CHAPTER 4

BATCH ADSORPTION STUDIES ON PREPARED ACTIVATED CARBONS FOR METHYLENE BLUE, PHENOL AND SALICYLIC ACID

4.1 Introduction

Conventional wastewater treatments are relatively ineffective to remove pharmaceutical residues such as Acetaminophen, Ibuprofen, Estradiol and a various chemicals compounds. This is one of the reasons of the detection of pharmaceutical residues in treated water including drinking water (Ferreira et al., 2015). Activated carbon is strongly believed to be the most effective wastewater treatments in removing the pharmaceuticals residues from the water environment (Wu et al., 2009).

Batch adsorption study is a method to investigate the adsorption capacity of an activated carbon to a specific adsorbate/s in an aqueous solution. With a known amount of activated carbon added to a solution with known concentration in a controlled system, adsorption at equilibrium can be achieved in an experiment. At the end of the experiment, the resultant solution is used to measure the final concentration (Desta & Lucia, 2013).

The initial adsorbate concentration can be a serious factor to overcome any possible resistance that created between the aqueous and solid phases during the adsorption process. The increase in initial concentration of the adsorbate can decrease the strength of the resistance force. It improves the interaction between the adsorbate and the adsorbent which lead to improvement of the adsorption uptake (Ahmad & Alrozi, 2011).

The purpose of this work was to investigate the performance of the prepared activated carbon from cocoa nibs (CNAC) as low-cost adsorbent for the removal of methylene blue, phenol and salicylic acid from aqueous solution using batch equilibrium tests.

4.2 Materials

The adsorbent used was the prepared activated carbon from cocoa nibs (CNAC). All chemical reagents used in this work were procured from the Merck, Malaysia (hydrochloric acid 30%), Essex, UK (sodium hydroxide 99 %), Friendemann Schmidt Chemical (salicylic acid in powder form), PC Laboratory Reagent (Liquefied Phenol) and Hamburg Chemical GmbH (Methylene blue in powder form).

4.3 Methods

Batch equilibrium studies were carried out for adsorption of methylene blue, phenol and salicylic acid on all the activated carbons produced. The effects of initial adsorbate concentration, contact time and solution pH on the adsorption uptake and percentage removal were investigated. The stock solutions (1000 mg/L) of methylene blue, phenol and salicylic acid were prepared prior experiments.

In order to prepare 1000 mg/L of methylene blue solution, approximately 1.0 gram of methylene blue (powder) was weighed and transferred into 1000 mL of volumetric flask. About 1000 mL of deionized water was added to the mark. The absorbance of methylene blue concentration was determined at 668 nm using a UV-Vis spectrophotometer. The calibration curve was obtained from the spectra of the standard solutions (5 - 100 ppm).

An aqueous stock solution of phenol (1000 ppm) was prepared by dissolving phenol solution in deionized water. Aqueous phenol solution with different concentration of phenol was prepared by successive dilution of the stock solution with water. The phenol concentration was determined using the absorbance (at 270 nm) of the solution after getting the UV spectra of the solution with a spectrophotometer. The calibration curve was obtained from the spectra of the standard solutions (10 - 100 ppm).

In order to prepare 1000 mg/L of salicylic acid solution, approximately 1.0 gram of salicylic acid in powder form was weighed and transferred into 1000 mL of volumetric flask. About 1000 mL of ultrapure water was added. The mixture was stirred for about one and a half hour to dissolve all the salicylate powder. The absorbance of salicylic acid concentration was determined at 295 nm. The calibration curve was obtained from the spectra of the standard solutions (10 - 100 ppm).

All stock solutions were stored in dark place to prevent direct sunlight to avoid decolourization and degradation. All chemical wastes were collected in proper containers before disposal.

The sample solutions were withdrawn at equilibrium to determine the residual concentration. The concentrations were measured using UV-Visible spectrophotometer at the maximum wavelength of the respective adsorbate. The amount of adsorbate adsorbed at equilibrium, q_e (mg/g) was calculated according to equation 4.1 and the percent removal of adsorbate was calculated as expressed in equation 4.2 (Tan et al., 2009).

