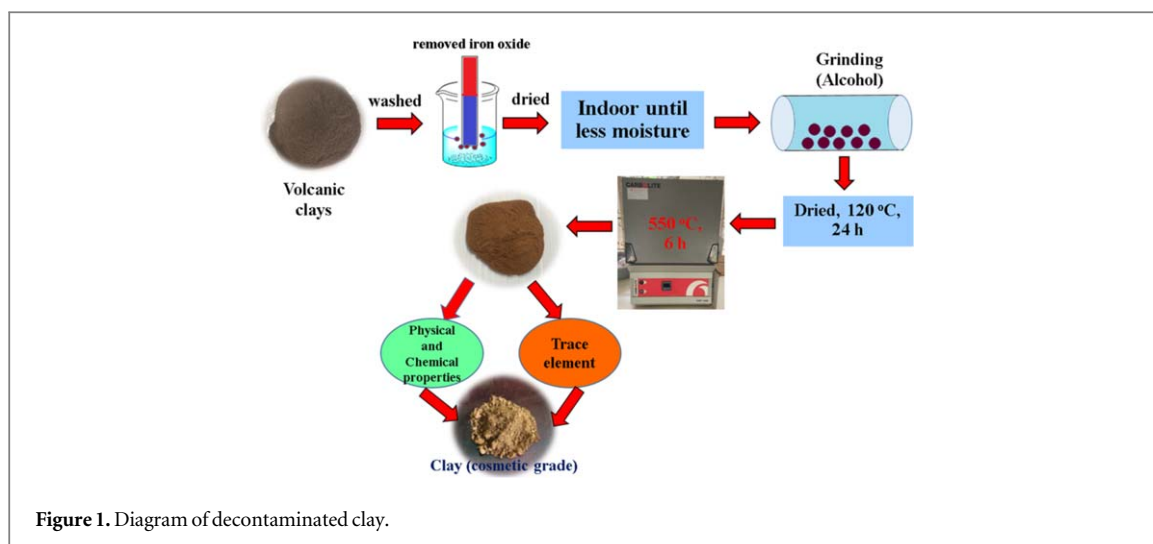
Figure 1. Diagram of decontaminated clay.

for a minimum duration of 1 h has also suggested [5, 11]. In addition to assessing decontamination processes, it is necessary to determine the accuracy of microbiological tests for certifying product quality as well as consider the risks of external impurities for all storage processes [12–14].

In this study, volcanic clay was obtained locally from Buriram Province and decontaminated to reduce possible health risks. By testing the utility of this approach, the purpose of this research was to characterize the decontamination of Buriram volcanic clays, which are similar to commercial red cosmetic clay, and study the suitability of these clays for its use as cosmetic ingredients.

2. Materials and methods

2.1. Materials
In this research, samples were referred to as clay A, B, C, and D, and were obtained as raw materials from the Nang Rong and Chaloem Prakiat Districts, Buriram Province (different locations, as shown in figure 1). Iron oxide impurities were removed using magnetic separation. Some clays were separated from other samples and retained for future use. Clays of each type are products in a final stock of approximately 20 kilograms. The clays were dried and subsequently weighed and homogenized. A 70% ethanol cosmetic grade solution was used at a 1:10 (w/v) ratio. The clays were soaked in the solvent for 6 h using a ball mill. Various mixtures were recovered using a filtration method. All experiments were performed in triplicate to ensure accuracy. Next, the clay samples were dried overnight in a hot air oven at 120 °C. The clay from the decontamination process followed the procedures [11] and supported by the World Health Organization hand hygiene observation method [15]. The clays were heated from an ambient temperature to 550 °C for 6 hwith a heating rate of 10 °C min^{-1}; 550 °C was the temperature required to obtain TGA results. The dried clays were sifted through a sieve of 325 mesh (approximately 0.044 mm) and were retained for future use. All experimental procedures used cosmetic grade chemicals and distilled water. The workflow of the clay decontamination process is shown in figure 2.

