

## CHAPTER V

### RESULTS AND DISCUSSION

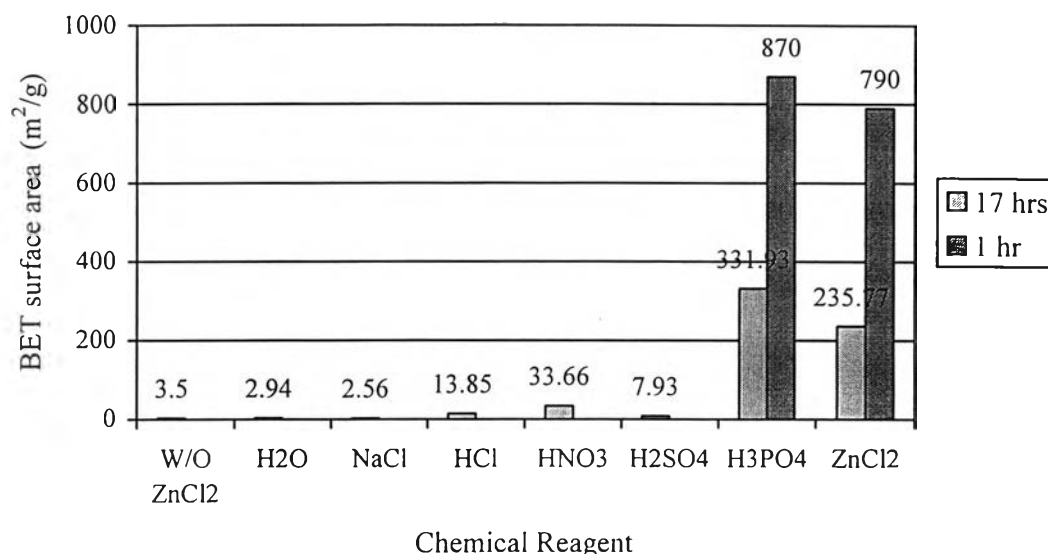
#### 5.1 EFFECTS OF CHEMICAL REAGENTS

Dried, ground water hyacinth was mixed with various chemical reagents, including water for comparison. Then, the reaction was allowed to occur at the temperature of 110°C in the oven. They were observed for physical changes after 1, 2, 3, 4, 5, 6 hours until the 17th hour. The observation results were shown in Table 5.1.

All carbon adsorbents prepared from water hyacinth by the reaction with various chemicals were characterized by nitrogen adsorption (BET surface area) at the normal boiling point of nitrogen (77K) by using a micromeritic BET model ASAP 2000 comparing with the carbon adsorbent which was carbonized only. The nitrogen-adsorbed surface area of carbon adsorbent prepared from water hyacinth was shown in Figure 5.1.

Table 5.1 Observation results of carbon adsorbents from water hyacinth reacted with the various chemical reagents at the temperature of 110°C, 17 hours in the oven

Chemical Reagents Physical Changes	11.64M HCl	5.13M NaCl	4.41M ZnCl <sub>2</sub>	9.52M HNO <sub>3</sub>	6.12M H <sub>3</sub> PO <sub>4</sub>	6.12 H <sub>2</sub> SO <sub>4</sub>
Water hyacinth used (g)	19.97	19.98	19.98	19.98	19.98	19.98
Immediately after mixing with chemical reagents	deep black	light brown (raw material colour)	light brown	yellowish-orange	light brown (raw material colour)	slightly black
1 hour	more black	more brown	more brown	yellow	partly black	more black (but less than HCl)
2 hours	black	brown with some white salt crystals	partly black	yellow	more black	more black
3 hours	black	brown with more white salt crystals	more black	yellow	more black	more black
4 hours	black	brown with more white salt crystals	more black	pale yellow	more black	more black
5 hours	black, drier	brown with more white salt crystals	more black	pale yellow, drier	more black	more black
6 hours	black, drier	brown with more white salt crystals	more black	pale yellow, drier	more black	more black
17 hours	black, dried	brown, dried with many salt crystals	black, not dried	pale yellow, dried	black, not dried	black, not dried



**Figure 5.1** BET surface areas of nitrogen adsorption of carbon adsorbents from water hyacinth which reacted with various chemicals at prereaction time of 1 and 17 hours at 110°C

The carbon adsorbent prepared from dried water hyacinth by carbonization at the temperature of 400°C for an hour provided BET surface area about 3.5 m<sup>2</sup>/g, which was comparable with carbon adsorbents from other carbonaceous materials, such as coconut shell [Kriangsak, 1999] and corncobs [Supaporn, 1998] under the same condition and chemical reagent.

Without oxygen, cellulose in water hyacinth was carbonized to amorphous form, referred to as “water hyacinth charcoal.” It was not appropriate for using as an industrial adsorbent because of the low surface area.

Hydrochloric acid solution is a strong corrosive reagent and can dissociate completely, so the concentration of hydrogen ion (H<sup>+</sup>) is 11.64 moles/liter. From the observation results, it is found that the mixture became black immediately after

mixing at the room temperature. The reaction between cellulose of water hyacinth and hydrochloric acid was violent and is similar to that of carbonization at high temperature. Thus, it could be concluded that the reaction of hydrochloric acid had a high rate comparable with the rate of carbonization. Thus, dried water hyacinth was partial corroded when mixed with hydrochloric acid, and then carbonized this mixture under at the temperature of 400°C for an hour. It provided surface area about 4 times of water hyacinth charcoal as shown in Figure 5.1. But this surface area was less than that of industrial carbon adsorbent (more than 1,000 m<sup>2</sup>/g) about 100 times. Because an increased in temperature affected the less soluble of hydrogen chloride in water, consider Figure 5.2 (1) [Perry and Green, 1997]. During the reaction in the oven at the temperature of 110°C, the reaction occurred in the short period because hydrogen chloride was not able to dissolve in water at the temperature above 50°C. Water was also vaporized at the temperature above 100°C. Then the remaining was carbonized at the temperature of 400°C as water hyacinth charcoal. Although the concentration of hydrogen ion is very high comparable with another chemical reagent, but it can react in a very short time, so hydrochloric acid can develop a small fraction of additional surface area (about 14 m<sup>2</sup>/g).

