

Comparative Effects of Soxhlet Extraction and Thermal Treatment on the Physicochemical Properties of Spent Bleaching Earth for Sustainable Reuse

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Abstract

This study evaluates the effects of solvent extraction and thermal treatment on the structural, mineralogical, and physicochemical properties of spent bleaching earth (SBE) from a palm oil refinery, aimed at sustainable reuse strategies. The SBE was subjected to Soxhlet extraction using n-hexane, as well as another process through calcination between 300 and 1000°C. Products were characterized by XRF, XRD, TGA/DSC, laser granulometry, SEM/EDS, and FTIR. The raw industrial bentonitic material exhibited a typical aluminosilicate composition: montmorillonite, illite, and kaolinite. Solvent extraction virtually removed residual oil from the bleaching process of palm oil, without significant changes in chemical composition or crystalline structure, preserving lamellar morphology, although with an increase in amorphous content. In contrast, thermal treatment promoted transformations, including structural collapse of montmorillonite, dehydroxylation of clay minerals, and formation of thermally stable phases, as well as particle agglomeration. Thermal analysis along with chemical extraction indicated approximately 25 wt.% residual oil content, and mass loss of about 40 wt.% from volatile materials. Results show that solvent extraction favors partial reactivation for adsorptive applications, whereas calcination produces a structurally modified material with potential for ceramic applications, possibly contributing to circular economy practices in vegetable oil refining.

1. INTRODUCTION

Palm oil, derived from *Elaeis guineensis*, is the most produced consumable vegetable oil in the world [1–3]. Marketed worldwide as crude palm oil (CPO), a crude state precursor obtained from the pulp of oil palm [3, 4] it mainly consists of carotenoids, free fatty acids, glycerides, trace metals, and other undesirable organic compounds [1, 3, 5]. After extraction, CPO requires filtration, degumming, neutralization of free fatty acids, bleaching, and deodorization [1, 3, 6, 7]. The bleaching process of palm oil is accomplished by mixing natural or acid-activated materials to natural oil phases to reduce the content of contaminants and undesirable characteristics [3, 7, 8]. Bleaching palm oil can be accomplished with bentonitic clays [1, 6, 9]

Bentonite is a clay ore in which montmorillonite constitutes the principal active mineral phase, although other clay minerals such as sepiolite and attapulgite have also been employed as bleaching earths [4, 6, 9–11]. Even though the terms bentonite and fuller's earth are often employed interchangeably, bentonite denotes a clay ore in which montmorillonite is the active component [6, 7, 12]. Not only does bentonite have, due to its mineral structure, a large surface area [7, 9, 12] allowing it to absorb a significant amount of material, but acid-activating bentonite, enhances its surface area and adsorption efficiency [9, 13], although also simultaneously alters the crystallochemical structure of the clay minerals [6]. Being an inexpensive material makes it a cost-effective option for removing impurities from palm oil.

Globally, based on a 1 wt.% bleaching earth usage, 200 million tons of edible oils and fats refined, an estimated 2 million tons of SBE equivalent is available yearly [14]. The landfilling disposal of spent bleaching earth remains a significant environmental concern due to its high residual oil content, potential for spontaneous combustion [8, 15], and generation of large quantities of industrial waste from the refining of vegetable oils. The traditional disposal methods are unsustainable and fail to align with circular economy [12]: landfilling, mainly involved large and secondary pollution [8, 15, 16], incineration, emitting hazardous waste [15–17], and composting it alone cannot be effectively used, requiring another source of composting agent [7, 14, 15]. Incineration of SBE remains the main disposal method in Europe [17], as well as in the largest producer of CPO, Malaysia [14]. However, in Europe 44% of bentonite in products are recycled at end-of-life, however, only for particular applications [18]

Exploring the reuse or repurposability of spent bentonitic clay could help mitigate environmental risks and promote circular economy practices within the palm oil industry. Due to the increasingly high cost of disposal, it is desirable to use, or reuse, the material instead of landfilling it [8, 16, 17, 19]. Proper destination for spent bleaching earth (SBE) is much anticipated to create a circular economy [15, 20] as well as traceability of the of the CPO production [21]. Although

bleaching efficiency of bentonitic clay and SBE is well documented [8, 9, 16, 22], comparatively fewer studies have focused on the structural and crystallochemical modifications induced by bleaching, solvent extraction, thermal decomposition processes [8, 15, 22–24]. Industrial bleaching earths normally deviate from ideal mineral structures as consequence of natural and artificial isomorphous substitutions, partial amorphization, and acid activation, leading to poorly defined lamellar microstructures [6, 10, 25].

Solvent extraction methods, particularly Soxhlet extraction, have been reported as effective for partial recovery of residual oil from SBE [16, 24] while largely preserving the crystalline framework of clay minerals [15]. Nevertheless, thermal analysis indicates that strongly adsorbed organic fractions remain, even after prolonged extraction [17, 24, 26]. In contrast, thermal treatment promotes structural transformations, including smectite layer collapse and dehydroxylation of associated clay minerals [13, 27–29], ultimately resulting in the formation of thermally stable phases at elevated temperatures [30].

In this context, a systematic investigation of the effects of solvent extraction and thermal treatment on the structural, mineralogical, and physicochemical properties of bentonitic clays is essential to advance the understanding of SBE reactivation mechanisms and to support sustainable reuse strategies consistent with circular economy principles.

2. EXPERIMENTAL

2.1. Raw Material

The spent bleaching earth (SBE) sample was supplied by Amazon Refining, Agropalma S/A (Brazil). This material was subjected to solvent chemical extraction and thermal treatment, and raw material and the subsequent products were subjected to mineralogical and physicochemical characterizations. For comparison purposes, a raw bentonitic material (RaB), representing the industrial material in its raw state prior to the bleaching process used at the same palm oil refinery, in which the SBE collected was being produced, was analyzed as reference material as the state prior to saturation.

2.2. Methods

2.2.1. Chemical Treatment by Solvent Extraction

The SBE was subjected to solvent extraction according to the following procedure. Initially, SBE was dried in a forced-air oven at 65°C for 24 h to remove free moisture, following conventional clay pre-treatment practice [24]. After drying, approximately 100 g of SBE was loaded into a cellulose thimble and extracted in a Soxhlet apparatus using n-hexane as solvent, a traditional choice for de-oiling bentonitic adsorbents due to its non-polarity and established industrial use [3]. During the process, n-hexane was heated to 70°C in the bottom flask, generating solvent vapor that continuously percolated through the clay contained in the thimble. The vapor was subsequently condensed in the water-cooled condenser and refluxed back into the extraction chamber, ensuring uninterrupted solvent cycling through the sample bed. The extraction was carried out under continuous reflux for 10 h. At the end of the extraction, the clay was removed from the thimble and dried to eliminate residual solvent. A total of 76 g of de-oiled and reactivated bentonite was recovered and designated as solvent-extracted bentonitic material (ExB), which represent around 24 wt.% loss of oil for this treatment. Hexane extraction of SBE is economically feasible for stable oils [16, 17], but for the purposes of this research, it was used for crystallochemistry analysis, similar in literature [24]. Due to its high oil saturation, SBE could not be adequately pulverized for solid-state analysis.

2.2.2. Thermal treatment

To evaluate the thermal behavior of the SBE upon heating, calcination trials were carried out using 20 g of SBE per sample prepared. The thermal analysis indicated at which temperature SBE loses most of its mass due to oil ignition and subsequent loss. Therefore samples were calcined in an electric furnace in air using ceramic crucibles in temperatures ranging from 300°C to 1000°C, in increments of 100°C for each individual sample, with a dwell time of 2 hours at each target temperature.. The calcined products were labeled according to the maximum calcination temperature: CaB300, CaB400, CaB500, CaB600, CaB700, CaB800, CaB900, and CaB1000.

