CHAPTER 7

GENERAL DISCUSSION AND CONCLUSION

7.1 Introduction

In this chapter, the main findings with regard to the research questions are summarized and general conclusions based on the findings of the studies presented in this thesis are described. The strengths and limitations of this thesis are also considered.

7.2 The Used of Cocoa Nibs Waste as Precursor for Activated Carbon

Agricultural wastes have been used in numerous studies as precursor in preparation of activated carbon by various researchers. Agricultural wastes are rich in carbonaceous materials such as coconut shell, palm shell, saw dust and tropical wood that are suitable to be used to produce activated carbon. These materials are abundant, inexpensive and readily available materials which are high in lignocellulose.

In Malaysia alone, approximately 203,093 tons of cocoa beans were ground in 2016 that would correspond to approximately 1,350 ton cocoa nibs waste per year. Therefore, the Malaysian industry of chocolate manufacturing had generated large quantities of cocoa nib waste, most of which are discarded together with other cocoa waste (cocoa pod, cocoa husk and cocoa shell) to the soil environments. The decomposition of these wastes could lead to generating various chemicals and microorganisms that can contaminate the environment in an uncontrolled manner.

Therefore it is necessary to find a use for this waste in order to avoid environmental problems, with sustainable solution. The proposed solution was to use the nibs as precursor in preparing a highly microporous activated carbon using chemical activation. Successfully, the precursor was converted into activated carbon which gained 1,313 m^2/g of surface area where 77 % (1,019 m^2/g) of the surface area was microporous in nature. The result indicated the effectiveness of the activating agent used (K_2CO_3) and the temperature applied during the process. In fact, the application of hydrochloric acid in acid treatment had improved the surface area (including the micropore) which resulted in 1,932 m^2/g of surface area with 25 % increase in microporous structure.

It was proven that the carbonization at higher temperature (800 °C) can increase the development of microporous structure. The applied temperature eased the elimination of tarry and disorganised matter in the carbon to improve more accessible pore structure. The surface areas were also increased due to the application of hydrochloric acid during washing process and demineralize treatment. The acid managed to leach out (de-ash) mineral and mineral oxides from the carbon structure to reduce the ash content and to offer more pores.

7.3 Evaluation of the Prepared Activated Carbon in Adsorption

In order to investigate the performance of the prepared activated carbon in adsorption, batch equilibrium studies were carried out using three different adsorbates: methylene blue, phenol and salicylic acid. The focus of the study was on the effects of initial adsorbate concentration, contact time and solution pH on the adsorption uptake.

It was understood from the study that the adsorption capacity of the adsorbates was increased when initial concentration increased from lower concentration (25 mg/L) to higher concentration (300 mg/L). Initial concentration offered the driving force to overcome resistance during mass transfer between the liquid and solid phase. Therefore, once the driving force increased, the mass transfer increased.

The second parameter was the solution pH, which generally effected by the surface chemistry of the adsorbent. When the point of zero charge pH (pH_{pzc}) was determined, the pH_{pzc} for the prepared activated carbon was found to be around 7.

Since opposite attracts the opposite, the positively charged solution was attracted to the negatively charged sites on the activated carbon surfaces to initiate adsorption. At low pH value, the adsorbent offered a small number of negatively charged sites but more positively charged surface sites available.

The pH of the prepared activated was determined by the adsorbates used. When the pH of the adsorbates was above the isoelectric point (pI) of the activated carbon, the activated carbon was negatively charge and therefore attracted to positively charge molecules. When the pH of the adsorbates was below the pI of the activated carbon, the activated carbon was positively charge and was attracted to the negatively charge molecules. As the prepared activated carbon was introduced to the adsorbate which its pH value was equal to the pI value, the adsorptions stop.

Therefore, at very low pH values, the surface of activated carbon was accumulated with many positive charges, which gave a large static repulsion force. When the pH value increased, the static repulsion forces decreased and the adsorption increased for methylene blue and phenol. The adsorption capacity in salicylic acid was decreased when the pH increased from pH 2 to pH 9, where the most adsorption happened at the lowest pH (pH 2).

The different pattern was observed in salicylic acid was due to the fact that it is acid in nature. Therefore, when the pH value increased, the acidity will decrease which simultaneously changed the nature of the solution that can be captured by the decreased in adsorption.

