Citric Acid Leaching Process for Silica Extracted from Oil Palm Ash for Zeolite Synthesis

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LIST OF ABBREVIATIONS

Al	Alumina
Al_2O_3	Aluminium Oxide
ASTM	American Society for Testing and Materials
BET	Brunauer, Emett and Teller
Ca	Calcium
CaO	Calcium Oxide
CEC	Cation Exchange Capacity
DSP	Desilication Product
EDX	Energy-Dispersive X-Ray Spectroscopy
Fe_2O_3	Iron Oxide
FTIR	Fourier Transform Infrared Spectroscopy
G	Gismondine
H	Hour
K	Potassium
K_2O	Potassium Oxide
LOI	Lost On Ignition
M	Molar
Mg	Magnesium
MgO	Magnesium Oxide
Na	Sodium
NaOH	Sodium Hydroxide
Q	Quartz
SEM	Scanning Electron Microscopy

Si	Silica
SiO_2	Silicon Oxide
TEOS	Tetraethylorthosilicate
XRD	X-ray Diffraction
XRF	X-ray Flouresence

Proses Larutlesap Silika daripada Abu Kelapa Sawit menggunakan Asid Sitrik untuk Pensintesan Zeolit

ABSTRAK

Hasil buangan pertanian seperti abu kelapa sawit mempunyai kemungkinan untuk digunakan sebagai sumber penghasilan tenaga diperbaharui dan silika (SiO_2). Kajian lanjut telah dijalankan untuk mengekstrak silika daripada sisa pertanian kerana silika merupakan bahan mentah yang berguna untuk aplikasi industri. Abu kelapa sawit terhasil daripada proses pembakaran sisa kelapa sawit seperti serat, tempurung dan tandan kelapa sawit. Abu kelapa sawit mengandungi sejumlah besar silika. Kajian ini telah dilaksanakan untuk mengekstrak silika daripada abu kelapa sawit menggunakan asid sitrik melalui proses larutlesap. Kesan keadaan tindak balas seperti kepekatan asid (1 hingga 6 %), masa tindak balas (30 hingga 180 minit), suhu (30 hingga 90 °C) dan nisbah pepejal/cecair (1:50 – 1:10) kepada proses larutlesap telah dikaji. Kemudian, kesan setiap parameter ini terhadap proses larutlesap dianalisa menggunakan XRF, FTIR, XRD dan SEM. Keadaan pengekstrakan optimum dicapai pada kepekatan asid sitrik 3%, suhu larutan 70 °C, tindak balas selama 60 minit dan nisbah pepejal/cecair 1:25. Keputusan XRF menunjukkan bahawa silika dapat diekstrak dari abu sawit menggunakan proses larutan asid citrik. Ketulenan silika yang diekstrak adalah 92%. Ujian awal telah dijalankan untuk mengkaji kemungkinan pensintesan zeolit menggunakan silika yang telah diekstrak daripada abu kelapa sawit. Pensintesan zeolit telah dilakukan di bawah keadaan hidroterma dengan pengaktifan menggunakan larutan natrium hidroksida. Pelbagai parameter eksperimen, seperti kepekatan alkali (1 hingga 4 M), masa tindak balas (6 hingga 24 jam) dan suhu (40 hingga 100 °C) telah dikaji. Sifat-sifat zeolit yang disintesis dinilai menggunakan XRF, XRD, SEM dan CEC. Keputusan menunjukkan bahawa keadaan optimum untuk mensintesis zeolit menggunakan silika yang diekstrak daripada abu sawit terawat telah dicapai dengan kepekatan alkali lebih daripada 2 M, 12 jam tindak balas dan suhu 80°C. Keputusan XRD menunjukkan bahawa Zeolit gismondine ($CaAl_2Si_2O_8 \cdot 4(H_2O)$) adalah dominan dalam semua produk sebagai fasa utama, manakala kuarza ditemui sebagai fasa minor. Hasil kajian mendapati zeolit boleh disintesis dengan menggunakan bahan-bahan kos rendah seperti abu kelapa sawit terawat.

