EVALUATION OF CASSAVA STEM BASED ACTIVATED CARBON AS POTENTIAL WASTE WATER TREATMENT ADSORBENT

by

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmet-Teller
RSM	Response Surface Methodology
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
pHzpc	pH at zero point charge
EDX	Energy Dispersive X-ray
XRD	X-ray Diffractometry
TGA	Thermogravimetric Analysis
MC	Moisture Content
NaOH	Sodium hydroxide
$ZnCl_2$	Zinc chloride
$CaCl_2$	Calcium chloride
MB	Methylene blue
OFX	Ofloxacin
ppm	Parts per million
ACS-Na05	Activated cassava stem modified with 0.5 M sodium hydroxide
ACS-Na20	Activated cassava stem modified with 2.0 M sodium hydroxide
ACS-Ca05	Activated cassava stem modified with 0.5 M calcium chloride
ACS-Ca20	Activated cassava stem modified with 2.0 M calcium chloride
ACS-Zn05	Activated cassava stem modified with 0.5 M zinc chloride
ACS-Zn20	Activated cassava stem modified with 2.0 M zinc chloride

PENILAIAN KARBON TERAKTIF BERASASKAN BATANG UBI KAYU YANG BERPOTENSI SEBAGAI PENJERAP RAWATAN AIR BUANGAN

ABSTRAK

Tujuan utama kajian ini adalah menyiasat potensi batang ubi kayu untuk digunakan sebagai bahan mentah kos rendah dalam pembuatan karbon teraktif. Batang ubi kayu telah diubahsuai kepada karbon teraktif oleh proses pengaktifan sendiri. Parameter pengaktifan terbaik ditentukan menggunakan program kaedah gerak balas permukaan. Potensi karbon teraktif batang ubi kayu dikaji selanjutnya melalui modifikasi permukaan dengan merawatnya secara kimia menggunakan natrium hidroksida, kalsium klorida dan zink klorida dengan kepekatan 0.5 M dan 2.0 M. Karbon teraktif dan karbon teraktif batang ubi kayu dengan permukaan termodifikasi digunakan dalam penjerapan fasa cecair pewarna biru metilena dan antibiotik ofloxacin dengan penggunaan batang ubi kayu asli sebagai perbandingan. Ciri-ciri termasuk kandungan karbon tetap, bahan meruap, abu, holoselulosa dan lignin batang ubi kayu asli, karbon teraktif dan karbon teraktif batang ubi kayu dengan permukaan termodifikasi dianalisa. Ciri untuk semua jenis penjerap batang ubi kayu kemudiannya dianalisa menggunakan analisa luas permukaan, analisa elemen, mikroskop pengimbasan elektron, tenaga serakan sinar X, pH pada caj titik sifar, analisa spektrometer inframerah, analisa termogravimeter, dan analisa penguraian sinar X. Kajian penjerapan kumpulan, kajian termodinamik, kajian kinetik dan kajian isotermik dilakukan untuk memeriksa kapasiti penjerapan dan sifat penjerap pada keadaan berlainan. Keputusan ciri batang ubi kayu asli menunjukkan bahawa batang ubi kayu sesuai untuk diubahsuai kepada karbon teraktif dengan permukaan lebih luas dan hasil yang lebih tinggi, sementara ciri karbon teraktif batang ubi kayu menetapkan bahawa bentuk karbon teraktif mempunyai sifat untuk berkhidmat sebagai satu penjerap yang baik berbanding yang asli. Tambahan pula, ciri yang ditunjukkan oleh karbon teraktif batang ubi kayu dengan permukaan dimodifikasi dilihat dapat memberi kapasiti penjerapan yang lebih tinggi berbanding bentuk karbon teraktif kecuali yang dirawat dengan zink klorida berkepekatan rendah. Penjerapan untuk kedua-dua metilena biru dan ofloxacin mendedahkan bahawa karbon teraktif batang ubi kayu mempunyai sifat penjerapan yang baik berbanding yang asli. Walau bagaimanapun, karbon teraktif batang ubi kayu dengan permukaan dimodifikasi menunjukkan sifat penjerapan yang baik berbanding karbon teraktif kecuali yang dimodifikasi dengan zink klorida berkepekatan rendah. Karbon teraktif yang dimodifikasi dengan natrium hidroksida mempunyai sifat penjerapan yang paling baik, diikuti oleh sampel yang dimodifikasi dengan kalsium klorida dan zink klorida. Dari segi kepekatan, 0.5 M natrium hidroksida dan kalsium klorida mencukupi untuk menyediakan karbon teraktif batang ubi kayu dengan sifat penjerapan yang bagus. Tetapi, 2.0 M zink klorida diperlukan untuk memberi kesan yang sama seperti yang dimodifikasi dengan natrium hidroksida dan kalsium klorida. Penjerapan kedua-dua metilena biru dan ofloxacin berlaku secara penjerapan fizikal, mono-lapisan, endotermik secara semulajadi, menuruti model isotermik Langmuir dan model kinetik pseudo tertib kedua. Ia boleh disimpulkan bahawa batang ubi kayu memiliki potensi yang bagus untuk digunakan sebagai bahan mentah kos rendah untuk menghasilkan karbon teraktif dengan kerja yang terbaik dalam aplikasi penjerapan.

