ASSESSMENT OF SPENT BLEACHING EARTH EMPLOYMENT IN THE IMPROVEMENT OF PALM OIL BIODIESEL FILTERABILITY

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IN THE

SCHOOL OF CHEMICAL ENGINEERING

FACULTY OF PHYSICAL-CHEMISTRY

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DEDICATION

This study is wholeheartedly dedicated to my beloved parents, who have been my source of inspiration and gave me strength when I thought of giving up, who continually provide their moral, spiritual, emotional, and financial support.

To my brother and sisters, who shared their words of advice and encouragement to finish this study.

To my dear friends Cristian Angulo, Dante Bayona, Esteban Luna, Jennifer Nuñez, Angela Ortiz, Lina Ramos, who teach me the real value of a friend and help me through this journey with kind words.

And lastly, I dedicated this book to the Almighty God, thank you for the guidance, strength, power of mind, protection and skills and for giving us a healthy life. All of these, I offer to you

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LIST ABBREVIATION

ASTM: American Society for Testing and Materials.

CBE: Calcinated Bleaching Earth.

CSFT: Cold Soak Filtration Test.

DG: Diglyceride.

EBE: Extracted Bleaching Earth.

EDS: Energy-Dispersive X-ray Spectroscopy.

FSG: Free Steryl-Glycoside.

MG: Monoglyceride.

OIT: Oxidation Induction Time.

PC: Particle Content.

POB: Palm Oil Biodiesel.

RBE: Regenerated Bleaching Earth.

SBE: Spent Bleaching Earth.

SEM: Scanning Electron Microscope.

TG: Triglyceride.

TG-CURVE: Thermogravimetric- Curve.

VBE: Virgin Bleaching Earths.

XRD: X-Ray Diffraction.

RESUMEN

TÍTULO: EVALUACIÓN DEL USO DE LAS TIERRAS DE BLANQUEO USADAS EN EL MEJORAMIENTO DE LA FILTRABILIDAD DEL BIODIESEL DE PALMA AFRICANA [*]

AUTOR: OMAR ADOLFO ROJAS GARCIA [**]

PALABRAS CLAVE: Remoción de Precipitados, Cold Soak Filtration Test, Reciclo de Tierras de Blanqueo, Tratamiento térmico, Tratamiento con ácido.

DESCRIPCIÓN:

El biodiesel ha recibido mucha atención en los últimos años debido a su potencial para reemplazar el combustible Diesel convencional; sin embargo, la formación de precipitados se ha convertido en una preocupación para los productores de biodiesel. Los precipitados presentes en el biodiesel inducen varios inconvenientes, por lo cual se desarrolló una prueba (CSFT) la cual mide la capacidad del biodiesel de obstruir los filtros de combustible. La norma ASTM D6571 establece que el biodiesel debe tener un tiempo de filtrado por debajo de 360 s, el biodiésel de aceite de palma (POB) se caracteriza por una filtrabilidad muy pobre. Después del blanqueamiento de los aceites comestibles, las tierras de blanqueo usadas (SBE) se convierten en contaminantes y se vierten en los rellenos sanitarios sin ningún tratamiento, lo que genera graves problemas ambientales. Por este motivo, la reactivación y la reutilización de SBE en la refinación de aceites comestibles se han propuesto como una forma de reducir la contaminación derivada de la eliminación inadecuada de estos residuos. Ningún estudio ha demostrado el uso de SBE reactivado en la purificación de biodiesel, aunque el tratamiento de biodiesel con tierras de blanqueo vírgenes (VBE) fue propuesto como una manera efectiva de eliminar el precipitado y, en consecuencia, mejorar su filtrabilidad. Por lo tanto, el objetivo primario de este estudio fue evaluar el uso de SBE reactivado para mejorar la filtrabilidad POB. SBE se reactivó mediante (1) lavado con hexano, (2) calentamiento a 500 ° C durante 1 h, y (3) tratamiento con solución de HCl 0.1 M. Como resultado, se descubrió que la extracción con disolvente del aceite residual por sí sola no es un método eficaz para la reactivación de SBE; en cambio, el CSFT superior proporcionado por calentamiento o por tratamiento ácido (75 s en promedio) evidenció que un adsorbente capaz de lograr la filtrabilidad necesaria se puede obtener mediante la reactivación de SPB. Esto fue consistente con una reducción en el contenido de precipitados. No hubo diferencias significativas entre CSFT de biodiesel tratado con los adsorbentes reactivados, por lo que el calentamiento debe preferirse al tratamiento con ácido.

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[*] Proyecto de grado

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ABSTRACT

TITLE: ASSESSMENT OF SPENT BLEACHING EARTH EMPLOYMENT IN THE IMPROVEMENT OF PALM OIL BIODIESEL FILTERABILITY [*].

AUTHOR: OMAR ADOLFO ROJAS GARCIA[**]

KEYWORDS: Precipitate removal, cold soak filtration test, bleaching earths recycling, heating treatment, acid treatment.

DESCRIPTIONS:

Biodiesel has received special attention in the last years due to its potential for replacing conventional diesel fuel; however, precipitate formation has become a concern for biodiesel producers. Precipitate induces a number of undesired consequences, so a cold soak filtration test was developed to determine if biodiesel is sufficiently free of precipitate capable of clogging fuel filters. ASTM D6751 standard specification requires that biodiesel have a cold soak filtration time (CSFT) below 360 s; however, palm oil biodiesel (POB) is characterized by a very poor filterability, resulting in failing CSFT. After bleaching of edible oils, the spent bleaching earths (SBE) become a pollutant and are dumped in landfills without any treatment, resulting in severe environmental troubles. Thus, reactivation and reuse of SBE in edible oil refining have been proposed as a way to reduce the pollution arising from inappropriate disposal of this waste. No study has been reported on the use of reactivated SBE in biodiesel purification, even though treatment of biodiesel with virgin bleaching earths (VBE) was proposed as an effective way to remove the precipitate, and consequently, to improve its filterability. Therefore, the primary objective of this study was to evaluate the use of reactivated SBE to improve POB filterability. SBE was reactivated by (1) washing with hexane, (2) heating at 500 °C for 1 h, and (3) treatment with 0.1 M HCl solution. As a result, solvent extraction of residual oil alone was found not to be an effective method for reactivation of SBE; in contrast, the superior CSFT provided by either heating or acid treatment (75 s in average) evidenced that an adsorbent capable of achieving the needed filterability may be obtained by reactivation of SPB. This was consistent with a concomitant reduction in the precipitate content. There was no significant difference between CSFT of biodiesel treated with the reactivated adsorbents, so heating should be preferred over acid treatment.

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INTRODUCTION

Biodiesel has received special attention in the last years due to its potential for replacing conventional diesel fuel. It offers the advantage that it is renewable, biodegradable, and non-toxic. It also improves lubricity and reduces greenhouse gas emissions when blended with diesel (Knothe, 2005). However, the precipitate formation has become a concern for biodiesel producers. The precipitate may affect process equipment upstream of the tank farm in biodiesel facilities and settle at the bottom of tanks where biodiesel is stored. As a consequence, frequent maintenance is necessary for biodiesel facilities (Van Hoed et al., 2008). It may also cause clogging of fuel filters in engine fuel delivery systems and form deposits on vehicle injectors, thereby causing potential customers to view biodiesel unfavorably (Dunn, 2009).

A cold soak filtration test was developed by the American Society for Testing and Materials (ASTM) in an effort to address the fuel filter clogging potential of biodiesel [ASTM D7501]. This test was intended to determine if biodiesel is sufficiently free of precipitate capable of clogging fuel filters. The ASTM D6751 standard specification requires that biodiesel have a cold soak filtration time (CSFT) below 360 s [ASTM D6751]. However, palm oil biodiesel (POB), which is currently produced in Colombia with an annual production of 986,000 tons, is characterized by a very high precipitate content, and consequently, very poor filterability, resulting in failing CSFT (Tang, Salley, & Simon Ng, 2008).

