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SPENT BLEACHING EARTH: SYNTHESIS, PROPERTIES, CHARACTERISATION, AND APPLICATION

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Abstract: Spent bleaching earth (SBE) is hazardous solid waste generated from the edible oil industry through the oil bleaching process, as it is used to purify the edible oil to accomplish the strict standards required for edible oil on colour, taste and hence oil's shelf-life. It has diverse applications for energy, construction, and agriculture, which are attributed to its remarkable physical and chemical properties. Waste generation can be reduced by utilising SBE for applications that include biogas production, bio-organic fertiliser, lubricating grease, and foamed concrete incorporating SBE. In line with this background, this paper compiled and reviewed the literature on the synthesis of SBE through the activation of bentonite, edible oil bleaching process, properties of SBE and characterisation techniques for SBE. Finally, the merits and demerits of the application of SBE are expounded. The overall performance of SBE in their respective applications is enhanced by free cations and residual oil present. Finally, future research considerations are also discussed for the co-pyrolysis application of SBE and other biomass substrates as an economically significant prospect. It is noted that reusing SBE appears to improve the oil refining industry's sustainability and in turn the cities and communities.

Keywords: Edible oil bleaching, oil adsorption, residual oil, spent bleaching earth, waste management.

Introduction

Spent bleaching earth (SBE) is a 2:1 unit layer structured alumino-silicate mineral consisting of montmorillonites (Loh e*t al.*, 2015a; Liu *et al*., 2020) mainly of clay minerals (Abdulbari *et al*., 2011; Malakootian *et al*., 2011). It is a solid residual adsorbent waste generated in the edible oil industry after discolouration (Pollard *et al*., 1991; Huang & Chang, 2010; Suhartini *et al*., 2011; Fahmil *et al*., 2014). SBE is currently discarded directly in landfills near the factories without treatment (Lee *et al*., 2000; Kheang *et al*., 2006; Nursulihatimarsyila *et al*., 2010; Mana *et al*., 2011; Cheong *et al*., 2013; Prokopov & Mechenov, 2013; Bachmann *et al*., 2020b). This is so because SBE would have lost its adsorption properties, necessitating additional transport costs from the oil refinery and treatment before being dumped at the landfill site. SBE after the bleaching process, contains residual oil of 20-40% by weight and after being left on landfill sites, it comes into contact with air (Nursulihatimarsyila *et al*., 2010; Beshara & Cheeseman, 2014a; Fahmil *et al*., 2014; Oladosu *et al*., 2017). Thus, it may self-ignite, causing hazardous fires (Kheang *et al*., 2006; Yuan *et al*., 2020) through spontaneous combustion. Disposing of SBE in landfills causes environmental pollution problems emanating from residual oil content, water content, leachable trace heavy metal, degradation of organic compounds and is a source of odours (Saleh Alhamed & Al-Zahrani, 1999). This is caused by impurities extracted from the unrefined oil and its exposure to atmospheric air resulting in residual oil oxidation accelerated by bleaching the earth's high surface area. SBE is therefore considered a hazardous waste because of its high organic content (Beshara & Cheeseman, 2014a). Similarly, the disposal of SBE in landfills is considered problematic to the environment, hence the need to properly manage SBE waste.

Between 1.5 and 2.0 million tonnes of SBE are generated annually based on the world's cooking oil production of 128.2 million metric tonnes in 2007. In Malaysia, bleaching earth added per tonne of crude palm oil (CPO) amounts to 5-10 kg resulting in up to 170,000 tonnes of SBE generated per annum (Loh *et al*., 2015). A palm oil refining plant in the cooking oil industry with a production capacity of 1,000 tonnes daily will need 109,000-436,000 tonnes of bleaching earth annually. Generation of SBE is estimated to exceed 2 million tonnes per year based on vegetable oil world consumption of 128 million tonnes (USDA, 2009) and assuming 1 wt.% of bleaching earth is used relative to the amount of edible oil processed (Beshara & Cheeseman, 2014). In Saudi Arabia, the estimated amount of the spent clay produced annually (assuming 2 wt.% is used in bleaching) is 5,200 tonnes/year (Saleh Alhamed & Al-Zahrani, 1999) whilst in Algeria, Poland, and Japan, edible oil refineries produce about 8,000, 40,000, and 80,000 tonnes respectively of SBE per year mostly in oil refining (Mana *et al*., 2011; Krzyśko-Łupicka *et al*., 2014).

SBE originates from bentonite clay after the adsorption of impurities from crude oil during the bleaching. Bentonite or natural bleaching earth is an inorganic, green, low-cost adsorbent and non-toxic 2:1 layer clay material (Maged *et al*., 2020) found in many parts of the world. Bentonite can exchange ions on the surface (Darmawan *et al*., 2020) with acid activation of bentonite producing Si-rich phase which is more acidic through the dissolution of non-clay components mainly in the octahedral layer and exchange of cations with hydrogen ions which then results in improved surface area, porosity, bleaching effectiveness, interlayer sites hydrophilic properties (Soetaredjo *et al*., 2021) and strongly protonated clay mineral surface (Shattar *et al*., 2020). Various methods have been used for the activation of bentonite using acid. Methods recorded by researchers differ with the type of acid used, the concentration of acid, clay-to-acid ratio, contact time and activation temperature. Because bentonite possesses excellent chemical, physical and sorption properties, it is used for the adsorption of varying pollutants, including removing impurities from vegetable crude oil through oil bleaching.

Oil bleaching is considered an integral part of oil processing to improve the taste and appearance of oils through reduction of heavy metals, phosphorous and to improve by reducing Bentonite activated with acid are the common bleaching agents and their selection for this purpose is favoured by their superior bleaching properties such as specific surface area and porosity. During the bleaching process, activated bentonite adsorbs oxidation products, peroxides (Usman *et al*., 2012), pigments and fatty acids, salts residuals (Gharby, 2022), phosphatides, gums, trace metals, phospholipids, soap, carotenoids, xanthophylls, lipid peroxidation products, chlorophyll, tocopherols, and gossypol (Kirali & Laçin, 2006; Foletto *et al*., 2011). These impurities affect the market value of the oil by giving it a colour that is not appreciated by customers, creating odour, and shortening shelf life. In addition, they degrade oil quality by altering its taste, thereby losing its flavour. The green colour in oil is mainly caused by chlorophyll, while carotenoids are the red/yellow colour pigments, so the bleaching capacity is primarily based on these two elements but more conveniently measured by chlorophyll adsorption because β-carotene molecules decompose to form shorter molecules (Bayram *et al*., 2021). These elements are removed during the bleaching process under vacuum conditions at high temperatures of 80-120ºC for up to 40 min with adsorbent dosages varying from 0.1 to 3%, resulting in the generation of spent bleaching earth as waste material. After the bleaching process, the sensory quality and oxidative stability of deodorised oil are improved. It should be noted that the quality of SBE produced depends on the activation process of bentonite, the bleaching process involved, and the type of oil to be bleached. Presented in Figure 1 is the mechanism of bleaching process reaction.

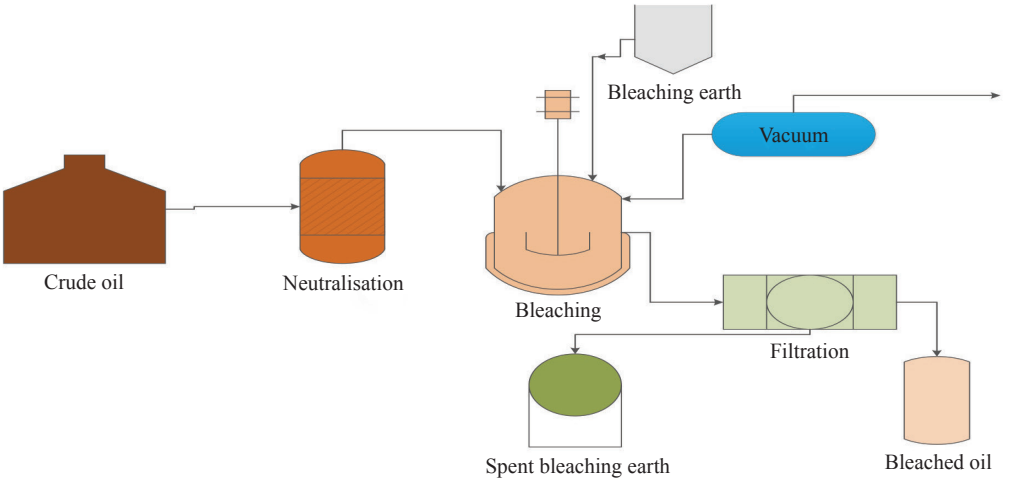

Figure 1: Mechanism of bleaching process and production of SBE

SBE possesses lower bulk density, high amorphous phase content, high cation exchange capacity and lower thermal conductivity, thus, making it one of the most studied industrial wastes. Additionally, application of SBE in fields of engineering and science include production of biogas (Ward, 2012; Moshi, 2017), biodiesel (Fahmil *et al*., 2014), biomass briquettes (Suhartini *et al*., 2011), biofuel (Sapawe & Hanafi, 2018), clay polymer bricks (Beshara & Cheeseman, 2014a), bio-organic fertiliser (Loh *et al*., 2015) and lubricating grease (Abdulbari *et al*., 2011). Furthermore, SBE can be regenerated for adsorption in water treatment plants (Malakootian *et al*., 2011; Mana *et al*., 2011; Tang *et al*., 2015) and as an adsorbent in the bleaching process (Saleh Alhamed & Al-Zahrani, 1999).

Studies on SBE include a review paper on the treatment of SBE with perceptions on interactions of SBE on crops and soils as a fertiliser (Loh *et al*., 2017), technologies for recovering edible oil from SBE (Oladosu *et al*., 2017) and ways of treating spent earth as suggested by other authors have been recorded (Dijkstra, 2020). Despite SBE research efforts, a review of synthesis, properties and SBE applications is not common. This review paper provides insight into SBE synthesis through activating bentonite and the bleaching process, properties, characterisation, and applications.