Citric Acid Leaching Process for Silica Extracted from Oil Palm Ash for Zeolite Synthesis

ABSTRACT

Agricultural wastes such as oil palm ash have a possibility to be utilized as a useful renewable source for production of energy and silica (SiO_2). Extensive researches have been carried out to extract silica from agricultural wastes, due to silica as a useful raw material for industrial application. Oil palm ash is one of the waste material from the palm oil industry where is was obtained from the burning process of solid waste such as empty fruit bunch, shell and fiber. Oil palm ash contains a large amount of silica. This study has been conducted to extract silica from palm ash by removing impurities using citric acid via leaching process. Various experimental parameters, such as acid concentration (1 to 6 %), reaction time (30 to 180 minutes), leaching temperature (30 to 90 °C) and solid/liquid ratio (1:50 – 1:10) were investigated. Then, the effect of each parameter towards extraction process was evaluated using XRF, FTIR, XRD and SEM. The optimum extracting condition was achieved at 3% concentration of citric acid, 70°C of solution temperature, 60 minutes of reaction time and 1:25 ratio of solid/liquid. XRF results show that the content of silica in treated palm ash can reach up to 92% after citric acid leaching treatment. The transmittance peaks at 798 - 778 cm^{-1} show that silica element is absent in the treated palm ash. Preliminary tests have shown that there is a possibility of using silica extracted from palm ash to synthesize zeolite. The zeolite synthesis was carried out under hydrothermal conditions by activation with sodium hydroxide solution. The parameters that have been studied were alkali concentration (1 to 4 M), reaction time (6 to 24 hours) and reaction temperature (40 to 100 °C). The properties of zeolite synthesized was evaluated using XRF, XRD, SEM and CEC. The results indicated that the optimum condition to synthesize zeolite by using silica extracted from palm ash was achieved with alkali concentration of 2 M, after 12 hours reaction time and reaction temperature of 80°C. Phase analysis by x-ray diffraction show that the zeolite gismondine ($CaAl_2Si_2O_8 \cdot 4(H_2O)$) was dominant in all products as major constituent phase, whereas quartz was found as minor phase, while the highest CEC value obtained was 100 meq/100g. The outcomes have significant motivation for the production of zeolites by using low cost material such as treated oil palm ash.

CHAPTER 1

INTRODUCTION

1.1 Research Background

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 in the earth's crust. Nowadays, most silica was produced from quartz or silica sand by the extraction process. For this production of silica, it was used to fulfil the requirement in its major applications such as for ceramic product, electronic component, additives in concrete, pharmaceuticals, cosmetics and detergents industries as a bonding and adhesive agents. Silica also has been utilized as a major precursor for a mixture of inorganic and organometallic materials which have applications in synthetic chemistry as catalysts and in thin films or coatings for electronic and optical materials (Ayegba, 2015).

Most of the industries require high purity silica, currently produced by smelting quartz in a high temperature furnace. Tetraethylorthosilicate (TEOS), sodium silicate, and tetramethylorthosilicate are widely used for production of commercial silica. These compounds can have a negative impact on health (Novie Permatasari *et. al.,* 2016). Furthermore, these conventional practices are really expensive and energy intensive (Khushboo *et. al.,* 2013). Thus, further approaches to find the source of silica that is safer, cheaper and more environmentally friendly is inevitable.

Silica which is abundant in soil and rock can also be transmitted to the tissue of root plants. A large amount of silica has been extracted from various types of agricultural waste such as rice husk ash, rice hull ash and bagasse ash (Khushboo *et. al.*, 2013). Several techniques such as acid leaching or by gasification of rice hull with a pilot flame in a modified fluidized bed as well as by burning the rice hull ash at high temperature have been reported for the extraction of silica (Hariharan & Sivakumar, 2013). The large amount of agricultural waste can be a new source of silica production in this country. Therefore, recycling waste and recreating it into a high-value material are important because it not only beneficial for the environment but also as promising resource (Novie Permatasari, 2016).