To resolve the high precipitate content of POB, different studies have been performed with two types of approaches; the first focused to decrease the amount of the minor compounds causing of precipitate formation (Plata, Gauthier-Maradei, & Kafarov, 2015) and another one leads to remove the precipitate once that is formed (Plata, Haagenson, Daƚdelen, Wiesenborn, & Kafarov, 2015). The present study can be considered in the last approach and propose the effective use of bleaching earth, commonly used in the refining of vegetable oils, to remove the precipitate on POB.

Refining of edible oils typically involves four steps: degumming, neutralization, bleaching, and deodorization (Mba, Dumont, & Ngadi, 2015). During the bleaching step, pigments[1] and other undesirable substances are removed from the oil by treatment with bleaching earth (Boukerroui, Belhocine, & Ferroudj, 2017)], a type of phyllosilicate with a 2:1 layer structure[2] containing exchangeable cations Na+ and Ca2+ between the layers, and where cations Si4+ are partly substituted with Al3+ in the tetrahedral layer and cations Al3+ are replaced by Mg2+ and Fe3+ in the octahedral layer (Hussin, Aroua, & Daud, 2011a).

After being used, the bleaching earth loses its adsorption properties and becomes a pollutant, which is dumped in landfills without any treatment (Meziti & Boukerroui, 2011). This waste, known as spent bleaching earth (SBE), contains up to 30 mass% of the residual oil that rapidly oxidizes to the point of spontaneous auto-ignition and

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[1] Chlorophyll-α and β-carotene

[2] Two silica tetrahedral sheets bonded to a central alumina octahedral sheet

produces unpleasant odors (Boukerroui & Ouali, 2000a). Heavy metals composing the residual oil may also penetrate into the groundwater and even infiltrate water-bearing horizons, causing severe environmental and public health troubles (Krzyśko-Łupicka, Cybulska, Wieczorek, Możdżer, & Nowak, 2014). Thus, environmental legislation has been imposing increasingly strict regulations on solid waste management on edible oil refineries (Mana, Ouali, Lindheimer, & Menorval, 2008).

Reactivation and reuse of SBE have been proposed as a way to reduce the pollution arising from the inappropriate disposal of this waste. Reactivation may be done by heating or chemical treatment, with or without solvent extraction, or the combination of these methods (Meziti & Boukerroui, 2011). When chemical treatment is employed, strong acids are preferred (Hussin, Aroua, & Daud, 2011b). Some studies may be found regarding reactivation and reuse of SBE in edible oil refining (Boukerroui et al., 2017; Boukerroui & Ouali, 2000a; Foletto, Alves, Sganzerla, & Porto, 2002; Girgis, 2005). In other studies, the possibility of using reactivated SBE as a sorbent for different pollutants has been evaluated (Malakootian, Fatehizadeh, Yousefi, Ahmadian, & Moosazadeh, 2011; Mana et al., 2008; Wambu, Muthakia, wa-Thiong'o, & Shiundu, 2009). However, to the best of our knowledge, no study has been reported on the use of reactivated SBE in biodiesel purification. Recently, treatment of biodiesel with virgin bleaching earth was proposed as an effective way to remove the precipitate, and consequently, to improve its filterability (Plata, Haagenson, et al., 2015). Therefore, the primary objective of this study was to evaluate the use of reactivated SBE to improve POB filterability. Related objectives were to examine the effect of adsorbent treatment on biodiesel oxidative stability and to investigate the effect of reactivation method on properties of reactivated SBE.

OBJECTIVE

General objective

To assess the use of spent bleaching earth frequently employed in the oil industry for the improvement of palm oil biodiesel filterability by the removal of its precipitate.

Specific objectives

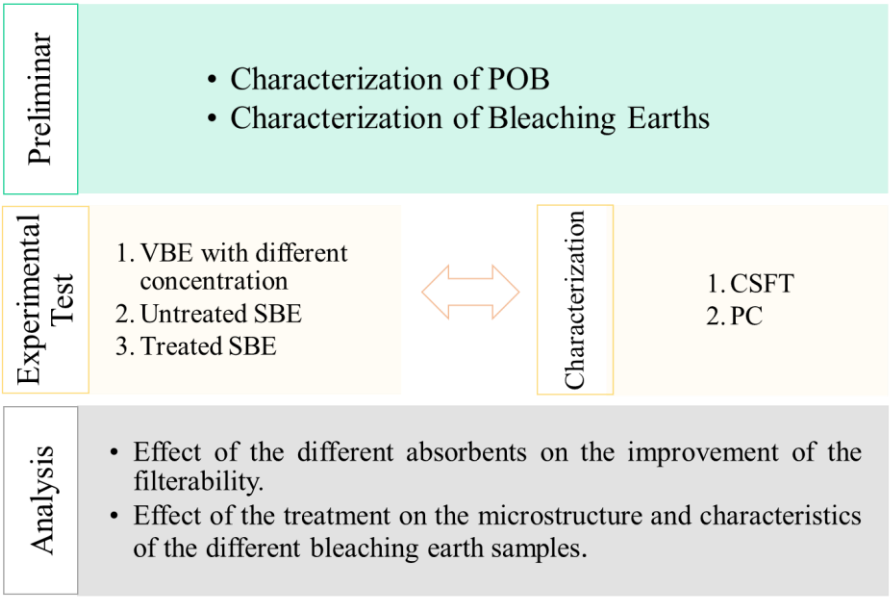
-To determine the effect of the virgin and non-treatment spent the bleaching earth on the removal of precipitate present in palm oil biodiesel.

-To establish a pretreatment for the spent bleaching earth and its effect on the removal of the precipitate present in palm oil biodiesel.

1. MATERIALS AND METHODS

The methodology is shown in the next Figure 1, each step is explained in detail below.

Figure 1: Schema of the methodology employed in this study.



1.1 MATERIALS

A sample of virgin bleaching earth (VBE) (Pure-Flo B-80, Chicago, IL, USA) and spent bleaching earth was supplied by an edible oil refinery (Aceites Manuelita S.A., Villavicencio, Colombia) where palm oil is processed. POB was also supplied by the same company. The POB was prepared from degummed, bleached, and deodorized palm oil. It was obtained dynamically from a sampling loop in a distribution line in the processing facility and supplied in a 20 L plastic container. All solvents were Carlo Erba Reagents (Milan, Italy) and Honeywell International Inc. (Morris Township, NJ) ACS reagent grade.

1.1.1 Biodiesel characterization. The fatty acid composition of the as-received POB was provided by Aceites Manuelita S.A. Samples collected after filtration through the bed of adsorbent and the Whatman No. 2 filter paper were analyzed to examine the effect of adsorbent treatment on biodiesel oxidative stability. Oxidation Induction Time (OIT) was determined in accordance with the ASTM E1858 Standard Test Method, and the analyses were all performed twice for each replicate of treated biodiesel.

1.1.2 Adsorbent characterization. As-received VBE sample was analyzed to determinate the reason of their effect on the biodiesel's treatment. Scanning Electron Microscopy SEM-EDS brand Instrument Quanta FEG 650 was used to observe the microscopic structure and composition of the virgin, calcinate, and regenerate bleaching earth (VBE, CBE, and RBE, respectively) sample at 20kV. Before the SEM test, gold coating is required for bleaching earth samples.

The crystalline phases present in each bleaching earth was determined by an X-ray diffractometer (Burker D8 Advance with DaVinci geometry) using Cu-Ka radiation. The powder patterns were recorded between 3.5° and 70° (2θ) at a scanning speed of 1° min^{-1}. VBE, CBE, and RBE were analyzed by X-ray powder diffraction equipment to observe the effect of the treatment on the smectite layers.

