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SYNTHESIS AND CHARACTERIZATION OF LIQUID-SILICATE FERTILIZER FROM TREATED AND UNTREATED ASH RICE HUSK

(Sintesis dan Kajian Sifat-Sifat Baja Cecair-Silikat daripada Abu Sekam yang Dirawat dan Tidak Dirawat)

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Abstract

Rice husk ash (RHA) is an agricultural waste material that is abundantly available in all rice-producing Asian countries. The RHA is rich in silica (Si), which can be extracted as silicate sources for many industries, such as fertilizer, building material, insulation material, or fuel. In this research, organic acid, which is a phosphoric acid (H_3PO_4), was used to treat RHA. RHA was treated with H_3PO_4 at various temperatures (60°C, 80°C, and 100°C) and molarity (1 M, 2 M, and 3 M), and followed by an extraction process of untreated and treated RHA using potassium hydroxide (KOH) at 2 and 3 hours of extraction time and 1 M and 2 M of KOH. The extracted liquid-silicate was determined by using Fourier Transfer Infra-Red (FTIR), X-ray fluorescence (XRF), and Particle Size Analyzer (PSA). The highest silica content (40.910%) in liquid-silicate fertilizer (LSF) was recorded for the treatment condition of 2 M H_3PO_4 at 80 °C based on the XRF result. The highest wave number was 1008.78 cm^{-1} from treated RHA at 2 M H_3PO_4 80 °C. According to PSA data, the smallest particle size (1465.9µm) was recorded after leaching with H_3PO_4 at 2 M 80 °C as compared to untreated RHA at 1639.75µm.

Keywords: rice husk ash, liquid-silicate fertilizer, acid leaching, phosphoric acid, silica extraction

Abstrak

Abu sekam padi (RHA) adalah bahan buangan pertanian yang banyak terdapat di semua pengeluar beras untuk negara Asia. RHA kaya dengan silika (Si), yang boleh diekstrak sebagai sumber silikat untuk banyak industri seperti baja, bahan binaan, bahan penebat atau bahan api. Dalam penyelidikan ini, asid organik, iaitu asid fosforik (H_3PO_4) digunakan untuk merawat RHA. RHA dirawat dengan H_3PO_4 pada pelbagai suhu (60 ℃, 80 ℃, dan 100 ℃) dan kemolaran (1 M, 2 M dan 3 M). diikuti dengan proses pengekstrakan RHA yang tidak dirawat dan dirawat menggunakan kalium hidroksida (KOH) pada 2 dan 3 jam masa pengekstrakan dan 1 M dan 2 M KOH. Cecair-silikat yang diekstrak ditentukan dengan menggunakan Inframerah transformasi Fourier (FTIR), pendaflour sinar-X (XRF) dan penganalisa saiz partikel (PSA). Kandungan silika tertinggi (40.910%) dalam baja silikat cecair (LSF) direkodkan untuk keadaan rawatan 2 M H_3PO_4 pada 80 °C berdasarkan keputusan XRF. Nombor gelombang tertinggi ialah

1008.78 cm^{-1} daripada RHA yang dirawat pada 2 M H_3PO_4 80 °C. Menurut data PSA, saiz zarah terkecil (1465.9µm) direkodkan selepas larut lesap dengan H_3PO_4 pada 2 M 80 °C berbanding RHA yang tidak dirawat pada 1639.75µm.

Kata kunci: abu sekam padi, baja cecair-silikat, asid larut lesap, asid fosforik, pengekstrakan silika

Introduction

In 2019, the world's total paddy rice production was estimated to be 757 million tons [1]. China is the world's leading producer of rice and paddy. As of 2019, China's paddy rice production was 211 million tons, accounting for 27.92% of global paddy rice production. The remaining top five countries which account for 71.54% of the production are India, Indonesia, Bangladesh, Vietnam, and Thailand. Malaysia's paddy rice production in 2019 was 2.91 million tons. From the production of paddy rice, about 1.2 million tons per year of agricultural waste is disposed of in Malaysia's landfills [2]. During the paddy rice cultivation, several by-products are also generated such as broken rice, the husk, and the bran layer. Hence, the utilization of these by-products or agricultural solid waste has been done to save the environment. In this study, rice husk ash (RHA) was the targeted waste material from paddy rice cultivation that can be converted into a potential liquid-silicate fertilizer (LSF).

