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Extraction of Silica from Palm Ashvia Citric Acid Leaching Treatment

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ABSTRACT

Agricultural wastes such as palm ash and rice husk have a possibility to be used as a usefully renewable source for production of energy and silica (SiO_2). Extensive researches have been carried out to extract silica from agricultural wastes such as rice husk, due to silica as a useful raw material for industrial application. In the previous studies, the strong acid leaching treatment was carried out to remove metallic impurities and organics contained in rice husk. A strong acid leaching treatment, however, is significantly hazardous to the environment and people [1].In this study, the environmentally benign and economically effective process to produce SiO_2 materials from palm ash has been established by using citric acid leaching, not the conventional strong acids. Results showed that silica can be extracted from palm ash using citric acid leaching treatment under the optimum extracting conditions with 70^0C of solution temperature, 60 minutes of reaction time and concentration of citric acid of more than 2%. The purity of silica extracted is more than 90%.

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INTRODUCTION

Silicon dioxide (SiO_2) or commonly known as silica is one of the basic materials and the valuable inorganic multipurpose chemical compounds. Silica is occurring naturally as quartz, sand or flint. It can exist in gel, crystalline and amorphous forms. It is the most abundant material on the earth's crust. Nowadays, most silica was produced from quartz or sand by the extraction process. Sodium silicate, the precursor for silica production is currently manufactured by smelting quartz sand with sodium carbonate at 1300^0C [2].From this production of silica, it will be used to fulfil the requirement in its major applications such as for ceramic product, electronic component and additive in concrete. However, manufacturing of pure silica is energy intensive.

Silica also can be found in agricultural waste such as palm ash. The large amount of this waste can be a new source of silica production for this country. For example, According to the Malaysian Palm Oil Board, the amount of palm ash produce in Malaysia in 2007 approximately 3 million tons [3]. Even though the production of silica from the agricultural wastes are not much compared to the production from quartz or sand, it is still can be used to fulfil the industrial demands.

Leaching treatment is a proper route to extract the silica. Sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3) solutions are conventionally used in leaching treatment to prepare silica materials [1, 4]. Beside hazardous to the environment and humans, the strong acid leaching treatment also has an economical problem due to a necessary use of expansive materials with corrosion resistance to strong acid and a special disposal treatment of used strong acids.The objective of this study was to study the possibility in developing a method to extract and characterized raw silica from palm ash using organic acid leaching method.

MATERIALS AND METHODS

Palm Ash:

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Palm oil is an important export commodity in tropical countries and especially in Malaysia due to its wide spectrum of an acknowledged usability such as precursors of food products and biofuel. Extraction of the oil from fresh oil palm fruitlets requires separation of the fruitlets from empty fruit bunches prior to further processing. These empty fruit bunches, which consists of fibres and shells, are often used as boiler fuel by palm oil mill to produce steam for electricity generation and palm oil extraction [5]. Combustion produces approximately 5% of palm ash.

Typically, oil palm ash is characterized by a spongy and porous structure in nature, of which its main components are in the angular and irregular form, with a sizable fraction showing cellular textures [6].The main chemical composition of oil palm ash is silica. The ash produced sometimes varies in tone of colour from whitish grey to darker shade based on the carbon content in it.Because of limited uses for palm ash, it is currently disposed of as landfill; this could lead to environmental problems in the future.

Leaching Process:

Leaching generally refers to the removal of a substance from a solid via a liquid extraction media. The desired component diffuses into the solvent from its natural solid form. There are three important parameters in leaching which are temperature, contact time per area and solvent selection. The temperature can be adjusted to optimized solubility and mass transfer. Leaching can be divided into two categories which are percolation and dispersed solid. For percolation, the solvent is contacted with solid in a continuous or batch method and widely used for extreme amount of solids. In dispersed solids, the solid are usually crushed into small pieces before being contacted with solvent. In simple words, percolation is for liquid added into solid while dispersed solid is for solid added into liquid [1, 7-9].