2.2. Clay characterization
2.2.1. Physical and physicochemical characterization
The ammonium replacement method [16] was used to determine cation exchange capacity (CEC); soil organic matter was determined following the Walkley and Black method [17]; pH levels were determined using a pH-meter (model HQ411d pH/mV, Hach Company, USA) dispersed in water and KCl (1:1) and conductivity was measured using a conductivity meter (model HQ430d flexi, Hach Company, USA). The results are summarized in table 1 and are compared with those of red clay (cosmetic grade), purchased from the Chemipan Company, Thailand. All experimental procedures used analytical-reagent grade chemicals and the tests were repeated three times. The specific surface areas were analyzed using the Brunauer–Emmett–Teller (BET) method (model TriStar_ll 3020, Micromeritics Instrument Corporation, USA).

2.2.2. Chemical analysis
Volcanic and decontaminated clays were classified using x-ray fluorescence spectrometry (XRF, model Horiba/XGT 52000, Japan). To assess certain trace elements in the samples, extraction using perchloric acid and nitric acid in a ratio of 1:2 was performed; subsequently, quantification was performed using a flame atomic

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Table 1. Physical properties.

Clay samples	Region	Color	pH	Organic matter (%)	CEC (cmol kg^{-1})	Conductivity (dS cm^{-1})
Clay A	Ban Charoen Suk, Chaloem Phra Kiat District	Black	7.29 ± 0.22	2.40 ± 0.24	86 ± 6.93	0.00 ± 0
Clay A-after decontamination		Brown	6.56 ± 0.08	0.18 ± 0.15	7 ± 1.15	0.00 ± 0
Clay B	Ban Thawon, Chaloem Phra Kiat District	Brown	6.56 ± 0.45	2.60 ± 0.15	38 ± 4.93	0.00 ± 0
Clay B-after decontamination		Brown	6.56 ± 0.01	0.19 ± 0.33	3 ± 2.31	0.00 ± 0
Clay C	Ban Hin Lat, Nang Rong District	Black	5.76 ± 0.02	5.66 ± 0.31	107 ± 1.53	0.00 ± 0
Clay C-after decontamination		Brown	6.56 ± 0.05	0.60 ± 0.29	6 ± 2.00	0.00 ± 0
Clay D	Ban Khok Sawang, Nang Rong District	Brown	5.82 ± 0.01	5.82 ± 0.65	88 ± 4.73	0.00 ± 0
Clay D-after decontamination		Brown	6.56 ± 0.04	0.48 ± 0.35	8 ± 1.15	0.00 ± 0
Red clay (cosmetic grade)	Cosmetic grade	Red	5.72 ± 0.08	0.34 ± 0.23	5 ± 1.26	0.00 ± 0