The RHA can be obtained from the combustion process of RH in the furnace under a controlled temperature, which is below 700 ℃. A suitable temperature and burning environment can provide a better quality of RHA as its particle size and specific surface area are dependent on burning conditions. For every 1000 kg of milled paddy, it will produce around 200 kg (20%) of RH, and when this husk undergoes a burning process in the boilers or incinerators, around 50 kg (25%) of RHA is produced [3]. Usually, a completely burnt RHA will be observed in physical color changes from grey to white. From the burning of RH, the ash contains mainly amorphous silica (Si) and carbon black residue, which is also called carbonaceous siliceous material [4]. The silica group minerals are framework silicates with the composition of SiO_2. They belong to the silicate mineral class. The most common silica mineral is quartz. Besides quartz, other silica polymorphs include cristobalite, tridymite, coesite, and stishovite [5].

The burning conditions can affect the amount of silica and carbon black in the ash. As proven by many researchers, RHA has a high content of silica, which is 94% of the total content, while the remaining 6% contains potassium oxide (K_2O), calcium oxide (CaO), magnesium oxide (MgO), aluminum oxide (Al_2O_3), and phosphorus pentoxide (P_2O_5) in decreasing concentrations [2]. Because of that, it has been utilized in many industries such as fertilizer, coating, and paint industries.

To obtain RHA, RH will undergo a carbonization process. Carbonization is a method by which solid residues with increasing carbon element content are produced from organic material in an inert atmosphere, typically by pyrolysis. Mehta proposed that essential amorphous silica can be obtained by holding the temperature for prolonged periods below 500℃ and under oxidizing conditions or the temperature can be increased up to 680 ℃ but with a hold-time of not more than 1 minute [6]. Other researchers have claimed that the burning of RH in extreme temperatures (i.e. high temperature) or long duration of time would result in the formation of crystalline phases [7]. The partially crystalline phase of RHA is caused by burning the RH for more than 1 hour in a temperature range between 973 and 1073 Kelvin. Burning RH at temperatures above 1073 Kelvin for more than 1 hour has been documented to lead to the formation of a complete crystalline phase.

Good quality biogenic silica can be produced by the treatment process. Several researchers have carried out the experiments by using a leaching process with hot acid treatment with inorganic acids such as hydrochloric acid (HCl), nitric acid (HNO_3), and sulfuric acid (H_2SO_4) or hot basic treatment with inorganic bases such as ammonium hydroxide (NH_4OH) and sodium hydroxide (NaOH) [8-11]. Acid leaching treatment of RHA by using organic acid is highly encouraged because it has many economic and ecological benefits compared to a strong acid [12-13]. It is a proper route for silica extraction to remove substances from solid organic

materials via the liquid extraction method. Based on the results obtained from the previous paper, an organic acid solution such as citric acid was considered a more environmentally friendly process during the acid-leaching treatment. However, phosphoric acid (H_3PO_4) was used as a pH adjustor in liquid fish fertilizers, as an inert ingredient in pesticide products, and as a sanitizer for dairy equipment [14].

A method based on acid treatment before the alkaline extraction is developed to produce high-purity silicate with minimal contaminants. This process does not provide any harm to the life of organisms, moreover, it is more economical. In addition, a chelating reaction occurs between the carboxyl group (-COOH) and metal cations, which leads to the removal of metal impurities in the RHA. Conventionally, the removal of metallic impurities is done by using inorganic acids such as HCL, HNO_3, and H_2SO_4. However, the use of inorganic acid has caused harm to human beings and the environment. Furthermore, the expensive materials with corrosion resistance needed for the leaching process using inorganic acid can cause an economic problem. There is also a high consumption of water to remove the acid, as well as the need for a special disposal system [12]. That is the reason why organic acid should be used as the substitute for inorganic acid, to comply with the environmental requirements for less exposure or disposal of hazardous or corrosive chemical waste. For this paper, organic acid which is H_3PO_4 was used to treat the RHA before the liquid-silicate extraction process. This study aimed to synthesize LSF from treated (acid leaching) and untreated RHA and to compare the results of the characterization of LSF by using XRF, FTIR, and PSA techniques for both treated and untreated RHA.