Palm ash from local palm oil mill was used as raw materialsto produce silica materials. Citric acid powders were dissolved in the distilled water at the ambienttemperature to prepare citric acid solutions. 10 to 30 g palm ash (having a mean particle size of 75 µm) was put into 500 ml citric acid solution in beaker. The concentration and temperature of the citric acidsolution, and stirring time in the solution were selected as the operatingparameters. This is because the chelate reaction between–COOH groups and metallic impurities strongly depend on theabove parameters. The concentrationwas controlled from 1% to 6% by changing the mixing ratioof citric acid powders and distilled water. The beaker was placed on the hot plate magnetic stirrer), and the solution temperature was changedfrom 30^0C to 70^0C. The reaction time recorded was 30 to 90 minutes. After the acid leaching process, the water rinsing treatmentof the palm ash was carried out in the distilled water at room temperatureto remove the citric acid content from the ash. The materials were driedat 60^0C for 60 min in the oven, and thencombusted at 800^0C for 30 min in the tube furnace. The combustiontemperature of 800^0Cwas used in this study to prevent thecrystallization of amorphous silica contained in the ash[10]. The airflow rate in the combustion was set to 0.5 ml/s using a small air-compressor system.

The content of each ashes containing metallic oxideimpurity was measured by X-ray fluorescence spectroscopy (XRF). Identification the presence of certain functional group in the molecule was analysed by Fourier transform infrared spectroscopy (FTIR) and surface morphology was carried out by using scanning electron microscopy (SEM).

RESULT AND DISCUSSION

In this study citric acid is seen as a viable alternative to replace strong acid in the leaching process. This is because, as an organic acid, ithas low level of hazardous effect comparing to the usage of a stronger acid. This study is in line withother research all over the world that isfocusing on ways to establish environmentally benign process to produce silicafrom agricultural wastes.

Effect of Acid Concentration:

Acid concentration is one of the key factors in achieving good results in leaching treatment process. Table 1 shows the chemical compositions of treated palm ash via the citric acid solution leaching treatment with different concentrations. The solution temperature of acid citric was 70^0C, reaction time of 60 minutes and burned at 800^0C.

Table 1: Chemical compositions of palm ash via the citric acid solution leaching treatment with different concentrations.

Acid Concentration (%)	SiO_2	MgO	Al_2O_3	P_2O_5	K_2O	CaO	Fe_2O_3	Others
Palm Ash	45.50	3.20	5.40	5.38	23.30	12.80	3.26	1.16
1	66.70	6.00	-	2.88	12.00	6.62	4.10	1.70
2	89.00	1.00	-	-	4.22	1.30	2.55	1.93
3	92.00	-	-	-	3.58	1.22	2.13	1.07
4	92.00	-	-	-	3.56	0.85	3.07	0.52
5	92.00	-	-	-	3.54	0.80	2.97	0.69
6	92.00	-	-	-	2.84	1.00	2.53	1.63

As shown in Table 1, the purity of silica (SiO_2) dramatically increased from just 45.5% in palm ash up to 92% when employing the citric acid solution with a concentration of 2% and higher. The content of metal oxide impurities in palm ash also reduced when concentration of solution was increased.

Thus, it is shown in these figures that citric acid leaching treatment is significantly useful and effective to remove impurities and increased the purity of silica in palm ash. Organic acids such as citric acid have carboxyl groups and therefore can act as chelating agents. These carboxyl groups, tend to donate protons (H+), resulting in the negatively charged carboxyl group that is capable of forming stable complexes with several metal ions. The impurities were removed from the ash via chelate reaction between carboxyl groups (-CHOOH) and the metal elements [1]. Therefore it is possible that these negatively charged carboxyl groups are able to form stable complexes with Ca^+ and K^+cations present, resulting in their removal from the palm ash. Al_2O_3 and P_2O_5 have been completely removed from the palm ash using the citric acid solution with 2% or higher concentration. The content of K_2O and CaO also extremely reduced. The content of MgO in palm ash, however, was completely removed with concentration of 3% and higher.

Effect of Solution Temperature:

Table 2 shows the chemical composition of palm ash via citric acid solution treatment under different solution temperature. The solution of citric acid concentration of 3% and reaction time of 60 minutes were used.

Table 2: Chemical composition of palm ash via citric acid solution treatment under different solution temperature.