EVALUATION OF CASSAVA STEM BASED ACTIVATED CARBON AS POTENTIAL WASTE WATER TREATMENT ADSORBENT

ABSTRACT

The main purpose for this study is to investigate the potential of cassava stem to be utilized as a low cost precursor in activated carbon production. The cassava stem was converted to the activated carbon by self-activation process. The optimum activation parameters were determined by using Response Surface Methodology programme. The potential of activated cassava stem as adsorbent was further examined through surface modification with sodium hydroxide, calcium chloride and zinc chloride with concentrations of 0.5 M and 2.0 M. The activated and surface modified activated cassava stem were then employed in liquid phase adsorption of methylene blue dye and ofloxacin antibiotic with raw cassava stem as comparison. The characteristics of raw, activated and surface modified activated materials were analysed including the content of fixed carbon, volatile matter, ash, holocellulose, and lignin. All types of cassava stem adsorbents were then analysed using surface area analysis, Elemental analysis, Scanning Electron Microscopy, Energy Dispersive X-ray, pH at zero point charge, Fourier Transform Infrared Spectroscopy, Thermogravimetric Analysis and X-ray Diffractometry Analysis. Batch adsorption studies, thermodynamic studies, kinetic studies and isothermic studies were done to examine the adsorption capacity and behaviour of the adsorbents at different conditions. The results on the characteristics of raw cassava stem showed that the cassava stem is suitable to be converted into the activated carbon with higher surface area and yield while the activated cassava stem characteristics indicated that the activated form possesses better properties to serve as a good adsorbent than its raw form. Furthermore, the characteristics showed by the surface modified activated cassava stems determined that these samples hold higher adsorption capacity than the activated form excluding those treated with low concentration of zinc chloride. The adsorption studies of both methylene blue and ofloxacin exposed that activated cassava stem have better adsorption properties than its raw precursor. However, the surface modified activated cassava stem showed better adsorption properties than the activated form excluding the one modified with low concentration of zinc chloride. Activated carbon modified with sodium hydroxide owned the best adsorption properties, followed by those modified with calcium chloride and zinc chloride. On concentration basis, 0.5 M of sodium hydroxide and calcium chloride was enough to provide the activated cassava stem with better adsorption properties. However, 2.0 M of zinc chloride is required to give the similar effects as those modified with sodium hydroxide and calcium chloride. The adsorption of both methylene blue and ofloxacin occurred by physisorption, mono-layer, endothermic in nature, following Langmuir isothermic model and pseudo-second order kinetic model. It can be concluded that the cassava stem had a great potential to be utilized as a low cost raw material for making activated carbon with excellent job for the adsorption application.

CHAPTER 1

INTRODUCTION

1.1 General introduction

Cassava plant (*Manihot esculanta*) from the family *Euphorbiaceae* can grow easily in various types of soil (Hillocks et al., 2002). It is one of the most drought tolerant crop that capable of growing on marginal soils. The main purpose of planting this plant is for its starchy roots which serve as staple food and as important source of starch in many tropical countries. In different countries, cassava or its starchy root was known for diverse names such as tapioca-root, manioc, manioc root, mandioca, kamoteng kahoy, balinghoy, mogo, and yucca (Lebot, 2009). Locally, Malaysian recognizes cassava as ubi kayu. Other than starchy root, cassava plant comprises of short-lived leaves and stems that branch irregularly as well (Hillocks et al., 2002).

Generally, all parts of the cassava plant can be used or turned into the value added products. The most valuable part is absolutely the starchy roots of the cassava plant. The root of the cassava plant was mostly turned into the food products such as breads, cassava flour, alcoholic beverage, tapioca, or non food products such as a laundry starch (Gupta, 2016). The first and second largest sources of food carbohydrates are rice and maize, respectively (Frei et al., 2003). Meanwhile, cassava root serves as the third largest food carbohydrates sources. The world's leading producer and exporter of cassava root is Nigeria and Thailand, respectively (Lebot, 2009). Leaves are the second part of the cassava plant that can be consumed. The sustainable supply of the leaves can be confirmed throughout the year if the plant receives enough water. Generally, the young shoots were taken and boiled for at least 10 minutes before they consumption. The leaves of the cassava plants are a good source of lysine and can be used in various dishes (Hancock, 2012). In rural area, cassava leaves could serve as a source of income as they were sold at the market. Cassava stem is the only part of cassava plant which is not being used as food source or other commercial uses. Only few cassava stems were used for the replanting purposes. Most of them were left to decay or burned after the root of the cassava was harvested (Lebot, 2009, Hillocks, 2002).

Generally, activated carbon can be described as a material that contains lot of pores that leads to a large surface area, which is valuable for the adsorption of gases as well as adsorbates from the aqueous solution (Okibe et al., 2013). Adsorption is described as the accumulation of substances at a surface or interface. Meanwhile, the adsorbing material is termed as the adsorbent and the material being adsorbed is known as adsorbate (Bansal and Goyal, 2005). The term adsorption and absorption carries different meaning where adsorption refers to a surface phenomenon in which the solutes are concentrated at the surface of the adsorbent, while absorption refers to a bulk phenomenon where the substance is uniformly distributed throughout the body of the solid (Krishnamurthy et al., 2014). The activated carbon has found its usages in recovery of solvents, elimination of organic contaminants, separation of gases, and as a catalyst support owing to its large surface area (Adinata et al., 2007). Commonly, the activated carbon can be derived from all that comprise high fixed carbon content. The coal such as anthracite, bituminous and lignite, softwood, hardwood, coconut shells, peat and petroleum based residues are the most regularly used raw materials to be converted into activated carbon (Serp and Machado, 2015).

The surface functional groups anchored on carbons or within carbons were found to be responsible for the variety in physicochemical and catalytic properties of the activated carbon (Szymański et al., 2002). This modification gave effects by changing, forming or introducing new types of surface chemical groups on the surface of the activated carbon. This will serve activated carbon with good properties by improving its adsorption behaviour. The carbon surfaces can be modified either physically, chemically or biologically. Physical surface modifications involved exposing of carbon to heat or gases such as ammonium and nitrogen gases. Meanwhile, chemical surface modification involved the exposing of carbon to basic or acidic chemicals (Shafeeyan et al., 2010).

1.2 Research background

The researches on the utilization of lignocellulosic waste as raw materials for the production of activated carbon have been widely done. These include sago waste, apricot stones, pumpkin stem waste, sugarcane bagasse, macadamia nut-shell, coconut shells, corn cob, ceiba pentandra hulls, and cassava peel (Okibe et al., 2013). According to the knowledge of the author, there is only few research that have been done to study the utilization of cassava stem as potential precursor to be converted to the activated carbon.