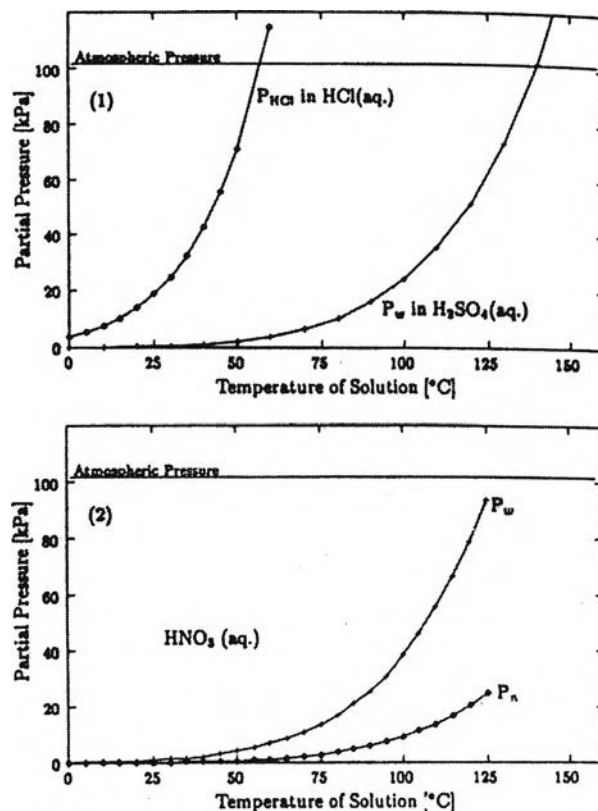


Figure 5.2 (1) Partial pressure of hydrogen chloride gas in hydrochloric acid solution and partial pressure of water in sulfuric acid, and (2) partial pressure of water vapour and hydrogen nitrate in nitric acid solution

Sulfuric acid solution ( $H_2SO_4$ ) is strongly corrosive and very reactive. It could ionize to hydrogen ion ( $H^+$ ) in two steps, the overall concentration of hydrogen ion [ $H^+$ ] is about 6.12 moles/liter for a single step. From the observation results, it is found that the mixture became black gradually. After 3 hours, it became black completely, and at the 17th hour, it was not dry. Then the mixture was carbonized and reacted at the temperature of  $400^\circ C$  for an hour. During the mixture was reacted at the temperature of  $110^\circ C$ , although the reaction could occur but in a short period only and due to the mechanism, the hydrogen ion was limited because of the vapourization of

water, consider Figure 5.2 (2). Sulfuric acid solution is gradually concentrated and could be rarely ionized to give hydrogen ion, and then only pure sulfuric acid is remained before the carbonization and reaction step and it could not react with the remained cellulose. Thus, it could provide BET surface area 2 or 3 times more than water hyacinth charcoal, as shown in Figure 5.1.

Nitric acid solution ( $\text{HNO}_3$ ) is a strong oxidizing agent and highly corrosive like hydrochloric acid solution, the yellow colour that could be observed from the reaction which occurs at the temperature of  $110^\circ\text{C}$  is due to the release of nitrogen dioxide on exposure to light or heat. Although the hydrogen nitrate compound is in the liquid phase at the normal condition, and ionizes to hydrogen ion and nitrate ion ( $\text{NO}_3^-$ ). The concentration of hydrogen ion is 9.52 moles/liter. Cellulose structure was corroded and rapidly decomposed at the temperature of  $110^\circ\text{C}$  and had a longer period for reaction. Then the solution was completely vapourized after preparation step (see Figure 5.2 (2)), and then was carbonized and reacted at the temperature of  $400^\circ\text{C}$  which was the same as the water hyacinth charcoal. So it provided the BET surface area greater than approximately tenfold to the water hyacinth charcoal as shown in Figure 5.1.

For phosphoric acid solution and zinc chloride solution, although they could dissociate to give less hydrogen ion (about 0.21 mole/liter for phosphoric acid and 0.001 mole/liter for zinc chloride) but they could maintain in liquid phase longer than other solutions which is mentioned above. Zinc chloride solution is a dehydrating and condensing agent, as well as phosphoric acid. So they could not be dried at the temperature of  $110^\circ\text{C}$  (as it was observed from the experimental results in Table 5.1).

When they were introduced to the muffle furnace to the carbonization and reaction step at the temperature of 400°C, although water might be vaporized or chemicals might be decomposed to another compound at that temperature, the process would consume a period about 30–40 minutes from the room temperature to that temperature. Under this circumstance, the reaction of chemical solution with cellulose was accelerated by temperature, and resulted the product in nitrogen adsorption providing BET surface area about 80–100 fold value of the surface area of water hyacinth charcoal as shown in Figure 5.1. When the reaction time was reduced to 1 hour, and followed by the same carbonization and reaction step at 400°C, the carbon adsorbents which were reacted by phosphoric acid and zinc chloride solutions provided a surface area of nitrogen adsorption not less than 800 m<sup>2</sup>/g approximately.

For sodium chloride solution, as the water was vaporized during the pre-reaction step at 110°C, sodium chloride was remained in the sample as the solid. When the sample was carbonized and reacted at the temperature of 400°C, sodium chloride was still in the form of solid phase that could not react with the water hyacinth (m.p. of NaCl is 801°C) [Lewis, Sr., 1993] and hydrogen ion concentration was too low to react with water hyacinth. So the surface area was the same as water hyacinth charcoal as shown in Figure 5.1.

The acidic reagent or the salt which dissolved in water and gave an acidic solution could dissociate to give hydrogen ion or hydronium ion (H<sub>3</sub>O<sup>+</sup>) which came from 2 sources, that is water and the acid, but the major source was the acid. The hydrogen ion was the reactant that reacted with the cellulose in the raw material (water hyacinth). So if more H<sup>+</sup> could be produced and maintained for longer period

of the reaction, the results might be well for developing BET surface area or other characteristics of carbon adsorbents.

## 5.2 CHARACTERIZATION OF CARBON ADSORBENTS

### 5.2.1 Effects of Reaction Temperature and Reaction Period

Carbon adsorbents from water hyacinth, rice husk, and sugar-cane bagasses activated isothermally with 600 grams/liter of zinc chloride solution at the temperature of 400, 500, and 600°C and the period of 1, 2, and 3 hours provided different specific surface areas, iodine numbers, as well as yields.

Without zinc chloride, a carbon adsorbent from water hyacinth, rice husk, and sugar-cane bagasses yielded 43.20, 57.80, and 39.49%, respectively. While the reaction process with zinc chloride produced carbon adsorbents less than 35, 52, and 35%, respectively, as shown in Figure 5.3–5.5. The results suggested that the reaction period affected the yields slightly, while the yield decreased as an increase in reaction temperatures for a given period of reaction. According to the Arrhenius' law, the rate of reaction increased exponentially with an increase in temperatures. With the limitation of chemical reagent, therefore, the amount of carbon remained at 400°C was larger than that at 600°C for the same raw material. The results agreed well with many researchers' results [Boonchai, 1984; and Pongstorn, 1995].