Materials and Methods

Materials

In this experiment, the RHA was obtained from a rice mill, DIBUK Sdn. Bhd., located in Perlis, Malaysia. Chemicals such as 45% potassium hydroxide (KOH) and 85% phosphoric acid (H_3PO_4) were obtained from Reichle & De-Massari (R&M), Switzerland.

Material preparation

An amount of 3 kilograms of RHA was obtained directly from the factory. The rice husk ash (RHA) had already undergone the carbonization process at the factory at 650 °C. After that, RHA was cleansed by using distilled water and dried in the oven to remove any impurities and reduce the moisture content. This was to avoid any effects during the treatment and extraction. The sample was dried at 60 °C for 60 mins [15]. Once the RHA was completely dried, the RHA was grounded using a mechanical grinder until it turned powdery. A few grams of the sample were kept without further treatment process as an untreated sample (blank sample).

Acid leaching treatment process

200 g of RHA were soaked in each beaker containing H_3PO_4 at various molarities (i.e.1 M, 2 M, and 3 M) to undergo acid-leaching treatment. During the treatment process, these acid-treated samples were placed on the hot plate magnetic stirrers to heat the mixture until they reached various temperatures at 60, 80, and 100 °C and were kept constant for 2 hours for each sample [16]. After the acid leaching treatment was completed, each sample was washed using distilled water to neutralize the sample. The pH of the sample must be monitored until it reaches pH 7. After that, all samples were desiccated in an oven at 100 °C for 2 hours.

Extraction process of treated and untreated RHA

100 g of treated and untreated RHA were soaked in beakers containing various molarities of KOH (i.e., 1 M, 2 M, and 3 M) for the extraction process. During the extraction process, each sample was placed on a hot plate magnetic stirrer to heat until the temperature reached a constant 100 °C at 2 and 3 hours for each sample, respectively. Next, the samples were desiccated in an oven at 100 °C for 2 hours.

Chemical composition analysis and characterization of treated and untreated rice husk ashes

Fourier transform infrared (FTIR) spectroscopy, X-ray fluorescence (XRF) spectroscopy, and particle size analyzer (PSA) were used to determine and compare the difference between the composition of silica in treated and untreated RHA in their potential as an LSF. The FTIR technique was used to characterize the major chemical groups present within the LSF using an FTIR spectrometer model L1280044 manufactured by Perkin

Elmer USA. After launching the spectrum software, the sample was placed on the sample holder followed by the operation of the spectrometer, and each spectrum was finally collected until complete spectra were projected on the monitor.

Next, the XRF spectrometer, PAN analytical MiniPAL 4 X-ray (Philips, UK) was used to characterize the number of chemical compounds within the liquid silicate [2]. Each sample was placed in a cup that was covered using a suitable foil, usually Kapton material. After that, the sample was placed into the XRF spectrometer.

Finally, RHA characterization was performed by using PSA Malvern Mastersizer 2000 (Malvern, UK). PSA was used to determine the size and distribution of the particles that comprise a material. The characterization and analysis of the composition of RHA were conducted using the Standard Operation Procedure (SOP) instructions. Then, the sample was added into the water to ensure an adequate amount of sample was aliquoted (one drop at a time) to turn the Laser Obscuration bar green (i.e. until it achieved the mid-value) [17-18]. The sample was measured and the outcome (size distribution) was computed. The recorded measurement was saved to a measurement file automatically.