A previous study by Antonio-Cisneros and Elizalde-González (2010) on cassava stem utilization for activated carbon had been done mainly on adsorption capacity of the activated carbon. The stem was separated into 3 parts, the rind, vascular system and pith. No optimization of production parameters was done previously. Therefore, this study focused on the optimization of the production process parameters. On the economical factor, outer part of the cassava stem was chosen as it contributes to higher portion availability. Table 1.1 simplified the previous researches that have been done on the cassava stem. These include production of bio-ethanol, starch extraction, production of alpha-cellulose, particleboard, and biochar.

Table 1.1 Previous research on the products based on cassava stem

Products	Authors
Bio-ethanol	Sovorawet and Kongkiattikajorn (2012)
Bio-ethanol	Nuwamanya et al. (2012)
Biochar	Noor et al. (2012)
Starch extraction, biofuel	Zhu et al. (2013)
Alpha-cellulose	Urip and Sumada (2013)
Bio-ethanol	Klinpratoom (2014)
Biochar	Prapagdee et al. (2014)
Particleboard	Aisien et al. (2015)

Due to the increasing number of pollutants (World Health Organization, 2018), activated carbon must have different characteristics that suit the pollutant behaviour. Therefore, most researchers focused on how to modify as well as to characterize the surface functional groups of the carbon materials in order to improve or extend their practical applications (Yin et al., 2007). Chingombe et al. (2005) had done a thermal and chemical modification on the surface of coal-based activated carbon by using nitric acid. The produced sample was then treated with five different ways. The first one was washing with water and the second sample was washing with 0.1 M sodium hydroxide, followed by treatment with 0.1 M hydrochloric acid and washed with water. The third sample was heated at a temperature of 580 K. The fourth sample was undergone the annealing process. The last sample was taken from the fourth sample and further treated with acetic anhydride and sulphuric acid, followed by washing with deionised water. The characterization with FTIR, pH titration, zeta potential and sodium capacity analysis showed that different ways of surface modification gave activated carbon with different chemical characteristics.

The effect of surface modification by nitric acid and sodium hydroxide on pitch-based activated carbon fibers for metal removal was done by Shim et al. (2001). This study showed that the surface modification by nitric acid and sodium hydroxide increased the adsorption of copper and nickel ions. This happened as surface functional groups of pitch-based activated carbon fibers were altered due to the exposure to those chemicals. Some of the research that had been done on the surface modifications of agriculture wastes based activated carbon were simplified in Table 1.2. The surface modifications were done chemically by using various chemical such as sodium hydroxide, nitric acid, hydrogen peroxide, ammonium persulphate, zirconium chloride, ferric chloride, ammonia, sulphuric acid, and phosphoric acid. Various chemical surface modification agents will give different effects to the lignocellulosic waste due to the different characters of the surface modification agent and raw materials.

Table 1.2 Several researches on the modification of the activated carbon surface

Raw materials	Surface modification agent	Authors
Pitch fiber	Sodium hydroxide, Nitric acid	Shim et al. (2001)
Coconut shell	Nitric acid, Hydrogen Peroxide, Ammonium persulphate	Edwin Vasu (2008)
Oil palm shell	Zirconium chloride, Ferric chloride	Rahman and Yusof (2011)
Coconut shell	Ammonia, Sodium hydroxide, Nitric acid, Sulphuric acid, and Phosphoric acid	Li et al. (2011)
Pine sawdust	Ferric chloride	López Leal et al. (2012)
Rice husk	Phosphoric acid	Mohammad et al. (2015)

1.3 Problem statement

Activated carbon has a potential to be used in many sectors. However, high cost involved in the production of activated carbon from certain precursors such as coal, peat and anthracite have limiting its usage only for certain applications. The reduction of high production cost is urgently needed as activated carbon is well known as the most widely and effective material used for large-scale water purification process (Alam et al., 2008, Babel and Kurniawan, 2003). Research on cost analysis of activated carbon production by Stavropoulos and Zabaniotou (2009) revealed that the most important factor for reducing the cost is the raw material where in the conclusion, he repeated that cheap and free materials is a must for cost reduction. Some of the material analysed were used tires, wood, pet coke, charcoal and lignite with production cost were estimated at 2.24 USD/kg, 1.56 USD/kg, 1.6 USD/kg, 1.6 USD/kg and 1.56 USD/kg, respectively. Therefore, lignocellulosic wastes with high reproducibility have been gaining the attention of many researchers to be utilized as low cost raw materials for the production of activated carbon.

Cassava plant is a fast growing species that was planted mainly for food source derived from its roots and nutritious leaves (Lebot, 2009). Grow up to ~5 m in height and 2.5 to 8.0 cm in diameter, cassava stem contributes to half mass of the root production and mainly seen as a waste. Cassava plant can be grown and harvested throughout the year, ensuring the continuous supply of its stem. According to a report by Department of Agriculture Peninsular Malaysia, 61,160.6 tonnes of cassava was produced in 2016 (Department of Agriculture Peninsular Malaysia, 2017). The cassava production that amounts to 19.4 metric tonnes per hectare leads to the huge amount in cassava stems waste. This increasing amount of cassava stem waste opens up a new opportunity for turning it into the value added product. Hence, this study explores the potential of cassava stem as a low cost raw material for the activated carbon production. High production cost of the activated carbon is also challenging researchers to increase the adsorption capacity of the activated carbon. Therefore, this study also investigates the effects of chemical surface modification treatment on the adsorption behaviour of the cassava stem based activated carbon.