Production of Spent Bleaching Earth

This section explains the bentonite structure, different approaches to bentonite activation, and bleaching procedures are also discussed. This will help to understand this waste's chemical and physical properties, and the reader will relate the properties of spent bleaching earth to its origin. It will also help to compare one activation method over other given methods.

Bentonite Structure

Bentonite, named after Fort Benton, Wyoming, whose largest sources are found (Moosavi, 2017), consists mainly of crystalline clay minerals and other non-clay minerals (Önal & Sarikaya, 2007).

It has two tetrahedral silica layers sandwiching a central octahedral alumina layer attracted to each other by electrostatic forces through exchangeable cation balance (Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+}) as presented in Figure 2. Isomorphous substitution of Fe^{3+} or Mg^{2+} for Al^{3+} in the octahedral layer and Al^{3+} for Si^{4+} in the tetrahedral layer results in a negative charge on the surface of the clay (Eren *et al*., 2009) with cations (Na^{+} and Ca^{2+}) balancing the structure and surrounding edges as well as positioned between the layers.

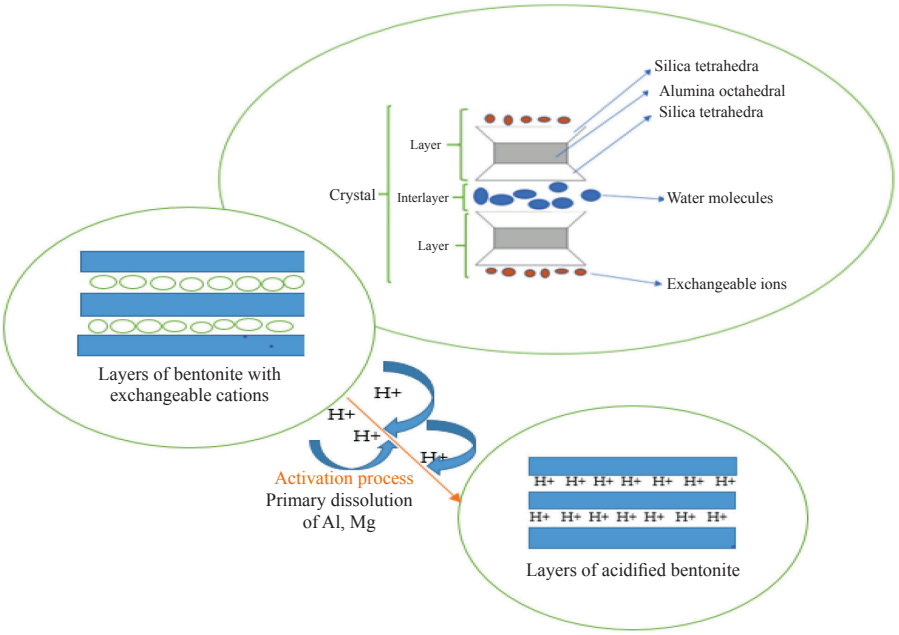

Figure 2: Bentonite and activation of the bentonite reaction mechanism

Bentonite Acid Activation

Bentonite activation is the physical or chemical modification applied for bentonite to adsorb impurities and colouring matter in oil with an increase in surface area of 200-300 m^2/g and pore diameters ranging from 2-6 nm (Figure 3). At first, exchangeable cations are replaced by H^+ ions, followed by Al, Fe, and Mg ions leaching from the tetrahedral and octahedral sheets with the silica groups remaining intact (Steudel *et al*., 2009). Therefore, activation involves exchangeable cations substitution from the octahedral sheet of Mg^{2+}, Fe^{2+}, and Al^{3+} against protons.

Several researchers have investigated the activation of bentonite using varied parameters (Table 1). Although acid activation improves the structure of bentonite, it usually involves high temperatures (up to 105ºC) and concentrated acids mainly H_2SO_4 and HCl with H_2SO_4 being favoured over HCl because of cost reasons. The properties of activated bentonite are largely affected by variables which include the nature of inorganic acid (Anyikwa *et al*., 2022), temperature, dry acid/clay ratio, treating time, particle size of bentonite, drying temperature of activated clay and washing procedure (Días & Santos, 2001).

From the literature, surface area and porosity increase with increasing concentration of acid (Foletto *et al.*, 2011; Motlagh *et al.*, 2011; Usman *et al.*, 2012; Alamery & Ahmed, 2021) and treatment time (Alamery & Ahmed, 2021) amounted to a decrease in pH from raw to acid activated clay due to cation substitution in the octahedral and tetrahedral sites. Surface area increases because at first, there are unoccupied spaces after Al^{3+}, Mg^{2+}, and Fe^{3+} leave the layers then as activation proceeds, larger empty spaces are formed resulting in micropores being changed to mesopores. In some locations, decomposition of the crystal structure begins to occur with some of the mesopores disappearing, hence reduction in specific surface area. Further acid concentration increases result in crystal structure destruction because of Al^{3+}, Mg^{2+}, and Fe^{3+} leaching from the octahedral sites, hence, causing a decrease in surface area. Optimum activation conditions for maximum bleaching

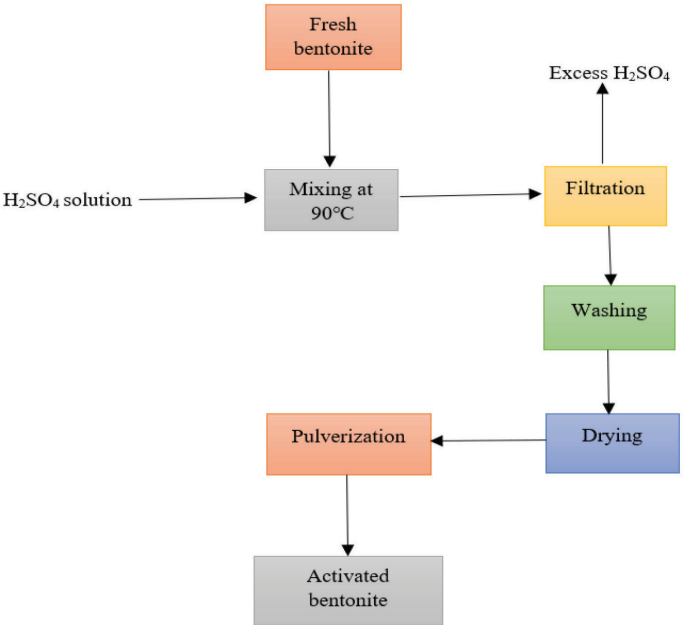

Figure 3: Summarised acid activation process

efficiency were reported as 98% H_2SO_4 acid concentration (34%), temperature (90ºC) and contact time (7 h) after an investigation using 3^3 factorial design (Didi *et al*., 2009) and 1N HCl acid concentration, contact time (6 h), 4% moisture and 0.5 solid to liquid ratio using 2^4 full factorial design (Kirali & Laçin, 2006). Table 1 summarises the methods of acid activation of bentonite.

Bleaching Process

The bleaching process involves the adsorption of oil impurities because of the acidity and the high surface area of activated bentonite since it is now more chemically active and efficient (Vaisali *et al*., 2015).

Several mechanisms are involved during bleaching, which include chemical bonding (ionic or covalent bonds), physical adsorption (Van der Waals forces) and chemical decomposition (Chakawa *et al*., 2019) as shown in Figure 4. The bleaching process is affected by the quantity and quality of activated bentonite, mixing, residence time, temperature, dosage rate/ amount, and vacuum or atmospheric pressure. The acid concentration used for bentonite activation affects bleaching efficiency. When acid concentration increases, it improves the bleaching capacity by removing cations in the octahedral sheet and, consequently causes the attack on the bentonite structure (Foletto *et al*., 2011; Motlagh *et al*., 2011) Iran, was submitted to acid activation with sulphuric acid. Sample aliquots (5gr. The quality of bentonite can also be improved by removing the moisture content using a vacuum system to prevent contact with oxygen in the air. Activated bentonite may catalyse oxidation at high temperatures in aerobic conditions and this causes degeneration of oil thus reducing its shelf life (Usman *et al*., 2012). Under vacuum conditions, bleaching contact time ranges from 20-40 min and temperatures vary from 80-120ºC (Table 2).

An increase in contact time and temperature results in a higher bleaching efficiency because of a decrease in oil viscosity resulting in an improved dispersion of particles, hence more flowability and clay-oil interactions. Initially, vacant surface sites will be available to remove impurities but will later be occupied as bleaching progresses, reducing bleaching

Table 1: Summary of activated bentonite synthesis for refining oil

Fresh Bleaching Earth Size (mm)	Activating Agent	Conditions	Characterisation	Activated Bleaching Earth Size (mm)	Challenges	Prospects	Reference
0.074	HCl (density = 1,16 kg/L; 32 kg HCl/0.1 L @ 9 mol * dm^{-3})	Conditions: Dry acid/clay (w/w) 0.64; 80ºC; contact time (3 h)	XRD	74	The test was conducted under moderate conditions which may not lead to the optimum bleaching capacity.	Optimisation of the parameters give a better indication of whether bleaching capacity will improve.	(Días & S., 2001)
0.075	HCl (1-5 N)	Conditions: Solid: Liquid ratio (0.1-0.5 g/mL; 95ºC; contact time (2-6 h)	XRD, BET N_2, XRF	-	HCl is a strong acid (indicated by low pKa). Washing off with distilled water will result in potential land pollution.	It is easier and safer to use H_2SO_4 or HNO_3.	(Kirali & Laçin, 2006)
0.045	HCl (4 and 6 N) (37%, density = 1.165 g/cm^3)	Conditions: 50% solid content; (3, 4, and 6 h); bentonite/acid (5:1); 70-80ºC	XRD, XRF, BET N_2	-	Washing off with hot water after activation results in more energy requirements.	Activated bentonite can be washed off using distilled water at room temperature.	(Alamery & Ahmed, 2021)
0.18	HCl (0, 0.2, 0.5, 1, 2, and 3 M)	Conditions: Clay: Acid (50 g: 250 mL); 105ºC; 30 min	XRD, AAS	0.18	Effect of acid concentration was analysed.	Optimisation of other parameters.	(Usman *et al.*, 2012)
0.35	$HN0_3$ (69%), H_2SO_4 (98%), HCl (37%) 15%, 20%, and 25% concentrations for all acids:	Clay: Acid (1:10); 90ºC; 30 min	XRF, XRD, FTIR	0.35	The study did not include activation time effects.	Effect of increasing activation time to be analysed.	(Yassin *et al.*, 2022)