Results and Discussion

Acid leaching treatment with phosphoric acid (H_3PO_4)

Acid leaching treatment on rice husk ashes was done by using H_3PO_4. The purpose of this treatment is to remove some amounts of metal impurities [15]. Based on the XRF data in Table 1, the highest silica content was at 1 M 60 °C sample with 57.676% and had the lowest potassium (K) and Iron (Fe) content, which are 1.413% and 39.357%, respectively. To proceed with the next stage of the experiment, which was the extraction process, the highest silica content from each proposed molarity was chosen. Hence, 1 M at 60 °C, 2 M at 80 °C, and 3 M at 60 °C were chosen to undergo the extraction process later. From previous studies, it has been demonstrated that the phosphoric acid activation of lignocellulosic [19] precursors produced carbons having not only a well-developed porosity, but also considerable amounts of acid surface groups. [20]

Table 1. XRF data for acid leaching treatment of RHA

Samples	Temperature (°C)	Si (%)	K (%)	Fe (%)	Traces Element (%)
	60	57.676	1.413	39.357	1.554
1 M	80	55.363	1.825	41.176	1.636
	100	54.400	1.758	42.205	1.637
	60	53.835	1.877	42.633	1.655
2 M	80	54.360	1.874	42.107	1.659
	100	53.593	1.754	43.002	1.651
3 M	60	51.378	1.885	45.061	1.676
	80	51.323	1.806	45.248	1.623
	100	51.139	1.731	45.487	1.643

Note: Data are given in mass percentage. The trace elements are Na, Mg, Al, P, Ca, Cu, and Zn

Extraction process using potassium hydroxide (KOH)

The extraction process was done by using KOH for treated and untreated RHAs. The purpose of extraction is to produce LSF. Further characterization was carried out to observe the content, such as silica content in the LSF.

XRF spectroscopy

Two types of sample conditions were tested, which are untreated and treated RHA. The chemical composition was analyzed by using an XRF spectrometer. Table 2 shows the chemical composition of treated and untreated RHA. Untreated RHA recorded the lowest silica content. Meanwhile, treated RHA at 1 M 2 H yielded the highest silica content, which is 40.910% at the treatment

condition of 2 M 80 °C, compared to untreated RHA, in which the silica content was 29.157%.

The other metallic elements such as iron and potassium are presented in the LSF of both treated and untreated RHA. The results indicated that most iron was reduced when the RHA underwent leaching treatment. Similar results were exhibited for the effect of acid-leaching treatment on the potassium content. The removal of these metallic cations after chelating with H_3PO_4 improved the chemical composition of a leached sample to be rich in alkaline metals, which are water-solubles such as potassium. Hence, the unwanted impurities were washed away by the distilled water used in the neutralization process. The impurities in the husk were removed using a chelate reaction between carboxyl groups (-COOH) and metal elements [2]. This is because the majority of elements absorbed during the leaching process were silica which was extracted from RHA. As a result of the strong covalent bond that exists between silicon and oxygen in the properties, silica becomes very hard and rigid [2], which makes it the end product of this leaching process for its useful real-life application as an agricultural fertilizer.

As shown in Table 2, H_3PO_4 leaching treatment was significantly useful and effective in removing impurities and increasing silica purity in RHA. However, the silica content for treated 2 M 2 H and 2 M 3 H was observed to decline from 21.317 to 18.477% and 19.148 to 18.212%, respectively when undergoing the treatment process. As shown in Table 2, the iron content was the highest compared to silica and potassium content. This correlates with the literature finding that, iron is very essential in plant growth. Iron is required for many vital plant functions, including enzyme and chlorophyll production, nitrogen fixation, development, and metabolism. Even though iron is abundant in soil, plants frequently suffer from iron deficiency due to its low solubility, particularly in alkaline calcareous soils. Hence, our liquid silicate fertilizer is very suitable for the plant as it has a high content of iron.