The adsorption behaviour of cassava stem based activated carbon was tested through liquid phase adsorption. The liquid phase adsorption was chosen due to the vitality to increase the supply of clean water nowadays. The shortage of clean water problem was expanding due to the several main factors such as increasing in population, industrialization and unplanned urbanization. The illnesses in developing countries are 70-80% resulted from the contaminated water (Bhatnagar and Sillanpaa, 2010). In view of the importance of continuous clean water supply, a number of adsorbents should have been developed since the adsorbents have been proven to be effective for water purification (Alam et al., 2008).

1.4 Research questions

Several research questions were generated for this study, and will be answered through the achievement of the objectives of the study. List of research questions to be answered through the implementation of this study were as follow:

1. Are the chosen raw material, cassava stem is suitable as the activated carbon production precursor?
2. What is the optimum activation parameters for the production of the activated carbon from cassava stem?
3. Are there any changes in the characteristics of raw cassava stem, together with characteristics of cassava stem based activated carbon before and after surface modification process?
4. How well the performance of cassava stem-based activated carbon in cleaning the water from contaminants?
5. Can chemical surface modification increase the adsorption capacity of the produced activated carbon?

1.5 Objectives of the study

The principal objective of this study is to investigate the potential use of stem from cassava plant (*Manihot esculenta*) as a new low cost adsorbent in the activated carbon form. This study was further extended to find out the potential use of cassava stem based activated carbon after underwent chemical surface modification process. In order to achieve these objectives, several points to be studied are listed as followed:

1. To examine the suitability of the cassava stem as the activated carbon precursor through chemical characteristics analysis.
2. To determine the optimum activation parameters for the production of the activated carbon from cassava stem.
3. To identify and differentiate the characteristics of raw cassava stem, together with characteristics of cassava stem based activated carbon before and after surface modification process.
4. To investigate the potential of cassava stem based activated carbon and the effectiveness of the chemical surface modification for methylene blue adsorption.
5. To evaluate the potential of cassava stem based activated carbon and the effectiveness of the chemical surface modification on the adsorption of ofloxacin from liquid phase.

1.6 Significant of the study

This study is very important in order to explore new way of utilization for commonly wasted cassava stem biomass. Activated carbon from cassava stem can be used as a material in water purification system where activated carbon acts as a pollutant absorber from water. This study is important to understand the adsorption behaviour of the activated carbon produced from cassava stem as well as the parameters that are suitable to achieve the maximum adsorption capacity. Other than that, this study is intended to explore new way to increase the adsorption capacity of the activated carbon from cassava stem through the surface modification treatments. This was done in order to ensure full utilization of every single gram of the activated carbon produced.

CHAPTER 2

LITERATURE REVIEW

2.1 Cassava plant (*Manihot esculenta*)

The cassava plant is a dicotyledons plant that was categorized in a Euphorbiaceae family with a botanical name of *Manihot esculenta Crantz.* The word 'cassava' was derived from the Arawak language (South America) which is *cazabi* or *casavi* that brings the meaning of bread (Lebot, 2009). The origin of the cassava is remains unclear until the late of 19th century, the authors coincide that the South America is the discoverer of the cassava plant. The other archaeological and historical evidence showed that the major centres of origin for cassava is in Central America (Guatemala, Mexico and Honduras) and northeastern Brazil (Grace, 1977, Lebot, 2009).

The introduction of cassava plant to the Africa started at 1550s when the Portuguese settlers introduced the cassava plant into Africa after they found the Tupinamba Indians or native Indians in eastern Brazil growing this crop. The cultivation of the cassava plant was spread to the weastern coast of Africa by the slaves in about the sixteenth century (Hancock, 2012). Later, the Portuguese brought and cultivate the cassava plant to Benin, Sao Tome, Principe as well as around the Congo River (Cabinda). Around the 17th century, the cultivation of this crop spread to the other areas in Angola, Guinea Gulf and Zaire. Cassava was known as a food plant in the Far East, around 1835. Around 1854, the flour made from cassava was introduced in Angola by Livingstone and consequently Stanley spread the usage of cassava in making flour to Congo. In 1850, the cultivation of cassava to the territories of African had increased. This was due to the tough effort by the Arabians and Europeans to bring this crop as a staple food in Africa as they acknowledged the value of cassava in reducing the starvation among the Africans (Grace, 1977).

In around 1850, cassava was first introduced to Java, Malaya and Singapore as the plant was transported straight from Brazil. The cassava cultivation spread to the other parts of Indonesia as rubber had started gained attention as the more profitable plant on the Malay Peninsula. Approximately 98% of all cassava flour was manufactured in Java during the 1919 to 1941. However, Brazil had increased and enhanced the cassava flour manufacturing during the Second World War (Grace, 1977). The cassava plant has a vast variety of names for different countries like ubi kettella or kaspe in Indonesia, mandioca or aipim in Brazil, manioca, rumu or yucca in Latin America, tapioca in India and Malaysia, manioc in Madagascar and French-speaking Africa, cassava and sometimes cassada in English-speaking regions in Africa, Thailand, and Sri Lanka. In Europe and the United States of America, the term cassava or manioc is frequently referred to the roots of the cassava plant, while the term tapioca is applied to the baked products based on cassava flour (Lebot, 2009). In Malaysia, cassava was also locally known as ubi kayu, as shown in Figure 2.1.

Figure 2.1 Cassava tree or locally known as Ubi kayu

The cassava cultivation area is increasing rapidly due to fast growth, has great yields and less affected by diseases and pests. The cassava plant is grown for its edible starchy roots, that function as a source of an important starch and staple food in most of humid countries. Its function as a crop to reduce the famine has long been acknowledged (Lebot, 2009). The function of cassava roots in reducing the famine had been proven during the Second World War in parts of the Far East as countless people survived on cassava roots. Moreover, the cassava roots served as a main food source for mining and industrial centres workers in Africa. Nowadays, the plant was grown extensively as a food crop or for the purposes of food industries that expands every year throught the world (Hancock, 2012).