-	H_3PO_4 (1, 2, 3, and 4 M)	30-120ºC; 5-60 min	-	-	Variation in activation time used in the study was too small.	Activation time to be increased up to 8 h.	(Anyikwa *et al.*, 2022)
-	H_2SO_4 (4 and 6 N)	Clay: Acid (1:10); 90ºC; 3.5 h	TGA, XRF, IR	0.074	Higher concentrations of H_2SO_4 were analysed.	Variation of concentrations from 1-6 N.	(Foletto *et al.*, 2011)
0.074	H_2SO_4 (15%, 20%, 25%, 30%, 40% and 45%)	Clay: Acid by mass (1:2); 4 h; 96-98ºC;	DTA, TG, XRD	0.074	Effect of activation time and activation temperature was not analysed.	Optimisation of all activation parameters which include activation time and activation temperature.	(Wu *et al.*, 2006)
0.149	H_2SO_4 (2-7 N)	Clay: Acid ratio (5 g:100 mL); 80ºC; 2 h	-	0.149	Effect of activation time and activation temperature was not studied.	Optimisation of the activation process parameters.	(Motlagh *et al.*, 2011)
0.074	H_2SO_4 (0-70% by mass)	97ºC; 6 h	XRD, BET	0.074	Effect of activation time and activation temperature was not studied.	Optimisation of all activation process parameters.	(Noyan *et al.*, 2007)
0.074	H_2SO_4	Temperature (25-250°C). Time (2.5-20 h) acid concentration (0.1-0.7 mass fraction of acid)	XRD, AAS	0.074	Very high activation time and temperature were used after 10 h and 150 °C, respectively.	Optimisation of process parameters to be conducted.	(Bayram *et al.*, 2021)
-	H_2SO_4 (98%)	Temperature (60, 90, and 120°C) Contact time (4 h, 6 h, and 8 h) Acid concentration (28%, 32%, and 36%)	-	0.075	Interaction of combined parameters is weak compared to individual interactions.	Factorial designs can be applied to determine the effects of activation parameters.	(Didi *et al.*, 2009)

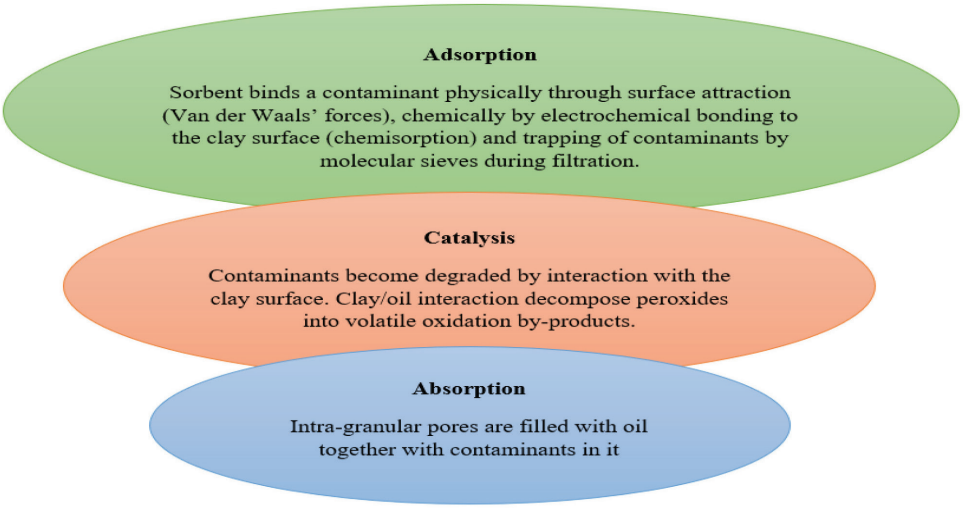

Figure 4: Bleaching mechanisms

capacity. Dosage increase results in an increase in bleaching efficiency as more adsorption sites become available but once equilibrium is reached, there will be no pigment removal. The dosage of bleaching earth also varies with the oil type. After bleaching, the bleaching earth-oil mixture is filtered first using filter plates. The SBE is then blown to remove the oil from the earth, followed by removal of the earth from the plate filters and then stored or disposed of.

Structural Characterisation of Spent Bleaching Earth

The following spectroscopic techniques can be used to evaluate and characterise SBE; X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) and Thermogravimetry Analysis (TGA) for the identification of crystalline phase, functional groups, thermal decomposition or thermal stability, respectively. X-ray Diffraction analysis (XRD) is a microstructural analysis providing crystallographic structure information, physical properties, and chemical composition of a material and includes atomic arrangements. SBE X-ray powder diffraction patterns in Figure 5 (a) show the presence of quartz impurities and peaks of the montmorillonite (M) (at 2θ = 20.89º and 26.65º) (Mana *et al*., 2011). Fired SBE waste (950ºC for 4 h) for making bricks showed the presence of cristobalite, anorthite, dolomite and muscovite (Eliche-quesada & Corpas-iglesias, 2014).

From the literature, diffraction peaks of SBE were detected at 2θ = 8.5º, 13.8º, 16.5º, 19.8º, 21.5º, 23.1º, and 27.6º (Tang *et al*., 2017). The infrared spectrum of absorption and emission of liquid, solid, and gas is obtained by FTIR, and it helps researchers get information about the intensity and wavelength of absorption and the functional groups present in a given compound. SBE absorption bands at 3,552, 3,436 and 1,631 cm^{-1} are a result of -OH stretching and bending vibrations of the adsorbed water and absorption bands at 1,744 cm^{-1} are attributed to stretching vibration of the carboxyl groups (Tang *et al*., 2017). Strong bands attributed to residual oil in SBE are indicated at wavelengths (2,914 and 2,853 cm^{-1}) due to $-CH_2$ symmetric and asymmetric stretching, -C = O stretching (1,736 cm^{-1}) and $-CH_2$ rocking bending (716 cm^{-1}).

TGA is a powerful technique for understanding the thermal decomposition of materials. Changes in the weight of a specimen are measured under predetermined heating rate and temperature conditions. Thermal decomposition of SBE displays three peaks

Table 2: A summary of research studies on the bleaching process

Type of Oil	Bleaching Process Parameters Varied	Characterisation after Bleaching	Significant Findings	Research Gap	References
Cotton seed	80ºC, 20 min, acid-activated bentonite/oil ratio (2 wt.%). Bleaching was conducted in a round-bottom three-necked flask with a stirrer, contact thermometer and a three-way valve (vacuum breaking or application).	Bleaching capacity = $\frac{C_0-C}{C_0}$ x 100 Colour determined spectro-photometrically at the best wavelength of 408 nm (Shimadzu UV160A). β-carotene equivalents compared against calibration curve prepared with 0-20 mg/L β-carotene solutio-s in petroleum ether.	Highest bleaching capacity was obtained for bentonite activated at 1 N HCI concentration, 0.5 solid-to-liquid ratio, 4% moisture for 6 h. Lowest bleaching capacity was obtained for bentonite activated for 2 h, 0.1 solid-to-liquid ratio, 4% moisture of bentonite with 1 N HCI concentration.	The study revealed the effect of activation time, solid-to-liquid ratio, acid concentration and bentonite moisture. Effect of activation temperature was not investigated.	(Kirali & Laçin, 2006)
Sunflower seed oil	Bleaching process parameters are not given.	Red and yellow colour index	Bleached oil had a lower colour index compared to unbleached oil.	Optimisation study on parameters not conducted.	(Alamery & Ahmed, 2021)
Palm oil	Varying parameters: Adsorbent dosages (1.0-3.0 g); reaction temperatures (30-120°C); and reaction time (5-60 min).	Edible oil moisture content; free fatty acids content; peroxide value; iodine value	Bleaching effectiveness is directly proportional to the acid concentration of the activated clay. Temperature, clay dosage and contact time also affected the process. Equilibrium adsorption concurred well with Freundlich and pseudo-second order kinetic model. Exothermic, physical and spontaneous adsorption. Optimum conditions: Adsorbent dosage, 3 g of clay: 100 g of palm oil; time 30 min; temperature 120ºC	Industrial bleaching earth was not used for comparison. Authors did not specify the adsorbent ratio.	(Anyikwa *et al.*, 2022)

Niger seed oil	Varying parameters: Temperature (60, 70, 80, 90, and 100ºC); Contact time (10, 20, 30, and 40 min); Dosage (1, 1.5, 2 g in 25 g of oil) Bleached oil was cooled and centrifuged.	Bleaching efficiency $\frac{C_0-C}{C_0}$ x 100	Bleaching efficiency increased with increase in acid concentration.	Optimisation on parameters used was not studied.	Yassin *et al*., 2022
Sunflower oil	100ºC; 30 min; under a vacuum of 450 mmHg, mechanical stirring. N_2 flow is maintained above the oil surface. Filtration of hot oil and clay mixture under vacuum.	Bleaching capacity $\frac{C_0-C}{C_0}$ x 100	Increase in acid concentration, improved bleaching capacity.	Optimisation study on parameters used was not investigated.	(Foletto *et al*., 2011)
Cotton seed oil	3% by mass of oil; 96-98ºC; 25 min. Speed 240 rpm. Clay slurry is filtered using double-layer filter paper by vacuum suction.	Bleaching capacity; $BC\ \% = \frac{A_\lambda^0(Neutralised\ oil)-A_\lambda^0(Bleached\ oil)}{A_\lambda^0(Neutralised\ oil)}$ A_λ^0 *, is the optical density at wavelength λ.*	Acid-activated bentonite can decolorise cottonseed oil.	Optimisation results were not provided.	(Wu *et al*., 2006)
Soya bean seed oil	2% by mass of oil; 90ºC; 10 min. Bleaching was performed in a 250 mL round-bottom rotary evaporator. Stirring at 60 rpm. Suspension filtered using a filter paper.	acid value; peroxide value *Bleaching capacity (%)* $= \frac{(Ta-T0)}{(Ts-T0)}\ X\ 100$	Removal of cations from bentonite octahedral sites proportionally increases the bleaching efficiency.	Optimisation results for bleaching parameters were not provided.	(Motlagh *et al*., 2011) Iran, was submitted to acid activation with sulphuric acid. Sample aliquots (5gr
Soya bean oil	1% by mass of oil; 95-105ºC; 15 min. Bleaching experiment involved stirred suspension in an open 400 mL beaker.	Red and yellow colour index using Lovibond Automatic Tintometer. Bleaching power = $100(R_0\text{-}R) / R_0$.	Bleaching power is mainly controlled by particle size distribution.	Optimisation was on activation of bleaching earth and not the bleaching process.	(Noyan *et al*., 2007)