2.2.3. Chemical analysis

The chemical composition of RaB, ExB, CaB400, CaB500, CaB600, CaB700, CaB800, CaB900, and CaB1000 was determined using a Bruker S2 Ranger X-ray fluorescence (XRF) spectrometer equipped with a Pd X-ray tube operated at 50 kV. The measurements followed the classical pressed-pellet method, widely adopted in industrial clay and mineral feedstock analysis for its robustness and reproducibility. XRF analysis of CaB300 could not be performed using the pressed-pellet method because the residual oil content remained high enough to compromise pellet integrity and preparation.

2.2.4. Physical analysis

Granulometric analysis of RaB and SBE was performed by laser diffraction using a Malvern Mastersizer 3000. The analysis conditions were agitation at 2500 rpm, no ultrasound, sample density of 1.56 g·cm⁻³, refractive index of 2.25, absorption index of 0.1. Distilled water containing 10% sodium pyrophosphate solution was used as dispersing agent (refractive index of the dispersant: 1.39). Sodium pyrophosphate was employed to promote deflocculation of clay aggregates and minimize interparticle attraction, improving the dispersion of fine particles during analysis.

2.2.5. Mineralogical analysis

The mineralogical composition of RaB, ExB, CaB400, CaB500, CaB600, CaB700, CaB800, CaB900, and CaB1000, were determined by X-ray diffraction (XRD) (Bruker D2 Phaser) diffractometer with a Cu radiation source ($K\alpha_1 = 1.54056 \text{ \AA}$), operated at 1.8 kW ($\approx 40 \text{ kV}$, 40 mA; 1.6 kW) from 5° to 70° (2 θ). As an auxiliary discriminatory method to enhance basal reflections, oriented clay mounts were prepared. The oriented, glycolated, and 600°C calcined specimens were scanned over a 2° to 30° (2 θ) range.

Mineralogical quantification of RaB, ExB and CaB400 was performed using the Rietveld method. The measurements were carried out on an Empyrean diffractometer (Malvern Panalytical) equipped with a Cu radiation source ($K\alpha_1 = 1.54056 \text{ \AA}$), operated at 1.8 kW. The analysis conditions were: 45 kV, 40 mA, 2 θ goniometer, scanning from 2.5° to 70° (2 θ), with an angular step of 0.02°, sample stage rotation at 1 rpm, and 150 s per step. To estimate the amorphous phase content, an internal standard (10 wt.% anatase) was added to all samples prior to XRD measurement (Dinâmica Química Contemporânea Ltda., Brazil). Rietveld refinement used reference crystal structures from the ICSD database with the following entries: quartz (ICSD 63532), anatase (ICSD 202242), montmorillonite (ICSD 161171), illite (ICSD 90144), kaolinite (ICSD 87771), and microcline (ICSD 16597).

2.2.6. Thermal analysis

To evaluate the thermal transformations of SBE, thermogravimetric analysis (TGA) (Netzsch STA 449 F3 Jupiter) was used to determine mass loss, and differential scanning calorimetry (DSC) to assess thermal behavior. Approximately 30 mg of powdered SBE was heated from 25 to 1000°C at a heating rate of 10°C·min⁻¹, under a nitrogen (N₂) flow of 70 mL·min⁻¹, using a Pt/Rh crucible in a vertical cylindrical SiC furnace with a silicon carbide (SiC) heating element housed in a vertical cylindrical SiC furnace.

2.2.7. Micromorphology and microchemistry analysis

Morphological and microchemical analyses of RaB, ExB, CaB400 and CaB600 were performed by scanning electron microscopy (SEM) (Tescan Vega 3 LMU) coupled with energy-dispersive X-ray spectroscopy (EDS) (Oxford Instruments X-Max N detector).

2.2.8. FTIR Analysis

A Fourier transform infrared spectrometer (FTIR) (Bruker, Model VERTEX 70v) was used to analyze RaB, SBE and CaB400 equipped with an attenuated total reflectance (ATR) adapter with diamond crystal. The analyses were conducted in the 4000 to 400 cm^{-1} regions, with a resolution of 4 cm^{-1} , and 64 scans were averaged for each measurement. A blank spectrum was registered before the analysis for background correction to mitigate atmospheric interference. The powdered materials were placed in the ATR and pressed in the diamond crystal interface.

3. RESULTS AND DISCUSSION

3.1. Chemical characterization

Chemically the RaB presents major elements of SiO_2 (44.18%), Al_2O_3 (15.2%), Fe_2O_3 (~ 9%), K_2O (3.87%), CaO (~ 3%), MgO (~ 3%) and Na_2O (1.27%) and minor elements of P_2O_5 , MnO and Cl (Fig. 1). Virgin bleaching clay usually made with bentonitic and clay materials, consists mainly of SiO_2 , Al_2O_3 and smaller amounts of Fe_2O_3 , MgO , CaO , K_2O , Na_2O and TiO_2 [15, 19, 22, 31–33]. Nevertheless, the chemical compositions of bentonite usually vary because of the many substitutions that are isomorphic in smectite [31] and the higher percentage of Fe_2O_3 could be a characteristic of Brazilian smectites [31]. And in this paper, the variations can be attributed to the industrial manipulation of raw clay materials used to make this adsorbing material.

The ExB, CaB400, CaB500, CaB600, CaB700, CaB800, CaB900, and CaB1000, have similar chemical composition with virtually same composition (Fig. 1). The XRF results show chemical composition of the bentonitic material at different calcination temperatures. The RaB presented an LOI of 16 wt.%, which implies the amount of volatile and structural water present in the RaB, while the calcined samples showed an LOI of ~ 43wt.%, which represents the oil content, structural water in clay minerals and volatile contents in each sample.

Oxides detected in high percentages are typically associated with aluminosilicates and clay minerals, such as kaolinite, illite and montmorillonite (Fig. 1). Potassium concentration in every sample, can be associated with the illite and feldspar mineral phases. Magnesium can be associated with the montmorillonite phase or isomorphic substitutions in other phases, generally illite.

3.2. Physical characterization

The particle size distribution of RaB and SBE is presented in Fig. 2 and was interpreted according to ASTM D6913 standards [34]. Results indicate that the samples were similar in particle distribution, but the RaB is finer in distribution. The RaB exhibited grain sizes in the clay fraction of 1%, the silt fraction of 83%, and sand fraction of 16% and the average particle size was 22.7 μm . For SBE, the grain sizes were 0.35% in the clay fraction, 50% in the silt fraction, and 49.65% in the sand fraction and averaged particle size was 51.7 μm . It is observed that the raw bentonite is silty, while the SBE is sandy-silty [34]. Therefore, the granulometric data of both samples confirm an overall increase in grain size, both within the silt range, which is comparatively similar to other Brazilian natural bentonitic clay [32], despite having a bigger overall particle size distribution which is attributed to the saturation of the bentonite and the consequent expansion of the montmorillonite phase through palm oil adsorption, predominantly affecting the silt fraction of the material. The impurities and adsorbed oil present in the SBE made the particles agglomerate and form small clumps and large granules [20] shifting the particle size distribution, which affect filtration efficiency [7].