2.1.1 Cassava stem as potential adsorbents

The cassava plant is categorized as a perennial plant that can grow under cultivation. They comprises of several parts which are the roots, leaves, and stems, as shown in Figure 2.2. The palmate leaves of this plants are large and typically have five to seven lobes that joined to the stem by a long and slender leafstalk. The cassava leaves are usually located only toward the end of the branches. They serve as an excellent source of protein and therefore found its usage in Africa as a pot herb (Hancock, 2012). Even in Malaysia, the cassava leaves has been used as vegetables sources in many main dishes which usually serves for lunch and dinner and sometimes being used as animal feeding. Meanwhile, as the stem grows, the roots start to grow from the main stem just below the surface of the ground. Feeder roots that radiate vertically from the storage roots and the main stem can penetrate the ground to a depth in the range of 50-100 cm (Grace, 1977).

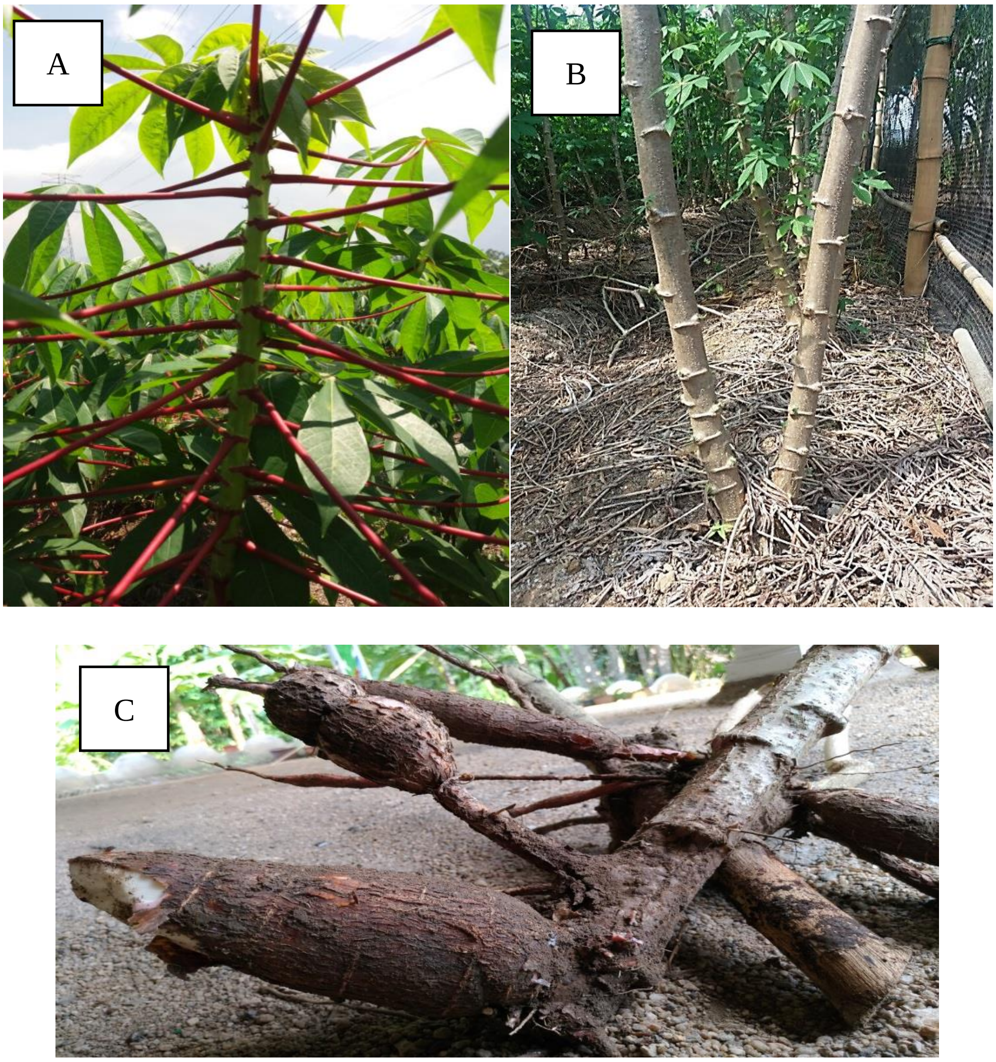

Figure 2.2 Leaves (A), stem (B) and root (C) of cassava

The branches were resulted from the dividing of the main stem as the plant grows. Some of the cassava plants having branches up to 3 branches and some of them grows as a single stem (Grace, 1977). This plant often matures as early as 9 to 12 months. Since the main purpose of its grown is mostly for its root and the leaves as their by-products, the component which is not fully being used is the stems. The cassava plant can grows to a height in the range of 2 to 6 meters. Normally only a small amount of cassava stem is used as propagation material for the next planting while the other is left to decay or burned. The waste of cassava stem was estimated to be as much as 50% from the mass of the root (Zhu et al., 2013).

Researchers had found potential used of cassava stems in the production of particleboard (Aisien et al., 2015), alpha-cellulose (Urip and Sumada, 2013) and biofuel (Sovorawet and Kongkiattikajorn, 2012, Nuwamanya et al., 2012, Klinpratoom, 2014). However, cassava stems had a great potential to be utilized as precursor to produce activated carbon as well. The advantage of using cassava stems as activated carbon rely in the reduction of the production cost of activated carbon since it was counting as waste lignocellulosic materials that can be obtained at low cost. Besides, the cassava stem can be obtained easily and continually since the planting of cassava is easy and the stem is obtainable as early as 6 months (Mombo et al., 2017).