(4.1) $$q_e = \frac{(C_o - C_e)V}{W}$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of adsorbate at initial and at equilibrium, respectively. V is the volume of the solution (L) and W is the mass of adsorbent used (g).

(4.2) $$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} x\ 100$$

4.3.1 Effect of Initial Adsorbate Concentration and Contact Time

In order to study the effects of initial adsorbate concentration and contact time on the adsorption uptake and percent removal, 100 mL of adsorbate solutions with known initial concentration (25, 50, 100, 200 and 300 mg/L) for methylene blue, phenol and salicylic acid were prepared in a series of 250 mL Erlenmeyer flasks. The amount of adsorbent that was added into each flask containing the adsorbates was fixed at 0.1 g, 0.3 g and 0.5 g respectively. The opening of the flasks were sealed with parafilm and the flasks were then placed in an isothermal water bath shaker at constant temperature (30 °C), with rotation speed of 120 rpm, until equilibrium point was reached. In this case, the solution pH was kept original without any pH adjustment.

4.3.2 Effect of Solution pH

The effect of solution pH on the adsorption process was studied by varying the initial pH of the solutions from 2 to 9. The pH was adjusted using 0.1 M hydrochloric acid and/or 0.1 M sodium hydroxide, and was measured using pH meter. The initial adsorbates concentration was fixed at 100 mg/L with adsorbent dosage of 0.1 g/200 mL. In this case, the solution temperature is at 30 °C.

4.3.3 The Point of Zero Charge (pH_{pzc})

The pH_{pzc} is an important tool in determining the acidity or basicity of the adsorbent and the net surface charge of the carbon in solution. To measure the pH_{pzc}, the pH of the solution is maintained by using 0.1N HCl and 0.1N NaOH solutions. The pH_{pzc} values of different activated carbon used for the adsorption experiment are determined by using solid to liquid ratio of 1:1000. For this, 0.1 mg of activated carbon is added to 100 ml of water with varying pH from 2 to 12 and stirred for 24 hours. Final pH of the solution are measured and plotted against initial pH of the solution (El-Sayed et al, 2014).

4.4 Results and Discussion

4.4.1 Effect of Initial Concentration of Adsorbates

Figure 4.1 shows the effects of initial concentration on the adsorption of methylene blue, salicylic acid and phenol onto CNAC at different initial concentrations (25, 50, 100, 200 and 300 mg/L) at 30 °C. It can be easily observed that the adsorption capacity of methylene blue, salicylic acid and phenol on CNAC increase with increasing of initial concentration of every adsorbate. This is due to the fact that the initial concentration provides the driving force to tackle resistance during mass transfer (Ahmad & Alrozi, 2011).

Relatively similar results have been reported in the literature for the removal of methylene blue and phenol on Fox nutshell (Kumar & Jena, 2016) and the adsorption of salicylic acid onto rice and coffee husk activated carbons (Raoul et al., 2015).

The adsorption equilibrium, q_e was increased from 25.0 to 201.89 mg/g when methylene blue initial concentration increased from 25 mg/L to 300 mg/L. Similar observations were made on salicylic acid and phenol, where the q_e increased from 18.24

to 197.07 mg/g and from 16.83 to 145.26 mg/g, respectively. The increase in mass transfer was due to the increased in the driving force, which was the initial concentration of the adsorbates. A reverse behavior was witnessed in percent removal, where the percent removal decreased when the initial concentration increased (Pathak et al., 2015).

All three adsorbates demonstrated a relatively similar trend; the quantity of adsorbate's molecules adsorbed was increased as the initial concentration increased (the amount of adsorbent used was fixed at 0.1 g for each experiment). Rao & Rao, (2006) explained at their similar finding – the ratio of the initial number of adsorbate molecules to the available surface area is high at higher adsorbate concentration. The total concentrations of adsorbates being adsorbed were varied although the initial concentration for each adsorbate was prepared at similar range. The graph shows that methylene blue was adsorbed the most in every initial concentration compared with salicylic acid and phenol.