Soya bean oil	2% by mass of oil; 105ºC; 15 min. The bleaching experiment was carried out in an open 400 mL beaker containing a stirred suspension.	Red and yellow colour index using Lovibond Automatic Tintometer. Bleaching power = $100(R_0\text{-}R) / R_0$ R_0 and R (red colour units on the Lovibond scale of the alkali-refined oil before and after bleaching).	0.8-3.2 nm is the most effective pore size for the best bleaching power.	Optimum parameters need to be determined individually for each raw bentonite and edible oil pair.	(Bayram *et al.*, 2021)
Colza oil	1% by mass; 100ºC; 20 min Bleaching is performed in a round-bottom three-necked flask with a contact thermometer, three-way valve (for breaking or applying vacuum) and a stirrer.	Chlorophyll; red and yellow colour.	Acid concentration and activation time greatly influence the bleaching capacity of bentonite.	The author did not investigate optimisation conditions for the bleaching process.	(Didi *et al.*, 2009)

(Yuan *et al*., 2020) that is, mass loss at 278ºC due to evaporation processes, with the evolution of oils or volatile products from the SBE sample, Figure 6. At temperatures of 341ºC and 400ºC, the peaks can be attributed to the burning and decomposition of SBE organic content (Mana *et al*., 2011; Eliche-quesada & Corpas-iglesias, 2014). Heating treatment at 500ºC confirms the removal of residual oil completely (Plata *et al*., 2020). Another author (Sapawe & Hanafi, 2018) highlighted a four-step weight loss, with the first step corresponding to the evaporation of adsorption water molecules and OH^- groups which are chemically bonded as a result of the bleaching process which produces SBE in an anhydrous condition, with second and third step being associated to burning and decomposition of organic materials (oils and volatile products) and residual oils carbonisation respectively. The fourth step is attributed to structural silica hydroxyl groups released from bentonite structure.

Spent Bleaching Earth Properties

This section discusses the properties of spent bleaching earth as an ideal material for different technologies. The reader will understand SBE important features as a perfect material for other technologies. SBE has high carbon content, creating a good energetic contribution to any firing process. It has a higher heating value of 72.575 kJ/kg (Eliche-quesada & Corpas-iglesias, 2014) due to bleaching earth's high surface area which can adsorb more oil and also expose oxygen to this residual oil during combustion reactions therefore, the high heating value is mostly due to the residual oil in the structure. The acidic, catalytic properties and trace heavy metals in the clay speed up the decomposition of hydroperoxides in residual oil and this ultimately results in less energy required during firing processes since FFA in the residual oil will be in an advanced oxidation state and hence oxidises more rapidly (Beshara & Cheeseman, 2014b).

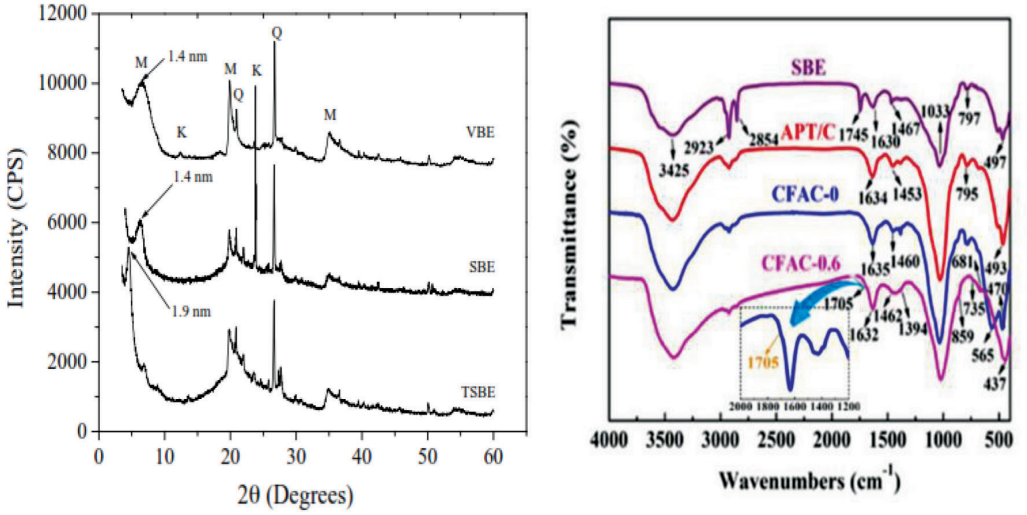

Figure 5: (a) XRD of TSBE (treated spent bleaching earth), SBE (spent bleaching earth) and VBE (virgin bleaching earth) (Mana *et al*., 2011) (b) SBE FTIR spectra (Tang *et al*., 2017)

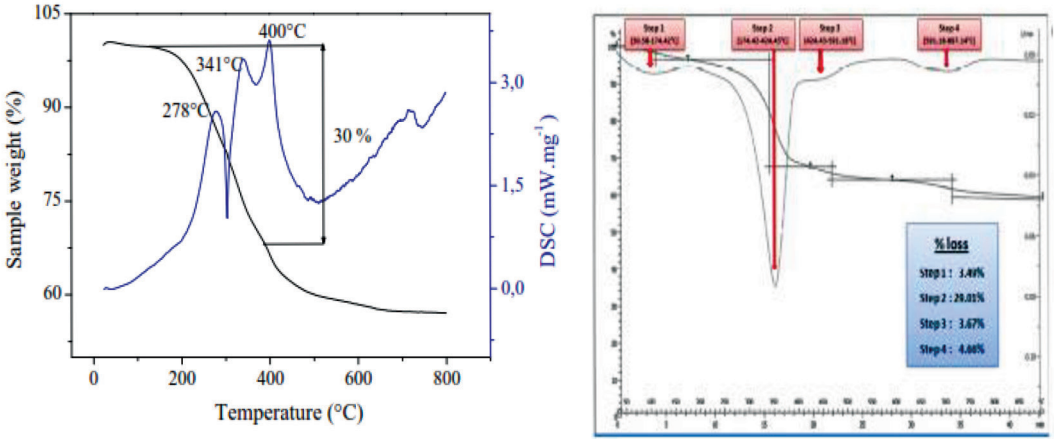

Figure 6: TGA spectra of spent bleaching earth (Eliche-quesada & Corpas-iglesias, 2014) (Sapawe & Hanafi, 2018)

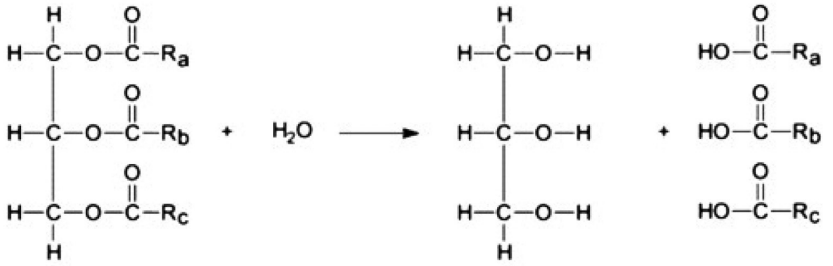

Figure 7: Reaction mechanism of lipids hydrolysis to form fatty acids and glycerol

Table 3: Summary of SBE characterisation from 2010 to 2020

Characterisation Parameter	Results (wt.% unless specified)	References
Moisture content	2.6%	(Beshara & Cheeseman, 2014b)
	2.6%	(Beshara & Cheeseman, 2014b)
	16%	(Suhartini *et al*., 2011)
	1.8%	(Kheang *et al*., 2013)
	7.92%	(Yuan *et al*., 2020)
	1.94%	(Moshi, 2017)
SiO_2	37.45%	(Mana *et al*., 2011)
	56.9%	(Kheang *et al*., 2013)
	70.87%	(Yuan *et al*., 2020)
	60.50%	(Moshi, 2017)
Al_2O_3	8.01%	(Mana *et al*., 2011)
	9.24%	(Kheang *et al*., 2013)
	11.83%	(Yuan *et al*., 2020)
	9.80%	(Moshi, 2017)
Carbon	17.4%	(Loh *et al*., 2015)
	26.99%	(Mana *et al*., 2011)
	15.5%	(Yuan *et al*., 2020)
	28.52%	(Moshi, 2017)
Nitrogen	0.06%	(Loh *et al*., 2015)
	0.06-0.71%	(Kheang *et al*., 2013)
	0.48%	(Yuan *et al*., 2020)
	0.08%	(Moshi, 2017)
C:N	293:1	(Loh *et al*., 2015)
	290:1	(Kheang *et al*., 2013)
	256.5	(Moshi, 2017)
pH	5.33	(Loh *et al*., 2015)
	4.5-5.3	(Kheang *et al*., 2013)
K_2O	0.27 ± 0.02%	(Loh *et al*., 2015)
CaO	3.58 ± 0.36%	(Loh *et al*., 2015)
MgO	1.55 ± 0.06%	(Loh *et al*., 2015)
Cu	41.4 ± 0.6%	(Loh *et al*., 2015)
Zn	30.1 ± 1.7 ppm	(Loh *et al*., 2015)
Mn	359 ± 4 ppm	(Loh *et al*., 2015)
Fe	10026 ± 663 ppm	(Loh *et al*., 2015)

SBE is rich in lipids attainable from the bleaching process and volatile solids (from adsorbed oil organic compounds) which is attributed to degradable organic matter for biogas production (Moshi, 2017). High ash content in SBE stresses mixing and pumping equipment during biodigestion.