2.1.2 Physical and chemical characteristics of cassava stem

The mature cassava stem is cylinder-shaped, with a diameter in the range of 2 to 8 cm, slender and having a whitish watery sap at the centre of the stem. Figure 2.3 showed the internal structure of the cassava stem. The internal structure of the cassava stem presented a typical structure of dicotyledons plants. The epidermis formed the first layer and the second layer was called the cortex. Beneath that is the ligneous layer of the wood. The prominent pith comprised of parenchymatous cells occupied the centre of the stem. The woody part of the stem will increase as the stem reached maturity age due to the accumulation of xylem in a huge amount. Physically, the cassava stems consists of 15-20% bark, 70-80% cambium or wood which is the sources of cellulose and 5-10% inner part which consist of cork or pith (Fernando, 1984).

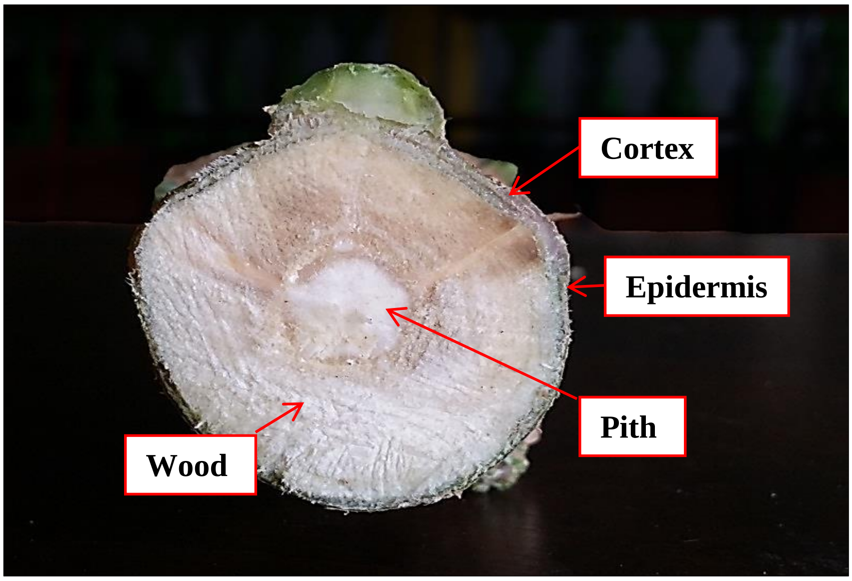

Figure 2.3 Internal structures of cassava stem (Taken by Nurul Syuhada Sulaiman)

The alternating nodes and internodes forming the external structure of the cassava stem as shown in Figure 2.4. The term node refer to the point at which a leaf connects to the stem, Meanwhile, the term internode refer to the empty part on the stem that exist between two sequential leaves. Length of the internodes varies between different species, age of the plant, and the planting environment. Some cassava plant tend to grow as a single stem (varieties with strong apical dominance) and some of them tend to branch. The branching differs as some of them having branch near the top and some have branch nearer the base. The cassava stems vary in colour with either being grey or silvery, green, greenish-yellow, reddish-brown, or streaked with purple (Fernando, 1984).

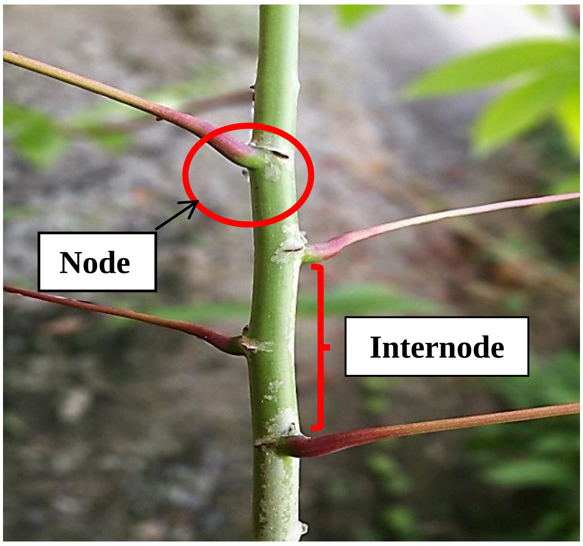

Figure 2.4 Node and internode of the cassava stem (Taken by Nurul Syuhada Sulaiman)

The chemical characteristics of cassava stems were shown as in Table 2.1. Martín et al. (2006) has differentiated the chemical composition of cassava stem into two groups, the stem with barks and the other one without the bark. The total carbohydrates (cellulose, xylan and arabinan) of cassava stem with bark less 103 g kg^{-1} than the stems without bark. However, the debarked cassava stem contained less extractives, lignin and ash content since the bark of many species are rich in mineral compositions, arabinans and extractives, especially phenolic compound.

Table 2.1 Chemical composition of cassava stems, w/g kg^{-1} (Martín et al., 2006)

Materials	Total carbohydrates^{1}	Extractives^{1}	Klason lignin^{2}	Ash^{1}	Acetyl groups^{2}
Cassava stems (with bark)	453 (4.6)	72 (3.1)	253 (3.6)	75 (3.7)	28 (1.5)
Cassava stems (debarked)	556 (4.2)	51 (0.7)	209 (4.2)	57 (0.4)	28 (1.0)

*Average of two (^{1}) and four (^{2}) replicates
*Values in parentheses indicates the standard deviation

2.2 Activated carbon

Activated carbon is a carbon-based material that contains a high degree of porosity and large interparticulate surface area. They can be derived from any carbon-based materials through combustion, partial combustion or thermal decomposition. The history of activated carbon had started in 1500 BC when the Egyptians had used activated carbon in the form of carbonized wood charcoal for medicinal purposes and as purifying agent as well. In India, the ancient Hindus used charcoal as purifying agent to purify their drinking water through filtration (Bansal and Goyal, 2005).