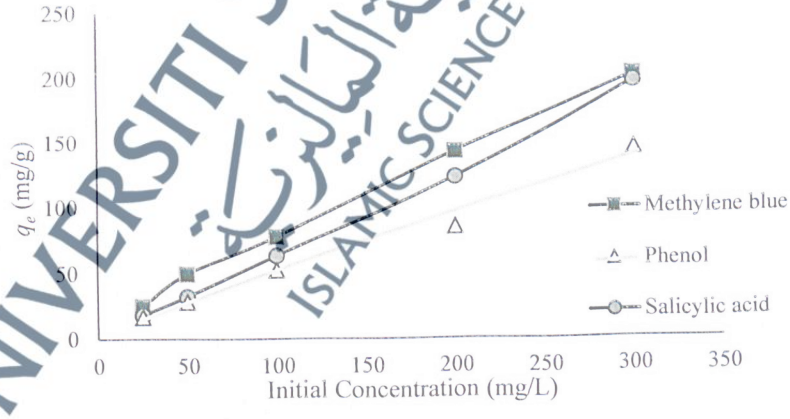

Figure 4.1 Adsorption uptakes versus initial concentrations at 30 °C for methylene blue, phenol and salicylic acid.

Methylene Blue, phenol and salicylic acid have different molecular sizes. Table 4.1 illustrates the molecular sizes and some of the properties of each adsorbate. The size

of methylene blue (0.46 nm^3) is bigger compared with salicylic acid (0.24 nm^3) and phenol (0.08 nm^3) has the smallest molecule size.

Adsorbates were removed by the adsorbent progressively due to available of a large number of vacant sites with active surface functional groups on the surface (Kumar & Jena, 2016). According to Raoul et al. (2015), the pore size of the adsorption sites and the size of the adsorbate is not the only factor that affects the adsorption when they experimented the adsorption of salicylic acid onto rice and coffee husk activated carbons.

Norzilah et al., (2011) described the higher adsorption of methylene blue onto carbon nanotubes was due to a dispersive interaction between the π electrons on the surface of the carbon and the free electrons of the methylene blue molecule (cationic dye) which present in the aromatic rings and multiple bonds. This explained the mass transfer for methylene blue is higher compared with the other adsorbates, although the size of methylene blue molecules are relatively bigger. In summary, the adsorption in liquid phase results from a relationship of electrostatic and non-electrostatic interactions between species in solution and carbon surface.

Table 4.1 Molecular size of adsorbates

Adsorbate	Molecular size (nm)	Reference
Methylene Blue	0.76 x 1.70 x 0.39 ~ 0.46 (cubic)	Arias et al., 1999
Phenol	0.67 x 0.80 x 0.15 ~ 0.08 (cubic)	Swiderska-Dabrowska & Schmidt, 2011
Salicylic acid	0.24 (cubic)	Zhou & Raphael, 2005

4.4.2 Effect of pH Solution

The solution pH is largely related to the surface chemistry of the adsorbent and on the chemistry of the adsorbate in solution. The surface chemistry of the prepared and

acid treated activated carbon has been studied by determining their point of zero charge pH (pH_{pzc}). Figure 4.2 shows the plot of the final pH against initial pH for the activated carbon. The intersection of each of these plots with the y = x function is considered to be the pH_{pzc}. The pH_{pzc} was found to be around 7 for the activated carbon.

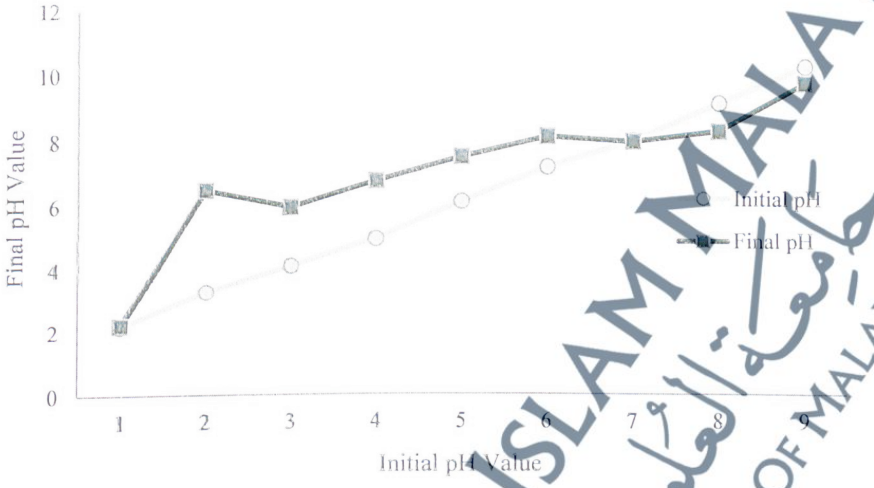

Figure 4.2 The final against initial pH plots for the studied activated carbons.