FT-IR spectra of the different bleaching earth samples (virgin, untreated and treated spent bleaching earth) were recorded in a Shimadzu IRTracer-100 to examine the variation of functional groups in the bleaching earth as a possible effect of the treatment. All the spectra were obtained in the wavenumber range of 4000 cm^{-1} to 400 cm^{-1} using an average of 16 scans, with a spectral resolution of 4 cm^{-1}, and air as the background.

TGA experiments were conducted using a TA instrument model TGA Q2050 under air atmosphere at a heating rate of 10 °C min^{-1} and a gas flow of 50 cm^3 min^{-1}. Each sample had a mass of about 5 mg and was heated from 30 °C to 800 °C.

The BET surface area and pore size distribution are determined from nitrogen adsorption isotherm at 77 K using a Micromeritics Tristar II instrument. Prior to analysis, the samples are outgassed 24 h under vacuum at 150 °C. The specific surface areas are determined according to the BET method at the relative pressure (p/p_o) in the range of 0.0025–0.95. The pore size distribution is calculated using the Barret–Joyner–Haleda (BJH) method using the adsorption isotherm.

1.2 EXPERIMENTAL TESTS

To attend the aims, two types of tests were performed in which the POB was treated with the bleaching earth. Firstly, the VBE was used in order to establish a set point to compare the performance of untreated- and treated- SBE with the difference in the removal of impurities in the POB. Subsequently, the SBE sample was analyzed in the same conditions of VBE.

1.2.1 *Sample conditioning.* Untreated POB was manually agitated for 5 min in accordance with the European Standard EN 12662 to resuspend sediments before withdrawing 400 ml samples. Each sample was placed in a 500 ml bottle and heated for 3 h in a water bath at 80 °C under a dry Nitrogen atmosphere to erase the thermal history of the sample[3]. This temperature was selected for this step because 40 °C is unsuitable to redissolve the sediments (Plata, Haagenson, et al., 2015). Each sample was then allowed to stand for 24 h at 25 °C before treatment with an absorbent.

1.2.2 *Adsorbent treatment with virgin bleaching earth.* POB samples were treated with VBE. The adsorbent was added to a 400 ml sample of POB and mixed at 250 rpm for 30 min, then filtered through Whatman No. 2 filter paper under vacuum. A bed of adsorbent of approximately 3 cm was formed above the filter paper during the filtration. The filter and adsorbent bed were washed with 50 ml n-heptane. The n-heptane collected after washing was evaporated at 110 °C, and the POB residue was weighed. After filtration, one portion (300 ml) of treated POB was tested for CSFT, as described below (Section 1.2.3). The other portion was stored in a 250 ml dark bottle at 25 °C under a dry Nitrogen atmosphere for further characterization. The adsorbent was evaluated at two concentrations (1 and 5 mass%) and one temperature (25

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[3] To redisolve the sediments present in the biodiesel due to the storage.

°C) in agreement with Tang et al. [2010], and each treatment was replicated two times.

1.2.3 Cold soak filtration test. A cold soak filtration test was performed in accordance to the ASTM D7501 with minor modifications (Plata, Haagenson, et al., 2015). After soaking at 4 °C for 16 h, 300 ml treated samples were allowed to warm to 25 °C in a water bath and held at this temperature for 4 h (Annex A). The samples were then filtered through a 0.7 μm glass microfiber filter (Whatman GF/F, 47 mm diameter, Piscataway, NJ, USA) under 70–80 kPa below atmospheric pressure. ASTM D7501 filtration apparatus comprises a funnel, a funnel base with a filter support, the glass microfiber filter, and a receiving flask assembled as a unit by a clamp. The filtration proceeded to completion, in contrast to the ASTM D7501 where filtration is stopped after 720 s. The time required for the biodiesel to pass through the glass microfiber filter was recorded as the cold soak filtration time (CSFT). The amount of precipitate retained on the glass microfiber filter was determined in accordance with the ASTM D7321 standard test method with minor modifications. After filtration, the sample container was rinsed with n-heptane previously filtered through a 0.45 μm glass microfiber filter (Millipore AP40, 47 mm diameter, Billerica, MA, USA), and the rinses were poured into the funnel and filtered through the glass microfiber filter. Similarly, the funnel was rinsed, and the rinses were filtered. With the vacuum applied, the funnel was carefully separated from the funnel base, and the periphery of the glass microfiber filter was washed with n-heptane by directing a gentle stream from the edge to the center. The vacuum was maintained for 10–15 s after washing to remove excess n-heptane from the glass microfiber filter. Using clean forceps, the glass microfiber filter was carefully removed from the filter support, and then dried in an oven at 110°C for 30 min, in contrast to the ASTM D7321 where the drying temperature is 90 °C. When cooled, the glass microfiber filter was weighed using an analytical balance, and the mass was recorded to the nearest 0.1 mg. The precipitate content was calculated from the increase in the mass of the glass microfiber filter and reported in ppm*.*

1.2.4 SBE treatment. A suspension of SBE in hexane (ratio 1:5 mass/volume) was stirred at 250 rpm and 40 °C for 10 min and then centrifuged at 2100 rpm and 25 °C for 30 min. After centrifugation, the hexane supernatant was discarded, and the pellet was centrifuged with fresh hexane. The supernatant was again discarded, and the pellet was dried in an oven at 55 °C for 30 min to remove any excess hexane. The resulting material was denominated as extracted bleaching earth (EBE).

A sample of SBE was also heated in a muffle furnace at 2.5 °C min^{-1} to 500 °C and then held isothermally for 1 h. The resulting material was denominated as calcinated bleaching earth (CBE) (Boukerroui & Ouali, 2000b). After heat treatment, one portion of the CBE was mixed with 0.1 M HCl solution (10 mass%), and the resulting mixture was stirred at 250 rpm and 25 °C for 1 h, and then filtered through Whatman No. 2 filter paper under vacuum. After filtration, the precipitate was washed with distilled water until it was chloride free, and then dried in an oven overnight at 80 °C (Boukerroui & Ouali, 2000b). The resulting material was denominated as regenerated bleaching earth (RBE).

1.2.5 Adsorbent treatment with untreated and treated spent bleaching earth. POB samples were also treated with untreated and reactivated SBE as described above (Section1.2.2), and the treated POB was also tested for CSFT (Section 1.2.3). However, since the required CSFT was not achieved with 1 mass% VBE, only a concentration of 5 mass% was used with untreated and reactivated SBE.

1.3 STATISTICAL ANALYSIS

Data were analyzed by ANOVA followed by the LSD test for multiple comparisons using Statgraphics Centurion software (free trial version, StatPoint Technologies, Inc., Warrenton, VA, USA). A *p*-value of <0.05 was considered statistically significant.

2. RESULTS

2.1 BIODIESEL ANALYSIS

CSFT of the as-received biodiesel was markedly higher than the 360 s limit specified in the ASTM D6751, confirming that POB had very poor filterability (Table 1). The precipitate content was also markedly higher in comparison with other biodiesel feedstocks (Tang et al., 2008), and this may have been due to the relatively high FSG content reported for POB (110.9 mg L-1, [Plata et al 2015a]). A high percentage of saturates (50.8 mass%) (Table 2), much higher than for other biodiesel feedstocks [Tang et al 2008a, Tang et al 2008b], was found for the as-received biodiesel. According to this, OIT was comparable to biodiesel feedstocks possessing high OSI values (De Melo, Santos, Rosenhaim, Souza, & Athayde Filho, 2011).