In carbonization and reaction step, volatile matters were eliminated, and the chemical reagent was used to reacted with the main composition of raw materials, i.e. cellulose spontaneously. The mass of raw material was lost in the form of gas



such as  $H_2$ ,  $CO$ ,  $CO_2$ , and  $H_2O$ . The reaction occurred by the reacting with cellulose in raw material and assisted by the heat to accelerate the reaction.

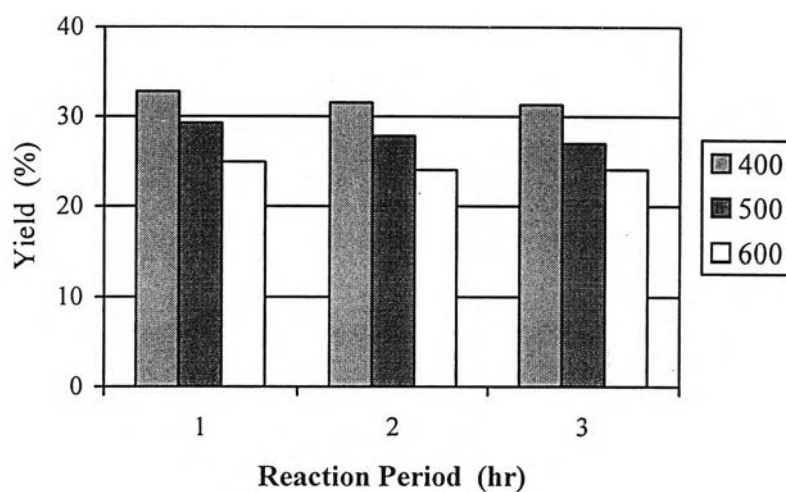


Figure 5.3 Carbon adsorbents yields from water hyacinth reacted with zinc chloride

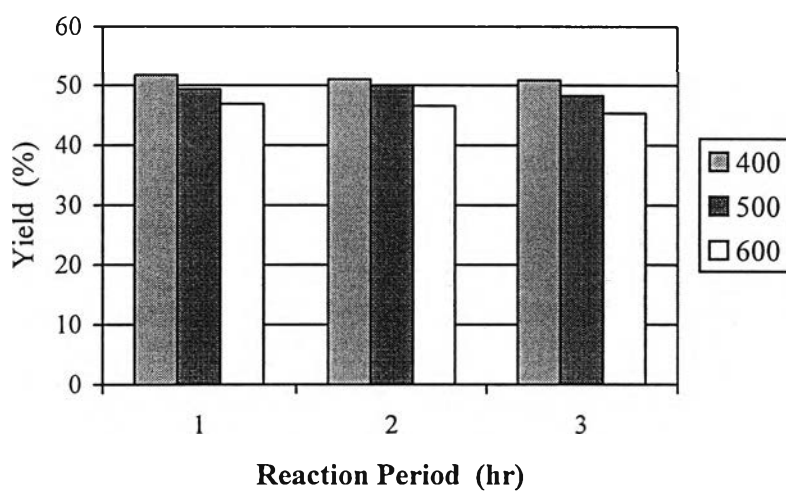


Figure 5.4 Carbon adsorbent yields from rice husk reacted with zinc chloride

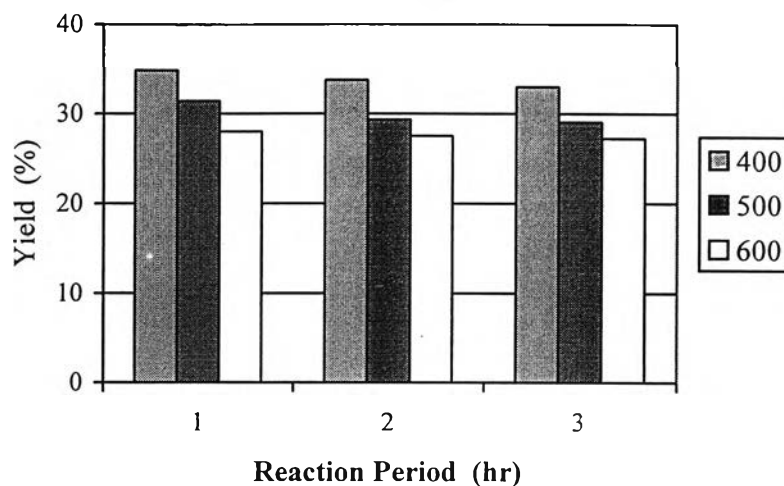
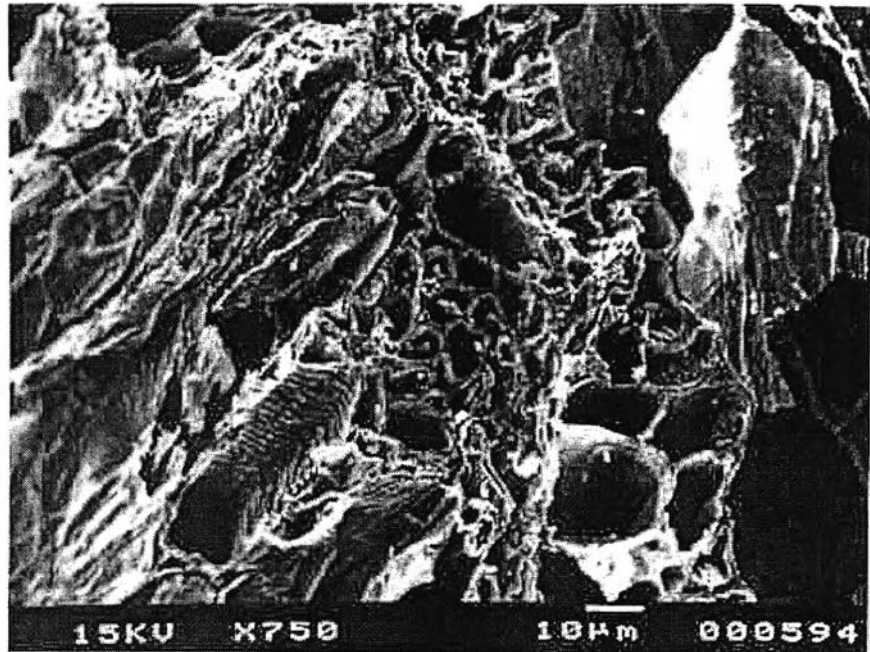
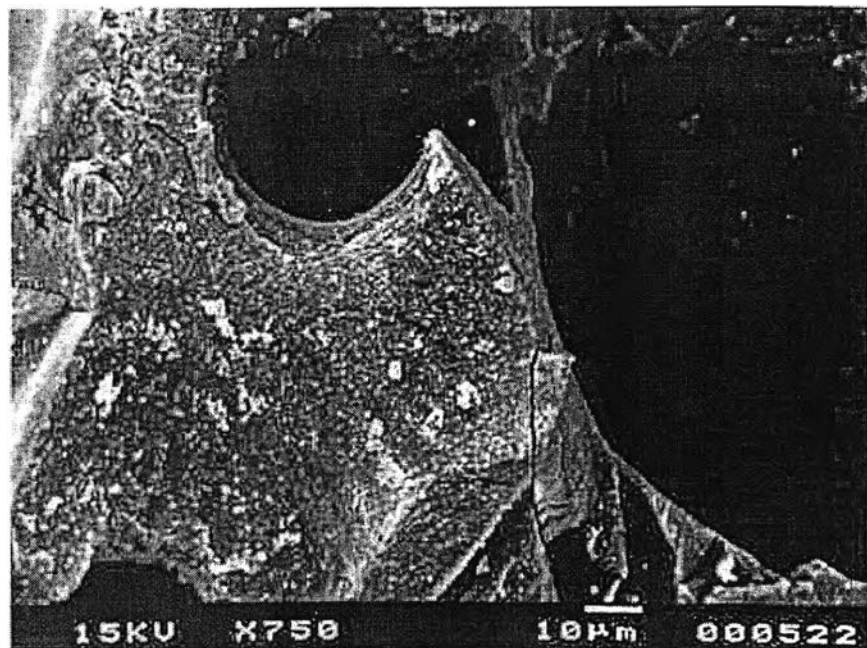