Figure 4.3 illustrates the effect of initial pH on the removal of methylene blue, phenol and salicylic acid onto CNAC. From the graph, it can be observed that methylene blue and phenol were having relatively similar binding pattern. The graphs were plotted in increase pattern until pH 7 and dropped when it reached pH 9. However, salicylic acid was plotted a relatively linear graph, which recorded decrease in percentage removal as the pH value increase.

It can be seen that the adsorption of methylene blue was increased with increasing pH from 2 to 7. The optimum pH value for methylene blue adsorption was at pH 7. Then, the adsorption performance decreased when the pH increased to 9. This is in agreement with the studies reported by Pua et al. (2013) and Nsami & Mbadcam (2013). Pua et al. (2013) examined the adsorption capacity of cocoa pod husk activated

carbon and Nsami & Mbadcam (2013) investigated the performance of cola nut shells activated carbon on the adsorption of methylene blue onto lignocellulosic adsorbents.

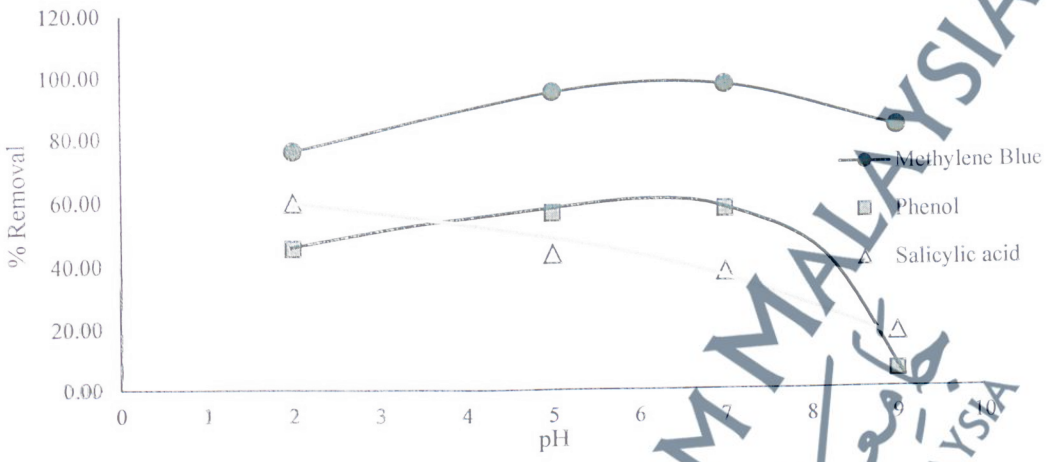

Figure 4.3 Effect of initial pH on methylene blue, phenol and salicylic acid removal.

Low pH value was unfavorable for methylene blue adsorption by CNAC. At low pH value, the adsorbent offered a small number of negatively charged sites but more positively charged surface sites available (Hamdaoui, 2006). Methylene blue is a basic dye, which also called a positive stain. Since opposites attract, the positively charged dye is attracted to the negatively charged sites (Angel, 2017). With more positively charged surface sites on the adsorbent, it did not favor the adsorption due to electrostatic repulsion (Hamdaoui, 2006). The presence of excessive proton (H^+) competed with dye cations of the methylene blue molecules for the adsorption sites via electrostatic interactions (Pua et al., 2013).

The edge sites of the basal plane on the surface of activated carbon represent active sites for oxygen chemical adsorptions (chemisorptions). This location is occupied by surface oxygen functional groups, either acidic or basic. Examples of the acidic groups are carboxyl, lactone, hydroxyl and carbonyl and the basic groups are chromene-

type and pyrone-type (Rakic et al., 2015). As discussed in the previous chapter, CNAC has carbonyl (C=O) oxygen functionalities, which is very polar as it is a hydrogen-bond acceptors (the carbonyl).