Residual oil in SBE is a major advantage of this waste as a substrate in anaerobic digestion. A high C:N ratio indicates a lack of nitrogen in SBE, as shown in Table 3. MgO and CaO in SBE are due to ionic forms of Mg and Ca saturated in the structural layer of SBE. Phosphorus content (Table 4) in SBE is because of the bleaching process of oil in the form of inorganic phosphate ($H_2PO_4^-$ or HPO_4^{2-}). The essential minerals (Mn, Fe, Ca, Mg, and Ti) and beneficial elements (Si and Na) play an important role as soil supplements for good plant growth.

Hydrolysis of lipids will lead to the formation of long-chain fatty acids and glycerol which will be converted to hydrogen and acetate and finally to methane gas by acidogenic, acetogenic, and methanogen bacteria. The isomorphous nature of SBE reduces the inhibition effect caused by long-chain fatty acids adsorption onto the microbial surface which affects nutrient transportation into a cell (Pereira *et al*., 2005). Phosphorus in residual oil in the SBE accelerates gas production in anaerobic digestion by activating many microorganisms in biological processes (Lei *et al*., 2010; Moshi, 2017). Trace elements in SBE, as well as minerals as part of clay material, are important for anaerobic digestion and iron present in SBE is an essential enzyme co-factor involved in the biochemical route of anaerobic digestion and is also considered to be among the trace elements that help stabilise the anaerobic digestion process and improve the growth of methanogens (Radhakrishnan *et al*., 2011; Mussoline, 2014).

SBE is acidic (Table 3), hence it can be added to alkaline soils to balance the pH. Cations present in SBE based in the structural layer are

Table 4: Characterisation of residual oil in SBE

Characterisation	Results	References
Free fatty acids, FFA (%)	12.6	(Kheang *et al*., 2013)
	13.01	(Moshi, 2017)
	11.5	(Kheang *et al*., 2006)
	24.1	(Huang & Chang, 2010)
Peroxide value, PV (meq/kg)	3.4	(Kheang *et al*., 2013)
	2.98	(Moshi, 2017)
	3.1	(Kheang *et al*., 2006)
Phosphorus, P (mg/kg)	18.7	(Kheang *et al*., 2013)
	19.3	(Kheang *et al*., 2006)
Iron, Fe (mg/kg)	1.24	(Kheang *et al*., 2013)
	0.22	(Kheang *et al*., 2006)
Copper, Cu (mg/kg)	0.38	(Kheang *et al*., 2013)
	0.32	(Kheang *et al*., 2006)
β-carotene (mg/kg)	6	(Kheang *et al*., 2013)
	0.401	(Moshi, 2017)
	3	(Kheang *et al*., 2006)
Total vitamin E (mg/kg)	38.8	(Kheang *et al*., 2013)
	39.03	(Moshi, 2017)
	0	(Kheang *et al*., 2006)

necessary for plant growth. It has a high cation exchange capacity (Loh *et al*., 2015) due to its substitutions of Si^{4+} and Al^{3+} with lower charge cations, for example, Fe^{2+} or Mg^{2+} which can hold and release NH_4^+ and reduce leaching of N nutrient (Cheong *et al*., 2013). High P content is attainable from the crude oil bleaching process and will be inorganic phosphate HPO_4^{2-} or $H_2PO_4^2$. Blending SBE with other fertilisers enables the exchange of micronutrients in the soil due to metal adsorption and desorption by silanol and aluminol groups in the clay material. SBE has a high C:N ratio; hence blending it with N-rich organic material improves nutritional balance (Loh *et al*., 2015).

The high cation exchange (36.02 ± 0.15 cmol kg^{-1}) exhibited by SBE improves the degraded charge properties of soils.

Deoiled SBE can be reactivated with an acid to enlarge the surface area for adsorption of impurities in biodiesel production (Fahmil *et al*., 2014), used as animal feed by mixing SBE with soya meal (Huang & Chang, 2010) or it can be a raw material for the bleaching process. For animal feed, 3% (Tippkötter *et al*., 2014) to 10% (Prokopov & Mechenov, 2013) of SBE can be added to animal feed for enrichment. Table 3 and Table 4 summarise the chemical composition of SBE analysed by different authors and the results of the composition of SBE residual oil, respectively.

Application of Spent Bleaching Earth

The presence of residual oil and free cations in SBE generates different applications, which preserve the environment, minimise waste disposal, reduce environmental pollution, lower production costs, recycle, and maintain the supply chain as explained in Table 5. It was found that all applications are suitable and effective for treating spent bleaching earth, however, each approach has different advantages and disadvantages. It is therefore advisable to select an appropriate approach based on the equipment and production of desired products. Many aspects in the given literature are untested yet, such as application effects to the real environment and parameter optimisation. Spent bleaching earth can make good, biodegradable lubricating grease and less toxic. Studies have proved that the incorporation of SBE in making bricks results in a decrease in bulk density of 1,341 kg/cm^3, lowering thermal conductivity (Sutcu *et al*., 2014). Additionally, the organic matter in SBE increases interconnected surface porosity, water adsorption and water suction. Higher water absorption values, lower bulk density and high content of amorphous phase add up to lower thermal conductivity, which acts as an insulator.

Residual oil contained in SBE can be used to develop biodiesel by in situ trans-esterification process. In this process, alkaline catalysts and methanol are used as the reactants for biodiesel and concurrently as the extraction solvent, reducing process steps and shortening the reaction time (Tuntiwiwattanapun *et al*., 2017). Biodiesel is also produced from residual oil in SBE through two-step esterification with the biodiesel product having a lower iodine number and higher cetane number compared to biodiesel from refined vegetable oils because of saturated fatty acids like palmitic acid in residual oil (Huang & Chang, 2010). Deoiled SBE can be reactivated with an acid to enlarge the surface area for adsorption of impurities in biodiesel production (Fahmil *et al*., 2014), used as animal feed by mixing SBE with soya meal (Huang & Chang, 2010) or can be a raw material for the bleaching process.

Long-chain fatty acids in residual oil are degraded anaerobically to H_2 and acetate which are then modified to methane. Anaerobic digestion encompasses metabolic reactivity chains such as hydrolysis Eq. (5), acidogenesis Eq. (6, 7, and 8), acetogenesis Eq. (9, 10, and 11) and methanogenesis Eq. (12, 13, and 14).

Trace elements in SBE improve performance with a faster substrate turnover and overall degradation process and prevent inhibition. Production of biogas through co-digestion of SBE with any other substrate contributes to utilising pollutants to be dumped

$$(C_6H_{10}O_5)n + nH_2O \rightarrow C_6H_{12}O_6 + nH_2 \quad (5)$$

$$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2 \quad (6)$$

$$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O \quad (7)$$

$$C_6H_{12}O_6 \rightarrow 3CH_2COOH \quad (8)$$

$$CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^+HCO_3^- + 3H_2 \quad (9)$$

$$C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (10)$$

$$CH_3CH_2OH + 2H_2O \leftrightarrow CH_3COO^- + 3H_2 + H^+ \quad (11)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (12)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (13)$$

$$2CH_3CH_2OH + CO_2 \rightarrow CH_4 + 2CH_3COOH \quad (14)$$

into the environment, save costs which results in improved industrial profitability since SBE was to be transported to landfill sites from the production plant and energy requirements are reduced because of biogas production. The oil in SBE is not extracted and is transformed for anaerobic digestion, producing biogas. A significant amount of biogas is economically produced from SBE (Moshi, 2017). Furthermore, SBE can be co-digested with manure, energy crops, industrial and municipal waste for biogas production and satisfactory levels of potassium and phosphorus are expected to improve the final bio-slurry after anaerobic digestion for fertiliser application. Briquettes are compressed blocks used as fuel. Compression allows the biomass to burn longer than if it were left loose. The high calorific values exhibited in SBE briquettes are due to residual oil in the waste. SBE can be blended with other fertilisers which enhances the exchange of micronutrients in the soil due to the presence of aluminol and silanol groups. Pyrolysis of SBE results in bio-oil or pyrolytic oil production, which is an alternative to fuels in industry.

Gap of Knowledge

Utilisation and recycling of SBE has been reviewed and discussed (Abdelbasir *et al*., 2023). Whereas different authors comprehensively cover several investigations on the application of SBE, other types of research questions have not been addressed adequately yet in the domain of pyrolysis of SBE. It is noted that literature highlighted pyrolysis of SBE to yield bio-oil with good similarity to petroleum-based fuels (Boey *et al*., 2011), the surface area of resulting solids after pyrolysis of over 100 m^2g^{-1} (Tsai *et al*., 2002), solids after pyrolysis of SBE having the capacity to adsorb tetracycline hydrochloride from aqueous solution (D. Wan *et al*., 2019) and high-quality bio-oil produced by catalytic pyrolysis of SBE (Xu *et al*., 2020).