Figure 5.5 Carbon adsorbent yields from sugar-cane bagasses reacted with zinc chloride

External surfaces of carbon adsorbents; reacted without zinc chloride and with zinc chloride at the same conditions, i.e. 400°C for an hour, were inspected with scanning electron microscope (SEM), as shown in Figure 5.6–5.11. It is found that the surface structure of the adsorbent from the process without zinc chloride was still similar to the original structure. While the surface structure of adsorbent reacted with zinc chloride was completely altered. The results illustrated that the adsorbent, with the original surface structure, might provide higher specific area than the former. Due to the limitation of the instrument, so the pore size of the carbon adsorbents having a magnitude order of  $10^{-10}$  m (Å) could not be seen by the SEM.



a)



b)

Figure 5.6 External surfaces of carbon adsorbents from water hyacinth: a) without zinc chloride and b) with zinc chloride at 400°C, 1 hour

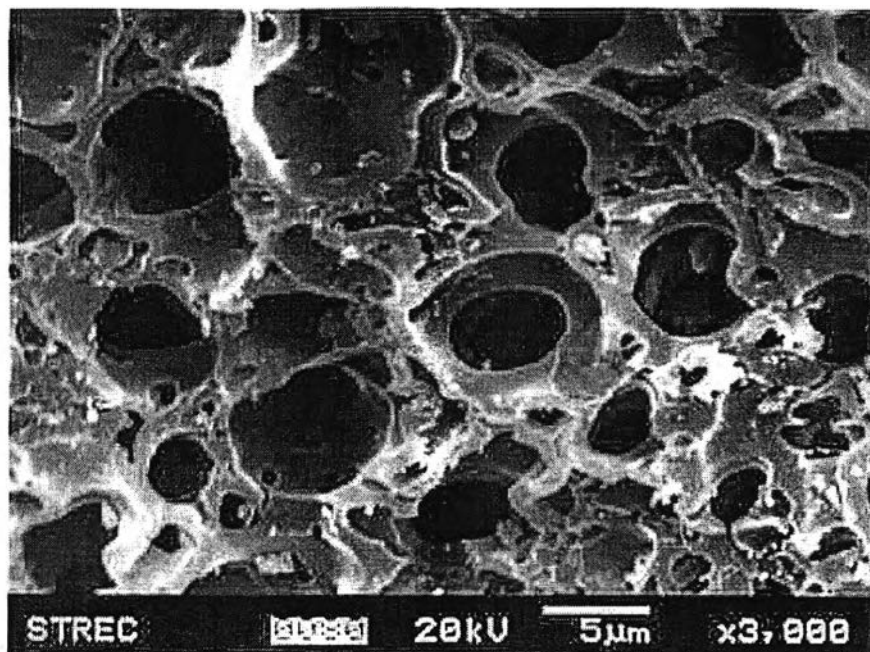


Figure 5.7 External surfaces of carbon adsorbents from rice husk reacted without zinc chloride at 400°C, 1 hour

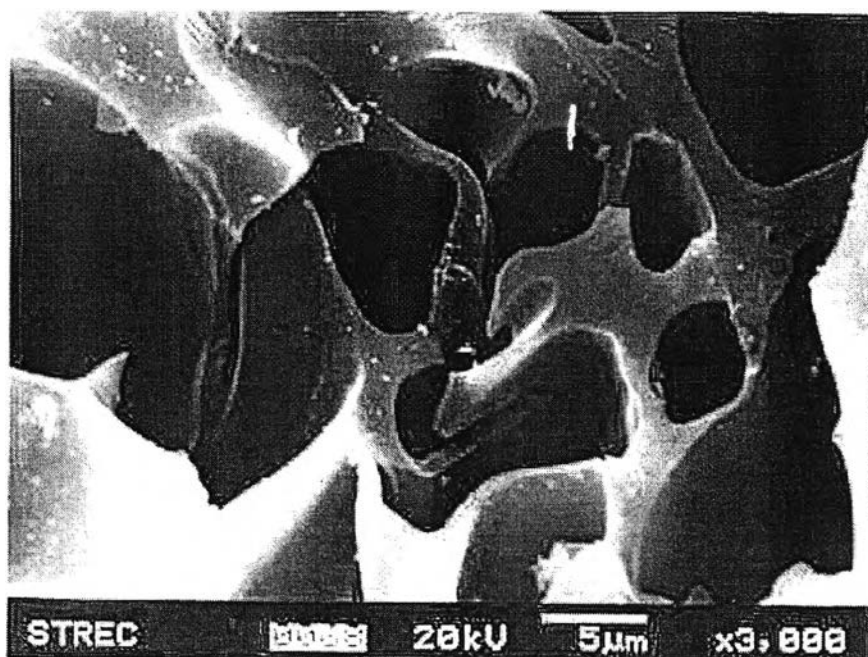


Figure 5.8 External surfaces of carbon adsorbents from rice husk reacted with zinc chloride at 400°C, 1 hour