A similar pattern of adsorption was observed in removal of phenol. This is in agreement with the studies reported by Norzilah et al. (2011) and by Ingole & Lataye (2015). The optimum pH for adsorption of phenol in this study was observed at pH 7.

At very low pH values, the surface of activated carbon was accumulated with many positive charges, which gave a large static repulsion force. As pH increased, the static repulsion forces decreased and the phenol adsorption increased. As pH was above 7, the decreased in phenol adsorption may be resulted from three factors (Abdel-Ghani et al., 2015).

First, the negatively charged of the activated carbon's surface increased with pH. However, at the same time phenol was changed from molecular state to ionic state which was significant for the repulsion force between phenol ions and the activated carbon. Second, the presence of a repulsion force between the phenol ions which were adsorbed by the activated carbon. Third, the negative charges on the activated carbon's surface were repulsive that blocked the disgregation of phenol ions and phenol adsorption (Abdel-Ghani et al., 2015).

The adsorption of salicylic acid onto the prepared activated carbon was relatively different from the other two adsorbates. The graph shows that the optimum pH for the adsorption was at pH 2. The adsorption capacity was decreased when the pH was increased from pH 2 to pH 9. A similar finding was reported by Raoul et al. (2015) when they studied the adsorption of salicylic and sulfosalicylic acid onto rice and coffee husks activated carbons.

As discussed earlier, the surface of the activated carbon was full with cation at lower pH (pH 2). The salt of salicylic acid (salicylate) formed anion ($C_7H_5O_3^-$) when dissolved in water (NCBI, 2017). A strong electrostatic interaction created between the surface of the adsorbent and the salicylate. More positive sites were available to more adsorbate anion which increased the adsorption capacity.

The adsorption performance was observed to decrease in every system when the pH value was increased to 9. In higher pH value, the adsorbates were believed to be more soluble. At the same time, more surfaces of the activated carbon became negatively charged. This situation creates repulsion interaction between the adsorbate anions and -OH groups of the surface of the material (Raoul et al., 2016). In addition, salicylic acid is naturally is acid. If the pH value increase, the acidity will decrease thus change the nature of the compound which translated into the decreased in percentage removal.

4.4.3 Effect of Contact Time

Figure 4.4 shows the effect of contact time in adsorption process performed in 30 minutes of experiments. The contact time between the adsorbent and the adsorbate is a significant parameter in determine the time necessary to reach equilibrium of an adsorption. The studies were performed on methylene blue, phenol and salicylic acid. The graph presents the pattern of the adsorption capacity of each compound with time at 30 °C.

The graph indicates that the quantity of adsorbate adsorbed at time, q_t is observed to increase with the increase in contact time. For 10 minutes of contact time, the q_t for methylene blue, phenol and salicylic acid was 31.02, 19.02 and 5.38 mg/g, respectively. After 30 minutes, the q_t could only increase up to 45.11, 36.79 and 14.61

mg/g for methylene blue, phenol and salicylic acid, respectively. Hence, the prepared activated carbon needs greater contact time to remove the maximum concentration of the adsorbates.

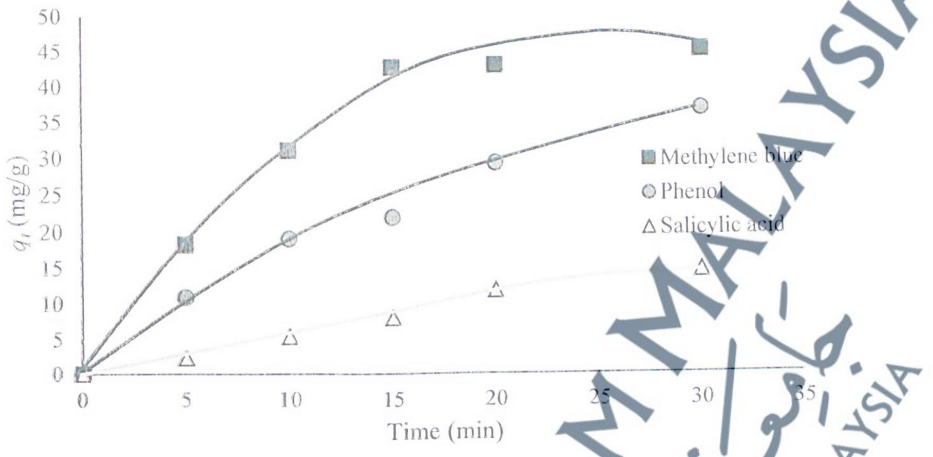

Figure 4.4 Effect of contact time on different adsorbates (30 min. experiments).