Solution Temperature (^{0}C)	SiO_2	MgO	Al_2O_3	P_2O_5	K_2O	CaO	Fe_2O_3	Others
30	87.00	1.80	-	-	4.96	1.35	2.78	2.11
50	90.00	1.20	-	-	4.17	1.07	2.43	1.13
70	92.00	-	-	-	3.58	1.22	2.13	1.07

Some investigators performed the leaching experiments at ambient temperatures. They states that temperatures tend to vaporize organic acids and water [11]. Table 2shows that, even 30^{0}C temperature leaching treatment is enough to remove Al and P impurities from palm ash.

The use of high temperatures can lead to an increase in the leaching performance as shown in Table 2, but the use of high temperatureswas seen to be limited with organic acidsdue to their low boiling temperatures and decompositions [11]. Table2 showed that with increase in the temperature, the content of impurities was decreased and the purification of palm ash silica (SiO_2) with 92% took place via the citric acid solution leaching at 70^{0}C.Furthermore, MgO content of the ashes decreased with rising temperature of solution. We conclude that using higher temperature in the process will improve the leaching result.

Effect of Reaction Time:

To find the effect of reaction time on the purity of silica powder, the reaction time was varied from 30 minutes to 90 minutes, while fixing the acid concentration (3%) and solution temperature (70^{0}C).The purity of silica increased with increasing of reaction time as shown in Table 3. When the reaction time increased from 30 minutes to 60 minutes, the purity of silica slightly increased by about 5%.However, no significant increase in silica purity was observed at longer reaction time than 60 minutes, so the reaction time of 60 minutes was confirmed to be the optimal reaction time.

Table 3: Chemical composition of palm ash via citric acid solution treatment under different reaction time.

Reaction Time (minute)	SiO_2	MgO	Al_2O_3	P_2O_5	K_2O	CaO	Fe_2O_3	Others
30	87.00	1.50	-	-	5.68	1.49	2.65	1.68
60	92.00	-	-	-	3.58	1.22	2.13	1.07
90	92.00	-	-	-	3.25	1.16	2.02	1.57

Fourier Transforms Spectroscopy (FTIR):

The silica powders obtained were confirmed by FT-IR examination in Figure 1. The absorption bands at 3445.01 and 1625.84 cm^{-1} were due to the H-O-H stretching and bending modes of the absorbed water, respectively. The peaks at 1099.00, 796.81 and 460.00 cm^{-1} were due to the asymmetric, symmetric and the bending modes of SiO_2 respectively [12].

In this study, hydrochloric acid solution is also used as the comparison in the leaching treatment. 2% and 3% of hydrochloric acid and citric acid solution was used. The temperature was controlled at 70^{o}C and 60^{o}C minutes reaction time.

Comparison FTIR patterns of palm ash and the products obtained in various stirring times and temperature using between citric acid and hydrochloric acid is shown in Figure 2. The transmittance peaks show silica element after leaching treatment between citric acid and hydrochloric acid is almost same because the transmittance peaks at (798 cm^{-1} - 778 cm^{-1}) was assigned as the Si-O stretching of quartz absence in the palm ash. It shows that it is possible to extract silica from palm ash using citric acid leaching method.

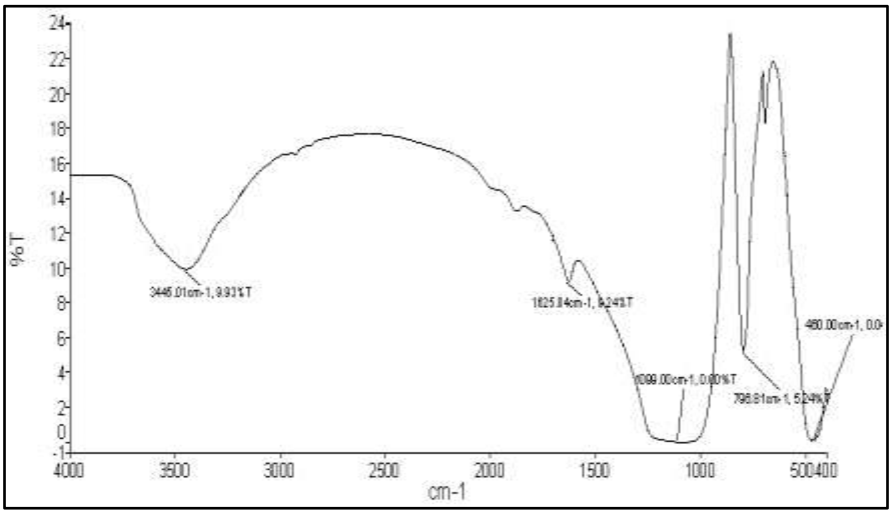

Fig. 1: Fourier transform infrared spectra of silica produced from palm ash.

