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Synthesis and Characterisation of Silica from Palm Oil Fuel Ash (POFA) Using Alkaline Fusion Method

Nur Athirah Adam[1], Alawi Sulaiman[1]*, Azhari Samsu Baharuddin[2], Mohd Noriznan Mokhtar[2], Zainuri Busu[3] and Tengku Elida Tengku Zainal Mulok[4]

[1]Tropical Agro-Biomass Research Group, Faculty of Plantation and Agrotechnology, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
[2]Faculty of Engineering, Universiti Putra Malaysia (UPM), 43400 Serdang, Selangor, Malaysia
[3]FTJ Bio Power Sdn. Bhd., Jalan Liku, 59100 Kuala Lumpur, Malaysia
[4]Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

ABSTRACT

Palm Oil Fuel Ash (POFA) is a biomass produced from palm oil industries. POFA is known to contain a high amount of silica and has been proven by XRF spectroscopy, in which the silicon dioxide content is 72.63%. In this study, silica was synthesised from POFA. To extract the silica, POFA was fused with alkaline agent (Na_2CO_3) before mixing with Cethyltrimetyl Ammonium Bromide (CTAB) and Sulphuric Acid (H_2SO_4). Sodium silicate solution from the fusion was used as silica precursor replacing conventionally used silica source, Tetraethoxilane (TEOS). XRD pattern showed that raw POFA dominantly consists of silica. Meanwhile, FTIR analysis of the synthesised silica exhibited spectra bands at 3393 cm^{-1}, 1635 cm^{-1}, 1028 cm^{-1} and 787 cm^{-1} that corresponded to the functional groups of Si-O and O-H. Thus, it could be concluded that silica was successfully extracted from POFA by the alkaline fusion method.

Keywords: Mesoporous silica, palm oil fuel ash (POFA), palm oil mill

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E-mail addresses:
n.athirahadam@gmail.com (Nur Athirah Adam),
dr_alawi@salam.uitm.edu.my (Alawi Sulaiman),
azharis@upm.edu.my (Azhari Samsu Baharuddin),
noriznan@upm.edu.my (Mohd Noriznan Mokhtar),
zainuri.b@feldaglobal.com (Zainuri Busu),
tetzm@salam.uitm.edu.my (Tengku Elida Tengku Zainal Mulok)
*Corresponding Author

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INTRODUCTION

Palm oil industries have been producing a variety of biomass, and are increasing annually (Yap et al., 2013). Biomass from the industry was subjected to combustion process as fuel for steam generation and yield POFA, or better known as boiler ash. POFA produced is 5% from the biomass combusted (Borhan et al., 2010). According to Yap et al. (2013), the produced POFA in Malaysia from 2007 to

2010 was 0.06 million tonnes. POFA was dumped to the open area of the palm oil mills without any beneficial returns. Furthermore, it can cause hazards to both human and environment (Tay & Show, 1995). POFA possesses pozzolanic properties due to high content of silica which is more than 50% (Hassan et al., 2015; Zarina et al., 2013). Due to the pozzolanic properties, many inventors have been conducting research utilising POFA as a replacement material to enhance the properties of cementitious composites (Noorvand et al., 2013).

Since POFA majorly consists of silica, it can be refined to produce pure silica. Thus, this study focused on extracting silica from POFA and equipped it with mesoporous characteristics. Sodium silicate from POFA acts as a precursor to yield high purity of silica. TEOS is conventionally used as silica source. TEOS is typically derived from sand as a raw material involving multi reaction pathways. These method yields silica with desired particle sizes, porosity and morphology. However, the silica precursor is expensive and has issues with sustainability (Ui et al., 2014). Thus, researchers are looking for another way to produce silica by using a greener approach with an affordable cost. Lately, researchers have come up with other source of silica such as rice husk (Wang et al., 2012), incinerator bottom ash (Liu et al., 2014) and coal fly ash (Hui et al., 2006).

