CHAPTER 1

PREPARATION, CHARACTERIZATION AND APPLICATIONS OF ACTIVATED CARBON FROM COCOA (*Theobroma cacao*) NIBS WASTE

1.1 Background of Study

Cocoa (*Theobroma cacao*) is best known for chocolates production. Cocoa trees can be found in the rainforest of the western hemisphere from 18 °N to 15 °S, which is from Mexico to the southern edge of the Amazon forests (Akinnuli et al., 2015). Cocoa is commercially cultivated in major cocoa producing countries such as Ivory Coast, Ghana, Nigeria, Brazil, Indonesia and Malaysia (Aprotosoaie et al., 2015).

Malaysia is relatively new in cocoa industry compared with West Africa and South America countries (Cadbury, 2017). Yet, Malaysia has becoming among the world leaders in cocoa bean production besides Ivory Coast, Ghana, Indonesia, Nigeria, Cameroon, Brazil, Ecuador and the Dominican Republic (Aprotosoaie et al., 2015).

Cocoa fruits are consist of three main products, which are cocoa pod and cocoa beans. Cocoa beans can be divided into cocoa shells and cocoa nibs. One cocoa pod could contain about 35 to 50 mucilaginous pulp (Aprotosoaie et al., 2015). Approximately, 50% of the cocoa beans consist of fat (Akinnuli et al., 2015), as the key ingredient in chocolate making (where usually called cocoa butter) (Spiegel, 2014). Cocoa pod husk is estimated to represent about 70 % (w/w) of the cocoa fruits (Daud et al., 2013).

Cocoa pods are usually discarded as waste during the cocoa harvesting (Rangga, 2013) and cocoa shells are discarded during winnowing (Awarikabey et al., 2014).

Unintentionally, cocoa nibs are becoming waste too during winnowing, if the nibs were broken into smaller fragments. In smaller fragments, the nibs were difficult to be separated from cocoa shells. Easily, the unseparated nibs will be discarded together with cocoa shells (Akinnuli et al., 2015).

At the early stage of cocoa beans harvesting, the defective cocoa beans are discarded from the processing area. The defective beans include the flat, germinated, moldy, slaty, insect damaged, insect infested and broken beans (MS, 2005). Diagrams of cocoa fruits, pod, beans, shells and nibs are as in Figure 1.1, 1.2, and 1.3, respectively.

According to Akinnuli et al. (2014), when a mass of 21,500 kg of cocoa beans were brought for processing, approximately only 18,096 kg (84.17 %) of cocoa beans were used to produce cocoa liquor, cocoa butter and cocoa cake. Others were discarded as wastes: approximately 143 kg (0.67 %) of foreign material, 318 kg (1.48 %) of cocoa beans waste, 1,512 kg (7.03 %) mass of shell and 1,430 kg (6.65 %) mass of cocoa nibs waste. Percentage wastes of cocoa shells and nibs were relatively high as compared to other waste. In other words, approximately only 10 % by weight of the cocoa fruit is commercialized while the other 90 % by weight is discarded as cocoa waste (Nfor et al., 2012).

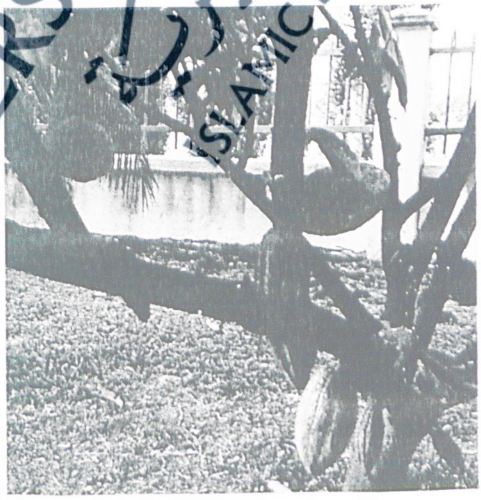

Figure 1.1 Cocoa fruits on cocoa tree (Nikman, 2017).

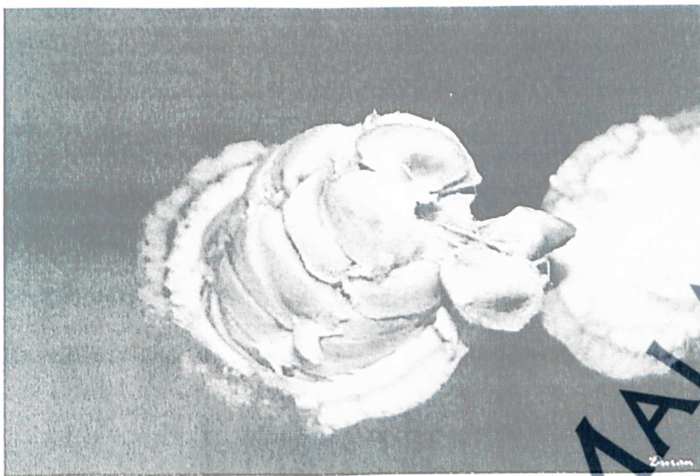

Figure 1.2 The opened cocoa pod displaying beans covered with pulp (Duran, 2010).

(a) (b) (c)

Figure 1.3 Picture of (a) cocoa beans, (b) cocoa shells and (c) cocoa nibs (Nikman, 2017).

Recently, researchers were using cocoa shells as precursor in the preparation of cocoa-based activated carbon. For example, Kalaivani et al. (2014) used cocoa shells to prepare activated carbon using chemical activation with sulphuric acid at 350 °C; followed by Ajifack et al., (2014) with phosphoric acid & potassium hydroxide at 400 °C; Saucier et al., (2015) with lime, zinc chloride & ion trichloride using microwave-assisted pyrolysis and Tejada et al., (2017) using chemical activation with zinc chloride at 350 °C.