Table 1: *Selected properties for the as-received POB. Data are means ± standard deviation of two replicates.*

Property	Method	Units	POB
CSFT	ASTM D7501	s	13868 ± 2688
Precipitate content	ASTM D7321	mg L^{-1}	261 ± 27
OIT	ASTM E1858	min	14.790 ± 0.124

Table 2: *Fatty acid composition of the as-received POB*

Fatty acid	POB (mass%)
C12:0	0.2
C14:0	1.1
C16:0	44.7
C16:1	0.5
C18:0	4.3

C18:1	39.9
C18:2	8.6
C18:3	0.2
C20:0	0.3
C22:0	0.1
C24:0	0.1
ΣSFA[a]	50.8
ΣUFA[b]	49.2

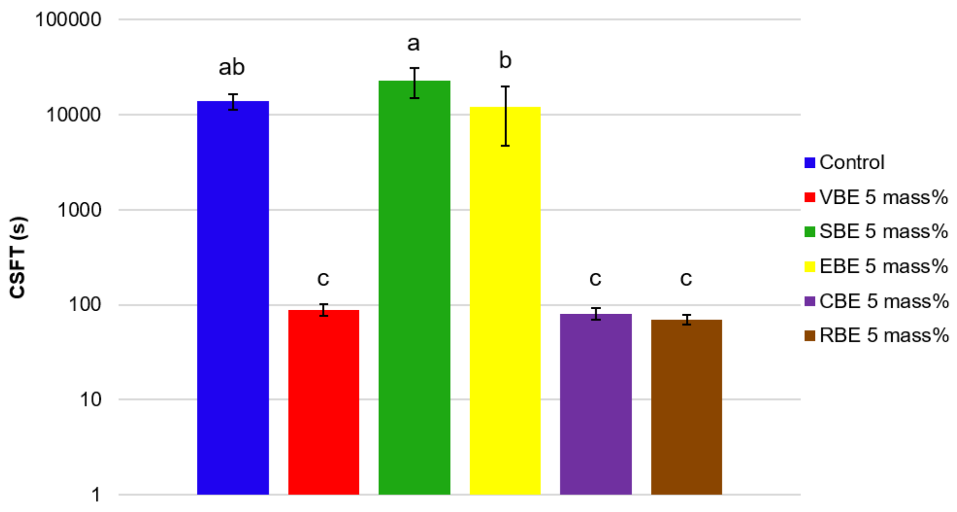
[a] ΣSFA=C12:0+C14:0+C16:0+C18:0+C20:0+C22:0+C24:0

[b] ΣUFA=C16:1+C18:1+C18:2+C18:3

2.2 ADSORBENT TREATMENT

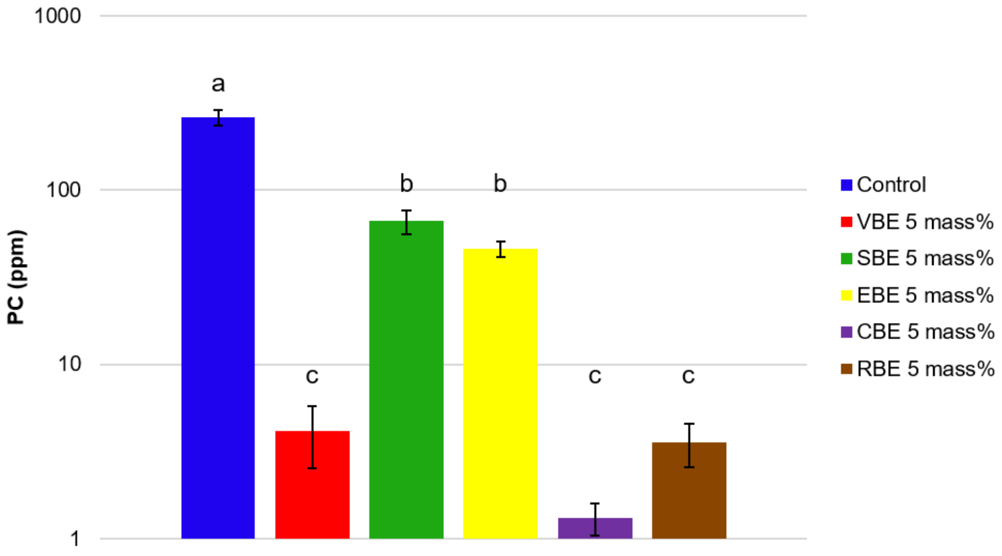
2.2.1 *Influence on CSFT.* Treatment with 5 mass% VBE resulted in POB that had a passing CSFT (< 360 s) (Fig. 2). This confirmed the potential of bleaching earth for improving POB filterability and was consistent with a significant reduction in the precipitate content (98.5 %) (Fig. 3). However, biodiesel treated with 1 mass% VBE failed to meet the ASMT limit for CSFT (1159 ± 958 s), indicating that an adsorbent concentration higher than this value is required to achieve the needed filterability.

Figure 2: CSFT for treated POB. Control denotes the untreated POB. Treatments having different letters are significantly different by LSD multiple range test (p-value <0.05) (Annex B). Error bars show standard deviation



Using 5 mass% SBE, the precipitate content was markedly lower than that for the untreated biodiesel (74.7 %). However, this was insufficient to decrease CSFT to below 360 s. POB treated with EBE had also a very high CSFT, even though the reduction in the precipitate content was higher (82.3 %). This was in agreement with Plata et al. [2005b], who examined the effect of the precipitate content on POB filterability and reported that biodiesel failed to meet the ASMT limit for CSFT once the precipitate content exceeded a threshold value (around 20 ppm). In addition, it indicates that solvent extraction of residual oil alone does not constitute an effective method for reactivation of SBE.

Figure 3: Precipitate content for treated POB. Control denotes the untreated POB. Treatments having different letters are significantly different by LSD multiple range test (p-value <0.05) (Annex B). Error bars show standard deviation.



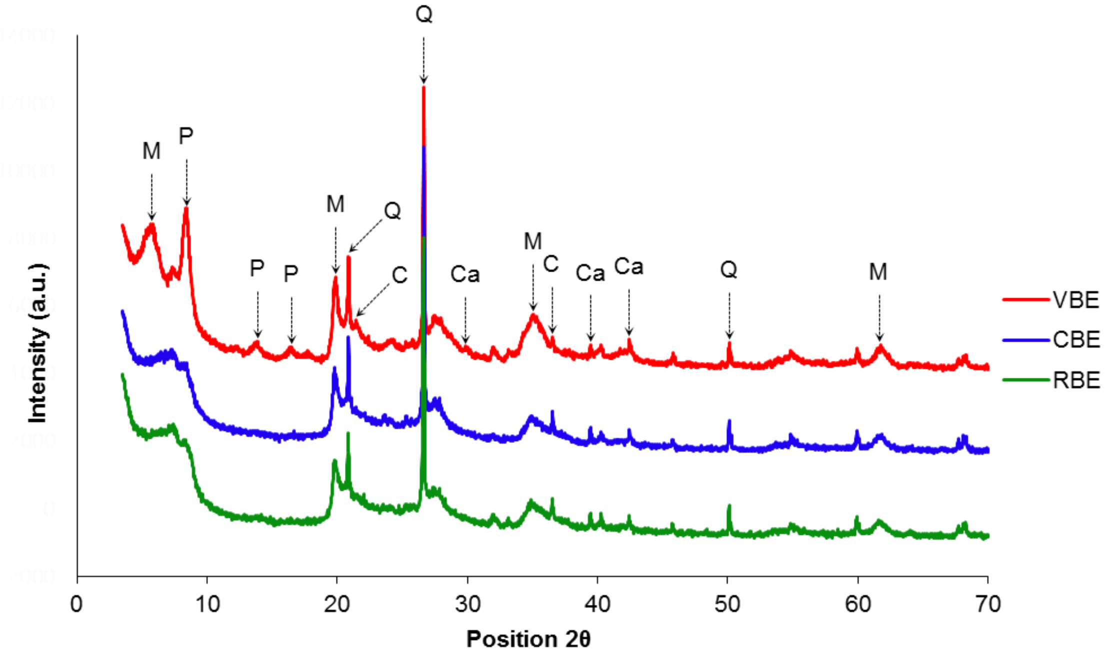
The superior CSFT provided by either CBE or RBE further confirmed that a precipitate content below the aforementioned threshold will result in biodiesel possessing a passing CSFT. More important, it evidenced that an adsorbent capable of achieving the needed filterability may be obtained by reactivation of SBE through heating treatment or a combination of heating and acid treatment. The performance of such adsorbent was similar to that of VBE, which was a clear indication that SBE recovered its initial adsorptive properties. Moreover, there was no significant difference in CSFT and the precipitate content between biodiesel treated with CBE and RBE, so heating treatment alone should be preferred.

