Faculty of Engineering

INVESTIGATION ON THE EFFECTIVENESS OF BIO-SILICA PRODUCED FROM SARAWAK BARIO RICE HUSK ASH (BRHA) AS SORBENTS

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Bachelor of Engineering with Honours

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This final year project report entitled **"Investigation on the Effectiveness of Bio-Silica Produced from Sarawak Bario Rice Husk Ash (BRHA) as Sorbents"** prepared by Patrick Anak Ajai (45974) as a KNC 4344 Final Year Project 2 course fulfillment for the Degree of Bachelor of Engineering with Honours (Chemical Engineering) is hereby read and approved by:

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INVESTIGATION ON THE EFFECTIVENESS OF BIO-SILICA PRODUCED FROM SARAWAK BARIO RICE HUSK ASH (BRHA) AS SORBENTS

PATRICK ANAK AJAI

A dissertation is submitted in partial fulfillment
of the requirements for the degree of
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Dedicated to my beloved parents, who always bestow me sustainable motivations, supports, and encouragements

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ABSTRACT

There are abundant of biomass wastes produced from paddy-based agricultural industries. For instant, most of the rice-producing countries will normally burn or dump the rice husk as wastes. This has led to increasing in many environmental problems such as greenhouse effects and pollutions. As rice husk wastes are rich in silica, as proven by many research analysis, this study aims to investigate the potential of bio-silica extracted from Sarawak Bario rice husk ash (BRHA) as sorbents for the absorption of moisture as well as adsorption of dyes and heavy metals at both laboratory and industry scales. Besides, as the conventional manufacturing (smelting) process of pure silica from natural quartz uses intensive energy up to 1300°C, this research work analyzes the capability of the extracted bio-silica produced at lower combustion temperatures to minimize the energy consumption. The collected raw material, which is the Bario Rice husk (BRH), initially undergoes acid pre-treatment using 1M hydrochloric acid (HCl) to remove the available impurities and increase the silica yield in the extraction process. The husks are then combusted at five different combustion temperatures; 400°C, 500°C, 600°C, 700°C and 800°C, before they undergo the silica extraction process in which the BRHA produced are gelified and aged at four different aging periods of 4, 6, 12 and 18 hours to produce the bio-silica sorbents. Several characterization analysis were carried out to determine the physicochemical properties of BRHA and chemical properties of produced bio-silica sorbents. This analysis includes colour analysis, weight loss analysis, Fourier Transform Infrared (FTIR), Brunauer-Emmet-Teller (BET), and X-ray diffraction (XRD). Lastly, several capability tests are conducted to test for the effectiveness of the produced bio-silica sorbents for the absorption of moisture and adsorption of dyes and heavy metals at both laboratory and industry scales.

Keywords: Bario Rice Husk, Bio-Silica, Colour Analysis, Weight Loss Analysis, FTIR, BET, XRD, Moisture Absorption, Dyes Adsorption, Heavy Metal Adsorption

ABSTRAK

Terdapat banyak sisa biomas yang dihasilkan daripada industri pertanian berasaskan padi. Untuk segera, kebanyakan negara pengeluar beras biasanya membakar atau membuang sekam padi sebagai sisa. Ini telah menyebabkan peningkatan dalam banyak masalah alam sekitar seperti kesan rumah hijau dan pencemaran. Seperti sisa sekam padi kaya dengan silika, seperti yang terbukti dengan banyak kajian penyelidikan, kajian ini bertujuan untuk mengkaji potensi bio-silika yang diekstrak dari serbuk sekam padi Bario (BRHA) sebagai sorben untuk penyerapan kelembapan serta penjerapan pewarna dan logam berat di kedua-dua makmal dan skala industri. Selain itu, proses pembuatan silika tulen yang dihasilkan daripada kuarza semula jadi menggunakan tenaga intensif sehingga 1300°C, kerja penyelidikan ini menganalisis keupayaan bio-silika yang diekstrak pada suhu pembakaran yang lebih rendah untuk meminimumkan penggunaan tenaga. Bahan mentah yang dikumpul, yang merupakan sekam padi Bario (BRH), pada awalnya menjalani rawatan pra-asid menggunakan asid hidroklorik 1M (HCl) untuk menghilangkan kekotoran yang ada dan meningkatkan hasil silika dalam proses pengekstrakan. Sekam kemudian dibakar pada lima suhu pembakaran yang berlainan; 400°C, 500°C, 600°C, 700°C dan 800°C, sebelum mereka menjalani proses pengekstrakan silika di mana BRHA dihasilkan sebagai jel dan menjalani tempoh penuaan yang berbeza iaitu 4, 6, 12 dan 18 jam untuk menghasilkan penyerap bio-silika. Beberapa analisis pencirian telah dijalankan untuk menentukan sifat-sifat fizikokimia BRHA dan sifat-sifat kimia silikon bio-silika yang dihasilkan. Analisis ini termasuk analisis warna, analisis penurunan berat, Fourier Transform Infrared (FTIR), Brunauer-Emmet-Teller (BET), dan X-ray difraksi (XRD). Akhir sekali, beberapa ujian keupayaan dijalankan untuk menguji keberkesanan sorben bio-silika yang dihasilkan untuk penyerapan kelembapan dan penjerapan pewarna dan logam berat di kedua-dua makmal dan skala industri.