Figure 2. Map of Buriram Province including the locations of Clay A (Ban Charoen Suk) Coordinates 14.551442, 102.866380; Clay B (Ban Thawon) Coordinates 14.517157 102.881146; Clay C (Ban Hin Lat) Coordinates 14.566635, 102.799916; and Clay D (Ban Khok Sawang) Coordinates 14.543095, 102.790615. Reproduced with permission from Chanatda Ratana; 2020 (unpublished figure)
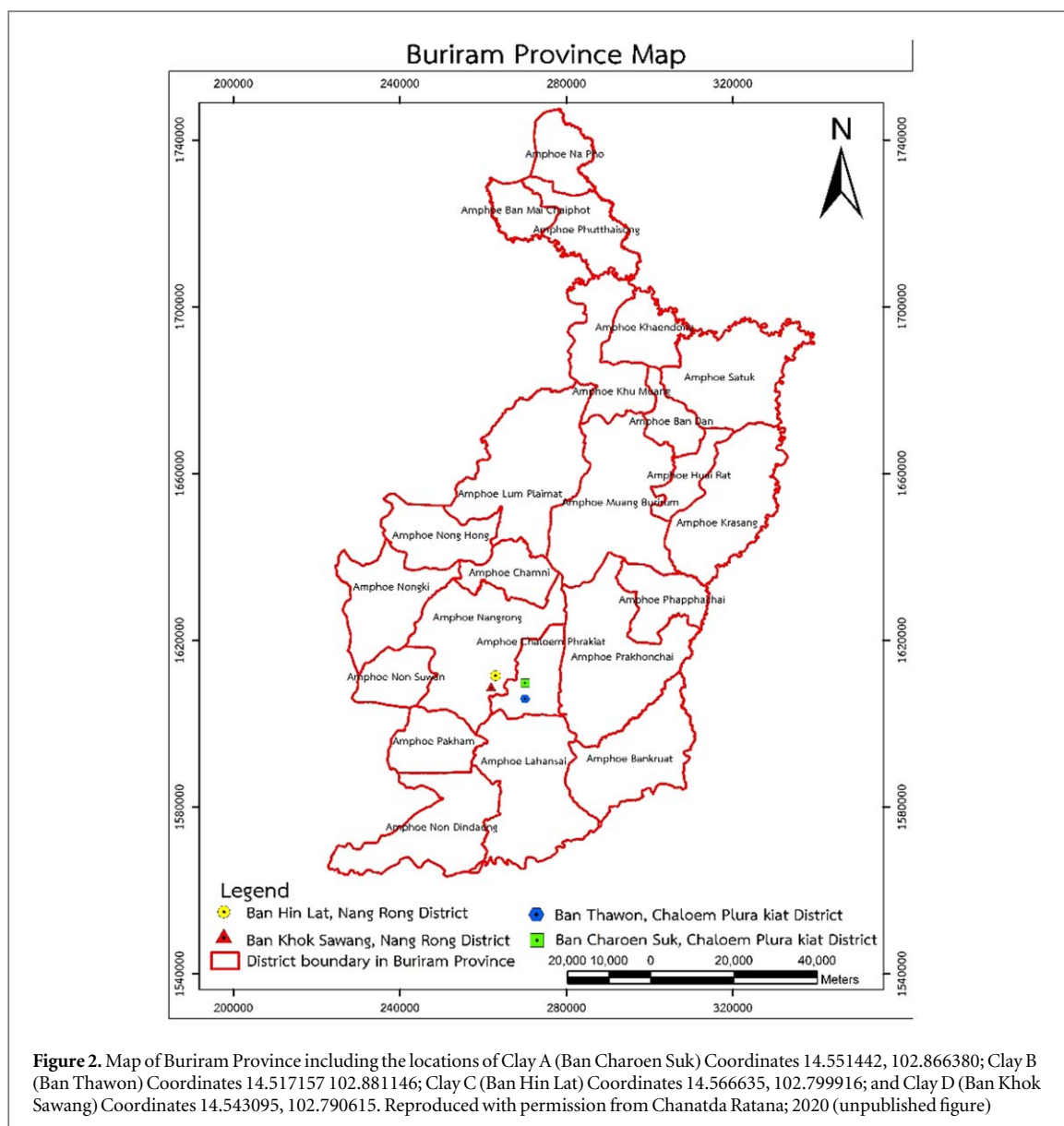
absorption spectrophotometer (F-AAS, model PinAAcle 900 F, PerkinElmer Inc., USA). The results are summarized in tables 2–4, and are compared with those of red clay (cosmetic grade). In all experimental procedures, analytical-reagent grade chemicals were used.

2.2.3. Thermal analysis
The loss in mass was dertermined using thermogravimetric analysis (model TGA-DSCll, Mettler-Toledo Inc., USA). A heating rate of 10 $^\circ$C min^{-1} was applied to increase the temperature from ambient to 1100 $^\circ$C under dynamic atmosphere of air.

2.2.4. Mineral composition
Mineralogical compositions were determined using x-ray powder diffraction (XRD-PANalytical, model X'Pert PRO MPD, Netherlands) with Ge monochromators and Cu-Kα radiation at a scan step of 3° min^{-1} with generator settings of 30 mA and 40 V (Expert 2Theta: 5°–60°).

2.2.5. Microbiological tests
Microbiological tests were conducted to determine whether *Escherichia coli*, fecal coliforms and total coliforms were present in the ingredients intended for cosmetic applications. Moreover, these procedures were conducted according to the US Pharmacopoeia [18].

Table 2. Chemical compositions before and after decontamination of clays A, B, C and D.