2.3 CHARACTERIZATION OF ADSORBENTS

X-ray powder analysis showed that VBE was composed of palygorskite, calcium-rich montmorillonite, and cristobalite in a descending order of abundance (Fig. 4). Palygorskite, the major component (49.1 %), was represented by a strong reflection appeared at 2θ equal to 8.38° and moderate reflections located at 13.45° and 16.04°, which are equivalent to basal spacing of 1.054 (d_{001}), 0.658 (d_{200}) and 0.552 (d_{130}) nm, respectively (Chen, Zhao, Zhong, & Jin, 2011). The characteristic diffractions peaks of the calcium-rich montmorillonite appeared at 5.70° (1.549 nm, d_{001}), 19.78° (0.448 nm, d_{110}), 34.84° (0.257 nm, d_{200}), and 61.44° (0.150 nm, d_{001}) (Noyan, Önal, & Sarikaya, 2007) whereas those of cristobalite were located at 21.44° (0.414 nm, d_{101}) and 36.51° (0.246 nm, d_{200}) (Jiang et al., 2012). The presence of quartz (20.86°, 0.425 nm; 26.65°, 0.334 nm; 50.09°, 0.182 nm) and calcite (29.42, 0.303 nm; 39.36, 0.229 nm; 42.47, 0.213 nm) as non-clay components in the parent clay was also observed (Ait Sidhoum et al., 2013).

The X-ray powder diffraction pattern of CBE was virtually the same as that of VBE, i.e., the characteristic peaks appeared at the same position. However, heat treatment produced a decrease in the intensity of the reflection at low angles, which may be attributed to the release of water from the parent clay (Ait Sidhoum et al., 2013). In crystal structure of palygorskite, there are three different states of water: zeolitic water, coordinated water and structural water, which may be selectively removed by heat treatment (Chen et al., 2011). Similarly, when heated, montmorillonite loses its interlayer water in the temperature range 100–250 °C and undergoes the loss of its structural hydroxyls[4] at around 500 °C (Mana et al., 2008). These thermal events were evidenced by FTIR and TGA, as described below.

Figure 4:XRD patterns of VBE, CBE, and RBE. Palygorskite (P), montmorillonite (M), cristobalite (C), quartz (Q), and calcite (Ca).



In relation to RBE, acid treatment resulted in no additional changes in the diffraction pattern compared to CBE. Therefore, reactivation of SBE through heating treatment or a combination of heating and acid treatment was found to have a negligible effect on the crystal structure of the parent clay. This is of interest as modification of the crystal structure may negatively affect the performance of reactivated SBE (Foletto et al., 2002).

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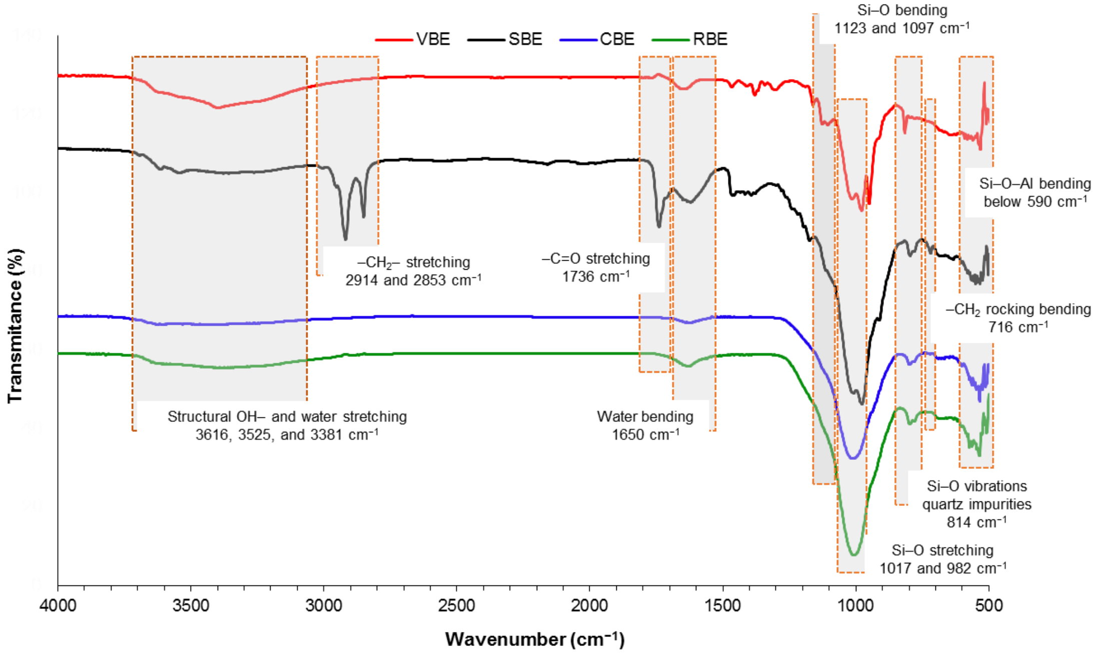
[4] Structural hydroxyls are hydroxyl groups bonded to Al3+ cations in the octahedral layer [Silva et al 2016]

FTIR spectrum of VBE displayed the characteristic absorption bands of palygorskite and montmorillonite (Fig. 5), particularly the bands in the higher wavenumber region (at 3616 cm^{-1}, attributable to stretching vibrations of the structural hydroxyls (Silva et al., 2016); at 3525 and 3381 cm^{-1}, due to stretching vibrations of zeolitic water in palygorskite (Suárez & García-Romero, 2006) and interlayer water in montmorillonite (Madejová, 2001) and the bands at 1650 cm^{-1} (attributable to zeolitic water bending (Silva et al., 2016) and interlayer water bending (Komadel & Madejová, 2006)), 1123 and 1097 cm^{-1} (due to Si–O bending), 1017 and 982 cm^{-1} (Si–O stretching), 814 cm^{-1} (Si–O vibrations of quartz impurities), and below 590 cm^{-1} (Si–O–Al bending) (Mana et al., 2008). The spectra of SBE showed the same absorption bands, but also displayed a series of strong bands attributable to the residual oil present in SBE, such as those due to $-CH_2$ asymmetric and symmetric stretching (2914 and 2853 cm^{-1}), –C=O stretching (1736 cm^{-1}), and $-CH_2$ rocking bending (716 cm^{-1}) (Mendoza et al 2018). These bands disappeared after heating treatment, indicating that the residual oil was completely removed (Boukerroui et al., 2017).