The activated carbon was not commercialized until 1794 when it was used in sugar refining industries. The preparation of activated carbon at that time was done through carbonization process. The precursors involve is a mixture of materials from vegetables origin. The carbonization process was done in the presence of metal chlorides or by activation of the charred material by CO_2 or steam. This occurrence leads to the beginning of research on the utilization of activated carbon in liquid phase (Bansal and Goyal, 2005). In the mid-19th century, the activated carbon was used in a large scale in gas phase application to remove nasty odours in London. However, the development of activated carbon happened during the First World War when the activated carbon find its usage as water treatment and removing vapours in gas phase other than in sugar refining process. The use of activated carbon was increasing in the 20th century due to the improvements in the medical and scientific field. The usage of activated carbon had increased with every decades, due to the stricter environmental regulations regarding water resources, gas purification and economic recovery of valued chemicals (Menendez-Diaz and Martin-Gullon, 2006).

The activated carbon material was first discovered by R. von Ostrejko that was considered as a father or inventor of the activated carbon. He had patented two different methods to produce activated carbon. The first is the basis of chemical activation by involving carbonization of lignocellulose materials with metal chlorides. Secondly, the produced chars were introduced to mild gasification with steam or carbon dioxide at high temperatures. This was the basis of thermal or physical activation (Bhatnagar et al., 2013). Recently, Shi and Xia (2014) had categorised self-activation as a third method in conversion of lignocellulose materials to the activated carbon. The self-activation process uses the gases emitted from the biomass during the carbonization process as the activation agent. Pyrolysis gases produced from the biomass usually contain H_2, CO, H_2O and CH_4. These gases serve as activating agents where the carbonization and activation are combined into one step. This one step method is more efficient in cost, environmental friendly and the product having comparable properties as those produce using the former methods. Activated carbon are described as unique and versatile adsorbents because of their extensively uses in wide applications in many areas but particularly in environmental fields. These include removal of organic and inorganic materials from domestic and industrial waste water, solvent recovery, air purification, removal of toxins and bacterial infections for medicine purposes, preparation of alcoholic beverages, decolourization of oil and fats, purification in electroplating operations, biogas purification, gold recovery and many others (Menendez-Diaz and Martin-Gullon, 2006).

2.2.1 Activated carbon from low cost materials

Activated carbon has been a popular choice as an adsorbent for the removal of contaminant from wastewater (Bhatnagar et al., 2013). However, high processing cost that related with commercial activated carbon demands the development of activated carbon from low cost and abundantly raw materials. The by-products from the agriculture and other industries could be assumed to be the low-cost adsorbents due to their abundance in nature and fewer processing requirements. Since these materials have little or no economic value, they frequently present as a disposal problem. Therefore, these low-cost by-products will offer an inexpensive and renewable supplementary source of activated carbon. The conversions of these materials into activated carbon will increase economic value, reducing the cost of waste clearance and offer a potentially inexpensive alternative to the existing commercial activated carbon (Rafatullah et al., 2010).

Biomass materials in its raw form derived from the agriculture or lignocellulosic waste such as leaves, fibers, fruits peels, seeds, etc. and waste materials from forest industries such as sawdust, bark, etc. have been used as adsorbents. They are available in large quantities, can be obtained at low cost and can be potential adsorbents due to their physico-chemical properties (Rafatullah et al., 2010). These agriculture or lignocellulosic wastes can be further transformed into activated carbon to increase their adsorption capacity. Numerous researches have been done to investigate the potential of activated carbon derived from lignocellulosic waste as adsorbents as shown in Table 2.2. Some of the lignocelluloses that have being investigated were derived from various parts of plants such as seed, stem, shell and fiber. These include *moringa oleifera* pod husk, jute stick, palm oil shell, pitch fiber, date bead, oil palm shell, and coconut bunch waste.

Table 2.2 Several research on the lignocellulosic waste based activated carbon

Precursor of activated carbon	Adsorbate	Types of activation	References
Moringa oleifera pod husk	Ofloxacin	Chemical activation using ammonium chloride	Wuana et al. (2015)
Jute stick	Carbon tetrachloride, Benzene	Steam activation	Asadullah et al. (2007)
Palm-oil shell	N/A	Pyrolysis, Steam activation	Vitidsant et al. (1999)
Pitch fiber	Copper ions, nickel ions	Steam activation	Shim et al. (2001)
Date bead	Lead ions	Chemical activation using zinc chloride	Danish et al. (2011)
Oil palm shell	Chromium ions	Pyrolysis followed by treatment with zirconyl nitrate	Rahman and Yusof (2011)
Coconut (*Cocos nucifera*) bunch waste	Methylene blue	No physical or chemical treatment	Hameed et al. (2008)

2.2.2 Factors influencing adsorption of activated carbon

The activated carbon adsorption process is influenced by various factors which are pH, temperature, chemical surface characteristics, surface area of the adsorbent, physical and chemical characteristics of the adsorbate and pores size of the adsorbent. Generally, the adsorption of organic pollutants by activated carbon at low pH value resulted in high adsorption capacity. This happen as at low pH value, neutralization of negative charges at the surface of the carbon occurred. This reduces the interference to diffusion and thus leads to extra active sites for adsorption. However, this effect depends on the types and activation technique during the activated carbon preparation (Cecen and Aktas, 2011).

Meanwhile, the decrease in temperature would result in high adsorption capacity. This was due to the exothermic reaction involved during the adsorption process. However, the increase in temperature would increase the rate of diffusion of the solute through the liquid to the adsorption sites, leading to high adsorption capacity. There is a specific relation between the properties of activated carbon and the solute during the adsorption process. Therefore, the quantitative effects of temperature would vary with all carbons and solutes (Hameed et al., 2008).

The chemical surface characteristics influenced the adsorption of activated carbon due to heterogeneity or homogeneity of its surface. Heterogeneity of the surface of activated carbon contributes to low adsorption capacity. This heterogeneity arises due to the surface oxygen groups which affect the acidity, polarity and charge of the activated carbon surface (Bhatnagar et al., 2013). Increasing in oxygen functional groups on the surface of the activated carbon would increase the polarity of the carbon surfaces. This would cause the activated carbon to adsorb water clusters. These water clusters would reduce the adsorption capacity of the activated carbon by preventing the pollutant access to the hydrophobic regions on the carbon surfaces, reduce the interaction energy between the pollutant and carbon surfaces and block the pollutant access to the micropores area (Nalwa, 2001).