3.3. Mineralogical characterization

The RaB is composed of quartz (SiO_2), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), montmorillonite ($(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$), illite ($\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$) and feldspar microcline ($\text{K}_{.5}\text{Na}_{.5}\text{AlSi}_3\text{O}_8$). The presence of the montmorillonite phase was confirmed by the discriminatory diffraction (Fig. 3) with peaks at $(14.23\text{\AA}) (6.2^\circ)$ when oriented, $(18.04\text{\AA}) (4.89^\circ)$ when glycolated and the peak disappears when heated to 600°C as well as the kaolinite peak $(7.14\text{\AA}) (12.39^\circ)$ that appears when oriented and glycolated. The biggest d-spacing varies from 9.6 up to 21 Å, hence the mineral is said to have an expanding lattice [10]. The mineralogical qualitative composition was consistent with the literature [22, 30, 32, 33, 35].

The mineralogical analysis of the RaB and ExB shows (Fig. 4) quartz, illite, montmorillonite and kaolinite as predominant phases. Band-like stretches can also be observed, indicating the presence of amorphous material, or amorphous fractions of the bentonitic material, or even oily-like material not completely extracted via low temperature solvent extraction. The well-defined peaks, however, indicate that the detected and predominant phases possess high crystallinity and did not suffer structural changes during the extraction process. In contrast to the calcined samples, the stable and crystalline phases suggest that the extracted bentonitic material kept their ordered structure, similar to their raw counterpart, essential to activation of bentonite.

The raw, extracted, and calcined bentonitic clay all samples have similar mineralogical composition (Fig. 4) and is consistent with the literature [22, 30, 32, 33, 35]. Quartz is present in all temperatures and is stable throughout the samples, illite also appears in all samples but due to its expansion and subsequent collapse the peaks are diminished with temperatures until its loss of characteristic peaks ($\sim 8^\circ$). Other mineral phases like kaolinite also start to lose their crystalline lattice at around 550°C and transform completely to metakaolin at 700°C , while the montmorillonite phase appears to collapse at temperatures lower than 300°C [13, 19, 27]. Even without the characteristic peak at low angles, it can be identified, up to 700°C , the broad characteristic band of montmorillonite caused by the turbostratic stacking disorder [25, 36]. As the temperature continues to rise, reaching between 600°C and 700°C , a continuous decrease in kaolinite peaks is observed, indicating a progressive transformation.

Hematite and mullite were identified only in the higher-temperature calcined samples (CaB800, CaB900 and CaB1000), indicating that thermal treatment promoted significant mineralogical transformations and recrystallization processes. Mullite formation is associated with the thermal decomposition of aluminosilicate clay minerals, whereas hematite likely originated from the crystallization of iron previously dispersed within the amorphous fraction, present as poor crystalline iron compounds, or incorporated into clay mineral structures through isomorphic substitution in clay minerals. This interpretation is supported by the XRF results (Fig. 1), which indicate relatively high Fe_2O_3 contents ($\sim 8 \text{ wt.}\%$) in all samples despite the absence of discrete iron-bearing crystalline phases in RaB and ExB diffractograms (Fig. 4). The appearance of hematite after calcination therefore suggests that thermal decomposition and structural reorganization promoted the segregation and crystallization of iron into a detectable crystalline phase.

Table 1
Mineral composition of bentonite samples

(%)	Quartz	Anatase*	Montmorillonite	Illite	Kaolinite	Microcline	Amorphous	RWP	GOF
RaB	4.8	10	6.3	24	3.4	2.8	48.7	12.1	10.25
ExB	3.6	10	4.1	17	3.3	1.8	60.3	9.8	6.69
CaB400	6.6	10	-	38.1	1.1	3.1	41.1	10.4	7.16

* Internal standard.

Table 1 shows a mineralogical quantification of RaB, ExB and CaB400, obtained through Rietveld refinement [37]. Overall, there is a predominant fraction of amorphous material in all samples, with values of 48.7% for RaB, 60.3% for ExB and 41.1% for CaB400, showing the structural alterations associated with different treatments. The relatively high amorphous contents may be associated with a combination of factors, including the natural heterogeneity of bentonitic materials, industrial processing, and residual organic matter prior to sampling. The RaB sample presents as majorly present crystalline phases, illite (24%), montmorillonite (6.3%) and quartz (4.8%), with other minor phases as kaolinite and microcline. After the extraction process, ExB has a reduction on illite percentage (17%), and increase in the amorphous content, which indicates structural disorder or possibly lixiviation of interlamellar cations. After the calcined process was analyzed, CaB400 showed the disappearance of montmorillonite, associated with the structural collapse of this phase, as well as an increase of the amount of illite (38,1%). Concurrently, there is a reduction of the amorphous phase comparatively to ExB, which indicates structural rearrangement thermically induced. The RWP e GOF values indicate robust quality of fit and refinement for all samples [38, 39].

Table 2

Montmorillonite phase lattice parameters.

(Å)	a	b	c
161171-ICSD	5.18	8.98	15.00
Raw Bent	5.22	8.95	16.87
Ext Bent	5.20	9.01	14.03
Viani et al (2002)	5.17	8.94	15.00
Porras et al (2021)	5.08	10.17	14.74

The refined lattice parameters are presented on Table 2. The unit-cell parameters for RaB were consistent with a typical 2:1 dioctahedral smectite structure reported in the literature [25, 27, 36]. After Soxhlet extraction, ExB presented slight variations in a and b parameters, with a pronounced reduction in the c parameter. The contraction along the c-axis implies partial removal of interlayer species, likely due to the residual organics or exchangeable interlamellar cations [27]. This behavior would be consistent with solvent-induced dehydration and partial collapse of the smectitic interlayer. The refined parameters for RaB and ExB remain within the expected range for triclinic montmorillonite [25, 36].

3.4. Thermal characterization

Thermal analysis was conducted on the SBE (Fig. 5). According to TGA/DTG between 100–200°C there is an initial 4% mass loss, attributed to evaporation of free water and humidity adsorbed on the mineral phases and on the material, this behavior is typical of bentonitic clays [30]. At 260°C, there is water loss from clay minerals crystal lattices [10, 22, 27, 40]. Between 280 and 420°C, there is considerable mass loss, around 25%, which can be attributed to the ignition of the residual palm oil [15] and residual fatty acids and lipidic degradation [41]. From Fig. 5, it could be inferred that the residual palm oil content in SBE was around 25 wt.% according to the weight loss ratio in that temperature range, which usually contains between 17–28 wt.% [8, 14, 17]. During the mass loss analysis, there was gaseous liberation due to the carbonization process, at around 380°C, which is similar to carbonization of residual soybean oil [15, 26]. The accumulation of mass loss up to 500°C is around 35%, representing the most important transformations of this bentonite. Around the range of 500 to 780°C there is a loss of approximately 5% from the clay mineral phases, kaolinite and montmorillonite [32]. From 780°C to 1000°C, there is noticeable mass stability. In total the mass loss is around 40 wt.%, which is attributed to ignition of oil in SBE [15, 41].