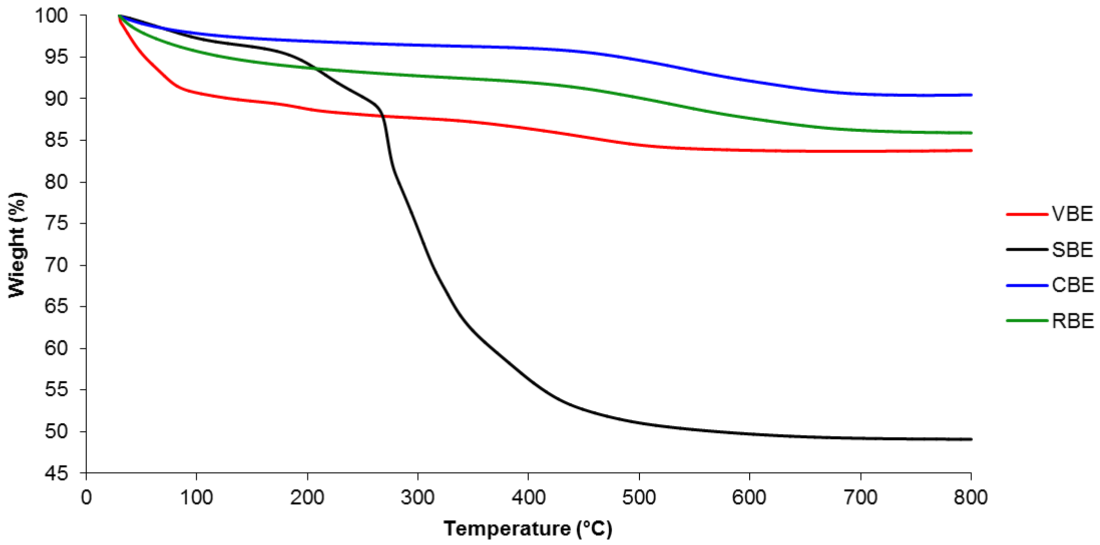
Figure 5:FTIR spectra of VBE, SBE, CBE, and RBE in the wavenumber range of 4000–400 cm-1.



As mentioned above, heat treatment resulted in the release of water from the parent clay. FTIR bands associated with vibrations of zeolitic and interlayer water not only decreased in intensity but also became diffuse, and therefore, it is obvious that modification of the clay was effected on this position (Akpomie & Dawodu, 2016).

Two main mass losses were observed during TGA of VBE (Fig. 6). These mass losses correspond to the release of zeolitic and interlayer water (in the temperature range 100–300 °C) and structural hydroxyls at around 500 °C (Rowland & Grim, 1942). An initial mass loss around 100 °C was also observed, which was related to removal of adsorbed water (Mana et al., 2008). The same two main mass losses were observed for CBE and RBE, but occurred at higher temperatures. In addition, as expected, the mass loss corresponding to the release of zeolitic and interlayer water was lower in comparison with VBE (Frini-Srasra & Srasra, 2008; Yildiz, Aktas, & Calimli, 2004).

Figure 6:TGA curves of VBE, SBE, CBE, and RBE.



TGA curve of SBE was similar to that of VBE, but showed a sharp mass loss starting at 250 °C, which overlapped the mass loss due to dehydroxylation. This corresponded to decomposition and burning of the residual oil present in SBE, in agreement with several other studies (Boukerroui et al., 2017; Mana et al., 2008; Meziti & Boukerroui, 2011), and was followed by no change of weight. Thus, heating treatment at 500 °C was confirmed to remove the residual oil completely, and consequently, this temperature was found to be the most suitable for reactivation of SBE.

The shape of nitrogen adsorption/desorption isotherms was similar to type IV according to the Brunauer, Deming, Deming and Teller (BDDT) classification with the hysteresis corresponding to type H3 of the International Union of Pure and Applied Chemistry classification (IUPAC) (Fig. 7) (Meziti & Boukerroui, 2011). Type IV isotherms are characteristic of mesoporous materials (Meziti & Boukerroui, 2011). However, the broader band displayed in the interval ranging from 1250 to 1100 cm^{-1} in the FTIR spectrum suggested the presence of micropores in CBE and RBE (Fig. 8). This band is attributable to amorphous silica, which may be formed during heat treatment (Hajjaji & El Arfaoui, 2009) and induce the formation of micropores (Meziti & Boukerroui, 2011).

Figure 7: Isotherms for the adsorption and desorption of nitrogen at 77 K on VBE, CBE, and RBE.

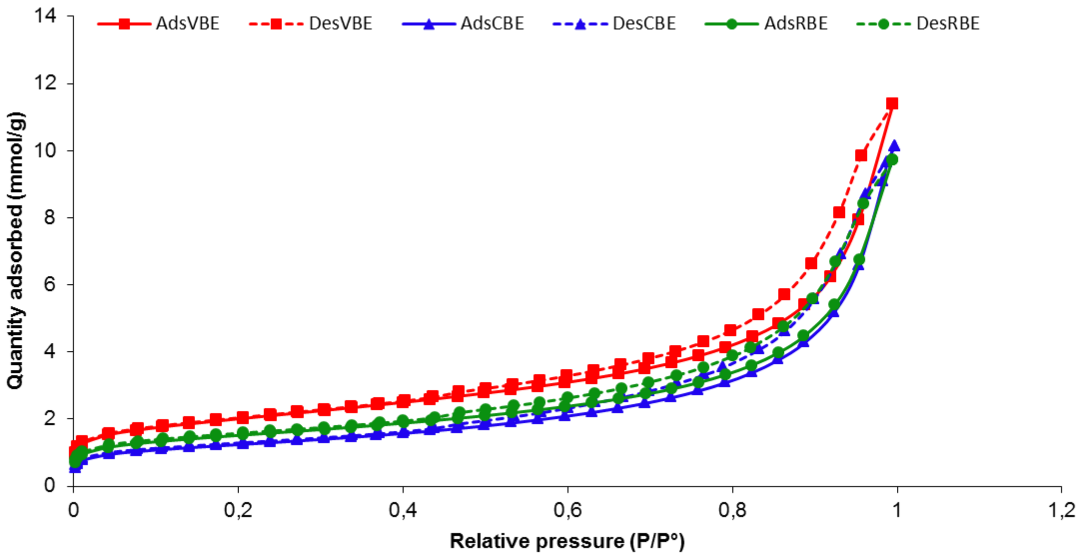
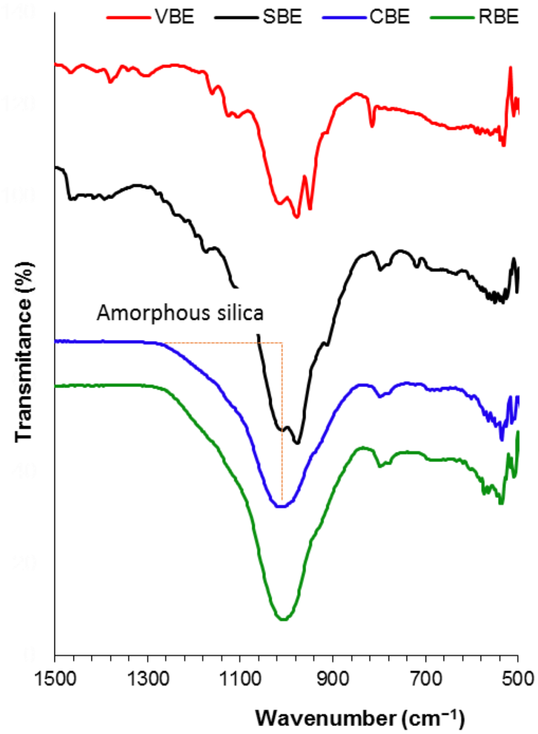
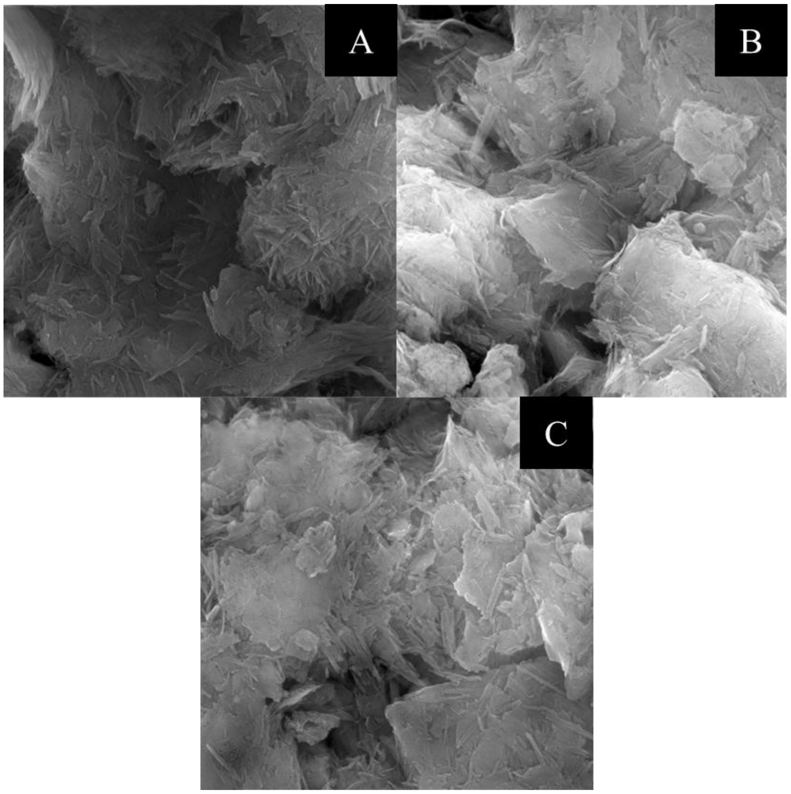