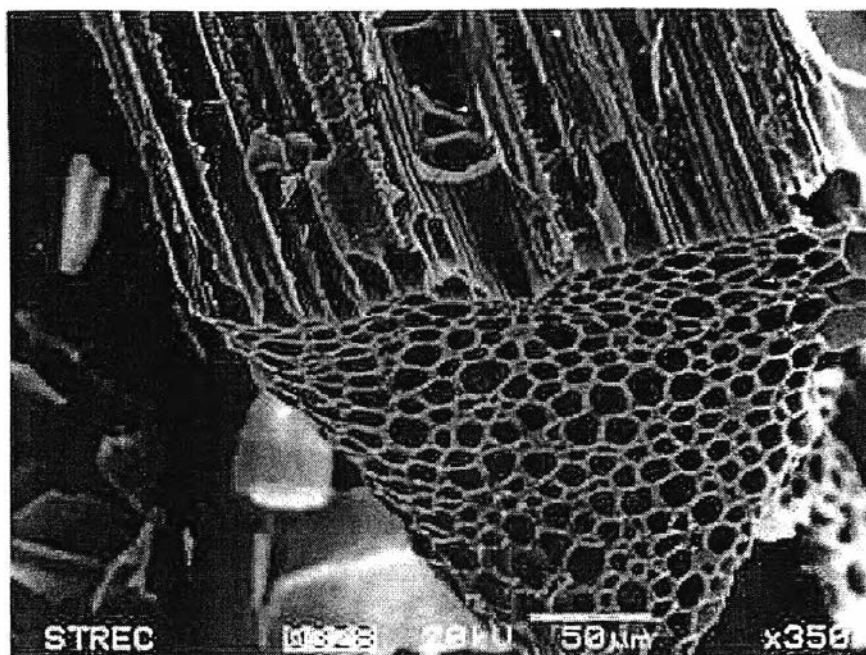


Figure 5.9 External surfaces of carbon adsorbents from sugar-cane bagasses reacted without zinc chloride at 400°C, 1 hour

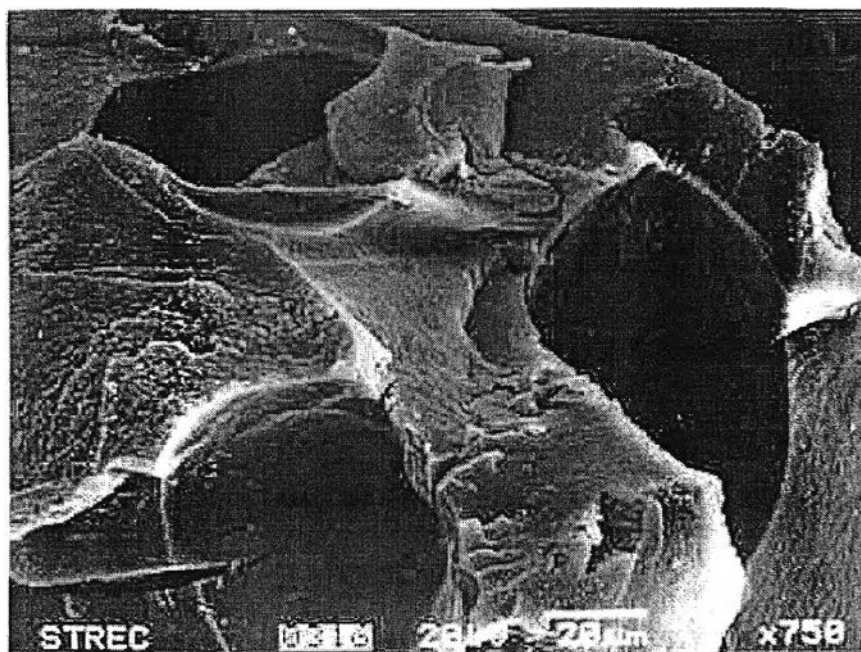


Figure 5.10 External surfaces of carbon adsorbents from sugar-cane bagasses reacted with zinc chloride at 400°C, 1 hour

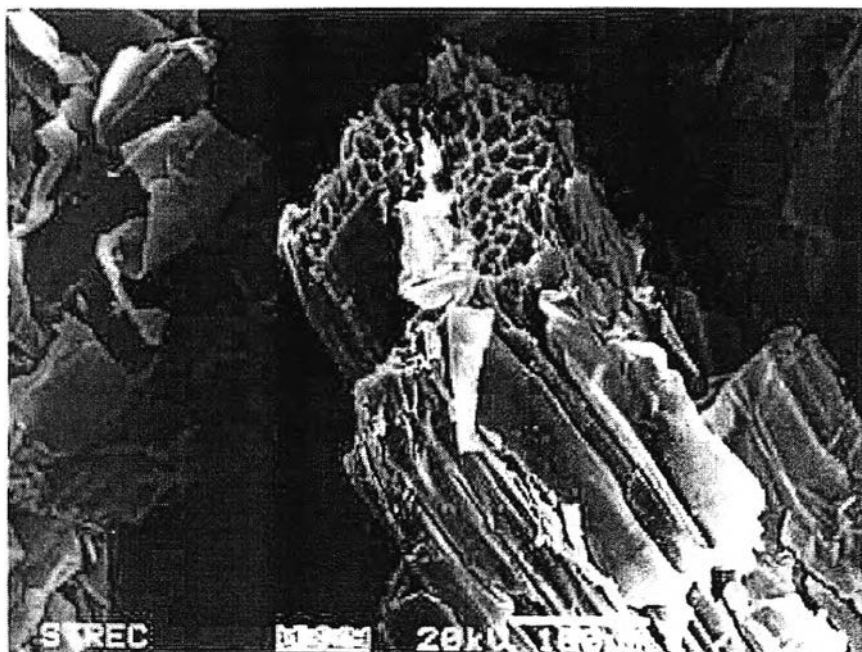


Figure 5.11 External surfaces of raw material (sugar-cane bagasses)

For the BET surface area, all the carbon adsorbents prepared from water hyacinth, rice husk, and sugar-cane bagasses were developed by the reaction of hydrogen ion from the chemical reagent. The reaction of  $H^+$  and cellulose of raw materials depending on the reaction period and temperature. From the experimental results in Figure 5.12–5.14, it is shown that the optimum reaction temperature was about  $500^{\circ}\text{C}$  and when the temperature was more than  $500^{\circ}\text{C}$ , the BET surface area approached a constant or slightly dropped. For the reaction period, it is found that the BET surface area was affected slightly by the reaction period because the reaction occurred within about 20–30 minutes of temperature-increasing period. After that, the hydrogen ion could not be maintained in the mixture any longer. The results were corresponded to the results of Phasuk et al. (1992) which studied the preparation of carbon adsorbents from coconut shell, pamyra palm meat, and cashew nut shell by

reacting with 50% (w/v) zinc chloride. They found that the optimum period was about 10–20 minutes and the reaction temperature was about 500–700°C.