Table 2. XRF data for treated and untreated RHA

Sample (RHA)	Treatment Condition	Si (%)	Fe (%)	K (%)	Traces Element (%)
Untreated Sample (Blank)	-	29.157	52.350	15.164	3.329
Treated 1 M 2 H	1 M 60 °C	37.685	51.053	9.769	1.493
Treated 1 M 2 H	2 M 80 °C	40.910	46.401	11.014	1.675
Treated 1 M 2 H	3 M 60 °C	29.777	50.891	13.906	5.426
Untreated 1 M 3 H	-	28.516	54.098	14.993	2.393
Treated 1 M 3 H	1 M 60 °C	39.285	45.704	13.417	1.594
Treated 1 M 3 H	2 M 80 °C	38.223	49.182	10.905	1.690
Treated 1 M 3 H	3 M 60 °C	34.004	49.943	13.555	2.498
Untreated 2 M 2 H	-	21.317	55.121	21.973	1.589
Treated 2 M 2 H	1 M 60 °C	21.711	55.087	21.680	1.522
Treated 2 M 2 H	2 M 80 °C	22.501	54.454	21.636	1.409
Treated 2 M 2 H	3 M 60 °C	19.477	56.551	22.794	1.178
Untreated 2 M 3 H	-	19.148	58.881	20.276	1.695
Treated 2 M 3 H	1 M 60 °C	27.767	50.150	20.857	1.226
Treated 2 M 3 H	2 M 80 °C	28.073	48.720	22.114	1.093
Treated 2 M 3 H	3 M 60 °C	18.212	52.906	27.465	1.417

Note: Data are given in mass percentage. The samples are from two conditions which are treated and untreated RHA. The trace elements are Na, Mg, Al, P, Ca, Cu, and Zn

FTIR spectroscopy

Figure 1 and Table 3 represent the infrared spectra of treated and untreated RHA at 1 M 2 H. Based on the XRF data tabulated in Table 2, the highest silica can be extracted from 1 M 2 H. Hence, the selected samples were used to further analyze the functional groups in treated and untreated RHA by using FTIR spectroscopy. The peak from 1095 to 1075 cm^{-1} or 1055 to 1020 cm^{-1}

showed the stretching of silicone, Si-O- [21]. Meanwhile, the peak from 1100 to 900 cm^{-1} showed the stretching band of silicate ions [21]. Because of the asymmetric stretching of the silicate ion, it demonstrated a peak at wave number 1006.88, 1001.13, 1008.78, and 1003.34 cm^{-1} for (a) untreated, (b) treated with 1 M 60 °C, (c) treated with 2 M 80 °C, and (d) treated 3 M 60 °C, respectively. The silicate ion present was due to the liquid silicate produced from the extraction process. Based on Table 3, it shows that the highest wavenumber was treated RHA at 2 M 80 °C. This can be proven based on the XRF results as it exhibited the highest silica content in the liquid silicate from the treated RHA of 2 M 80°C (1008.78 cm^{-1}) [22].