The specific surface area refers to the fraction of the total surface area that is accessible for adsorption. Generally, it is assumed that the specific surface area is proportional to the extent of adsorption. High finely divided and porous adsorbents were estimated to give high adsorption capacity per unit weight of adsorbent. The external surface was characterized as it exhibits cavities or bulges with depth less than width. Meanwhile, the surface was characterized as internal as it exhibits cavities and pores that have greater depth than width (Poulopoulos and Inglezakis, 2006).

The physical and chemical characteristics of the adsorbate influenced the adsorption of activated carbon due to molecular weight of the adsorbate, number of functional groups, polarity, dissociation constant and the existence of substituents groups on the surface of the adsorbate. Normally, a compound with high molecular weight and high amount of functional groups like halogens or double bond tend to be adsorbed. Activated carbon has a high tendency to adsorbed large molecules than small molecules. The solubility of the adsorbate also plays an important role in determining the adsorption properties of an activated carbon. The contrary relationship was expected to happen between the degree of adsorption of an individual adsorbate and its solubility in the solvent where the adsorption takes place. The adsorbate was said to have high solubility as the adsorbate-solvent bonds are stronger than the attractive forces of the adsorbate-adsorbent (Lens et al., 2002).

The other important factor is the polarity of the adsorbate. A nonpolar solute is preferably adsorbed by a nonpolar adsorbent, meanwhile a polar solute is tend to be adsorbed by a polar adsorbent. Activated carbon has a high affinity to adsorb nonpolar molecules than polar molecules. A great affinity between adsorbate and the solvent occurred as the solubility of the particular adsorbate is high. This fact cause the attraction of the adsorbate by the activated carbon is hinder. Subsequently, any alteration that raised the solubility may reduce the adsorption capacity. Therefore, polar groups that were characterized by an affinity for water typically reduce the adsorption of adsorbate from aqueous solution (Cecen and Aktas, 2011).

The degree of adsorption of activated carbon was influenced by the dissociation constants of weak acids and bases as well. This is due to the degree of ionization was determined by the dissociation constant. Activated carbon is much better adsorb the ionic form than the molecular forms. Consequently, high dissociation constant causes high formation of ionic form that frequently difficult to be adsorbed onto the surface of activated carbon (Cecen and Aktas, 2011, Poulopoulos and Inglezakis, 2006).

Additionally, the existence of substituent groups gives effect to the adsorption properties of activated carbon as well especially in the adsorption of organic contaminants. The substituent group and their effects were tabulated as in Table 2.3. The influence of the first substituent was frequently strengthened by the presence of a second or third substituent. Moreover, the positioned of the substituent groups like ortho, meta, and para will act as a contributor factor as well. Molecules with branched chain are easy to be adsorbed than molecules with linear chain. In addition, the increasing in chain length leads to the increasing in adsorbability of activated carbon. Lastly, the factor of spatial arrangements of atoms and groups in a molecule also give different effect to the adsorption properties of activated carbon. The aromatic compounds was said to better contributes in high adsorption of molecules on the activated carbon than aliphatic compounds of similar molecular size (Cecen and Aktas, 2011).

Table 2.3 Influence of substituent groups on adsorbability of organic compounds (Cecen and Aktas, 2011)

Substituent group	Influence
Hydroxyl	Generally reduces adsorbability
Amino	Generally reduces adsorbability
Carbonyl	Variable effect depending on host molecule
Double bonds	Variable effect depending on host molecule
Halogens	Variable effect depending on host molecule
Sulfonic	Generally reduces adsorbability
Nitro	Generally increases adsorbability

The last factor that influences the adsorption of activated carbon is pore size of the activated carbon. According to the International Union of Pure and Applied Chemistry (IUPAC), pores of activated carbon can be classified into three types which are the micropores, the mesopores (transitional pores) and the macropores. These types of pores were illustrated as in Figure 2.5.

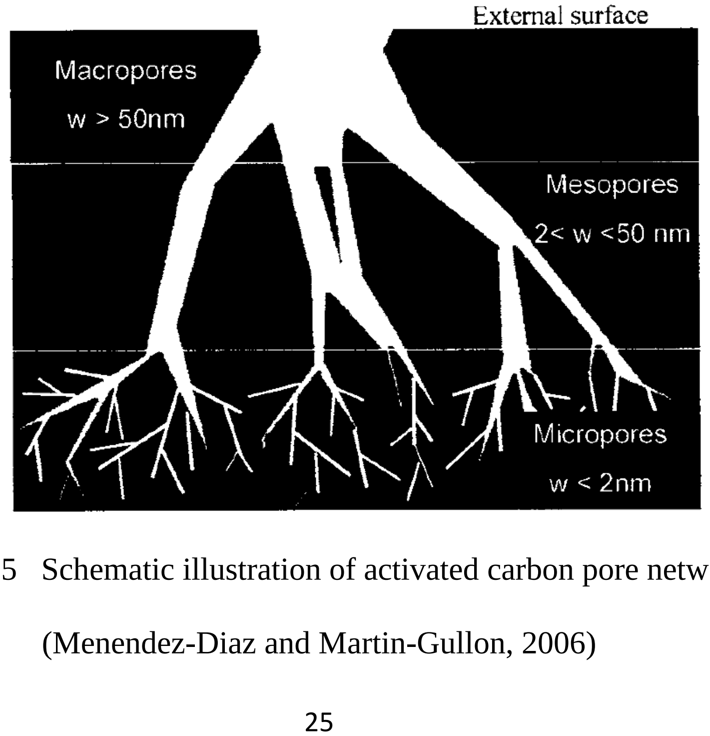

Figure 2.5 Schematic illustration of activated carbon pore network (Menendez-Diaz and Martin-Gullon, 2006)