There are several established methods used in order to synthesise silica. For example, silica is produced using stober method (Liu et al., 2006), hydrothermal synthesis (Wang et al., 2009), sol-gel process (Buckley & Greenblatt, 1994) and more. Mesoporous silica offers high surface areas of 500-1000 m^2/g and huge pore diameters. Hence, it would make a great support material for enzyme immobilisations. For biocatalyst reactions, this allows substrate to flow through in and out of the supporting materials freely. Mesoporous silica broadly applied in various fields such as drug delivery (Wang, 2009; Slowing et al., 2008), biomedical applications (Wang et al., 2015; Maleki et al., 2016), catalysis (Liu et al., 2016; Yokoi et al., 2012), and water treatments (Paseta et al., 2016), and so on. POFA is abundant in supply, available at low cost and it is another way to utilise solid waste material that gives a new wealth to the oil palm industries.

MATERIALS AND METHOD

Raw Materials and Chemicals

The raw material, POFA, was collected from Felda Sungai Tengi Palm Oil Mill, Kuala Kubu Baru, Selangor, Malaysia. All chemicals, sodium carbonate (Na_2CO_3), Cethyltrimetyl Ammonium Bromide (CTAB) and Sulphuric acid (H_2SO_4) used were analytical reagent grade and purchased from R&M Malaysia. POFA was ground by using a grinder and sieved to <250µm.

Extraction of Silica from POFA

Figure 1 shows the process flow diagram of silica extraction from POFA. The method was proposed by Liu et al. (2014). POFA was initially fused with Na_2CO_3 at 900°C in a furnace for 15 minutes. Before placing them in the furnace, POFA and Na_2CO_3 were mixed uniformly. After the fusion, the product was hydrolysed with deionised water. The solution was placed in an oven at 105°C for 24 hours. After being hydrolysed, the solution was filtered. The filtered resultant

solution contains silica, while the ash is referred to as desilicated POFA. The resultant solution is also known as sodium silicate solution and it will be further processed to yield silica powder.

Next, 1.2 g of CTAB was diluted in 20 g deionised water was added to the sodium silicate solution. Subsequently, 1M H_2SO_4 was introduced into the solution until the pH became 10, and constantly stirred for 3 hours. The initial pH value of the mixture before introducing sulphuric acid was in between 11-12. The mixture was then placed in oven for 48 hours at 105oC to allow hydrothermal reaction to take place. The solid produced was later filtered and dried before calcined in furnace at 550oC for 6 hours. The calcination process completed the production of silica.

Characterisation Study

Characterisation was carried out using Fourier Transform Infra-Red (FTIR) Spectrometer (Perkin Elmer Model 2000) in order to identify the surface functional group of the synthesized silica. The synthesised silica and POFA were also subjected to X-ray Diffraction (XRD) using Rigaku Ultima III X-ray diffractometer, with a 2Θ angle ranging from 10°- 90° to get the diffraction pattern. The composition of raw POFA was determined using X-ray Fluorescence (XRF) spectroscopy.