Co-pyrolysis involves different materials as feedstock (Abnisa & Wan Daud, 2014; Situmorang *et al*., 2021) under the same operating conditions (Ahmed & Hameed, 2020), thus combining favourable feedstock properties. With a few exceptions, co-pyrolysis studies of SBE with biomass wastes are deficient in the literature. Co-pyrolysis of SBE and polymeric waste (Abbas-abadi *et al*., 2020), SBE and corncob lignin (Wan *et al*., 2022) and SBE with low-density polyethylene (Zhang *et al*., 2022) were studied and recorded. As a result, an important gap that future researchers should fill is considering co-pyrolysis of SBE with biomass wastes to help reduce solid waste disposal challenges in the edible oil production industry (Adeboye *et al*., 2021). More rigorous research is required in this area of study, which will greatly impact improvement in terms of quantity and quality of bio-oil yield as well as make it more cost effective. Many studies have shown that the co-pyrolysis of biomass has successfully improved the oil quantity and quality without any

Table 5: Application of spent bleaching earth

Application	Synthesis Conditions	Significant Findings	Advantages	Disadvantages	References
Lubricating grease	A mixture of SBE with waste cooking oil was formed at room temperature (21ºC) to create a homogenised structure.	Very fine particles of SBE release and hold oil, hence, a special property for a thickener.	1. Lubricating grease from SBE requires less energy to manufacture and is easy to produce compared to lubricating grease manufactured from soap. 2. Lubricating grease can be produced from SBE without any additives.	1. There can be structure modification since waste cooking oil is prone to oxidation.	(Abdulbari *et al*., 2011)
Clay/vegetable oil polymer bricks	Compaction of SBE samples using 1 and 5 MPa uniaxial pressing pressures. Heat treatment at 60°C and 150°C for times between 0.5 and 48 h, then sample storage in a desiccator before testing and weighing.	Low-energy novel clay/ vegetable oil polymer blocks from SBE have the potential to be used in construction.	1. Formation of monolithic blocks with compressive strength (Beshara & Cheeseman, 2014a). 2. It can be used to produce clay/vegetable oil polymer blocks utilising less energy (Beshara & Cheeseman, 2014b). 3. 100% waste product recovered. 4. Reduction of landfilling by recycling SBE	1. A significant amount of residual oil is not recovered. 2. Some gases are formed during the incineration in brickmaking which can be dangerous.	(Beshara & Cheeseman, 2014a)

Application	Synthesis Conditions	Significant Findings	Advantages	Disadvantages	References
Biodiesel production	100 g of SBE reacted with 600 mL methanol and 1.5% (v/w) of H_2SO_4 catalyst for 3 h in a three-necked stirrer, a heater and a condenser with a stirring speed of 625 rpm at 65ºC.	Optimum conditions based on the response surface method to produce biodiesel were a concentration of 1.8% and a reaction time of 104.73 min. Hexane can be used as an additional solvent in biodiesel production resulting in increase in yield.	1. Deoiled SBE left can be used as an adsorbent during the purification of biodiesel (Fahmil *et al*., 2014). 2. Preliminary cost of production is lower than the biodiesel or diesel, which is produced from waste cooking oils or refined oil. 3. Deoiled SBE can be a raw material for the bleaching process directly or after activation with acids to be reused in bleaching (Fahmil *et al*., 2014). 4. It helps to minimise environmental pollution 5. Industry profits will increase since SBE removal costs are reduced.	1. Variations in the quality of biodiesel since oil processed vary in quality. 2. Production cost and return on investment are affected by expensive chemicals used and crude oil price (Huang & Chang, 2010).	(Fahmil *et al*., 2014)
Biogas production	Anaerobic digestion experiments carried out with a working volume of 300 mL in 500 mL glass bioreactors. A substrate to inoculum ratio was at 2:1 (in terms of VS). Stirrers operated at 46 rpm, 120 s off and 30 s on during the whole experiment.	Methane yield increased linearly with an increase in SBE (%) in the bioreactors. SBE can be co-digested with energy crops, manure, industrial, municipal wastes for biogas production.	1. Energy provision through biogas production. 2. No need for extraction of the oil when applying anaerobic digestion. 3. Improved bio-slurry after anaerobic digestion to boost vegetable production (Moshi, 2017).	1. High dry matter in SBE results in difficulties in pumping and mixing. 2. Sedimentation challenges and abrasive damage (Ward, 2012).	(Moshi, 2017)

Application	Synthesis Conditions	Significant Findings	Advantages	Disadvantages	References
Biomass briquettes	Diluted maltodextrin, 1:10 (w/v) was evaporated to a temperature of 70ºC; SBE was mixed with the maltodextrin liquid then stirred and fed into a mould, followed by pressurisation into an SBE briquette. SBE briquette was then dried in the oven at a temperature of 60ºC for 24 h.	Calorific value of SBE briquette (10.96 $MJ \times kg^{-1}$); SBE waste (7.28 $MJ \times kg^{-1}$) with the addition of 10% maltodextrin at a pressure of 100 $kg \times cm^{-2}$ having the highest calorific value.	1. High calorific value (Suhartini *et al*., 2011). 2. Process of densification requires more energy which SBE supplies. 3. Easy to store, handle and transport. 4. It replaces the usage of the conventional type of fuels.	1. Briquettes tend to loosen when exposed to water and high-humidity weather (S. A. Ahmed *et al*., 2014).	(Suhartini *et al*., 2011)
Bio organic fertiliser	Mixture of SBE with oil palm fronds, oil palm trunk and empty fruit bunches was homogenised using an automated continuous-mode stainless steel grinder then optimised blend was fortified with commercial mineral fertilisers.	Total nitrogen, potassium and phosphorus in the blend increased. The c:N ratio was reduced from 293 (raw SBE) to 36 (bioorganic fertiliser).	1. Enables low chemical fertiliser application. 2. It is a total solution to the treatment of SBE since it uses all the waste. 3. Preserves the environment and contributes to sustainable agriculture (Loh *et al*., 2015).	1. Extra costs are incurred if you want to produce a fertiliser blend; to achieve the targeted NPK of 2:2:2 mineral fertiliser is added (Loh *et al*., 2015).	(Loh *et al*., 2015)
Bio-oil	5 g of SBE was heated inside tubular coupled with furnace under N_2 atmosphere at a heating rate of 10°C/min with a flow rate of 375 mL/min until it reached 500°C.	Clay acts as a catalyst resulting in low pyrolysis temperatures. Compounds present; carboxylic acids were the major group of compounds present followed by alkenes and alkanes. Aldehydes and nitrogenated compounds were absent in this bio-oil.	1. Bio-oil can be used as chemical feedstock.	1. Polycyclic Aromatic Hydrocarbons (PAHs) present in biofuel are carcinogenic and/or mutagenic.	(Sapawe & Hanafi, 2018)

Application	Synthesis Conditions	Significant Findings	Advantages	Disadvantages	References
Non-fired wall tiles	SBE, laterite Soil and Fluvial Sand was dried for 2 h at 150ºC and sieved. All raw materials were mixed with 10% water by total materials weight. Total mixture pressed at 100 bar by uniaxial pressing, then water sprayed on the specimens and curing for seven days.	Bending strength is affected due to the replacement of SBE waste into main raw materials.	1. Cheap 0,00276 USD/100g	1. The composition of raw materials needs to be adjusted since the quality of SBE produced from plants is different due to the bleaching parameters used.	(Wangrakdiskul *et al.*, 2015)
Foamed concrete incorporating Processed Spent Bleaching Earth	Cement paste was prepared by dry mixing processed spent bleaching earth, cement, sand, and silica, then, water was added and mixed homogeneously. The foam was added and combined well. Slurry was used to cast cube specimen size and cylinder size. The specimens were cured using water immersion, natural curing, air curing, and water immersion for seven days, then, natural weather curing and water immersion for seven days, followed by air curing.	Incorporating processed foamed concrete as concrete replacement enhances chloride permeability, compressive strength, and porosity due to processed spent bleaching earth's pozzolanic reactions.	1. High silica and alumina content in processed spent bleaching earth generates calcium silica hydrate. 2. Improves internal structure of processed foamed concrete. It contains fewer voids, which results in a denser structure. 3. More resistance to chloride ion penetration.	1. Mixing process is difficult when not supported by proper equipment since it is a mixture of different materials.	(Othman, *et al.*, 2022)

Application	Synthesis Conditions	Significant Findings	Advantages	Disadvantages	References
Foamed concrete containing processed spent bleaching earth (sulphate resistance)	Foamed concrete with processed spent bleaching earth was added to the cement paste and mixed continuously until the slurry was homogeneously mixed. Fresh mix was filled into cube specimens. After 24 h, the specimens were removed from the mould.	Foamed concrete containing processed spent bleaching earth exhibited less deterioration after 52 weeks immersed in sulphate attack. There was less mass change, lower value of expansion of the bar.	1. Better durability towards sulphate attack. 2. Surface deterioration is minor. 3. Can be used in construction applications.	1. High mixing time.	(Othman, *et al*., 2022)
Mortar Containing Processed Spent Bleaching Earth	Processed spent bleaching earth, water and sand were measured and placed in a bucket, and water was added at ambient temperature. Mixing was conducted using a heavy-duty mud mixer. Moulds were filled in three layers uniformly and after 24 h, demoulding was conducted, followed by water curing for up to 28 days. Image analysis using Trainable Wega Segmentation and Fiji Particle was used to obtain the surface porosity of mortar specimens.	Partial replacement of cement with processed spent bleaching earth had high compressive strength but decreased mortar consistency. Pozzolanic reaction improves strength index and reduces water absorption rate.	1. Analysis method used only requires a digital camera. 2. Shooting distance does not have strict limitations. 3. Processing and analysis of images is easy to carry out. 4. The image processing method allows quantification of surface porosity.	1. Applicable for macro analysis of concrete. 3. Cement replacement using pozzolanic materials decreases the workability of cementitious products. 4. Pozzolanic reaction is a long-term process.	(Wei Chong *et al*., 2021)

improvement in the system process. Co-pyrolysis has attractive performance/cost ratios (Abnisa & Wan Daud, 2014) due to synergistic effects from the reaction of different feedstock during the process. A specific suggestion is to optimise and model co-pyrolysis parameters: reaction time, reaction temperature and feedstock ratio on the pyrolysis yield using a central composite experimental design (Adeboye *et al*., 2021). Developed models would then be evaluated using statistical parameters and response surface curves. More suitable models can be developed by studying these aspects to yield improved co-pyrolysis products (Uzoejinwa *et al*., 2019).

Conclusions

This review summarised the synthesis, properties, characterisation and application of SBE. SBE is an acidic alumino-silicate mineral generated in an oil refinery after a bleaching process containing 20-40% residual oil with high cation exchange capacity. Properties exhibited by SBE include high heating value, lower bulk density and high content of amorphous phase. Its generation is directly connected to environmental, economic and social activity and therefore it is pertinent to reduce its disposal and generate high-quality waste streams for reuse and recovery, which maximises both the value and the volume of resources within economies. Its treatment promotes edible oil production and other stakeholders who feed into the system to provide raw materials for oil production. Treatment of SBE supports efficient use of natural resources, thus securing animal feed, availability of food, renewable raw materials, soil fertility, and energy provision.