Oxide composition	Clay A Before	Clay A After	Clay B Before	Clay B After	Clay C Before	Clay C After	Clay D Before	Clay D After	Red clay (cosmetic grade)
SiO_2	20.49	38.08	3.04	56.55	13.67	56.55	7.67	22.42	7.01
Al_2O_3	4.66	4.26	2.73	2.65	5.06	2.65	4.00	5.92	5.82
Fe_2O_3	59.95	41.35	89.10	28.90	59.74	28.90	78.58	55.64	85.92
CaO	1.28	1.45	0.14	0.30	6.06	N.D.	1.15	1.85	—
K_2O	0.58	0.68	0.03	0.03	1.85	0.03	0.66	2.05	1.04
MgO	2.97	2.69	1.58	4.87	4.13	4.87	1.35	3.38	—
TiO_2	8.09	8.76	2.39	5.18	6.48	5.18	5.00	6.05	—
MnO_2	1.20	1.86	0.76	0.60	1.79	0.61	0.99	1.13	0.06
Cr_2O_3	0.08	0.06	0.09	0.08	0.05	0.08	0.13	0.89	—
CuO	0.04	0.06	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	—
ZnO	0.09	0.11	0.03	0.04	0.15	0.04	0.08	0.54	—
ZrO_2	0.45	0.54	0.07	0.80	0.59	0.80	0.17	0.49	—
Nb_2O_5	0.05	0.50	N.D.	N.D.	0.05	N.D.	N.D.	N.D.	0.08
SrO	N.D.	0.01	N.D.	N.D.	0.59	N.D.	0.11	0.23	—
NiO	0.10	0.04	0.05	N.D.	N.D.	N.D.	0.10	0.13	—
SO_3	—	—	—	—	—	—	—	—	0.07

Table 3. Trace element contents of the investigated clays.

Clay samples	Trace element (ppm) Ni	Pb	Cr	Se	Cu
Clay A	0.01	0.30	0.87	N.D.	0.05
Clay A-after decontamination	0.01	0.20	0.52	N.D.	N.D.
Clay B	0.02	0.30	0.64	10.23	0.32
Clay B-after decontamination	0.01	0.05	N.D.	N.D.	N.D.
Clay C	0.01	0.25	0.97	N.D.	0.25
Clay C-after decontamination	0.01	0.21	0.79	N.D.	0.09
Clay D	0.02	0.44	N.D.	10.38	0.12
Clay D-after decontamination	0.01	0.30	N.D.	N.D.	N.D.
Red clay (cosmetic grade)	0.45	0.39	N.D.	N.D.	0.63

3. Results and discussion

3.1. Characterization of clay samples

3.1.1. Physical and physicochemical characterization

Table 1 shows some of the physical properties of the clay samples. The colors of the clay before and after decontamination were examined and compared with cosmetic clay. A black color indicates a high amount of organic matter or humic substances based on CEC testing, and it is due to the presence of organic matter and clay minerals. These results confirmed that the influence of organic matter on the total CEC of clay is often important and is significantly better than that of clay minerals. Numerous results on the CEC values of clay minerals have been provided by many researchers including the finding that pH and conductivity values obtained were not significantly for different organic matter types or humic substances [19]. The organic matter and humic substances provide cation exchange sites, which are widely accepted and appear in carboxyl and phenolic hydroxyl groups; additionally, the CEC from organic matter and humic substances is influenced by the pH. A previous study has stated that the CEC from humic substances significantly decreased the pH levels. As a result, the organic matter or humic substances influenced the CEC values, which were tested under the pH levels of 7.0, 6.0, 5.0, and 4.0 [20]. The effect of the observed pH values on the clay CEC reduced, and decreased with different sources. The results showed that the content of organic matter decreased in certain decontaminated clays, especially in the 300 °C–550 °C range, as confirmed by the TGA results. Clay decontamination revealed a small amount of organic matter based on the lower CEC. The Buriram volcanic clay samples were classified only after decontamination based on their brown color. In this study, the pH value of some of the decontaminated clays was 6.56 [21]. The amount of organic matter is found to be the lowest after the decontamination of clays as compared to that before the decontamination of clays, which is important for its application in the cosmetic field. The observed CEC value decreased to approximately

Table 4. Surface area and volcanic clay colors.