Kata kunci: Sekam Padi Bario, Bio-Silica, Analisis Pewarna, Analisis Peurunan Berat, FTIR, BET, XRD, Penyerapan Kelembapan, Penyerapan Pewarna, Penyerapan Logam

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ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
BET	Brunauer-Emmett-Teller
BRH	Bario Rice Husk
BRHA	Bario Rice Husk Ash
Cd	Cadmium
CO_2	Carbon dioxide
FTIR	Fourier Transform Infrared
H_2O	Water
H_2SO_4	Sulphuric acid
H_3BO_3	Boric acid
HCl	Hydrochloric acid
HNO_3	Nitric acid
KBr	Potassium Bromide
Mg	Magnesium
Na_2SiO_3	Sodium silicate
NaCl	Sodium chloride
NaOH	Sodium hydroxide
No.	Number
Pb	Lead
pH	Potential of hydrogen
$Si(OH)_4$	Silicic acid
SiO_2	Silica dioxide
Si-O-Si	Bio-silica
TGA	Thermogravimetric
UV	Ultra Violet
XRD	X-Ray Diffraction
λ	Lambda

NOMENCLATURE

kg	Kilogram
^{o}C	Degree Celcius
hr	Hour
ton/ha	Tonne per hectare
%	Percentage
^{o}F	Degree Farenheit
N	Normality
M	Molarity
m	Metre
g	Gram
cm^{-1}	Per centimeter
m^2/g	Metre square per gram
cm^3/g	Centimeter cube per gram
rpm	Revolution per minute
ml	Milliliter
µm	Micrometer
$^{\circ}Cmin^{-1}$	Degree celcius per minute
mg	Milligram
°	Degree
mg/L	Milligram per liter
ppm	Parts per million

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The world population has grown tremendously over the past few decades. Food drives the world and this makes agriculture as one and most significant industry worldwide. An agricultural productivity is crucial not only due to country's balance of trade but the security and health of its population as well. This century portrays a significant switch from fossil fuel to the bio-based economy with agriculture as one of the leading sources of biomass feedstocks for renewable bio-products such as bioenergy and biomaterials. According to Selvakumar et al. (2014), biomass is considered as one of the renewable energy sources in the industrialized country. The large volume of biomass can be converted to a huge amount of energy and raw materials.

Southeast Asia is a big producer of paddy which produces a large number of biomass residues. The countries include Myanmar, Vietnam, Laos, Cambodia, Thailand, Brunei, Indonesia and Malaysia**.** Malaysia is one of the main rice producers whereby the annual production had increased from 1,588,456 tonnes in 2010 to 1,685,236 tonnes by 2013 (World Rice Production, 2017). Therefore, a proper waste management must be performed as the agro wastes may lead to many environmental problems.

According to Mohanta et al. (2012), for every 1,000kg of paddy milled, about 220 kg of husk is produced. This thus clearly shows that abundant of biomass wastes are produced from paddy agricultural activities. Most of the rice-producing countries will normally burn or dump the rice husk as wastes. These have led to environmental problems such as greenhouse effect and environmental pollution. Therefore, many research activities have been actively conducted to maximize the use of rice husk wastes to produce beneficial and useful products, thus minimizing the environmental adverse effect (Selvakumar et al., 2014).

One of the potential research is to study the extraction of bio-silica from Bario rice husk. Bio-silica is a type of desiccative made from biomass agro wastes which are harmless to the environment. Nowadays, there are many applications of bio-silica especially in building construction, marine environments, and nuclear power plants. Besides, bio-silica is also widely used in rubber industries as reinforcing and cleansing agents whereas in the food industries it is commonly used as an anti-cracking agent.

1.2 Problem Statement

Malaysia is a well-known country for its agricultural economy in producing rice. Due to this, there are abundant of rice husk wastes produced throughout the annual paddy production. Most of the time the rice husks are discarded at the dumping site and burned as they are not profitable. Generally, rice processors and farmers often burn the rice husk as wastes and this releases carbon dioxide, CO_2 into the atmosphere. The increase of carbon dioxide gas volume in the atmosphere causes global warming, commonly known as greenhouse effect as well as air pollution. However, recently, the rice husk biomass is used to produce marketable products as it has potential to be used as materials valorization for minerals. According to Madrid et al. (2012), thermal valorization is preferred to produce a silica-rich ash via calcination process to be used as pollutant absorbers or absorbents. Converting the biomass to marketable products does not only provide profits but it also helps to maintain the environment.