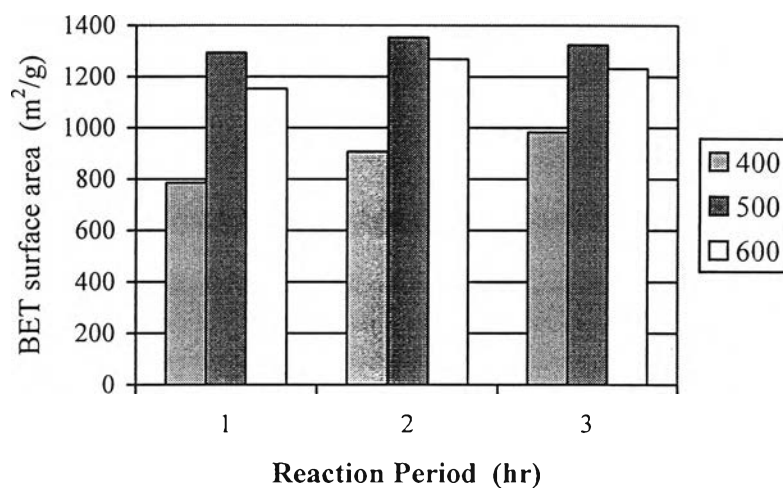


Figure 5.12 BET surface areas of carbon adsorbents from water hyacinth reacted with zinc chloride

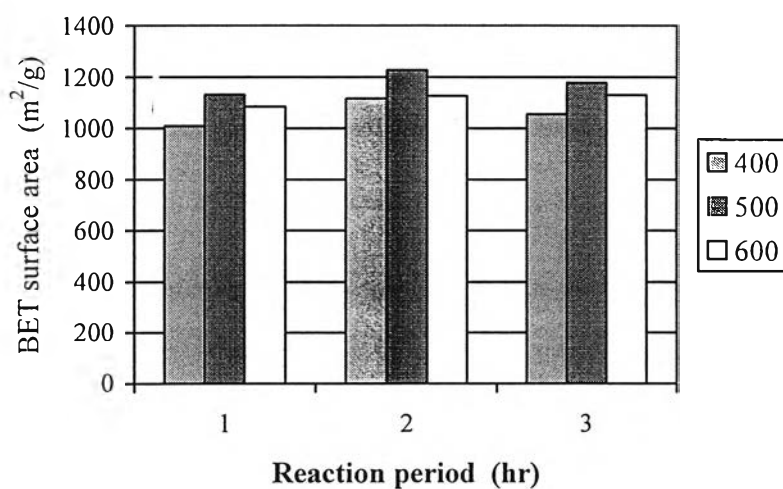
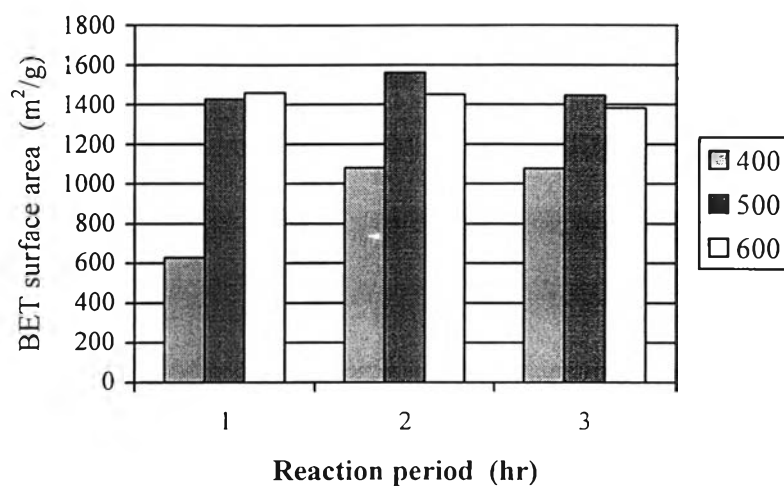


Figure 5.13 BET surface areas of carbon adsorbents from rich husk reacted with zinc chloride



**Figure 5.14** BET surface areas of carbon adsorbents from sugar-cane bagasse reacted with zinc chloride

From Kittiya's experiments (1999), coconut shell was reacted with 50% (w/w) zinc chloride solution at the temperature of 500°C by varying reaction period from 15, 30, 45, and 60 minutes. The results were shown in Table 5.2.

**Table 5.2** The experiment results using 50% (w/w) zinc chloride solution with coconut shell at 500°C

Time (min)	Characteristics	BET surface area (m <sup>2</sup> /g)	Iodine number (mg/g)
15		315	353
30		411	410
45		496	464
60		711	898

It was found from the results that as increasing in reacting period within the range of 15 to 60 minutes, the characteristics of carbon adsorbents (BET surface area and iodine number) increased. Thus, it is found in this experiment that if the

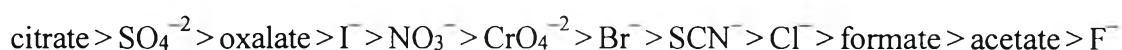


reaction period was about 1, 2, and 3 hours (more than 20 minutes), the BET surface area was not developed further. This is because the reaction occurred during carbonization and reaction was the reaction of hydrogen ions from the solution of zinc chloride. When the mixtures of raw material and zinc chloride solution were heated, hydrogen ions could react with the raw material if water was still maintained in liquid phase. But the water was vaporized by the heat added, so the reaction was slow down and only the heating effect was remained. Zinc chloride solution only had catalytic effect on the reaction [Suzuki, 1990]. From an experiment of Anuchit Kitsawas (1997) it was found that after the reaction, zinc chloride could be recovered from rice husk more than 90%. So it was assumed that zinc chloride was not used in the reaction, and it might performed as a catalyst in the reaction. The period that water was maintained in the sample could be roughly calculated by the heat added from the room temperature to the boiling point of water (100°C) and from water at 100°C to vapour at 100°C was 7 minutes approximately.

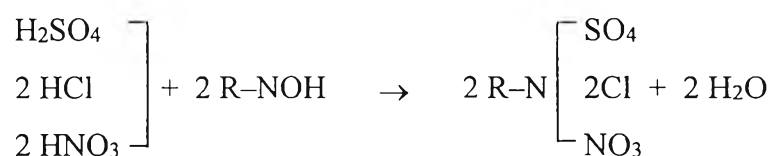
The carbon adsorbents which were reacted without zinc chloride provided BET surface area about 3.5 m<sup>2</sup>/g at 400°C, 1 hour. So, the increasing of BET surface area was partly affected by the reaction temperature and period. Although there was no results of BET surface area at the temperature of 500°C, 1 hour and 600 °C, 1 hour (reacting without zinc chloride) for comparison.