According to the DSC curve, there are several thermal events, as products of the amount of phases occurring in SBE. At 300°C there is an endothermic peak, commonly associated with water loss in lattices in kaolinite, montmorillonite, and

illite phases [10, 22, 40], as well as lattice expansion [27]. At 400°C is associated with the beginning of the dehydroxylation of the kaolinite phase [13, 40]; around 430°C, there is expansion of the illite lattice, to a mica-like structure [27]; at 470°C, associated with the beginning of dehydroxylation of the montmorillonite phase, in particular rich in iron [40], as well as the dehydroxylation of the illite phase [13, 28]. Although the dehydroxylation peak is pronounced, the absence of a major distinct kaolinite peak in Fig. 4 suggests that this event is primarily related to the smectite and illite phases. Since these thermodynamic events overlap within a narrow temperature range, distinguishing each individual process becomes challenging. Around the range of 500 to 780°C even without discernible endothermic peaks, end the dehydroxylation of the clay minerals [10, 13, 40], as well as the collapse of the crystalline lattice of kaolinite into metakaolin phase ($\text{Al}_2\text{Si}_2\text{O}_7$), which is typical for materials containing kaolinite. From 780°C to 900°C, there is noticeable mass stability which confirms the major stages of transition, crystallization loss and physical transformations have already occurred. Between 900°C and 1000°C, confirms the formation of new phases like hematite and mullite [22] a high temperature exothermic phase recrystallization around the 950°C temperature. The illite phase ultimately collapses around 1000°C and could be associated with the last thermal peak. The loss of mass throughout the N_2 heating atmosphere is also corroborated in the loss on ignition results presented in the XRF analysis (Fig. 1).

3.5. Micromorphology and microchemistry of bentonite materials

The SEM/EDS results (Fig. 6) illustrate the morphological and chemical differences of bentonitic clay through the various stages of extraction and thermal treatment. At its raw state (Fig. 6a), the bentonitic clay appears to be homogenous large particles and irregular micrometric thin sheets, which corroborate to their high specific surface area, and in some cases, form radial-lamellar (rosette-like) flaky-features or clumps. Nonetheless it is morphologically homogeneous. Kaolinite is believed to be observed in samples (Fig. 6b) as plate-like lamellae with a distinct hexagonal outline [10], whereas montmorillonite structures appear as thinner, less developed flakes clumps, an characteristic identifiable in the raw sample [13, 31]. The ExB sample shows smaller flake-like particles which illustrate the high specific surface area in slit/planes shapes, implying that the reactivation procedures do not change their macrostructure [24]. Smaller clumps of material are present on the surfaces of the flake particles and the overall structure of the ExB samples are agglomerated flake-like particles imbued with a concentrated amount of smaller particles.

The surface characteristics of CaB400 and CaB600 were similar, and both showed the damage of flake-like features and agglomerated particles that, due to higher temperatures, impurities, pigments, and adsorbed oil made the clay particles agglomerate and form from small clumps to large granule [20]. Due to temperature as well the volatile matter adsorbed were cracked and released, revealing specific surface properties and pore structures [15]. This agglomeration is corroborated by analysis of particle size (Fig. 2). The EDS spectrum of the mapped areas indicated the presence of silicon and aluminum in high concentrations, as well as the presence of homogeneously dispersed iron, magnesium, and oxygen, and minor concentrations of potassium and sodium. These elements are consistent with the expected composition of clay minerals [20] such as kaolinite, illite, and montmorillonite, confirming the predominantly aluminosilicate nature of the material, previously identified by XRD (Fig. 4). Although the XRF did not detect sodium in all temperatures, the EDS system managed to detect sodium in all samples homogeneously. SEM images reveal the complex surface morphology of clay samples, and these surface structures were consistent with previous relevant studies [15, 30, 33], and that temperature played a vital role, volatile matters gradually cracked and released from SBE with the increasing temperature, forming specific surface properties and pore structures [15].

3.6. FTIR Analysis

FTIR spectra of the RaB, SBE and ExB samples are presented in Fig. 7. All the samples present a strong band in around 1000cm^{-1} , mostly attributed to the stretching vibration in the plane of Si-O commonly associated with the presence of silicates and clay minerals like kaolinite and illite [19, 32, 33], as well as absorption band 3410cm^{-1} , which can be

attributed to the asymmetric and symmetric stretching of structural hydroxyl groups and adsorbed water [13, 19, 32]. Characteristic absorption of dioctahedral smectite can be observed in 3620, 1109 and 908 cm^{-1} [13, 19], although it diminishes with the saturation of palm oil (SBE) and subsequent extraction (ExB), a typical feature of Al-Al-OH octahedral sheet is present in 1633 cm^{-1} [13]. And at 797 cm^{-1} it can also be observed in the RaB a peak commonly attributed to quartz [13].

In the FTIR spectrum of SBE, absorption bands at 2932 and 2852 cm^{-1} are observed and are commonly attributed to the asymmetric and symmetric C–H stretching vibrations of methylene groups from aliphatic hydrocarbons [15, 24], which are characteristic of polyunsaturated fatty acids associated with crude palm oil (CPO) commonly reported in Malaysian mills [21, 41]. No significant absorption bands were observed in the triple-bond stretching region between 2500 and 2000 cm^{-1} , the band around 2350 cm^{-1} was attributed to the room CO_2 . A strong absorption band at 1744 cm^{-1} , within the double-bond region, is attributed to the C = O stretching vibration of carbonyl-containing compounds such as ketones, aldehydes, and carboxylic acids. [21, 41]. Additionally, the same band at 1633 cm^{-1} corresponding to octahedral sheets of smectite [13] could also correspond to C = C stretching vibrations of polyunsaturated fatty acids [15, 21], as well as -OH frequencies of water molecules [19], so they do not seem to alter intensity, but shape. The band at 1452 cm^{-1} is attributed to the C–H bending vibrations of methylene and methyl groups, which is characteristic of saturated aliphatic hydrocarbons, such as long-chain alkanes [41].

Observing comparatively with SBE, the ExB spectrum does not seem present the aliphatic or carbonylic peaks corresponding to polyunsaturated fatty acids or saturated aliphatic hydrocarbons [17, 26, 35]. Which comparatively, in these samples, shows the effects of the extraction by solvent, still it presents a diminished attributed water and montmorillonite peaks at 3692 and 3620 cm^{-1} , respectively. Comparatively, the samples present peaks at 908, 682 and 526 cm^{-1} , which given the clay nature of the samples, could correspond to Octahedral sheets stretching planes in the crystalline structure of montmorillonite [25, 32]. But the overall intensity of these stretching planes lose intensity in SBE and subsequently ExB.

3.7. Comparative effects of Soxhlet extraction and thermal treatment on bentonite properties.

Given the results obtained through the analyses, and the integrated discussion of the chemical, mineralogical, thermal, physical, spectroscopical and morphological characterizations, it is possible to establish the following comparisons in Table 3, substantiated in a classical approach to materials engineering and technology of bentonitic clays.

Table 3
Comparative effects of Soxhlet extraction and thermal treatment on bentonite properties

Aspect	Soxhlet extraction (ExB)	Thermal treatment (Calcination)
Bulk chemistry (XRF)	Preserves major oxide composition (SiO_2 – Al_2O_3 – Fe_2O_3 system), only Na_2O fluctuates within detection limits of analysis.	No change in bulk chemistry of aluminosilicate material other than apparent increase of chemical contents due to loss of volatile materials.
Structural integrity (XRD)	Clay mineral structure preserved; montmorillonite, illite and kaolinite remain crystalline.	Progressive structural collapse of smectite (< 300°C) and dehydroxylation of kaolinite/illite (600–700°C) high-temperature recrystallization (> 800°C).
Amorphous content	Increased amorphous fraction, attributed to residual oil and partial structural disorder attributed to industrial contamination and weathering.	Decrease at moderate temperatures (400°C) due to thermal rearrangement.
Organic matter removal	Chemical extraction removed 24wt.% of SBE oil content in sample.	Nearly complete removal below 400°C; thermal stability above ~ 780°C.
FTIR	The extraction is effective in removing oil adsorbed, with loss of crystallinity	Nearly complete removal below 400°C.
Microstructure (SEM)	Lamellar morphology preserved with oil-induced agglomerates.	Morphological changes and granular aggregates are due to thermal reorganization above 300°C.
Functional implications	Would maintain swelling and surface reactivity but limited full regeneration for adsorption.	Could be used as a thermally stable material, suitable for ceramic applications.