Clay samples	Specific surface area ($m^2 g^{-1}$)	Langmuir surface area ($m^2 g^{-1}$)	External surface area ($m^2 g^{-1}$)	Colors
Clay A	49.24	63.12	40.57	
Clay A-after decontamination	21.51	20.11	20.11	
Clay B	76.35	97.66	58.35	
Clay B-after decontamination	5.18	6.72	5.71	
Clay C	26.81	34.25	19.91	
Clay C-after decontamination	12.41	15.98	11.81	
Clay D	54.80	70.15	43.64	
Clay D-after decontamination	17.35	22.36	17.32	
Red clay (cosmetic grade)	11.92	15.29	12.66	

3–15 cmol kg^{-1} [1]; however, this range was acceptable and relatively suitable for cosmetics [22]. Additionally, the physical properties of decontaminated clay exhibited parameters similar to that of cosmetic clay, hence, decontaminated clay were acceptable as potential cosmetic ingredients.

3.1.2. Chemical analysis

The chemical compositions of Buriram volcanic clays are shown in table 2. They indicate the inconsistencies in the compositions of the clay sources studied, which probably occur because the clays are selected from various locations of the Chaloem Phra Kiat and Nang Rong districts and are compared with red clay (cosmetic grade). When referring to cosmetics use the chemical and mineralogical compositions are directly associated with clays for cosmetic applications. The chemical compositions of clay after decontamination are high in silica than that

before decontamination. Therefore, clay from different localities vary not just in chemical composition, but in various aspects. Thus, the thermal treatment at approximately 550 °C and transformation of clay initiates ferric oxide leaching. These amorphous phases are shown in mineralogy. Further, the clay responds to remove ferric oxide by releasing silica for dissolution. The silica content of volcanic clay is thought to be derived from the degradation of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) phase and primary quartz of volcanic clay. Several researchers have also investigated the application of clay in cosmetics. Therefore, clay can be applied to transform the amorphous phase, which includes a calcination step at a high temperature of 500 to 600 °C [23, 24]. This process proved to increase the activity of clay and high percentage fractions of silica, especially kaolinite phase from clay [3]. Low aluminum, and decreased amounts of iron oxide were observed after removal by magnetic separation; however when compared to red clay (cosmetic grade), higher contents of iron oxide and other chemicals were observed. As reported in previous studies, silicon in clay (if in sufficiently high concentrations) could renew skin tissues, induce tissue hydration, and moderate potential skin inflammatory routes [6]. Aluminum, as a secondary element was found in the clays. In the field of cosmetics, aluminum in raw materials as appropriate as it provides relaxation, color distribution, moisture treatment, and melanin adsorption. The minor chemical compositions of different clays include TiO_2, MgO, CaO and K_2O. According to the chemical composition of natural clays used in cosmetics, SiO_2 and Al_2O_3 were found to be the primary components and K_2O, MgO, Fe_2O_3, CaO, and TiO_2 were the minor components [4]. Furthermore, Clays with silicon, aluminum, iron, magnesium, zinc, calcium, potassium, and titanium have been used for their antiseptic, renewing, and antibacterial properties, which contribute to cell regeneration, contamination absorption, tissue invigoration and circulatory stimulation. The contents of trace elements are shown in tables 2 and 3, which indicates the prohibited toxic trace elements found in cosmetics [25]. Trace element analysis reveals a slight decrease in Cr_2O_3, CuO, NiO, and ZnO based on F-AAS. Moreover, the content of nickel, lead, selenium and copper is the lowest. The element limitations, found in the report of EC Regulation 1223/2009 (EC, 2009), indicate that considerable attention must be paid to the concentrations of certain metals that are traditionally considered as toxic metals, including arsenic, antimony, cadmium, cobalt, lead, zinc, mercury, selenium, tellurium and barium. They must be at extremely low concentrations as compared to those quantified by the pharmacopoeia, which limited the amount of lead to a maximum of 40 ppm [18]. Chromium, selenium and copper, which were low in concentration for some of the clay samples, were not detected.