Palm oil is an important export commodity in Malaysia due to its wide variety of acknowledged usability such as precursors of food products and biofuel. After the separation of fresh oil palm fruitlets from fruit bunches, further processing will be carried out to extract the palm oil from fruitlets. These empty fruit bunches, which consist of husk of oil palm and palm kernel shell are often used as boiler fuel by palm oil mill plants to produce steam for electricity generation and palm oil extraction (Chun, 2008). The ash produced after the combustion is called palm ash.

Utilization of oil palm ash is minimal and unmanageable, while its quantity increases annually and most of the oil palm ash are disposed of as waste in landfills causing environmental and other problems. Waste disposal from palm oil mills in Malaysia is one of the main environmental challenges for industries after meeting the demand for oil at domestic and global levels. This waste materials in large quantities can create a serious environmental problem. Hence, there is a need to adopt proper strategy to reduce the waste (Vaibhav et. al. 2014).

Palm ash is one of the agro waste ashes whose chemical composition contains a large amount of silica (Tangchirapat *et. al*, 2007). Due to the high silica content in the palm ash, its utilization as a raw material for the production of silica is an interesting issue at this time.

Extensive researches have been carried out for past 10 years to extract silica from agricultural wastes, because silica is a useful raw material for industrial application (Thuadaij & Nuntiya, 2008; Umeda & Kondoh, 2008; Adam *et. al.*, 2008; Adam *et. al.*, 2011; Ding & Su, 2012; Li *et. al.*, 2011; Ang *et. al.*, 2012; Zulkifli *et. al.*, 2012; Hariharan & Sivakumar, 2013; Gu *et. al.*, 2013; Noushad *et. al.*, 2014; Kongmanklang & Rangsriwatananon, 2015; Kumar *et. al.*, 2015). The silica content will be extracted from the agricultural wastes by removing the organic matter by using an acidic solution.

1.2 Problem Statement

In the previous studies (Umeda *et. al.* 2009; Hariharan & Sivakumar, 2013; Kumar *et. al.*, 2015), the strong acid leaching treatment was carried out on rice husk to remove metallic impurities and organics contained in them. The problem is most of leaching treatment was used strong acid such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3) as the extraction media. Although sulphuric and hydrochloric acids generally appear to be the most promising leaching agents, but these acids are not biodegradable, their leakage into the environment is a concern with regard to causing secondary pollution (e.g. sulphuric acid can cause respiratory problem). While nitric acid cannot be used due to severe regulation of the nitrogen content in water (Huang, *et. al.,* 2011).

In this study, a process to produce silica from agricultural waste has been established using the citric acid leaching treatment. Citric acid is a natural chelating agent containing three carboxylic groups and one hydroxyl group, which can form stable chelates with metal elements (Huang, *et. al.,* 2011). The advantages of the citric acid is that its environmentally benign characteristics and abundance in nature. Umeda & Kondoh (2008) has shown in their studies that high purity of silica can be produced using organic acid solution leaching treatment.

Since the main chemical composition of treated palm ash is silica, it has great similarities with raw materials typically been used as starting materials for synthetic zeolites. The inspiration for using silica extracted from oil palm ash as the forerunner in the synthesis of zeolites is motivated by many elements, such as the abundance in quantity, less costly to produce and minimal required ingredients for processing. With the intention to reduce costs, zeolites researches are seeking cheaper aluminosilicate bearing precursors, such as oil palm ash, to produce synthetic zeolites. However, a limited number of papers published to date have reported on using silica extracted from oil palm ashes to synthesize zeolite.

1.3 Objectives of the Research

The objectives of this study are:

1 To extract silica from oil palm ash using citric acid leaching process.

2 To study the influence of reaction conditions i.e: reaction time, acid concentration, temperature and solid/liquid ratio on the citric acid leaching process.

3 To determine the physical properties of silica extracted from the citric acid leaching method.

4 To synthesize zeolite from extracted silica using an alkaline hydrothermal treatment process.

1.4 Scope of Research

The major aim of the study is to extract silica from oil palm ash using citric acid leaching treatment and to look into the suitability of extracted silica as precursor to synthesize zeolites by alkaline hydrothermal treatment.