Effects of reacting temperatures and periods on the iodine adsorption were similar to those on the BET surface area as shown in Figure 5.15–5.17. As the reacting temperature increased, the BET surface area and iodine number increased. But the iodine number did not increase proportionally to the BET surface area. Due

to the molecular size of nitrogen is 3.7Å while the molecular size of iodine molecule is 10Å [Hassler, 1974], so iodine molecule can penetrate to the pore more difficult than the nitrogen molecules. Moreover, the adsorption of iodide ion ( $I^-$ ) with carbon adsorbent could be considered as an ion exchange. On the surface of the carbon adsorbent consists of several functional group (from FTIR results) such as hydroxyl group and carbonyl group. The hydroxyl group could exchange with iodide ions. Owing to the ion selectivity for the negative ion is as follow:



So the hydroxyl ion could be interchanged easily for iodide ion [Narong, 1986]. The reaction between weak-basic ion exchange (WB) with anion is as follow:



For the half-cell reaction of iodide ion and hydroxyl ion is as follow [Inthira, 1995]:



From the standard electrode potential (SHE), the hydroxyl group could release or exchange easily with iodide ion, thus the probability between the two negative ions to interchange is high.

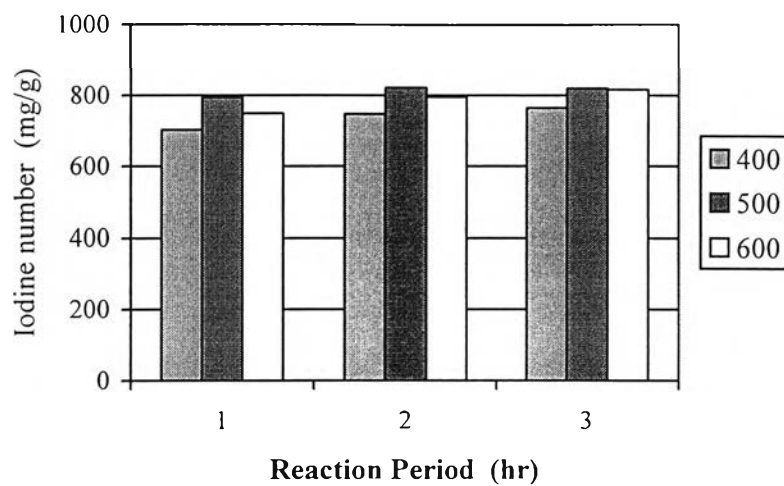


Figure 5.15 Iodine numbers of carbon adsorbents from water hyacinth reacted with zinc chloride

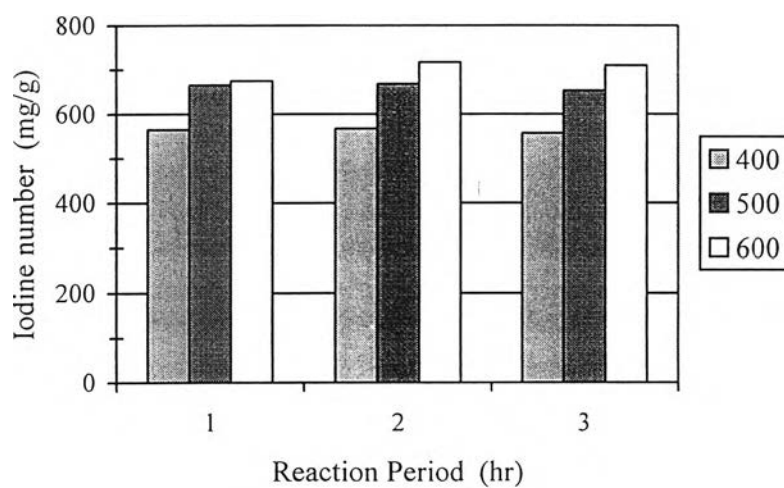


Figure 5.16 Iodine numbers of carbon adsorbents from rice husk reacted with zinc chloride

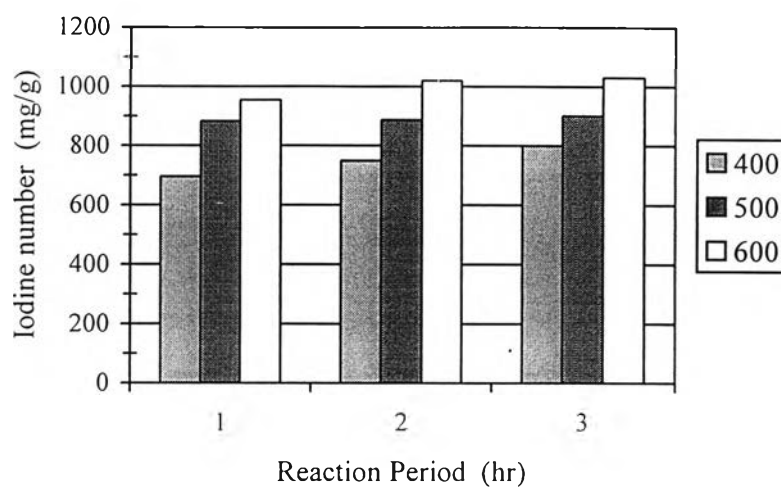


Figure 5.17 Iodine numbers of carbon adsorbents from sugar-cane bagasses reacted with zinc chloride

The average pore size of carbon adsorbents depended merely on the reaction temperature as shown in Figure 5.18–5.20. With slow rates of reaction, the carbon adsorbents from water hyacinth provided a relatively small pore size in comparison with the existing pore size, i.e. approximately  $40\text{\AA}$ , which could be obtained by the process without zinc chloride. On the contrary, the pore size of carbon adsorbents became relatively large with fast rate of reaction.

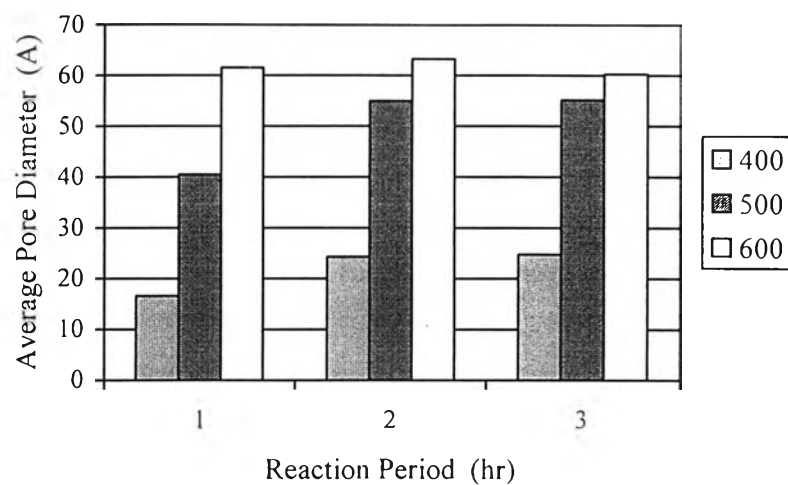


Figure 5.18 The average pore sizes of carbon adsorbents from water hyacinth reacted with zinc chloride