The specific surface areas of the decontaminated clays are shown in table 4. The areas of Clay A (21.51 $m^2\,g^{-1}$), Clay B (5.18 $m^2\,g^{-1}$), Clay C (12.41 $m^2\,g^{-1}$) and Clay D (17.35 $m^2\,g^{-1}$) are lower after decontamination. Moreover, the clays A, C, and D show greater specific surface areas as compared to that of the red clay (cosmetic grade); these results may indicate favorable properties for their use as cosmetic ingredients, and greater adsorption capacity as compared to that the different clays analyzed. A previous study has reported clay with a large specific surface area being used as an ingredient in creams, powders, and emulsions for cosmetics because these properties help the skin to form a film, replicating the effect to mechanical protection, and preserve skin oils [6]. This procedure reduced the decontamination of the clay to minimize the decrease in the specific surface area of decontaminated clay. If the soluble organic matter were principally adsorbed on the clay surface area, the specific surface area using BET would be greater owing to an increase in the concentration of soluble organic matter. Therefore, a constructive relationship exists between BET and total soluble organic matter [26], which was compared based on the results of the percentage of organic matter before and after decontamination. Evidently, pyrolysis hydrocarbons were found at temperatures from 300 to 600 °C.

Previous studies have revealed that rich organic matter in the interlayers of clay minerals at 300 °C will not be excluded unless the temperature reaches 550 °C [27]. The specific surface areas of decontaminated clay when heated to 550 °C were determined according to the TGA results. The color before decontamination was black, whereas it was brown after decontamination. This indicates a significant decrease in organic matter content; however, the value is not significantly different as compared to that of the red clay (cosmetic grade).