The repurposability of SBE represents a strategic pathway toward circular economy integration within the palm oil industry [15, 20]. Instead of disposal through landfilling, SBE can be reintegrated into productive cycles through controlled solvent extraction or co-solvent extractions, and thermal cycles. The integrated chemical, mineralogical, spectroscopic, and morphological characterizations show that each treatment route directs SBE toward distinct value-added pathways, functional regeneration and structural transformation. These strategies enhance material circularity, reduce waste generation, and align industrial mineral processing with sustainability principles by extending material life cycles and minimizing environmental impact.

4. CONCLUSIONS

The results show that the applied treatments exert distinct effects on the structural, mineralogical, and physicochemical properties of SBE, leading to different reuse pathways. Soxhlet solvent extraction proved to be a low-impact, structure-preserving process, capable of partially removing residual oil without inducing significant changes in bulk chemical composition, crystalline structure, or lamellar morphology. Consequently, swelling capacity was largely preserved, although complete regeneration of adsorption sites was not achieved. In contrast, thermal treatment induced irreversible structural modifications, including collapse of the montmorillonite lattice, progressive dehydroxylation of clay minerals, and recrystallization into thermally stable phases at elevated temperatures, accompanied by morphological alterations and increased particle agglomeration. These transformations resulted in the formation of materials with enhanced thermal stability and potential for technological applications, particularly in ceramic processing.

Therefore, the selection of the treatment method should be determined by the intended end-use of the spent bleaching earth, whether for partial reactivation and reuse as an adsorbent or for conversion into structurally stable materials.

These findings provide further insight into the modification mechanisms of bentonitic clays and support their valorization within the framework of circular economy strategies and sustainable industrial waste management.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Data Availability

The experimental datasets generated and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors' contributions

Author 1: Conceptualization, methodology, investigation, formal analysis, data curation, visualization, writing of the original draft, and project administration.

Author 2: Conceptualization, methodology, formal analysis, supervision, and writing, review and editing.

Author 3: Methodology, investigation, formal analysis, data curation, and review and editing.

Author 4: Methodology, investigation, formal analysis, and review and editing.

All authors read and approved of the final manuscript.

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Figures

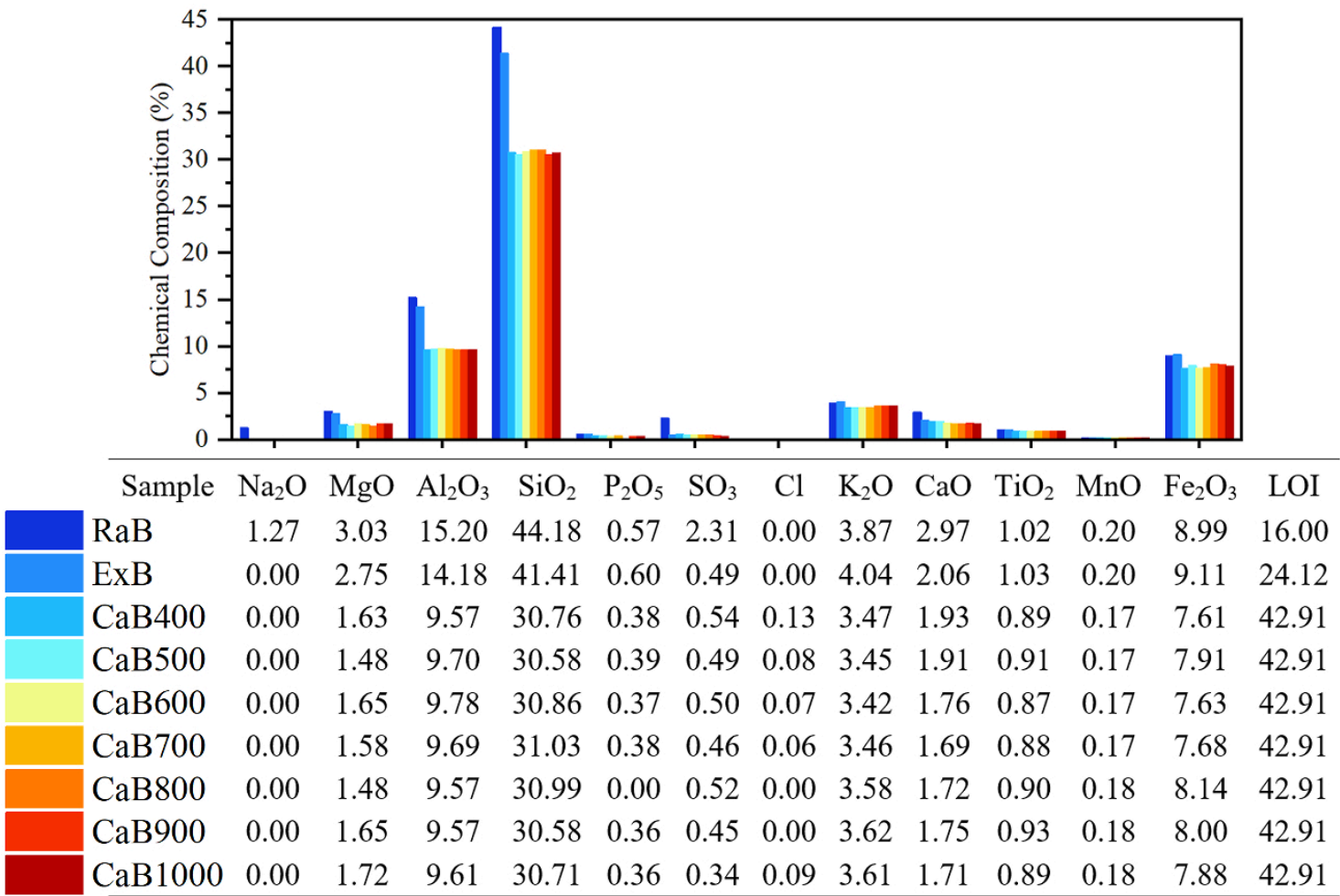


Figure 1

Chemical composition comparison of RaB, ExB, CaB400, CaB500, CaB600, CaB700, CaB800, CaB900, and CaB1000.