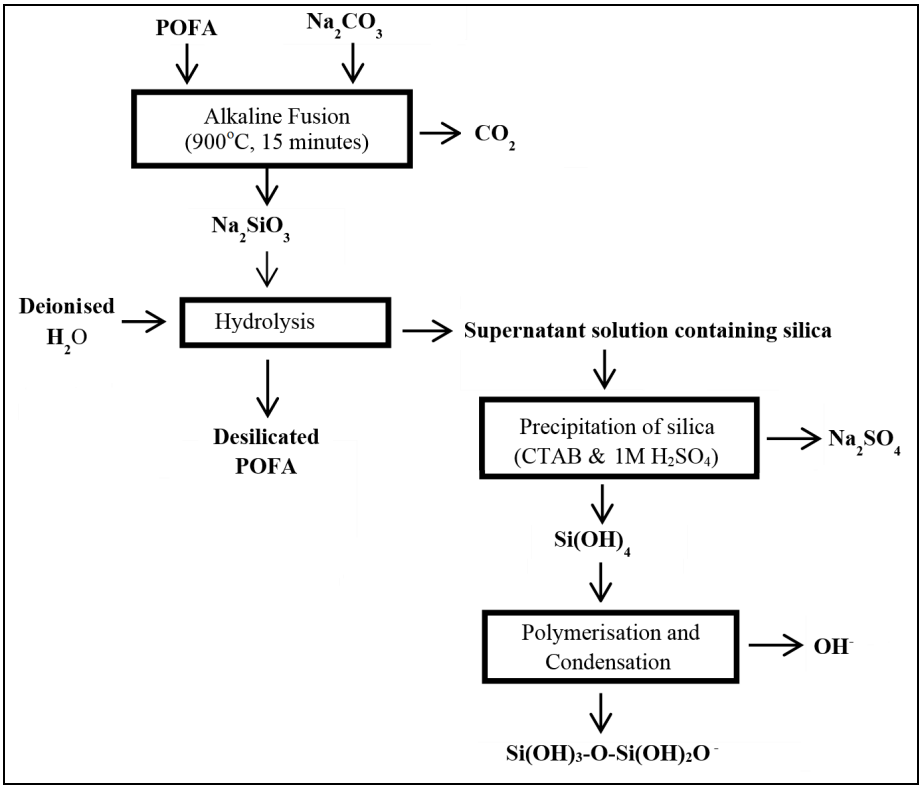

Figure 1. Silica extraction process from POFA

RESULTS AND DISCUSSION

Reaction Mechanisms

Equation 1 shows the reaction occurred when sodium carbonate was mixed with silicon dioxide at 900°C. This reaction yielded sodium silicate. As proposed by Grynberg et al. (2015), the surface of the silica was spread by the molten sodium carbonates and it led to the surface reaction generating sodium silicate.

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2 \quad [1]$$

Sodium silicate formed after the fusion was hydrolysed with deionised water, and thus allowing the leaching process of the fused sodium carbonate and silica of the POFA (Septawander et al., 2016). According to Liu et al. (2014), the silicates are readily soluble in water. The addition of sulphuric acid to the sodium silicate solution initiated the gelation of silica in the form of silicic acid, as in Equation 2. As explained in the methodology, sulphuric acid is added to sodium silicate solution until the pH reached 10. Approaching pH 10, white precipitate of silica started to appear. At this stage, the solution is stirred vigorously to promote the formation of silica. Liu's report (as cited in Mendelez-Ortiz, 2013) has stated that the required time for sodium silicate to yield silica decreases in alkaline pH.

$$Na_2SiO_3 + H_2O + H_2SO_4 \rightarrow Si(OH)_4 + Na_2SO_4 \quad [2]$$

Polymerisation of monomer silicic acid occurred results in the production of oligomeric silicic acid and water as by-product (Wilhelm & Kind, 2015). In the polymerisation process, as indicated in the Equation 3, the surface of the agglomerates is negatively charged.

$$Si(OH)_4 + Si(OH)_4 \rightarrow Si(OH)_3 - O - Si(OH)_2O^- + OH^- \quad [3]$$

In this study, CTAB acts as a template or structure directing agent to fabricate mesoporous silica materials. At the end of the process, the mesoporous silica was calcined to remove the CTAB template. As proven by the FTIR spectroscopy, no traces of CTAB were found in the synthesised silica from POFA. Figure 2 illustrates the mechanism of silica templated with CTAB to construct mesoporous structure. The agglomerates of silica after going through the polymerisation process are anionic, while the surfactant is cationic. As illustrated in Figure 2, the surfactant and anionic silica established connections through electrostatic forces.

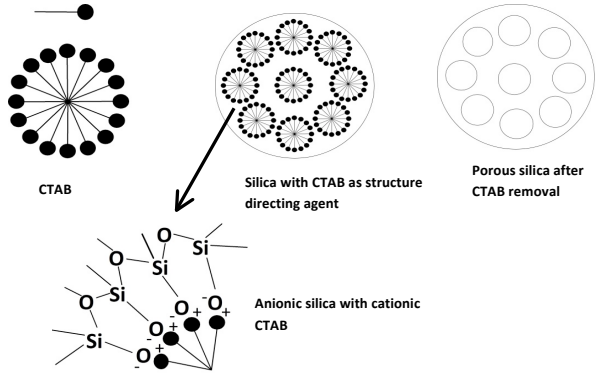

Figure 2. CTAB templated mesoporous silica

XRF Analysis

Table 1 below shows the chemical composition of raw POFA using the XRF analysis. From the table, analysed raw POFA contains SiO_2, K_2O, CaO, Al_2O_3, Fe_2O_3, MgO and P_2O_5. It can be observed that silica is the dominant compound in POFA, with the percentage of 72.63%. Thus, raw POFA can be used as raw materials for silica production.