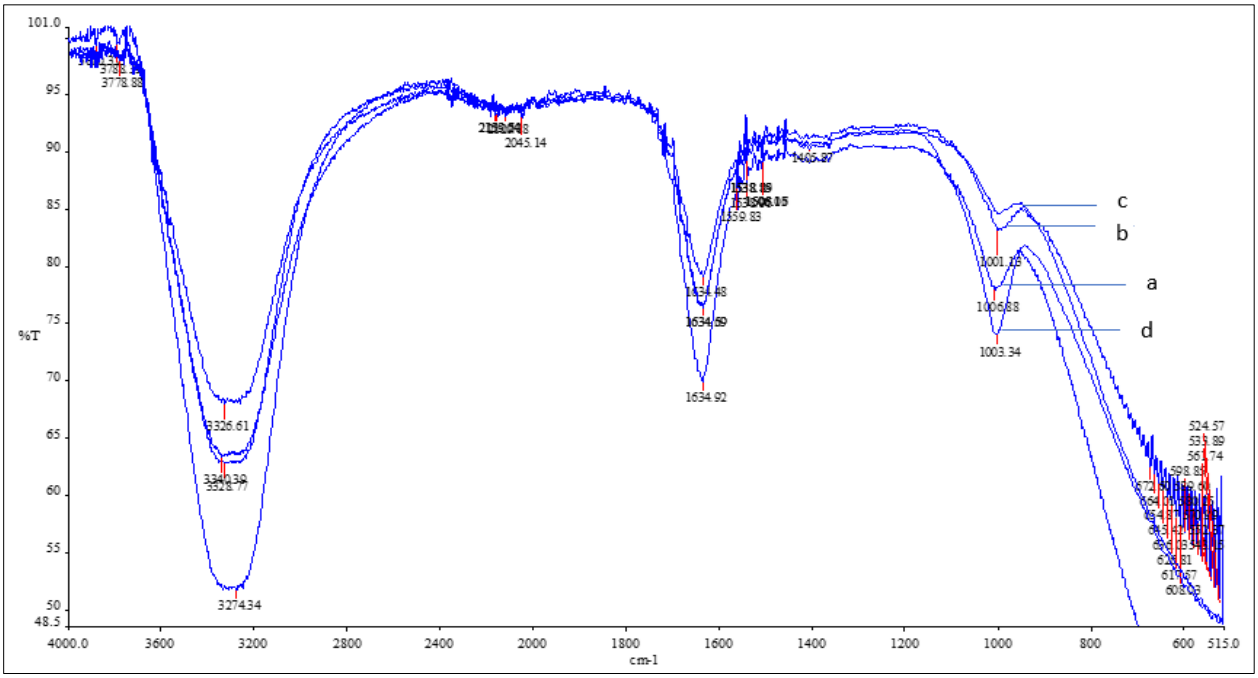

Figure 1. FTIR spectra of treated and untreated RHA of 1M 2H; (a) untreated RHA, (b) treated RHA with 1M 60°C, (c) treated RHA with 2 M 80 °C, and (d) treated RHA with 3 M 60 °C

The presence of O-H stretching was represented by both treated and untreated RHA spectrum, which shows broad characteristic peaks at 3274.34, 3326.61, 3328.77, and 3340.39 cm^{-1} for (a) untreated, (b) treated with 1 M 60 °C, (c) treated with 2 M 80 °C, and (d) treated 3 M 60 °C, respectively (Refer to Table 3). This O-H stretching indicates the presence of phenols and alcohols [23]. The reason for O-H stretching was due to the moisture content in the fibers, which contains hydroxyl groups in the form of lignin, hemicelluloses, and cellulose [24, 25].

Table 3. Wavenumber functional groups identified from treated and untreated RHA at 1M, 2H & 3M

	Wavenumber (cm^{-1})			
Vibration Band Assignment	**Untreated RHA**	**1M 60 °C**	**2M 80 °C**	**3M 60 °C**
Asymmetric stretching of silicate ion	1006.88	1001.13	1008.78	1003.34
O-H	3274.34	3326.61	3328.77	3340.39
O=C=O	2120.18	2155.60	2159.24	2045.14

The presence of O=C=O stretching was represented by both treated and untreated RHA spectrum, which is CO_2 at the wavelength of 2120.18, 2155.60, 2159.24, and 2045.14 cm^{-1} for (a) untreated, (b) treated with 1 M 60

°C, (c) treated with 2 M 80 °C, and (d) treated 3 M 60 °C, respectively (refer to Table 3). Major functional groups of O-H and O=C=O gave rise to bands above ~1500 cm^{-1}. However, the precise pattern of bands seen in the fingerprint region was specific to each compound. The presence of CO_2 in treated and untreated RHA was due to the carbonization process, which produced a gaseous product high in CO_2. However, as shown on the spectrum of treated RHA, the CO_2 formed was present after acid-leaching treatment. This shows that liquid silicate cannot remove volatile materials such as CO_2 [26].

PSA analysis

Table 4 displays the results of the PSA of the treated and untreated RHA at 1 M 2 H. The mean particle diameter decreased with the increase in treatment temperature. The mean particle diameter of H_3PO_4 at 2M 80 °C was recorded as the lowest as compared to other treatments.

Table 4. PSA data for treated and untreated RHA

Component	Untreated	Treated 1 M 60 °C	Treated 2 M 80 °C	Treated 3 M 60 °C
$D_{0.1}$	722.184	878.156	38.975	743.054
$D_{0.5}$	1165.935	1237.355	645.737	1168.995
$D_{0.9}$	1639.751	1645.679	1465.954	1642.913

Note: $D_{0.1}$, $D_{0.5}$, $D_{0.9}$ are the mean diameter for the smallest 10%, 50%, and 90% of the analyzed liquid silicate of untreated RHA, treated RHA at 1 M 60 °C, treated RHA at 2 M 80 °C and treated RHA at 3 M 60 °C.