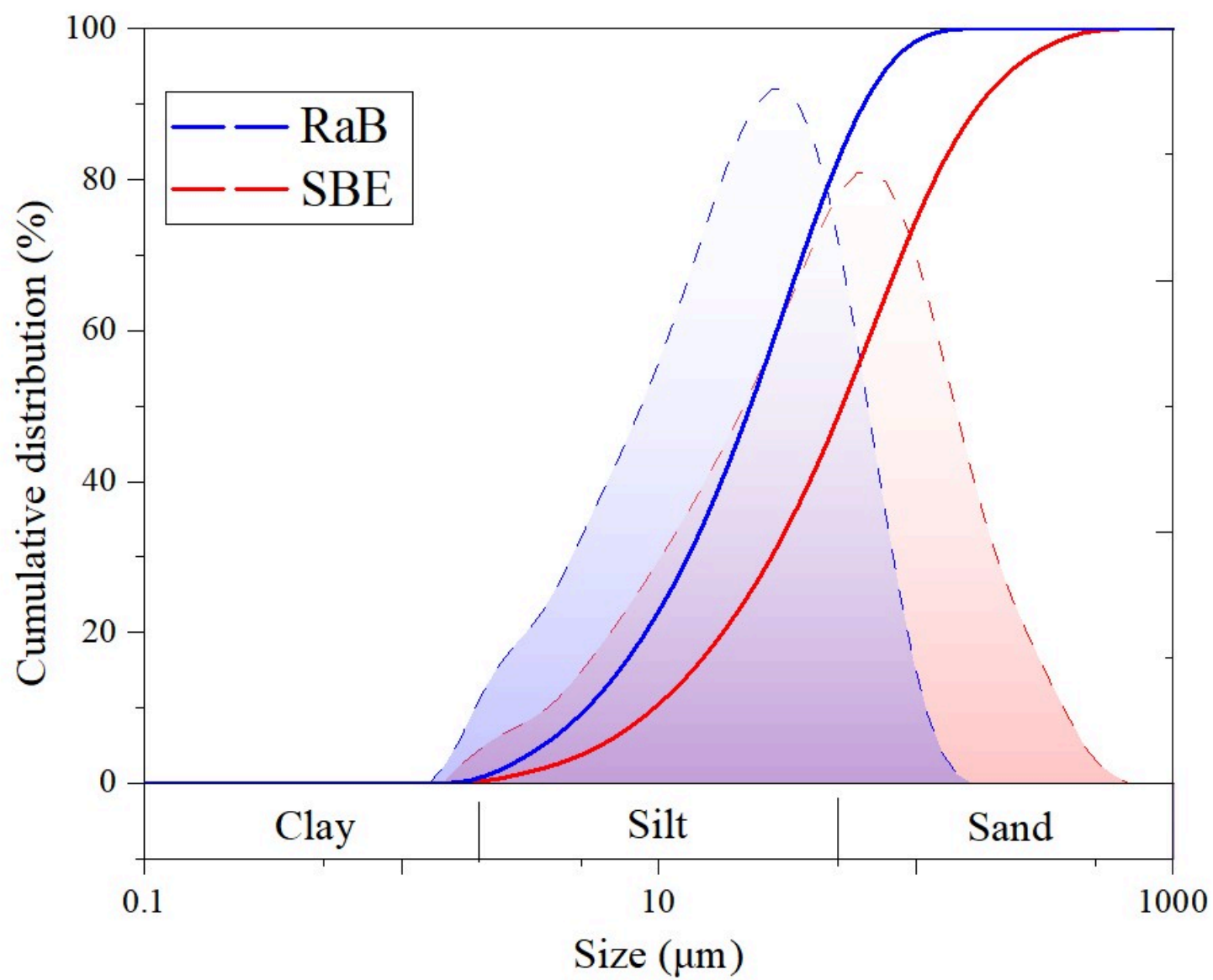


Figure 2

Cumulative particle size distribution of RaB and SBE.

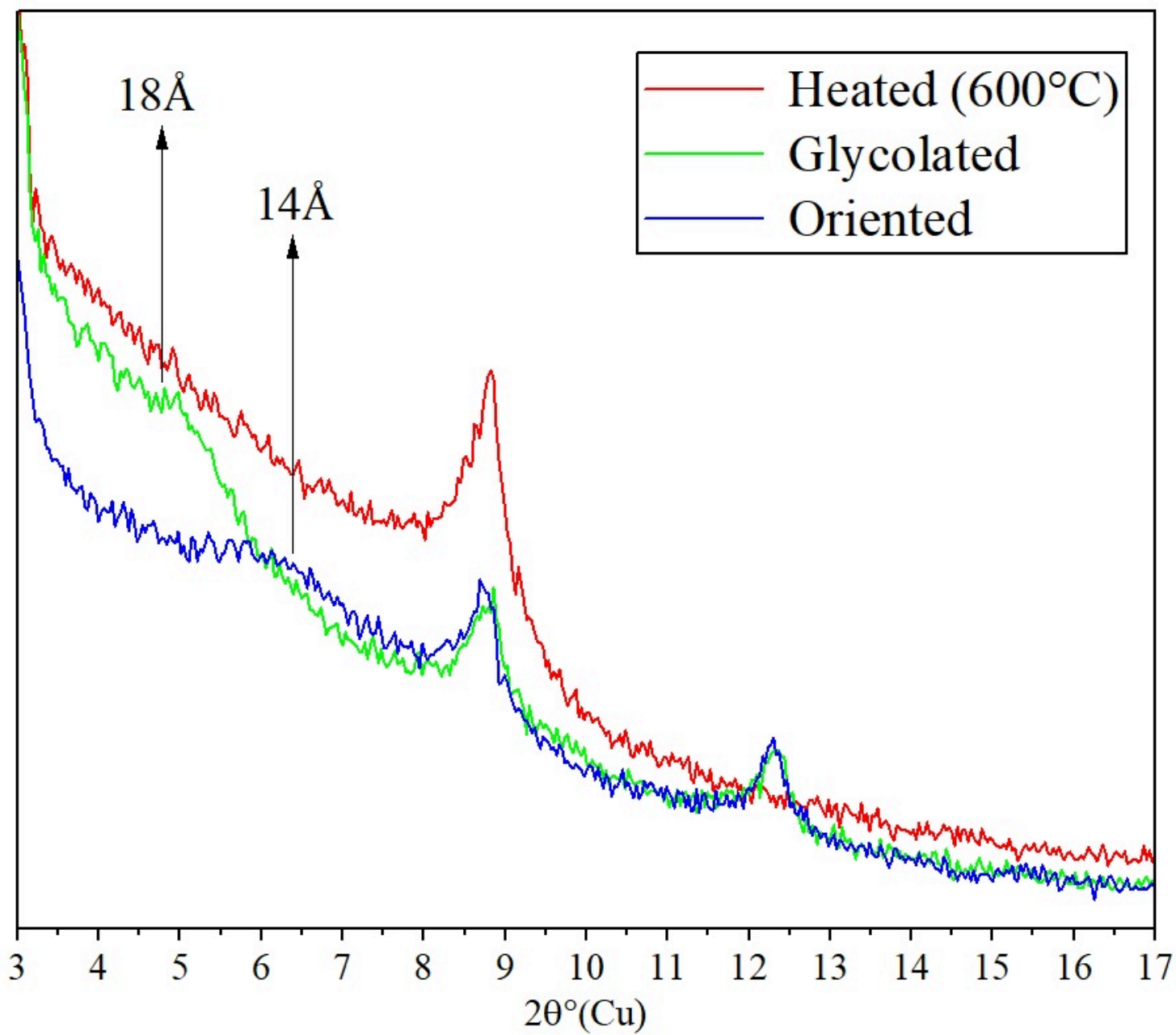


Figure 3

X-ray diffraction patterns of RaB oriented, glycolated and heated.