Table 1
The chemical composition of POFA

Compound	Content (%)
SiO_2	72.63
K2O	9.77
CaO	5.48
Al_2O_3	5.03
Fe_2O_3	3.53
MgO	3.39
SO_3	0.18

FTIR Spectroscopy

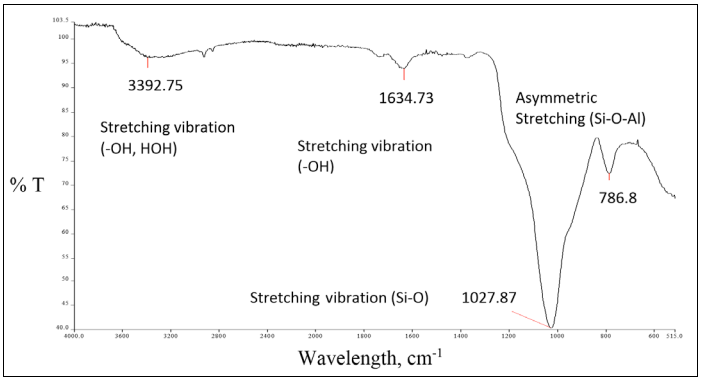

Figure 3. The FTIR spectra of silica synthesised from POFA

Figure 3 shows the spectra bands of silica extracted from POFA. Bands appearing at 3392.75 and 1634.73 attributed to the Si-OH stretching and bending and SiO-H bending, respectively. As discussed earlier, there are hydroxyl groups attached at the surface of the silica during the processes of precipitation and polymerisation. The bands appearing at 1027.87 and 786.80 show the asymmetric and symmetric stretching modes of Si-O-Si (Rahmat et al., 2016). There is no band that is corresponding to C-H vibrations observed. This shows that Cetyltrimethy Ammonium Bromide (CTAB), which is the template material used during silica extraction, has completely been removed during calcination. These results are aligned with the previous studies by Liu et al. (2014). This also confirms that silica can be extracted effectively from POFA by using alkaline fusion method.

XRD Analysis

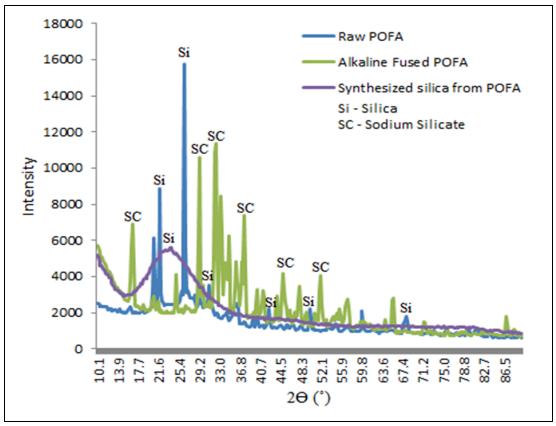

Figure 4. The XRD pattern of raw POFA, alkaline fused POFA and synthesised silica from POFA

The XRD pattern in Figure 4 shows the peaks of raw POFA, alkaline fused POFA and synthesised silica. The peaks indicate that silica is the major component in the raw POFA sample. More intense peaks appeared as POFA was fused with alkaline agent, Na_2CO_3 to produce sodium silicate. The peaks corresponding to the presence of sodium silicate as the surface of POFA, which is dominated by silica particles, are being surrounded by the molten sodium carbonate during the fusion process. This indicates that the alkaline agent successfully reacted with the POFA particles to form sodium silicate. The XRD pattern of silica extracted from POFA is consistent with the report by Liu et al. (2014).

CONCLUSION

In this study, silica was successfully extracted from POFA. The FTIR analysis results proved that silica particles extracted from POFA were of high purity and the XRD pattern of silica particles was found to be consistent with other studies. Sodium silicate solution, as the precursor silica produced from this study, can replace the expensive TEOS. On the other hand, the palm

wastes can be fully utilised for higher value-added products. Thus, this study has shown that the production of silica from POFA could be achieved using the alkaline fusion method.

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