The particle size was reduced after leaching with H_3PO_4 at 2 M 80 °C before the liquid silicate extraction process. This finding has proven that high temperature is suitable to produce a good small particle size. The temperature has a significant impact on particle size, with lower temperatures producing smaller particles with a larger surface area than higher temperatures [27]. As a result, as the particle size decreases, a greater proportion of the particles are found at the material's surface. Hence, acid leaching treatment is the most suitable method for extracting silica from the rice husk ashes for its application as a fertilizer.

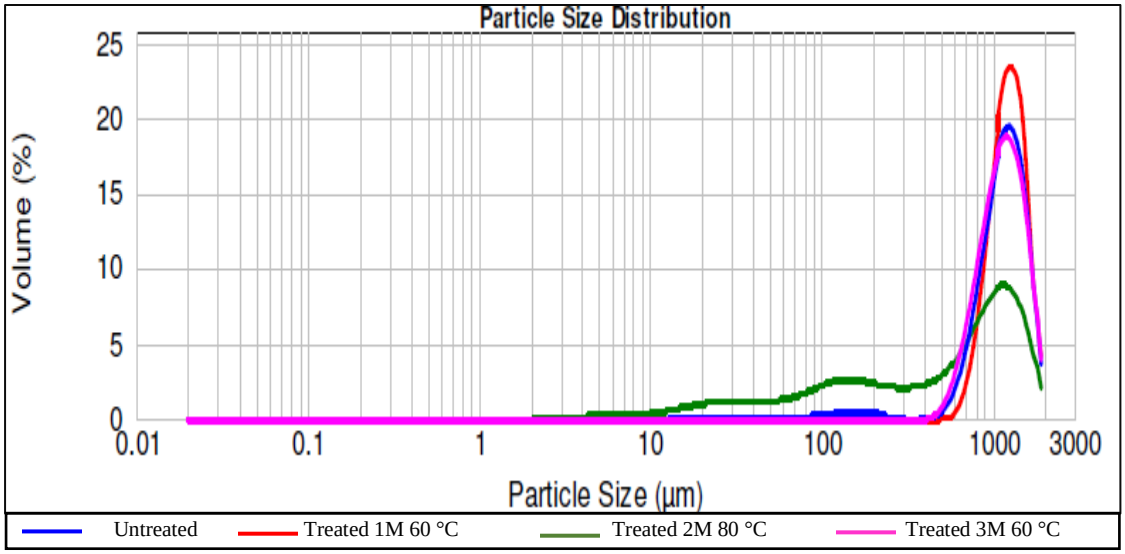

Figure 2. Particle size distributor of treated and untreated RHA at 1M 2H

All organic components dissolve in water, resulting in slow precipitation and small particles forming droplets. The removal of all organic compounds causes more silicate, iron, and potassium ions to be present. Hence, the high amount of silicate particles in the liquid silicate solution of treated RHA at 2 M 80 °C resulted in a decrease in the mean particle diameter.

Figure 2 demonstrates the comparison of particle size distributors between both treated and untreated RHA. As a result, the peak of the treated RHA at 2 M 80 °C was the broadest compared to the rest of the samples as a smaller particle size is preferable as a silicate particle. Besides, the rest of the peak only had a slightly different mean particle diameter. This proved that an acid-leaching treatment process somehow affects the formation of silicate particles.

Conclusion

The characterization of treated and untreated RHA via XRF spectroscopy, FTIR spectroscopy, and PSA of this study has demonstrated that acid leaching treatment using H_3PO_4 produces promising LSF as they contain silica, potassium, iron, and other trace elements, which are deemed to be suitable for plant growth. H_3PO_4 leaching treatment is significantly useful and effective in removing impurities and increasing the silica purity in RHA. Besides that, the alkaline extraction by 1M 2H KOH also exhibits the highest results of silica (40.91%), iron (46.40%), potassium (11.01%), and trace element (1.675%), respectively. These results are correlated with PSA and FTIR analysis. If RHA undergoes suitable treatment such as acid leaching treatment before the extraction process, it will produce high-quality LSF with the addition of other minerals such as iron and potassium.

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