Figure 8:FTIR spectra of VBE, SBE, CBE, and RBE in the wavenumber range of 1500–400 cm-1.



A type H3 hysteresis loop is typical of non-rigid aggregates of plate-like particles, and these particles are characteristic of solids composed of a layered structure (Boey et al., 2011). Thus, reactivation of SBE was found not to substantially alter the layered structure of the parent clay. This was in agreement with other studies (Boey et al., 2011; Tsai, Chen, Hsieh, Sun, & Chien, 2002) and our SEM analyses, where the same mixture of disorderly-packed plates, irregular in size and outline, typical of montmorillonite, and bundles of randomly-oriented fibers, characteristic of palygorskite [Berhane et al 2015], was observed for VBE, CBE, and RBE (Fig. 9).

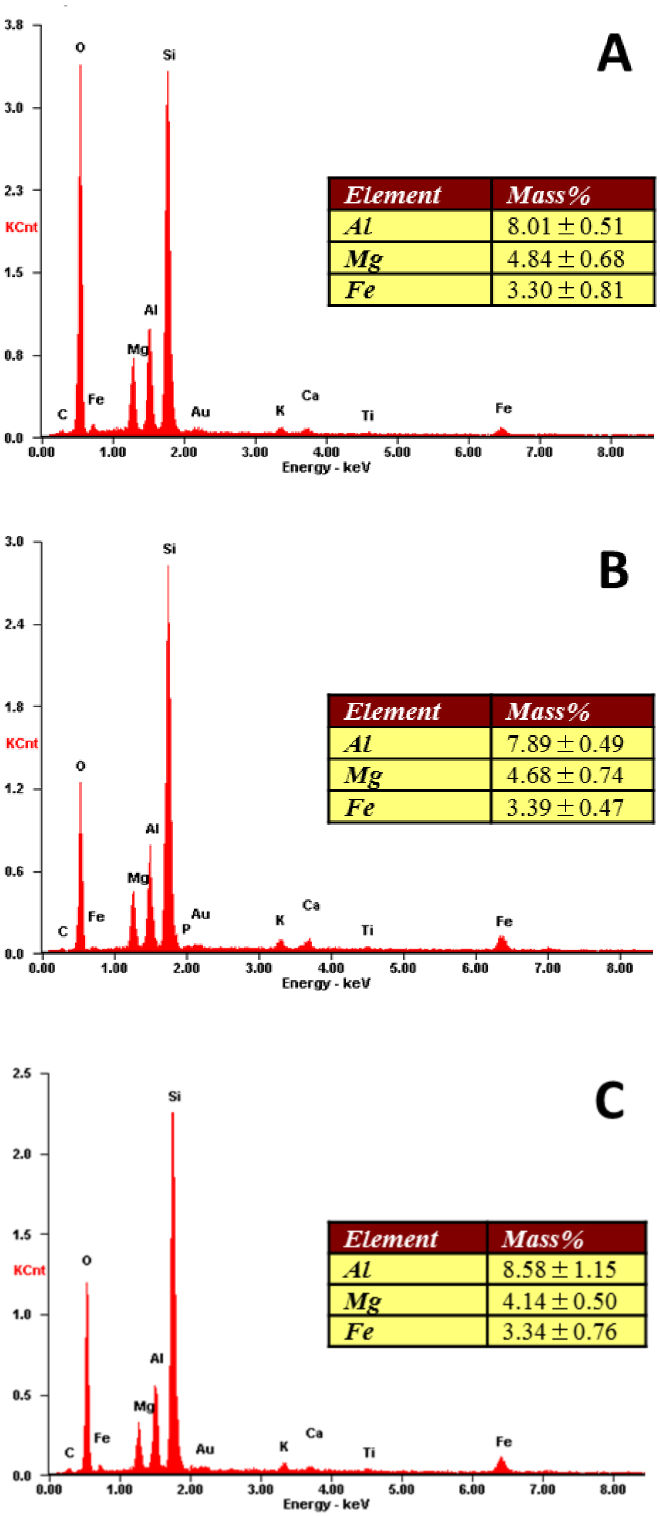
Figure 9:Scanning electron microscopy (SEM) images of (a) VBE, (b) CBE and (c) RBE with an enlargement of 2 µm



The BET specific area (S_{BET}) of CBE (98.94 m^2/g) was smaller than that of VBE (160.11 m^2/g). This may be attributed to pore blockage by the carbonaceous residues formed during decomposition and burning of the residual oil (Boey et al., 2011). Specific area is well known to play a significant role in the bleaching earth performance, and adsorption capacity is expected to decrease with decreasing values of specific area (Tsai et al., 2002). According to this, the amount of N_2 adsorbed by CBE was smaller than by VBE, although not markedly (Fig. 7). This is likely the reason why the performance of CBE was not statistically different from that of VBE.

In general, acids dissolve the residues formed during calcination of SBE, yielding a well-developed structure in the pores, i.e., without residues blocking pore entrances (Tsai et al., 2002). Acids also promote the substitution of the exchangeable cations by protons and the dissolution of the tetrahedral or octahedral cations, generating micropores (Hussin et al., 2011a). As a result, there is an increase in specific area, and consequently, in adsorption capacity (Boey et al., 2011). According to this, acid treatment led to a rise in S_{BET} of RBE compared to CBE (121.70 m^2/g). However, it did not increase its adsorption capacity in comparison to VBE. This finding may seem contradictory, but was consistent with our EDS analyses (Fig. 10). The content of Al^{+3}, $Mg^{+}2$, and Fe^{+3}, the tetrahedral and octahedral cations susceptible of being dissolved during acid treatment, was not statistically different between RBE and either VBE or CBE.

Figure 10: Representative EDS spectra of VBE (A), CBE (B), and RBE (C). Data are mean ± standard deviation of four replicates.