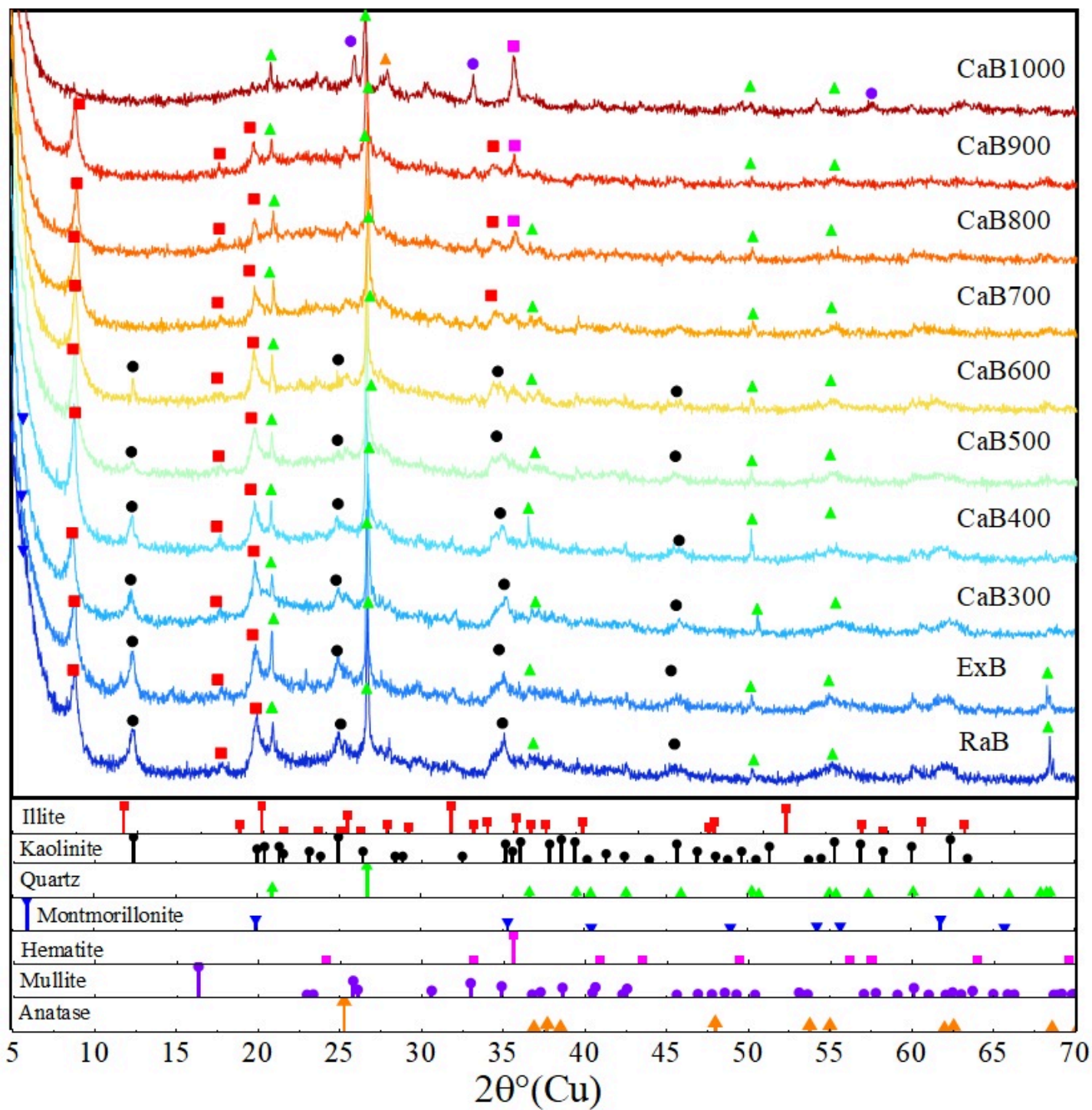


Figure 4

X-ray diffraction patterns of RaB, ExB and CaB. Illite: PDF: 00-002-0050, Kaolinite: PDF: 00-005-0143, Quartz: PDF: 01-085-0335, Montmorillonite: PDF: 00-003-0015, Hematite: PDF: 01-073-0603, Mullite: PDF: 00-041-1480, Anatase: PDF: 01-071-1167.