A study conducted by Syuhadah and Rohasliney (2012) confirmed that agro-wastes produced from rice husks have capabilities to be converted into bio-silica absorbent and this provides advantages to the environment as large volume of rice husk can be utilized to produce absorbents. Besides, according to Faizul et al. (2013), the manufacturing pure silica by smelting natural quartz sand with sodium carbonate uses intensive energy up to the temperature 1300^{o}C. This high energy consumption could be reduced if the silica is produced from natural biomass wastes (Kero et al, 2015). Hence, the production of bio-based silica from agro-wastes is proposed with the aim to minimize the energy consumption.

According to Syuhadah and Rohasliney (2012), a proper research must be performed to fully utilize the agriculture wastes. The abundance and availability of agricultural by-products such as rice husk make them the good sources of cheap raw material for many silica applications. While there is a limited study conducted on BRH wastes from Sarawak agricultural industries, this research work will explore the extraction of bio-silica from BRHA and test its capability as a sorbent in several applications.

1.3 Aim of Research

The research's aim is to study the extraction of bio-silica from Sarawak Bario rice husk waste ash (BRHA) and its effectiveness as moisture absorbent as well as dye and heavy metals adsorbents through both laboratory and industry tests.

1.4 Scope of Research

The research used Sarawak Bario rice husks (BRH) as raw materials which are collected from Rice Mill Bario Ceria Sdn. Bhd. This research was conducted at Bio-Process laboratory at the Department of Chemical Engineering and Energy Sustainability and Plantation Ecology Laboratory at Faculty of Resource and Science Technology. The BRH is combusted in a furnace at varying temperatures of 400^{o}C, 500^{o}C, 600^{o}C, 700^{o}C, and 800^{o}C. BRHA produced after the combustion process is characterized and analyzed for its chemical and physical properties. Physical properties analysis includes weight loss analysis and colour analysis while chemical properties analysis includes FTIR and BET. After that, BRHA undergoes gelification process to extract the silica and then aged in an oven at 130^{o}C for four different aging periods; 4, 6, 12, and 18 hours. The extracted and treated bio-silica sorbents are characterized using FTIR, BET and XRD. The effectiveness of produced bio-silica sorbent is tested based on its capability to absorb moisture and adsorb dyes and heavy metals through both laboratory and industry tests.

1.5 Objectives of Research

The objectives of the research are outlined as followed;

i. **To analyze the relationship between the combustion temperatures and amount of silica in the burnt ash as well as its chemical and physical properties via characterization analysis**

   BRH is collected from local industry and burnt into ash at varying combustion temperatures of 400ºC, 500ºC, 600ºC, 700ºC, and 800ºC. The BRHA are analyzed by colour analysis, weight loss analysis, FTIR, and BET.

ii. **To produce bio-silica sorbents from BRHA and characterize its chemical properties via characterization analysis**

   BRHA undergoes gelification to produce bio-silica via silica extraction method. Then, the produced bio-silica sorbents are aged in oven operated at 130ºC at four different aging period of 4, 6, 12 and 18 hours. The treated bio-silica sorbents are analyzed by using FTIR, BET, and XRD to study its chemical properties.

iii. **To investigate the effectiveness of the produced bio-silica sorbents for the absorption of moisture as well as adsorption of dye and heavy metals via the laboratory and industry tests**

   The capability tests include moisture absorption as well as dyes and heavy metals adsorption tests. Moisture absorption and dyes adsorption tests are carried out at laboratory scale only while heavy metals adsorption test is carried out at both laboratory and industry scales whereby the wastewater was obtained from the Taiyo Yuden Company.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides an explanation on the availability of raw material, the bio-silica extraction steps and the characterization analysis related to the research study.

2.2 Overview of Bario Rice Husk in Sarawak

Malaysia is one of largest agricultural countries in producing rice in the world. According to World Rice Production (2017)**,** the annual rice production by Malaysia is about 1, 820, 000 metric tonnes in year 2017. According to Fallis (2013), Sarawak has the potential to produce up to 6 tonnes per hectare of paddy per season with 36.67 tonnes per hectare of paddy husk. In Sarawak, Bario rice is well known grown in several areas of Bario, Ba'kelalan, Long Semadoh and Long Bawang.