3.1.3. Thermal analysis

The TGA curves of Clays A-D are shown in figure 3. The TGA curves at temperatures from 100 °C to 300 °C indicate a loss in mass of approximately 2 to 3%. These losses were due to water molecules lost from the surface of the clay. Additionally, a small amount of free water was released at temperatures below 300 °C. This observation was above 300 °C, which showed the thermal balance curve. At approximately 450 °C, the effects of dehydration are evident. This is possibly due to clay sintering or transformations of crystalline phases. The clay minerals were modified to crystalline forms at approximately 1000 °C. Previous studies have reported decreased water adsorption, resulting in sustainability of pores [28]. This process was observed at a temperature of approximately 120 °C. Therefore, the water loss observed during thermal analysis was associated with the adsorbed free water, which was loosely bound on particle surfaces.
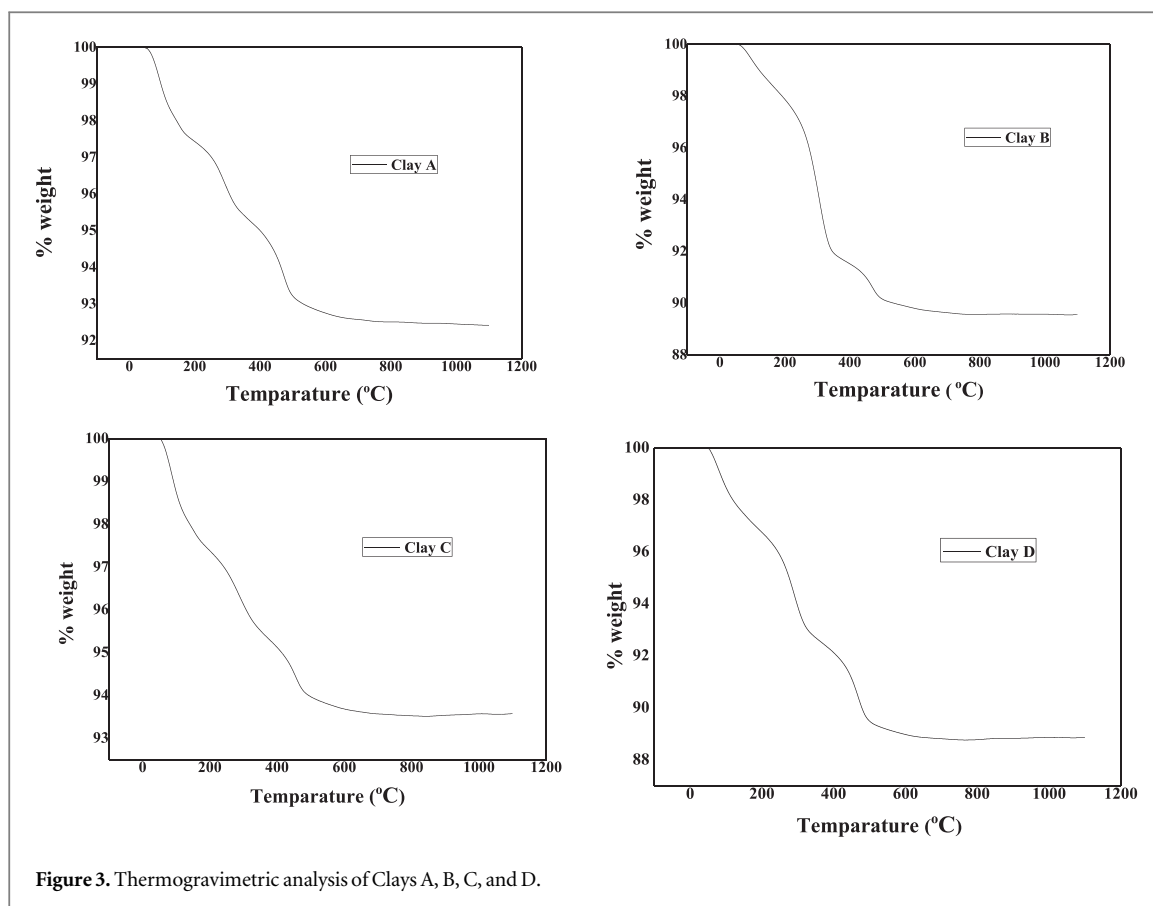
Figure 3. Thermogravimetric analysis of Clays A, B, C, and D.
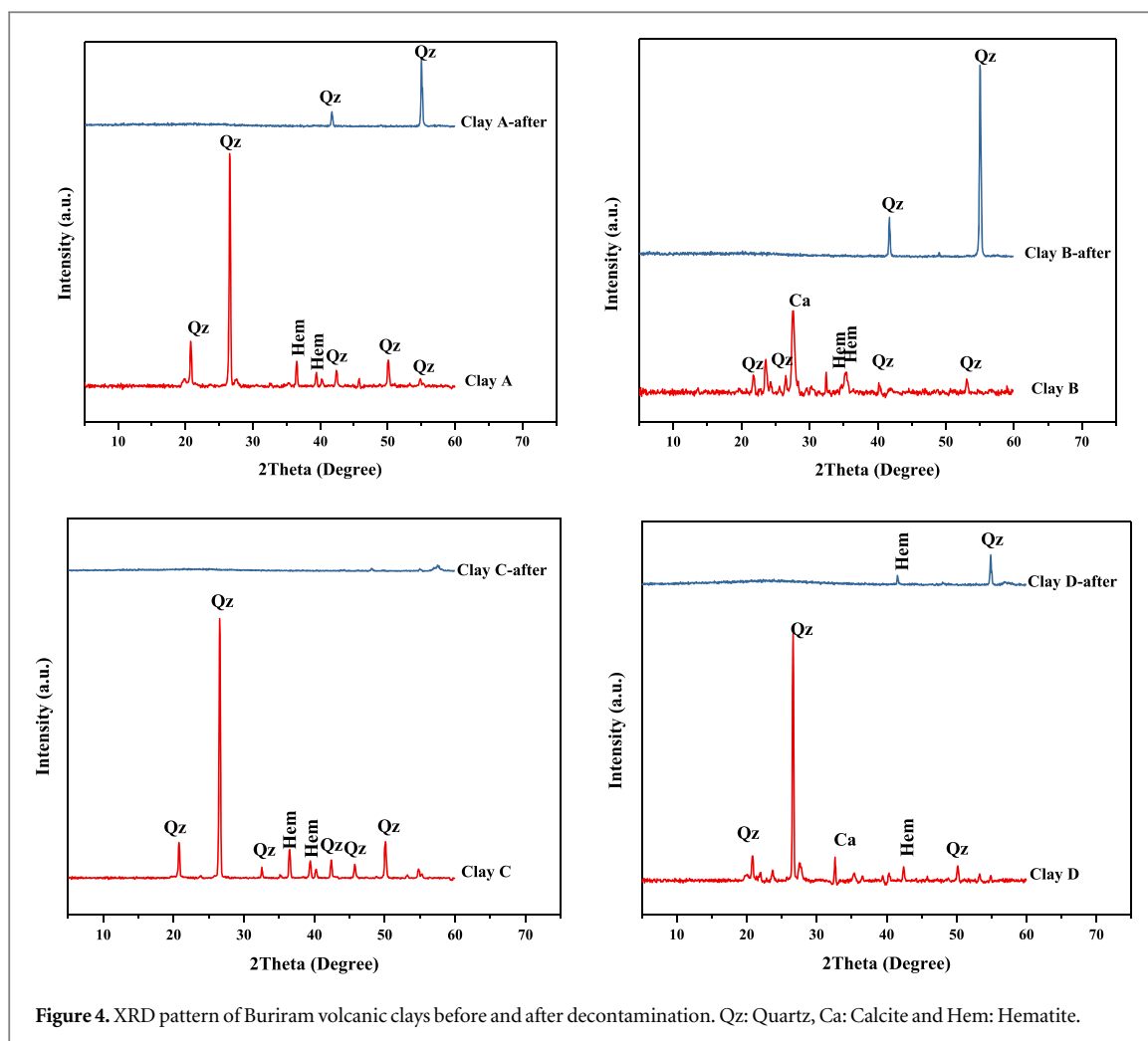
3.1.4. Mineral composition