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Conflict of Interest Statement

The authors declare that they have no conflict of interest.

References

Abbas-abadi, M. S., Jalali, A., Rostami, M. R., Haghighi, M. N., & Farhadi, A. (2020). The atmospheric, vacuum and pressurized pyrolysis of used bleaching soils along with polymeric wastes to reach the valuable and economical fuels. *Journal of Cleaner Production*, *255*, 120328.

Abdelbasir, S. M., Shehab, A. I., & Khalek, M. A. A. (2023). Resources, conservation & recycling advances spent bleaching earth; recycling and utilization techniques: A review. *Resources, Conservation & Recycling Advances*, *17*, 200124.

Abdulbari, H. A., Rosli, M. Y., Abdurrahman, H. N., & Nizam, M. K. (2011). *Lubricating grease from spent bleaching earth and waste cooking oil: Tribology properties*, *6*(20), 4695-4699.

Abnisa, F., & Wan Daud, W. M. A. (2014). A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil. *Energy Conversion and Management*, *87*, 71-85.

Adeboye, B. S., Adewole, B. Z., Adedoja, A. M., Obayopo, S. O., Asere, A. A., Kayode, O., Idris, M. O., & Okediran, I. K. (2021). Optimization and modeling of process parameters on the yield of enhanced pyrolysis oil during co-pyrolysis of cassava peel with polystyrene. *Environmental Challenges*, *5*, 100347.

Ahmed, M. J., & Hameed, B. H. (2020). Insight into the co-pyrolysis of different blended feedstocks to biochar for the adsorption of organic and inorganic pollutants: A review. *Journal of Cleaner Production*, *265*, 121762.

Ahmed, S. A., Kumari, A., & Mandavgane, K. (2014). A review on briquettes as an alternative fuel. *International Journal of Innovations in Engineering and Technology (IJIET)*, *3*(4), 139-144.

Alamery, H. R. D., & Ahmed, S. A. (2021). Purification and activation of the Iraqi bentonite for edible oil Production. *IOP Conference Series: Materials Science and Engineering*, *1090*(1), 012039.

Anyikwa, S. O., Nwakaudu, M. S., Nzeoma, C., & Yakubu, E. (2022). Kinetics and equilibrium studies of colour pigments removal from crude palm oil using acid activated Kaolin Clay and mathematical method. *International Journal of Science and Engineering Investigations, 16*(110).

Bachmann, S. A. L., Valle, R. D. C. S. C., Vegini, A. A., & Tavares, L. B. B. (2020). Determination of optimum conditions for thermal regeneration and characterization of a spent bleaching earth. *Journal of Environmental Chemical Engineering*, *8*(2), 103503.

Bayram, H., Ustunisik, G., Önal, M., & Sarıkaya, Y. (2021). Optimization of bleaching power by sulfuric acid activation of bentonite. *Clay Minerals*, *56*(2), 148-155.

Beshara, A., & Cheeseman, C. R. (2014a). Reuse of spent bleaching earth by polymerisation of residual organics. *Waste Management*, *34*(10), 1770-1774.

Beshara, A., & Cheeseman, C. R. (2014b). Reuse of spent bleaching earth by polymerisation of residual organics. *Waste Management*, 1-5.

Boey, P. L., Saleh, M. I., Sapawe, N., Ganesan, S., Maniam, G. P., & Ali, D. M. H. (2011). Pyrolysis of residual palm oil in spent bleaching clay by modified tubular furnace and analysis of the products by GC-MS. *Journal of Analytical and Applied Pyrolysis*, *91*(1), 199-204.

Chakawa, D. P., Nkala, M., Hlabangana, N., & Muzenda, E. (2019). The use of calcium sulphate dihydrate (CaSO4.2H2O) as a bleaching agent for crude soya bean vegetable oil. *Procedia Manufacturing*, *35*, 802-807.

Cheong, K. Y., Loh, S. K., & Salimon, J. (2013). Effect of spent bleaching earth based bio organic fertilizer on growth, yield and quality of eggplants under field condition. *AIP Conference Proceedings*, *1571*, 744-748.

Darmawan, M. A., Muhammad, B. Z., Harahap, A. F. P., Ramadhan, M. Y. A., Sahlan, M., Haryuni, Supriyadi, T., Abd-Aziz, S., & Gozan, M. (2020). Reduction of the acidity and peroxide numbers of tengkawang butter (Shorea stenoptera) using thermal and acid activated bentonites. *Heliyon*, *6*(12), e05742.

Días, F. R. V., & Santos, S. P. (2001). Studies on the acid activation of brazilian smectitic clays. *Quimica Nova*, *24*(3), 345-353.

Didi, M. A., Makhoukhi, B., Azzouz, A., & Villemin, D. (2009). Colza oil bleaching through optimized acid activation of bentonite. A comparative study. *Applied Clay Science*, *42*(3-4), 336-344.

Dijkstra, A. J. (2020). What to do with spent bleaching earth ? A review. *Journal of the American Oil Chemists' Society*, *97*, 565-575.

Eliche-quesada, D., & Corpas-iglesias, F. A. (2014). Utilisation of spent filtration earth or spent bleaching earth from the oil refinery industry in clay products. *Ceramics International*, *40*(10), 16677-16687.

Eren, E., Afsin, B., & Onal, Y. (2009). Removal of lead ions by acid activated and manganese oxide-coated bentonite. *Journal of Hazardous Materials*, *161*(2-3), 677-685.

Fahmil, A. S. Q. R. M., Gumbira-Sa'id, E., & Suryani, A. (2014). Biodiesel production from residual palm oil contained in spent bleaching earth by In situ trans-esterification. *EnvironmentAsia*, *7*(2), 30-35.

Foletto, E. L., Colazzo, G. C., Volzone, C., & Porto, L. M. (2011). Sunflower oil bleaching by adsorption onto acid-activated bentonite. *Brazilian Journal of Chemical Engineering*, *28*(1), 169-174.

Gharby, S. (2022). Refining vegetable oils: Chemical and physical refining. *Scientific World Journal*, *2022*(Table 1).

Huang, Y., & Chang, J. I. (2010). Biodiesel production from residual oils recovered from spent bleaching earth. *Renewable Energy*, *35*(1), 269-274.

Kheang, L. S., Foon, C. S., May, C. Y., & Ngan, M. A. (2006). A study of residual oils recovered from spent bleaching earth: Their characteristics and applications. *American Journal of Applied Sciences*, *3*(10), 2063-2067.

Kheang, S., James, S., Ngatiman, M., Yein, K., May, Y., & Soon, W. (2013). Enhancement of palm oil refinery waste – Spent bleaching earth (SBE) into bio organic fertilizer and their effects on crop biomass growth. *Industrial Crops & Products*, *49*, 775-781.

Kirali, E. G., & Laçin, O. (2006). Statistical modelling of acid activation on cotton oil bleaching by Turkish bentonite. *Journal of Food Engineering*, *75*(1), 137-141.

Krzyśko-Łupicka, T., Cybulska, K., Wieczorek, A., Możdżer, E., & Nowak, M. J. (2014). The effect of spent bleaching earth ageing process on its physicochemical and microbial composition and its potential use as a source of fatty acids and triterpenes. *Environmental Science and Pollution Research*, *21*(18), 10765-10774.

Lee, C. G., Seng, C. E., & Liew, K. Y. (2000). Solvent efficiency for oil extraction from spent bleaching clay. *Journal of the American Oil Chemists' Society, 77*(11),1219-1223.

Lei, Z., Chen, J., Zhang, Z., & Sugiura, N. (2010). Methane production from rice straw with acclimated anaerobic sludge: Effect of phosphate supplementation. *Bioresource Technology*, *101*(12), 4343-4348.

Liu, Y., Li, J., Wu, L., Shi, Y., He, Q., Chen, J., & Wan, D. (2020). Magnetic spent bleaching earth carbon (Mag-SBE@C) for efficient adsorption of tetracycline hydrochloride: Response surface methodology for optimization and mechanism of action. *Science of the Total Environment*, *722*, 137817.

Loh, S. K., Cheong, K. Y., Choo, Y. M., & Salimon, J. (2015). Formulation and optimisation of spent bleaching earth-based bio organic fertiliser. *Journal of Oil Palm Research*, *27*(1), 57-66.

Loh, S. K., Cheong, K. Y., & Salimon, J. (2017). Surface-active physicochemical characteristics of spent bleaching earth on soil-plant interaction and water-nutrient uptake: A review. *Applied Clay Science*, *140*, 59-65.

Maged, A., Kharbish, S., Ismael, I. S., & Bhatnagar, A. (2020). Characterization of activated bentonite clay mineral and the mechanisms underlying its sorption for ciprofloxacin from aqueous solution. *Environmental Science and Pollution Research*, *27*(26), 32980-32997.

Malakootian, M., Fatehizadeh, A., Youse, N., Ahmadian, M., & Moosazadeh, M. (2011). Fluoride removal using Regenerated Spent Bleaching Earth (RSBE) from groundwater: Case study on Kuhbonan water. *Desalination, 277*, 244-249.

Mana, M., Ouali, M. S., Menorval, L. C., Zajac, J. J., & Charnay, C. (2011). Regeneration of spent bleaching earth by treatment with cethyltrimethylammonium bromide for application in elimination of acid dye. *Chemical Engineering Journal*, *174*(1), 275-280.

Moosavi, M. (2017). Bentonite clay as a natural remedy: A brief review. *Iranian Journal of Public Health*, *46*(9), 1176-1183.

Moshi, A. (2017). Characterization of spent bleaching earth and its utilization for improving manure-based biogas production. *Biotechnology Journal International*, *17*(4), 1-13.

Motlagh, K., Youzbashi, A. A., & Rigi, Z. A. (2011). Effect of acid activation on structural and bleaching properties of a bentonite. *Iranian Journal of Materials Science and Engineering*, *8*(4), 50-56.