Another parameter was the contact time between the activated carbon and the adsorbates. The quantity of adsorbate adsorbed at time, q_t was increased when the contact time increased. This was due to a large number of surface sites available for the adsorbates molecules at the initial stage of adsorption to cause a rapid adsorption in the first 30 minutes of interaction. However, after some time, the presence of repulsion between the solute molecules of the solid and bulk phases caused some resistant for the remaining surface sites to be filled, and the adsorption was slowing up.

7.4 Efficiency of the Prepared Activated Carbon on Removal of Paracetamol

The prepared activated carbon was proven to be effective in removal of adsorbates such as methylene blue, phenol and salicylic acid. All the adsorbates are related to medical and health products, and it is beneficial to know the efficiency of the prepared activated carbon in removing these compounds.

In further analysis, Paracetamol batch adsorption study was performed to investigate the performance of the prepared and demineralized activated carbon. The percentage removal of 96.27 % at pH 3 was relatively similar to the result of salicylic acid adsorption. The removal efficiency of Paracetamol was found to decrease when the pH value was increased. This showed that the prepared activated carbon was efficient to adsorb Paracetamol in stomach environment which usually at high acidic value.

In addition, the adsorption of Paracetamol onto the surface of the activated carbon was due mainly to dispersive forces causing the hydrophobic interaction between adsorbate and adsorbent. The hydrophobic element of the adsorbate was likely to associate with the non-polar surface of the activated carbon with the hydrophilic group (carboxylic group) directed toward the aqueous phase.

7.5 Conclusion

Below are the conclusions of this study based on the overall experimental results obtained as presented and discussed:

i) Cocoa nibs were successfully used as agricultural wastes precursor for production of activated carbon using chemical activation method consisting of potassium carbonate (K_2CO_3) impregnation.

ii) The K_2CO_3 and char impregnation ratio (IR) and the carbonization temperature were important factors influencing the adsorption performance of the activated carbons produced from cocoa nibs for removal of methylene blue dye, phenol and salicylic acid in aqueous solutions. The optimum condition obtained for producing the activated carbons from the precursor were 3:1 and 800 °C for IR and carbonization temperature, respectively.

iii) Activated carbon produced was mesoporous in nature with relatively high mesopore surface area (400.34 m^2/g) with average pore diameters larger than 4.0 nm. Activated carbons produced from cocoa nibs demonstrated homogeneous type pore structures. FTIR analyses indicated the presence of functional groups such as hydroxyl, nitrile and amine on the surfaces of the activated carbon.

iv) An increased in methylene blue, phenol and salicylic acid initial concentrations and contact time increased the adsorption uptakes of the activated carbon tested. The activated carbon removal efficiency for methylene blue and phenol was at pH 7 and at pH 2 for salicylic acid.

v) The acid treatment was found to significantly increase the adsorption of methylene blue. The activated carbon was characterized by nitrogen adsorption isotherm to determine its BET surface area, mesopore surface area, micropore volume and pore diameter and the values were 2,448.70 m^2/g, 716.93 m^2/g, 1.41 cm^3/g, and 4.36 nm, respectively. However, the acid treatment process did not influence the composition of functional groups in the produced activated carbon. The SEM images showed the development of more pores after the treatment.

vi) The results of Principal Component Analysis (PCA) showed that activated carbon experienced with the acid treatment were clustered together with the commercial activated carbon indicating that these experimental activated carbons are having a similar properties as in the commercial activated carbon.

vii) The adsorption of methylene blue on the treated activated carbon was best represented with pseudo-second-order kinetic and Boyd models, while the adsorption isotherm was well explained by Langmuir and Temkin isotherm models. The adsorption process was governed by the film-diffusion-mechanism.

viii) The adsorption of paracetamol on the activated carbon produced was best at pH 3.2. The pseudo-second-order kinetic model was suitable to represent adsorption process while the isotherm models were best explained with Langmuir and Freundlich models.

7.6 Recommendation

Several recommendations for future work are suggested in view of their significance and importance related to the present research as the following:-

i) To further evaluate the adsorption performance of the activated carbons prepared in this study in removing paracetamol using human stomach contents as the adsorption performance and mechanism of the activated carbon may be interfered by various factors compared with using simulated gastric fluids (SGF) in controlled laboratory environment.

ii) To use physicochemical activation process where CO_2 gas or steam is applied to produce the activated carbon in order to achieve highest surface area and porosity.

iii) To apply potassium hydroxide (KOH) and phosphoric acid (H_3PO_4) as the activating agents during impregnation process to replace K_2CO_3.

iv) To use hydrogen fluoride (HF), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) to treat the produced activated carbon to remove cations and remaining minerals.