Figure 4 shows the diffractogram for all volcanic clays. Quartz or silica was determined using JCPDS no. 33-1161 as a reference, and hematite was determined using JCPDS no. 24-0072 as reference. The presence of these minerals was confirmed after the samples were heated to 550 °C, disappearance of the structure, and decrease in the stable crystalline phases at the expense of amorphous phases. In the amorphous phase, slight amount of silica (SiO_2) and hematite (Fe_2O_3) JCPDS no. 24-0072 were observed in clays A, B, C and D. Clay A also contained silica (natural volcanic clay D = 3.35) and a slight amount of aluminum (natural) [24]. The lack of crystal-like silica suggested that these samples have promising characteristics (security and chemical apathy) for use as cosmetic ingredients.

3.1.5. Microbiological tests

The microbiological test results confirmed the suitability of the decontaminated clays and colored clays as compared to that of the red clay (cosmetic grade) for cosmetic use. This finding is significant owing to the required absence of *Escherichia coli,* fecal coliforms, and total coliforms in the ingredients proposed for medicinal and cosmological use [14, 29]. It has been reported that, 39% ethanol is effective against environmental *Escherichia coli*. However, these results used 70% ethanol for the removal of microorganisms accordingly, *Pseudomonas aeruginosa* was inhibited using 37% ethanol, *Staphylococcus aureus* using 42% ethanol, *Enterococcus hirae* using 44% ethanol [30]. As evidenced in one case, the microorganisms were absent at ethanol concentrations of approximately 70%–90% v/v. Thus, the concentration of ethanol is relative to the poor activity of microorganism. Ethanol is used as essential quality control and safety indicator for pharmaceuticals and virucide, and it is being applied in the composition of other antiseptic products as well [31].

4. Conclusion

In this research, we investigate the suitability of decontaminated Buriram volcanic clays for use as cosmetic ingredients. The physicochemical properties of decontamination clays reveals that the lowest organic matter if the clay has a high percentage of organic matter, resulting in a high cation exchange capacity, enhances the adsorption of cations. However, the organic matter contains substances such as carboxylic and phenolic groups. When these compounds breakdown, they possess a negative charge adsorbs the cations contained in heavy metals (cadmium, copper, lead, and zinc) of clay, resulting in an increase in the heavy metals in the clay. This result of trace element experiments indicated that the decontaminated clays satisfied the standard limits as

Figure 4. XRD pattern of Buriram volcanic clays before and after decontamination. Qz: Quartz, Ca: Calcite and Hem: Hematite.

recognized by the cosmetic ingredients. The pH, conductivity, and CEC exhibited noncompliance with acceptable values related to the current specifications in cosmetics. The high specific surface areas of the contaminated clays were essential for application in cosmetics. The composition analysis revealed that SiO_2, Al_2O_3, and Fe_2O_3 were the major minerals present, whereas TiO_2, K_2O, CaO, and MgO, which were essential minerals for cosmetics field, were present in small amount. The microbiological exposes absence of *Escherichia coli*, fecal coliforms, and total coliforms. The four clays were analyzed as cosmetic ingredients. The results showed that clays A, B, and D are extremely suitable as cosmetic ingredients.

Acknowledgments

ORCID iDs

Pattaranun Thuadaij ⓘ https://orcid.org/0000-0003-4990-779X

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