1.2 Problem Statement

According to Akinnuli et al., (2014), 143.33 kg of cocoa nibs waste were collected when a mass of 21500 kg cocoa beans were processed. In percentage, approximately 0.665 % of the cocoa nibs were discarded during a single process of chocolate making. Using the data collected by Malaysian Cocoa Board, about 203,093 tons of cocoa beans were ground in 2016 (MCB, 2016). By referring to the price of cocoa beans in 2014, one ton of cocoa beans priced about RM 8,535 (Arshad & Abdulla, 2015).

In a simple calculation below:

- 0.67 % of 203,093 tons was equivalent to 1,350.8 tons (cocoa nibs waste).
- With USD 2,366 for one ton of cocoa beans, approximately USD 3,203,564 were recorded as lost (for 1,350.8 tons of cocoa nibs waste).

It showed a great loss to the grinding company when the nibs were discarded as waste. As cocoa beans are costly and valuable, the extracted nibs should totally be used to produce chocolate. Therefore, the amount of cocoa nibs separated from the shells and collected at the end of winnowing process were very critical.

Normally, the cocoa nibs waste together with other cocoa wastes was used as animal feed. However, it is a high time to produce an activated carbon from palatable, food grade and clean precursor such as cocoa nibs waste. The origin precursor of the commercially available activated carbons was not to known in term of palatability and food grading. Usually, bituminous coals were used as a precursor.

The prepared activated carbon was suggested to be used in human to treat cases of poisonings (such as from medication/drugs). Paracetamol is one of the common over-the-counter drugs that can easily to be used in attempt-suicide case. The prepared activated carbon from cocoa nib waste can be evaluated as potential adsorbent in Paracetamol poisonings.

This research was carried out to investigate the novel performances of cocoa nibs waste as activated carbon, which can be used in medicinal purpose. The main objective of this research is to prepare highly microporous activated carbon from cocoa nibs waste. The performance of the prepared cocoa nibs-based activated carbon was evaluated with batch adsorption experiments using methylene blue dye, phenol, salicylic acid and Paracetamol in aqueous solutions.

1.3 Research Questions

Based on the problem statement mentioned before, the following questions are constructed:

- Can the cocoa nibs waste converted into activated carbon?
- Can the chemical activation method develop a high quality micropore activated carbon from cocoa nibs waste?
- How can we evaluate the effectiveness of the proposed product in adsorption?
- How effective the proposed product in application of paracetamol removal?

1.4 Objectives of the Study

The main objective of this study is to prepare microporous activated carbon from cocoa nibs using chemical activation process. In order to achieve this main objective, some sub-objectives can be formulated. These objectives are as listed below:

1.4.1 To characterize the prepared activated carbon and the acid-treated activated carbon on the surface area, pore volume, surface morphology and surface chemistry using analytical instruments like Surface Area and Porosimetry, Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM).

1.4.2 To evaluate the performance of the prepared activated carbon on the adsorption of methylene blue, phenol and salicylic acid in aqueous solutions using batch adsorption studies.

1.4.3 To assess the adsorption capacity of methylene blue onto the acid-treated activated carbon.

1.4.4 To determine the performance of acid-treated activated carbon in Paracetamol removal in simulated gastric fluid.

1.5 Scope of Research

This study will focus on preparing an activated carbon using potassium carbonate as the activating chemical agent. The prepared activated carbon is estimated to have microporous structure and contains a large amount of surface area. The prepared activated carbon is expected to have oxygen functional group as to assist in the adsorption process. The prepared activated carbon will be treated with hydrochloric acid in order to achieve highly micropore structure and highest number of developed surface area. The prepared activated carbon and the treated activated carbon will undergo the adsorption process using some chemicals (methylene blue, phenol and salicylic acid) and drug (Paracetamol) to evaluate the adsorption performances. In addition, the adsorption isotherm and kinetics will focus on the applicability of the isotherm and kinetics models in describing the adsorption processes.

1.6 Organization of the Thesis

In this work, cocoa nibs-based activated carbon was produced using chemical activation technique. The experimental procedures and the results obtained were comprehensively and systematically presented. Besides the introductory chapter (Chapter 1), this thesis was divided into six chapters.

Chapter 2: This chapter described some of background information on the activated carbon structure, pore size distribution, raw materials, manufacturing processes, applications and researches related to the current work.

Chapter 3: This chapter discussed on the method to prepare the activated carbon, the technique used to demineralize the prepared activated carbon and the characterization of the prepared activated carbon and the acid-treated activated carbon. The following characteristics were determined: surface area, pore development, surface morphology and surface functional group. The chapter was ended with the description and discussion of the experimental results and application of Principal Component Analysis (PCA) as a statistical instrument to evaluate the relationship between the activated carbon's characteristics.

Chapter 4: This chapter evaluated the performance of the prepared activated carbon from cocoa nibs (CNAC) for the removal of methylene blue, phenol and salicylic acid from aqueous solution using batch equilibrium tests.

Chapter 5: This chapter discussed on the results obtained from adsorption of methylene blue onto the acid-treated activated carbon. The data for adsorption equilibriums, isotherm and kinetics studies were also included.

Chapter 6: This chapter investigated the effectiveness of the prepared activated carbon in the removal of paracetamol from aqueous solution. The adsorption capacity of the activated carbon was studied using batch equilibrium tests, adsorption isotherm and adsorption kinetics studies.

Chapter 7: This chapter was presented with the significant discussions, recommendations and conclusions reached from the research.