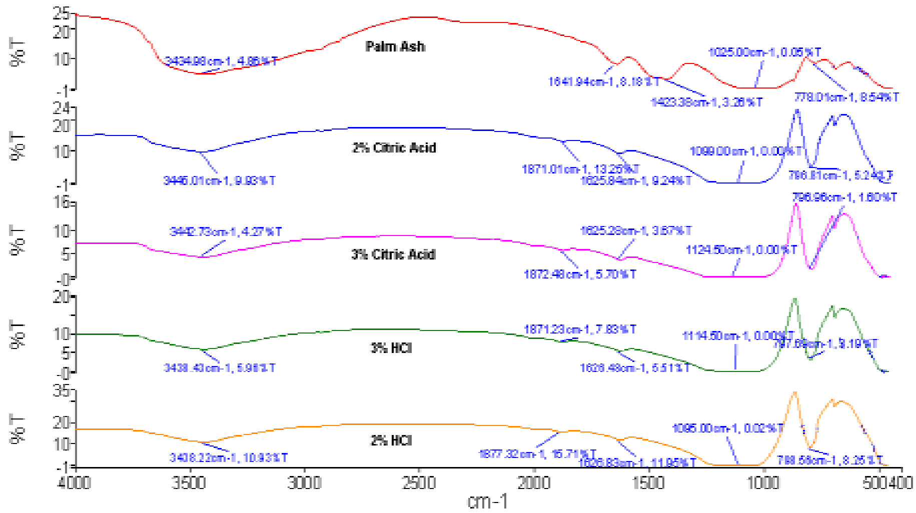

Fig. 2: Comparison FTIR patterns of palm ash and the products obtained in various stirring times and temperature using between citric acid and hydrochloric acid.

The colour of pulverised palm ash after citric acid leaching treatment was changed from dark grey to light creamy colour (Figure 3). Ash which has undergone maximum extent of combustion is highly desirable as it contains higher percentage of silica. It appears white-grey in colour when compared to the black coloured ash obtained from incomplete combustion. The carbon present is such ash hinders the main silica digestion reaction and may change the product characteristics (colour, etc) [13].

Fig. 4: Digital photo of palm ash (a) before (b) after citric acid leaching treatment.

Scanning Electron Microscopy (SEM):

Foo, K.Y. and Hameed, B.H. (2009) reported that the SEM micrograph for palm ash was evidenced consisting rather spherical particles with a median size of 183.0µm while medium and small particle ground palm ash were individually noted to contain crushed shape structures with a median of 15.9 µm and 7.4 µm [14]. Figure 5 shows that SEM micrograph images of the palm ash used in this research are in consistent which the research conducted by Foo, K.Y. and Hameed, B.H. (2009).

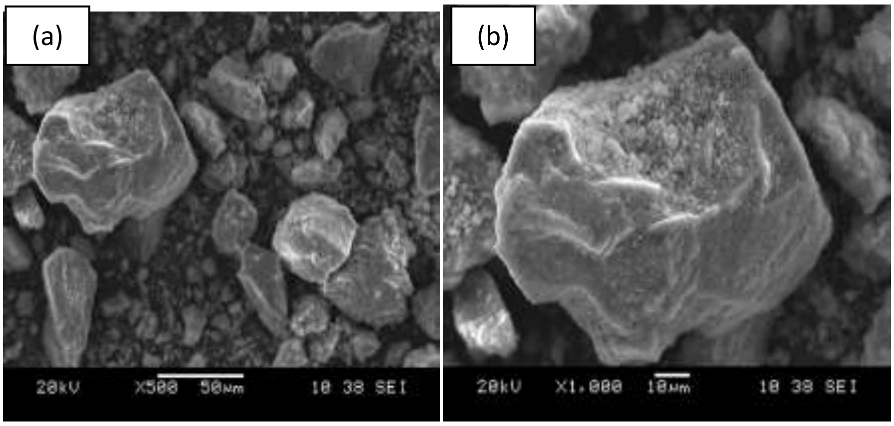

Fig. 5: SEM micrograph of palm ash raw material. (a) Magnification 500x (b) Magnification 1000x