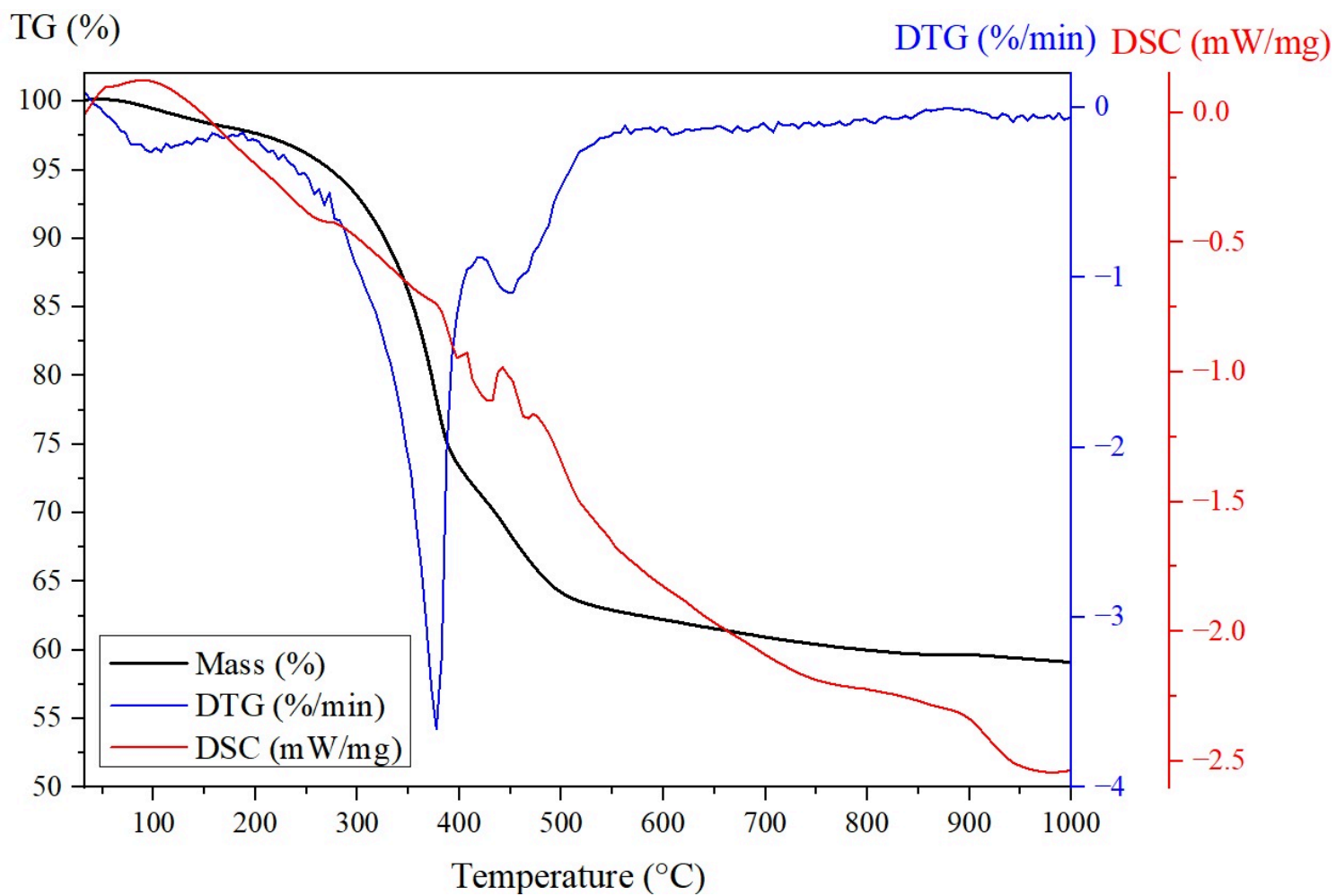


Figure 5

TGA/DTG and DSC curves analysis of SBE

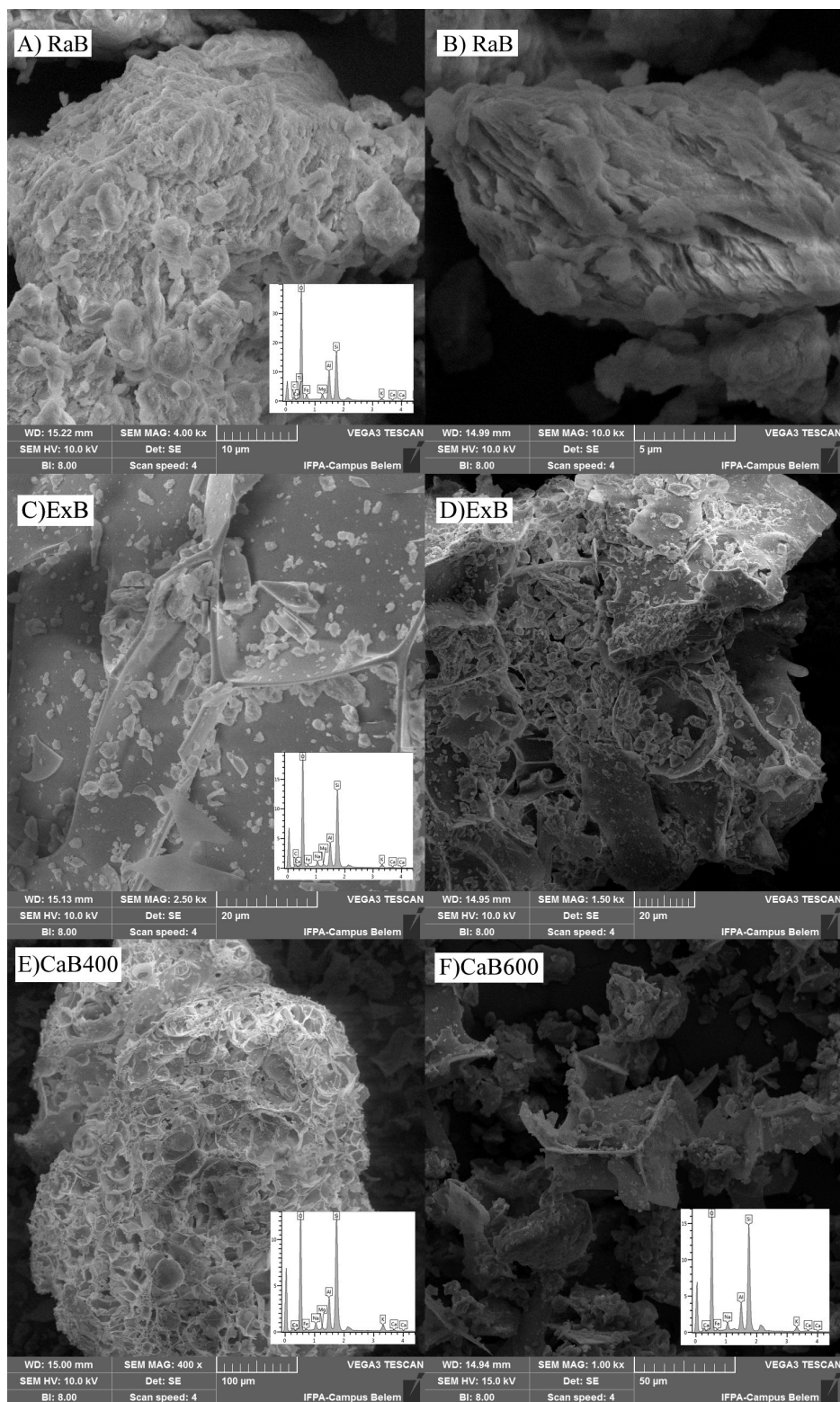


Figure 6

SEM/EDS results: A) and B) Raw Bentonite RaB, C) and D) Soxhlet extracted Bentonite ExB, E) Calcined SBE Ca400, F) Calcined SBE Ca600

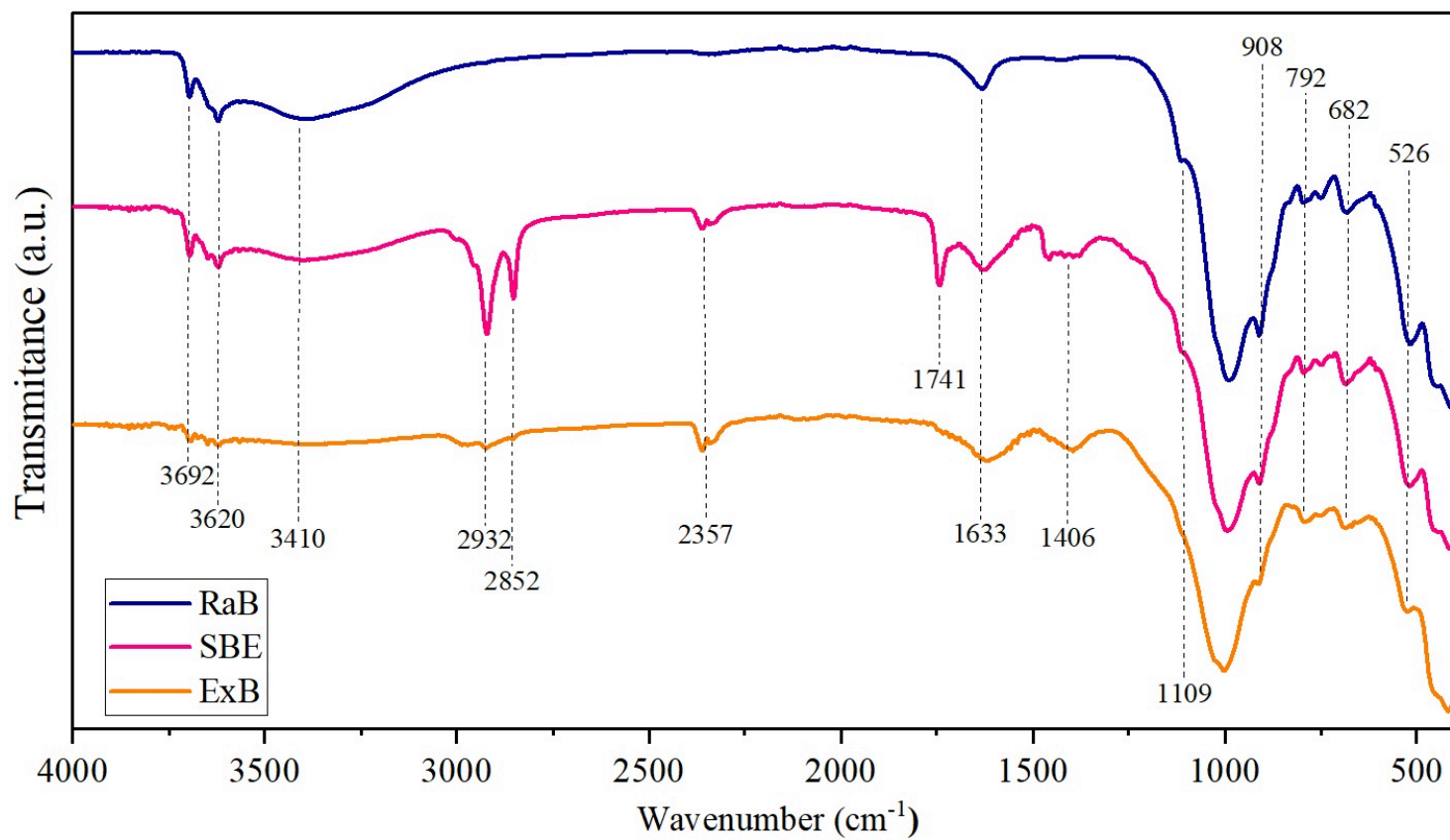


Figure 7

FTIR spectra of the samples RaB, SBE and ExB.