Mussoline, W. (2014). Enhancing the methane production from untreated rice straw using an anaerobic co-digestion approach with piggery wastewater and pulp and paper mill sludge to optimize energy conversion in farm-scale biogas plants.145.

Noyan, H., Önal, M., & Sarikaya, Y. (2007). The effect of sulphuric acid activation on the crystallinity, surface area, porosity, surface acidity, and bleaching power of a bentonite. *Food Chemistry*, *105*(1), 156-163.

Nursulihatimarsyila, A. W., Cheah, K. Y., Chuah, T. G., Siew, W. L., & Choong, T. S. Y. (2010). Deoiling and regeneration efficiencies of spent bleaching clay. *American Journal of Applied Sciences*, *7*(3), 434-437.

Oladosu, W. A., Manan, Z. A., & Alwi, S. R. W. (2017). Recovery of vegetable oil from spent bleaching earth: Stateof-The-Art and prospect for process intensification. *Chemical Engineering Transactions*, *56*, 133-138.

Önal, M., & Sarikaya, Y. (2007). Preparation and characterization of acid-activated bentonite powders. *Powder Technology*, *172*(1), 14-18.

Othman, R., Muthusamy, K., Duraisamy, Y., Sulaiman, M. A., Putra Jaya, R., Ahmad Abdul Ghani, N. A., & Mangi, S. A. (2022). Evaluation of the sulphate resistance of foamed concrete containing processed spent bleaching earth. *European Journal of Environmental and Civil Engineering*, *26*(8), 3632-3647.

Othman, R., Muthusamy, K., Sulaiman, M. A., Duraisamy, Y., Jaya, R. P., Wei, C. B., Al Bakri Abdullah, M. M., Mangi, S. A., Nabiałek, M., & Sliwa, A. (2022). Compressive strength and durability of foamed concrete incorporating processed spent bleaching earth. *Archives of Civil Engineering*, *68*(2), 627-643.

Pereira, M. A., Pires, O. C., Mota, M., & Alves, M. M. (2005). Anaerobic biodegradation of oleic and palmitic acids: Evidence of mass transfer limitations caused by long chain fatty acid accumulation onto the anaerobic sludge. *Biotechnology and Bioengineering*, *92*(1), 15-23.

Plata, V., Rojas, Ó., & Gauthier-Maradei, P. (2020). Improvement of palm oil biodiesel filterability by treatment with reactivated spent bleaching earths. *Fuel*, *260*, 116198.

Pollard, S. J. T., Sollars, C. J., & Perry, R. (1991). A lowcost adsorbent from spent bleaching earth. The selection of an activation procedure. *Journal of Chemical Technology and Biotechnology*, 277-292.

Prokopov, T., & Mechenov, G. (2013). Utilization of spent bleaching earth from vegetable oil processing. *Ukrainian Food Journal*, *2*(4), 489-498.

Radhakrishnan, K. (2011). *Impacts of the use of Magnesia versus Iron on Mesophilic Anaerobic digestion and odors in wastewater* (Masters Thesis). *V*irginia Polytechnic Institute and State University, 1-88.

Saleh Alhamed, Y. A., & Al-Zahrani, A. A. (1999). Techno-economical evaluation of oil recovery and regeneration of spent bleaching clay. *Journal of King Abdulaziz University: Engineering Sciences*, *11*(2), 115-126.

Sapawe, N., & Hanafi, M. F. (2018). ScienceDirect Analysis of the pyrolysis products from spent bleaching clay. *Materials Today: Proceedings*, *5*(10), 21940-21947.

Shattar, S. F. A., Zakaria, N. A., & Foo, K. Y. (2020). One step acid activation of bentonite derived adsorbent for the effective remediation of the new generation of industrial pesticides. *Scientific Reports*, *10*(1), 1-13.

Situmorang, Y. A., Zhao, Z., Chaihad, N., Wang, C., Anniwaer, A., Kasai, Y., Abudula, A., & Guan, G. (2021). Steam gasification of co-pyrolysis chars from various types of biomass. *International Journal of Hydrogen Energy*, *46*(5), 3640-3650.

Soetaredjo, F. E., Laysandra, L., Putro, J. N., Santoso, S. P., Angkawijaya, A. E., Yuliana, M., Ju, Y. H., Zhou, C. H., & Ismadji, S. (2021). Ecological-safe and low-cost activated-bleaching earth: Preparation, characteristics, bleaching performance, and scale-up production. *Journal of Cleaner Production*, *279*, 123793.

Steudel, A., Batenburg, L. F., Fischer, H. R., Weidler, P. G., & Emmerich, K. (2009). Alteration of swelling clay minerals by acid activation. *Applied Clay Science*, *44*(1-2), 105-115.

Suhartini, S., Hidayat, N., & Wijaya, S. (2011). Physical properties characterization of fuel briquette made from spent bleaching earth. *Biomass and Bioenergy*, *35*(10), 4209-4214.

Sutcu, M., Del Coz Díaz, J. J., Álvarez Rabanal, F. P., Gencel, O., & Akkurt, S. (2014). Thermal performance optimization of hollow clay bricks made up of paper waste. *Energy and Buildings*, *75*, 96-108.

Tang, J., Mu, B., Zheng, M., & Wang, A. (2015). One-step calcination of the spent bleaching earth for the efficient removal of heavy metal ions. *ACS Sustainable Chemistry and Engineering*, *3*(6), 1125-1135.

Tang, J., Mu, B., Zong, L., Zheng, M., & Wang, A. (2017). Facile and green fabrication of magnetically recyclable carboxyl-functionalized attapulgite/carbon nano-composites derived from spent bleaching earth for wastewater treatment. *Chemical Engineering Journal*, *322*, 102-114.

Tippkötter, N., Wollny, S., Suck, K., Sohling, U., Ruf, F., & Ulber, R. (2014). Recycling of spent oil bleaching earth as source of glycerol for the anaerobic production of acetone, butanol, and ethanol with Clostridium diolis and lipolytic Clostridium lundense. *Engineering in Life Sciences, 14*, 425-432.

Tsai, W. T., Chen, H. P., Hsieh, M. F., Sun, H. F., & Chien, S. F. (2002). Regeneration of spent bleaching earth by pyrolysis in a rotary furnace. *Journal of Analytical and Applied Pyrolysis*, *63*(1), 157-170.

Tuntiwiwattanapun, N., Monono, E., Wiesenborn, D., & Tongcumpou, C. (2017). In-situ transesterification process for biodiesel production using spent coffee grounds from the instant coffee industry. *Industrial Crops and Products*, *102*, 23-31.

Usman, M. A., Ekwueme, V. I., Alaje, T. O., & Mohammed, A. O. (2012). Characterization, acid activation, and bleaching performance of Ibeshe Clay, Lagos, Nigeria. *ISRN Ceramics*, *2012*, 1-5.

Uzoejinwa, B. B., He, X., Wang, S., Abomohra, A. E. F., Hu, Y., He, Z., & Wang, Q. (2019). Co-pyrolysis of macroalgae and lignocellulosic biomass: Synergistic effect, optimization studies, modeling, and simulation of effects of co-pyrolysis parameters on yields. *Journal of Thermal Analysis and Calorimetry*, *136*(5), 2001-2016.

Vaisali, C., Charanyaa, S., Belur, P. D., & Regupathi, I. (2015). Refining of edible oils: A critical appraisal of current and potential technologies. *International Journal of Food Science and Technology*, *50*(1), 13-23.

Wan, D., Wu, L., Liu, Y., Chen, J., Zhao, H., & Xiao, S. (2019). Enhanced adsorption of Aqueous Tetracycline Hydrochloride on renewable Porous Clay-Carbon adsorbent derived from spent bleaching earth via pyrolysis. *Langmuir*, *35*, 3925-3936.

Wan, Z., Wang, S., Li, Z., Yi, W., Zhang, A., Li, Y., & Zhang, P. (2022). Co-pyrolysis of lignin and spent bleaching clay: Insight into the catalytic characteristic and hydrogen supply of spent bleaching clay. *Journal of Analytical and Applied Pyrolysis*, *163*, 105491.

Wangrakdiskul, U., Khonkaew, P., & Wongchareonsin, T. (2015). Use of the spent bleaching earth from palm oil industry in non fired wall tiles. *The International Journal of Advanced Culture Technology*, *3*(2), 15-24.

Ward, A. J. (2012). Biogas potential of soapstock and bleaching earth. *Danish Centre for Food and Agriculture, Aarhus University, Report no. 004*.

Wei Chong, B., Othman, R., Jaya, R. P., Shu Ing, D., Li, X., Wan Ibrahim, M. H., Abdullah, M. M. A. B., Sandu, A. V., Płoszaj, B., Szmidla, J., & Stachowiak, T. (2021). Image analysis of surface porosity mortar containing processed spent bleaching earth. *Materials*, *14*(7), 1-16.

Wu, Z., Li, C., Sun, X., Xu, X., Dai, B., Li, J., & Zhao, H. (2006). Characterization, acid activation and bleaching performance of bentonite from Xinjiang. *Chinese Journal of Chemical Engineering*, *14*(2), 253-258.

Xu, L., Chen, S., Song, H., Liu, Y., Shi, C., & Lu, Q. (2020). Comprehensively utilization of spent bleaching clay for producing high quality bio-fuel via fast pyrolysis process. *Energy*, *190*, 116371.

Yuan, Z., Shen, Y., Yuan, H., Sui, A., & Zhu, N. (2020). A collaborative approach to in-situ oxysul fi des and oxynitrides fi xation in fl ue gas and energy recycling: Co-combustion of spent bleaching earth and coal. *Journal of Cleaner Production, 258*(2020), 120622.

Zhang, X., Ke, L., Wu, Q., Zhang, Q., Cui, X., Zou, R., & Tian, X. (2022). Microwave catalytic co-pyrolysis of low-density polyethylene and spent bleaching clay for monocyclic aromatic hydrocarbons. *Journal of Analytical and Applied Pyrolysis*, *168*, 105709.