After palm ash had been leached with citric acid (Figure 6 and 7), the particle became smaller with irregular and crushed shape. It is because the citric acid reaction was decomposed silica dioxide into the finer particle. Previous researchers reported on the morphology of raw material palm ash have found spongy and porous structures of varied shape [6]. Besides that, the particle shape of palm ash is characterized by irregular form with a sizeable fraction showing cellular textures. The images of silica grain at 3% citric acid concentration in Figure 7 are more porous than 2% citric acid concentration in Figure 6.

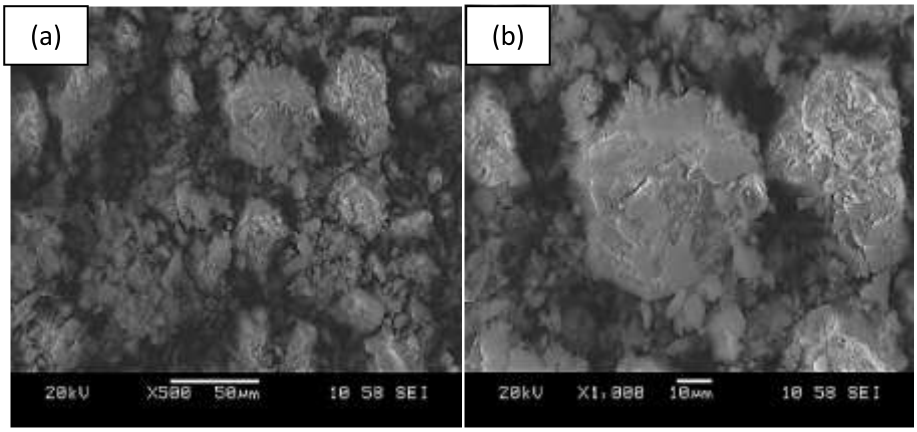

Fig. 6: SEM micrograph of palm ash after leaching treatment using 2 % citric acid (a) Magnification 500x (b) Magnification 1000x.

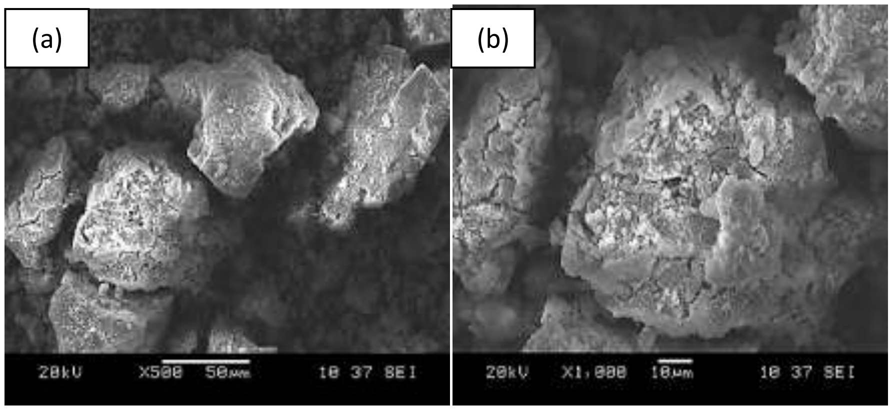

Fig. 7: SEM images of palm ash after leaching treatment using 3 % citric acid (a) Magnification 500x (b) Magnification 1000x.

Conclusion:

This study had shown that it is possible to extract silica from palm ash using organic acid leaching method. It consists of a citric acid leaching and air-combustion process. Citric acid leaching treatment is significantly useful and effective to remove the impurities and increased the purity of silica in palm ash. The purity of silica can reach up to 92% under the optimum extracting conditions which were $70^{0}C$ of solution temperature, 60 minutes of reaction time and concentration of citric acid is more than 2%.

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