2.2.1 Background of Bario Rice

According to Slow Food (2017), Bario rice is a local product which is originated in the Kelabit Highlands and located in northeast Sarawak, Malaysia. Bario rice is also called as Bareo or Adan rice which is cultivated by hand with no pesticides or herbicides. Bario Rice takes about six months to mature and only one crop can be planted annually. **Figure 2.1** shows the Bario rice that is cultivated over 1000 metres above the sea level and has cool day temperatures ranging from 19^{o}C to 22^{o}C. In addition, Bario rice is a special product due to its excellent sweet taste, fine grains, slightly sticky textures, and classified as medium grain rice size with marble white in colour (State Farmer's Organisation Sarawak, 2017).

Figure 2.1: Bario rice (Borneo Today, 2016)

2.2.2 Bario Rice Plantation

According to Fallis (2013)**,** the plantation of Bario rice within Sarawak includes the areas of Bario, Ba'kelalan, and Krayan. The area of the plantation is at an elevation range from 450 m to 1100 m above sea level. **Figure 2.2** shows the plantation of Bario rice at Bario Highlands in Sarawak.

Figure 2.2: Bario rice plantation (Rustic Borneo, 2017)

2.2.3 Production of Bario Rice

According to Abdullah and Asrina (2015), the current potential production of Bario rice is about 1.5 to 3.5 ton/ha. The variety is planted twice a year in July and January. The is very limited study conducted on the land for this rice production.

2.2.4 Rice Husk Waste

Rice husk or known as rice hull is defined as the by-product produced in the paddy mills. According to Pandey et al. (2012)**,** rice husk is usually separated from the rice itself and it is the outermost part of rice paddy which covers about 16% to 25% by weight. To be specific 1 ton of paddy rice could produce about 220kg of rice husk in most of the paddy mills (Abedin & Das, 2014)**.** Globally, the annual production of rice paddy is approximately about 600 million tons. On average 20% of the paddy is a husk, the estimated annual production of husk is around 120 million tons (Mohanta et al., 2012).

Currently, the rice husk produced from majority of rice mill industries is either burnt or dumped into the environment**.** Mohanta et al. (2012**)** stated that disposal of husk causes damage to land especially to the area where it is dumped. Same goes for BRH where the husk wastes contribute to pollution due to improper disposal. However, the researchers came up with an idea to utilize the huge amount of rice husk as it has a great potential to be used as raw material in generating electricity (Abedin & Das, 2014). According to Mohanta et al. (2012)**,** rice husk by-product can be transformed into the valuable material in many industrial applications due to the presence of a large amount of silica. Based on the chemical composition of rice husk ash as shown in **Table 2.1**, silica compound records the highest percentage (Química et al., 2011). However, the composition of Bario rice husks is yet to be known and will be further explored in this research.

Table 2.1: Composition of rice husk ash on dry basis (Química et al., 2011)

Compound	Percentage, %
Silica (SiO_2)	82.6
Alumina (Al_2O_3)	0.4
Ferric Oxide (Fe_2O_3)	0.5
Calcium Oxide (CaO)	0.9
Potassium Oxide (K_2O)	1.8
Manganese Oxide (MnO)	0.3
Sodium Trioxide (SO_3)	< 0.1
Magnesium Oxide (MgO)	0.7
Potash (P_2O_5)	0.9
Loss on Ignition	11.9

2.3 Silica

Silica or known as silicon dioxide is a naturally occurring mineral composing of silicon, Si, and oxygen, O_2. Silica compound is one of the most abundant compounds on earth, which is quartz, and it is the major component of making glass. According to Takaran et al. (2015), silica has nine different forms of crystalline with three main major forms of quartz. The most common are tridymite and cristobalite, for semi-precious stone are agate, onyx, and carnelian, granular varieties are jasper and flint, and diatomite and opal are in anhydrous forms. Many industries use silica due to its chemical and physical properties such as for colour, melting and boiling point, reactivity and hardness. Among the applications of silica are for building materials, abrasives, filters, dye water filtration and electronic components. Silica is crystallized mineral in solid form under normal conditions of pressure and temperature as shown in **Figure 2.3**.

Figure 2.3: Pure silica (Nejlepšíceny, 2017)

Based on Mohs scale, the hardness of silica is 7 whereas diamond is 10 which indicates that silica is categorized as one of the hardest material on earth. Besides, the melting and boiling points of silica are 3110^{o}F and 4046^{o}F respectively (Study.com, 2017). Thus, intensive energy is required to smelt the quartz in order to produce glass (Hubert et al., 2015). Therefore, Bureau (2011) stated that those industries that produce silica are categorized as the energy-intensive industries as they require large amount of energy to produce sodium silicate by fusing sand and sodium carbonate in various proportions. Moreover, pure silica is colourless but if contaminated, it might be colored. For instance, rose quartz is a silica with trace amounts of iron that is in pinkish hue