Figure 4.5 shows the quantity of adsorbates adsorbed in 240 minutes. As clearly observed in the figure, the quantity of the adsorbate adsorbed at time, q_t was increased with the increased in contact time. For the first 30 minutes of experiments, the q_t for methylene blue, phenol and salicylic acid were rapid where it reached 44.78, 53.53 and 13.32 mg/g, respectively. After 30 minutes, the adsorption plots were much horizontal, indicating a slower adsorption process. The q_t for each adsorbate at 240 minutes was recorded to be 77.12, 68.27 and 49.21 mg/g for methylene blue, phenol and salicylic acid, respectively.

It can be observed too from the graph in Figure 4.5 that the q_t was differed for every adsorbate. Similarly, the adsorptions were took place in two stages. The initial stage occurred in fast rate to show a rapid adsorption process. The next stage was much horizontal indicating a slower adsorption process. The second stage for methylene blue and phenol started earlier which was after 30 minutes of the contact time. For salicylic

acid, it was only started after 120 minutes of the contact time. The extension of the initial stage for the adsorption of salicylic acid was believed to be due the molecular size of salicylic acid, which is smaller in nature than the methylene blue and phenol. Hence, the molecules could occupy more available sites in a longer time compared with the other adsorbates.

During the initial stage of adsorption, a large number of surface sites were available for the adsorbates molecules to cause a rapid adsorption. After a lapse of 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 (Ahmad & Rahman, 2011).

It was also understood that during the first stage of adsorption, the adsorption of adsorbates onto the surface area of the activated carbon was facilitated by the functional groups available on the surface of the activated carbon. Then the second stage involved the occupation of porous structures, where more surfaces was provided in the mesopores structure. This indicated the ratio of the available surface area to the initial number of adsorbate molecules was higher at lower concentration (Rao & Rao, 2006).

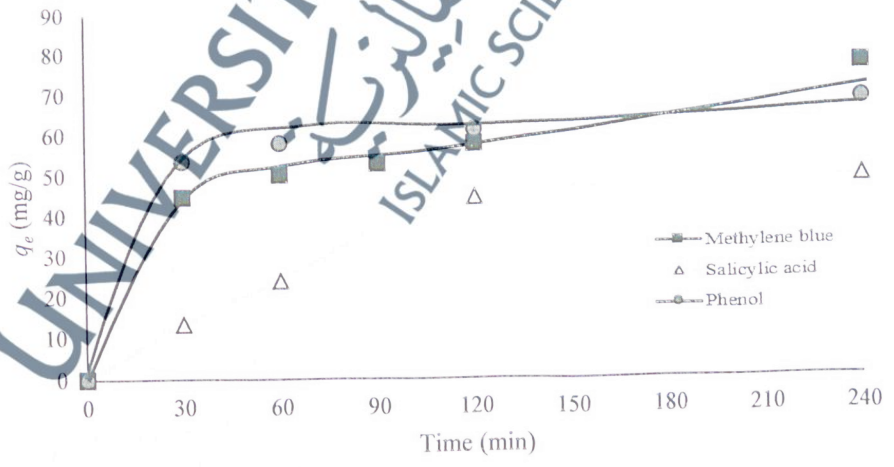

Figure 4.5 Adsorption of adsorbates onto CNAC in 240 minutes of contact time.

4.5 Conclusion

The adsorption of methylene blue, phenol and salicylic acid onto the prepared activated carbon showed distinguished performances of the activated carbon. The initial concentration of the adsorbates, their pH and the contact time between the adsorbates and the activated carbon affected the adsorption performance. The adsorptions were facilitated by available sites and surface functional groups on the activated carbon, together with the repulsion interaction between the charges.