A

Element	*Mass%*
Al	8.01 ± 0.51
Mg	4.84 ± 0.68
Fe	3.30 ± 0.81

B

Element	*Mass%*
Al	7.89 ± 0.49
Mg	4.68 ± 0.74
Fe	3.39 ± 0.47

C

Element	*Mass%*
Al	8.58 ± 1.15
Mg	4.14 ± 0.50
Fe	3.34 ± 0.76

3. CONCLUSION

POB as received from a local supplier was characterized by an exceptionally high CSFT (>4 h), confirming the poor filterability of POB. This was consistent with a high precipitate content (>261 ppm), much higher than for biodiesel from other feedstocks.

Treatment with 5 mass% VBE resulted in POB that had a passing CSFT (< 360 s), confirming the potential of bleaching earths for improving POB filterability. However, biodiesel treated with 1 mass% VBE failed to meet the ASMT limit for CSFT, indicating that an adsorbent concentration higher than this value is required to achieve the needed filterability.

Of the three methods tested, only heating treatment (CSFT = 81 ± 11 s) and a combination of heating and acid treatment (CSFT = 71 ± 8 s) were found to be effective for reactivation of SBE. However, since there was no significant difference in CSFT and the precipitate content between biodiesel treated with CBE and RBE, heating treatment alone should be preferred.

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ANNEX

ANNEX A: *Schema of CSFT procedure according to ASTM D7501 with minor modifications*

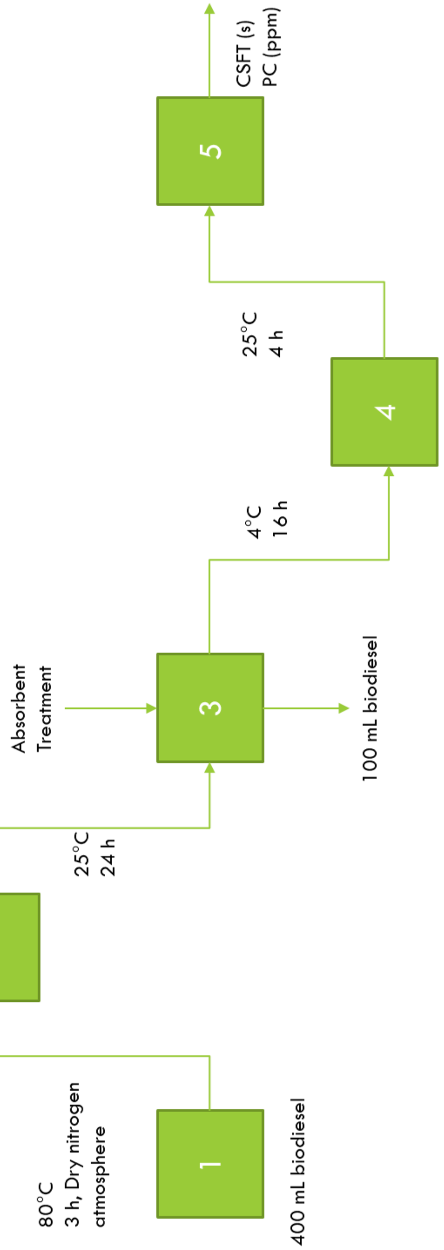

Figure A1: Schema of CSFT procedure according to ASTM D7501 with minor modifications

ANNEX B: *CSFT Statistical Analysis*

CSFT's data was analyzed by ANOVA followed by the LSD test for multiple comparisons using Statgraphics Centurion software (free trial version, StatPoint Technologies, Inc., Warrenton, VA, USA).

The ANOVA table (Table B1) decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio, which in this case equals 12.1457, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 6 variables.

Table B1: *CSTF's ANOVA*

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
Between groups	1.0872E9	5	2.17439E8	12.15	0.0014
Within groups	1.43221E8	8	1.79026E7		
Total (Corr.)	1.23042E9	13			

Using X's columns were identified 3 homogeneous groups (Table B2), this groups were identified in figure 2 with a, b, c letters (they are assigned in ascendant order), which means within there are no statistically significant. As an exception from the others, Control's sample is present in 2 different groups which means that it has the same effect from both groups. This groups were assembled estimating the difference between each pair of main, an asterisk has been placed next to 10 pairs (Table B3), indicating that these pairs show statistically significant differences.

Table B2: *CSFT's* LSD

	Count	*Mean*	*Homogeneous Groups*
ANOVA RBE	2	70.5	X
ANOVA CBE	2	81.0	X
ANOVA VBE	3	89.0	X
ANOVA EBE	2	12228.5	X
ANOVA Control	3	15432.7	XX
ANOVA SBE	2	22979.5	X

Table B3: *Difference between mains*

Contrast	*Sig.*	*Difference*	*+/- Limits*
ANOVA Control - ANOVA VBE	*	15343.7	7966.61
ANOVA Control - ANOVA SBE		-7546.83	8906.94
ANOVA Control - ANOVA EBE		3204.17	8906.94
ANOVA Control - ANOVA CBE	*	15351.7	8906.94
ANOVA Control - ANOVA RBE	*	15362.2	8906.94
ANOVA VBE - ANOVA SBE	*	-22890.5	8906.94
ANOVA VBE - ANOVA EBE	*	-12139.5	8906.94
ANOVA VBE - ANOVA CBE		8.0	8906.94
ANOVA VBE - ANOVA RBE		18.5	8906.94
ANOVA SBE - ANOVA EBE	*	10751.0	9757.06
ANOVA SBE - ANOVA CBE	*	22898.5	9757.06
ANOVA SBE - ANOVA RBE	*	22909.0	9757.06
ANOVA EBE - ANOVA CBE	*	12147.5	9757.06
ANOVA EBE - ANOVA RBE	*	12158.0	9757.06
ANOVA CBE - ANOVA RBE		10.5	9757.06

* denotes a statistically significant difference.

ANNEX C: *PC Statistical Analysis*

PC's data was analyzed by ANOVA followed by the LSD test for multiple comparisons using Statgraphics Centurion software (free trial version, StatPoint Technologies, Inc., Warrenton, VA, USA).

The ANOVA table (Table C1) decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio, which in this case equals 145.206, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 6 variables.

TABLE C1: *PC's ANOVA*

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
Between groups	100252.	5	20050.5	145.21	0.0000
Within groups	828.5	6	138.083		
Total (Corr.)	101081.	11			

Using X's columns were identified 3 homogeneous groups (Table C2), this groups were identified in figure 2 with a, b, c letters (they are assigned in ascendant order), which means within there are no statistically significant. This groups were assembled estimating the difference between each pair of main, an asterisk has been placed next to 11 pairs (Table C3), indicating that these pairs show statistically significant differences.

TABLE C2: *PC's LSD*

	Count	*Mean*	*Homogeneous Groups*
PCCBE	2	1.5	X
PCRBE	2	3.5	X
PCVBE	2	4.0	X
PCEBE	2	45.5	X
PCSBE	2	66.5	X
PCControl	2	260.5	X

TABLE C3: Difference between each main.

Contrast	*Sig.*	*Difference*	*+/- Limits*
PCCBE - PCControl	*	-259.0	28.7535
PCCBE - PCEBE	*	-44.0	28.7535
PCCBE - PCRBE		-2.0	28.7535
PCCBE - PCSBE	*	-65.0	28.7535
PCCBE - PCVBE		-2.5	28.7535
PCControl - PCEBE	*	215.0	28.7535
PCControl - PCRBE	*	257.0	28.7535
PCControl - PCSBE	*	194.0	28.7535
PCControl - PCVBE	*	256.5	28.7535
PCEBE - PCRBE	*	42.0	28.7535
PCEBE - PCSBE		-21.0	28.7535
PCEBE - PCVBE	*	41.5	28.7535
PCRBE - PCSBE	*	-63.0	28.7535
PCRBE - PCVBE		-0.5	28.7535
PCSBE - PCVBE	*	62.5	28.7535

* denotes a statistically significant difference.