In this study, extraction of silica from oil palm ash was carried out via a leaching process with a citric acid solution. Various experimental parameters, such as acid concentration (1 to 6 %), reaction time (30 to 180 minutes), leaching temperature (30 to 90 ^{o}C) and solid/liquid ratio (1:50 – 1:10) were investigated. The chemical compositions of each ashes measured by X-ray fluorescence spectroscopy (XRF). Identification of mineral phases and the presence of certain functional group in the molecule was analysed by X-ray diffraction and Fourier transform infrared spectroscopy (FTIR) respectively, while surface morphology was carried out using scanning electron microscopy (SEM).

Zeolite synthesis was carried out under hydrothermal condition by activation with sodium hydroxide (NaOH) solution. In this study, 20 g of extracted silica was mixed with NaOH solution, then the mixture was aged, crystallised and the solid product recovered for later study. Various experimental parameters, such as alkali concentration (1 to 4 M), reaction time (6 to 24 hour) and temperature (40 °C to 100 °C) were investigated. At the end of the process, the solid is separated by filtration, washed several times with distilled water and then dried overnight at 60 °C. The synthesized products were characterized using XRD (identification of phases) and XRF (chemical composition), SEM (surface morphology) using standard procedures. The product synthesized was also evaluated in terms of cation exchange capacity (CEC) value. Figure 1.1 illustrates the schematic diagram of the overall experimental work.

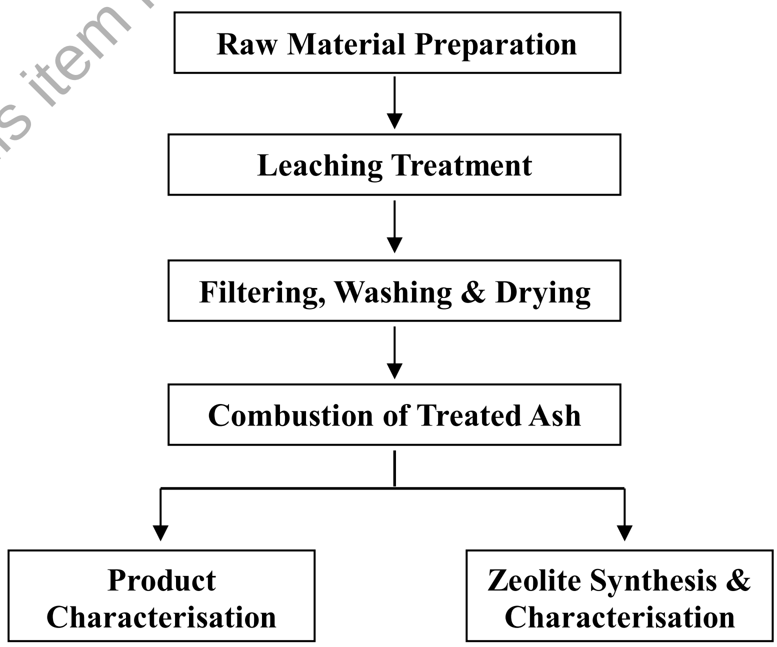

Figure 1.1: Schematic Diagram of the Experimental Work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter present background of silica and the related studies from other researchers regarding the extraction of silica from agricultural wastes. Extensive researches have been carried out to extract silica from agricultural wastes, because silica is useful raw materials for industrial uses. In the previous studies, strong acid leaching treatment was carried out on rice husks to remove metallic impurities and organics contained in them. Sulphuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3) solutions are conventionally used in leaching (Rajesh Ghosh, 2013). In this research, the environmental friendly and non-hazardous process to produce high-purity silica from palm ash has been established by using citric acid leaching treatment. Lastly, the chapter ends with quick reviews of synthesis of zeolite by hydrothermal treatment of treated palm ash.

2.2 Silica

Silica is synonymous with silicon dioxide (SiO_2), one of the most widely used industrial compounds and it can be considered the most important material in the manufacture of glass and ceramics. It is composed of the two most abundant elements on earth, silicon and oxygen. It also happens to be the basic building block for all