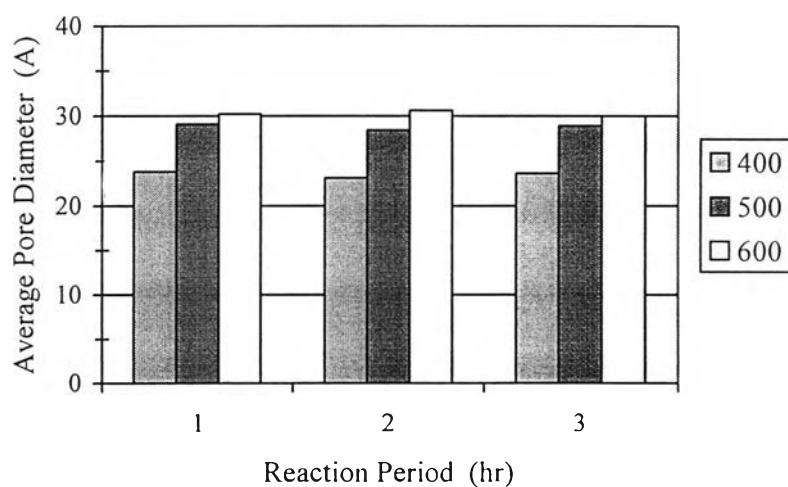


Figure 5.19 The average pore sizes of carbon adsorbents from rice husk reacted with zinc chloride

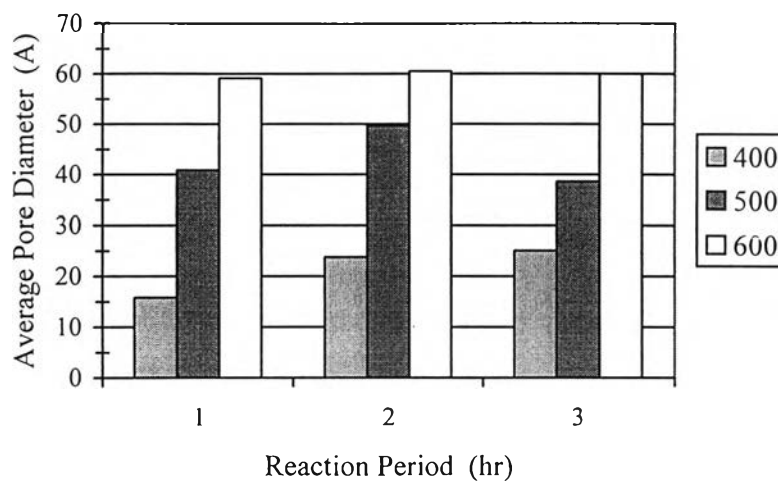


Figure 5.20 The average pore sizes of carbon adsorbents from sugar-cane bagasses reacted with zinc chloride

### 5.2.2 Functional Groups

From figure 5.21–5.29, all carbon adsorbents from water hyacinth constituted hydroxyl group, alkyl group, carbonyl group, carboxylic group, and ether group at the wave numbers of 3500, 2900, 1600, 1400, and 1200  $\text{cm}^{-1}$ , respectively. Generally, Y-axis or percent transmittance can be used to estimate the amount of the functional group, the higher percent transmittance, the higher amount of functional group.

Owing to the equal weight of all samples used and the relative peak height at the wave number of 3500 and 1600  $\text{cm}^{-1}$  can be calculated as they referred to hydroxyl group and carbonyl group, respectively. The data was shown in Table 5.3.

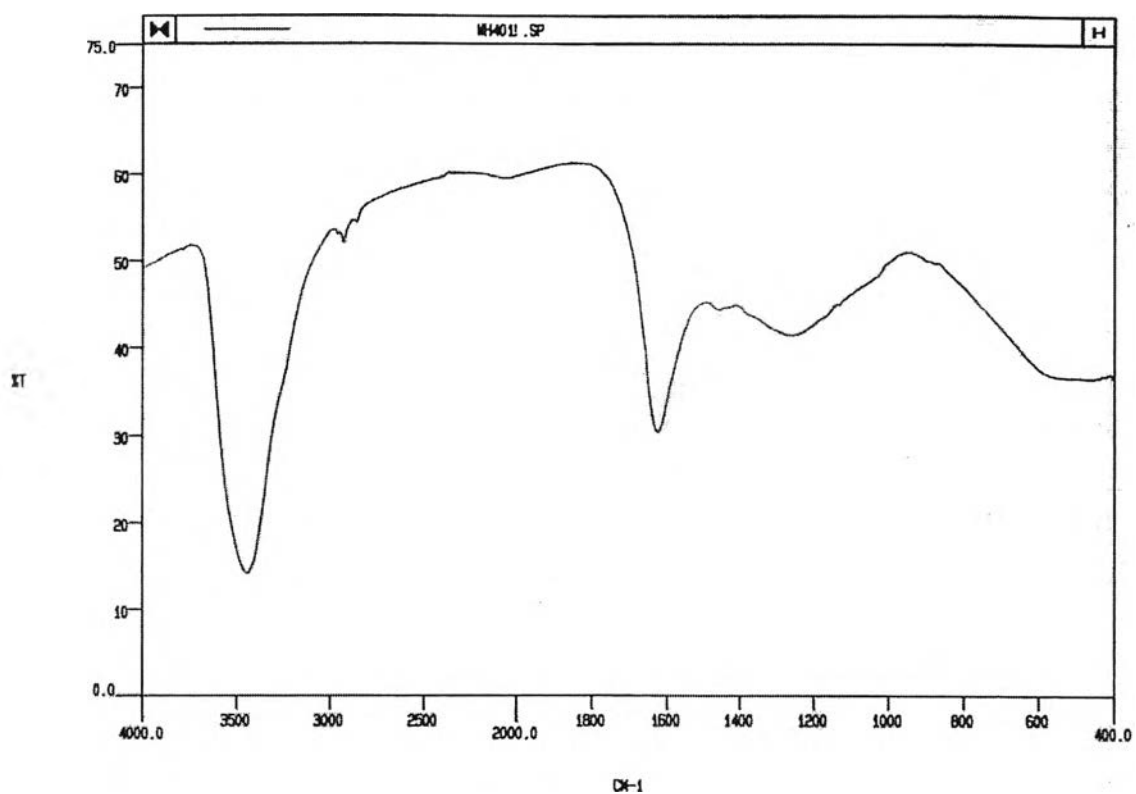


Figure 5.21 IR spectrum of carbon adsorbent WH401

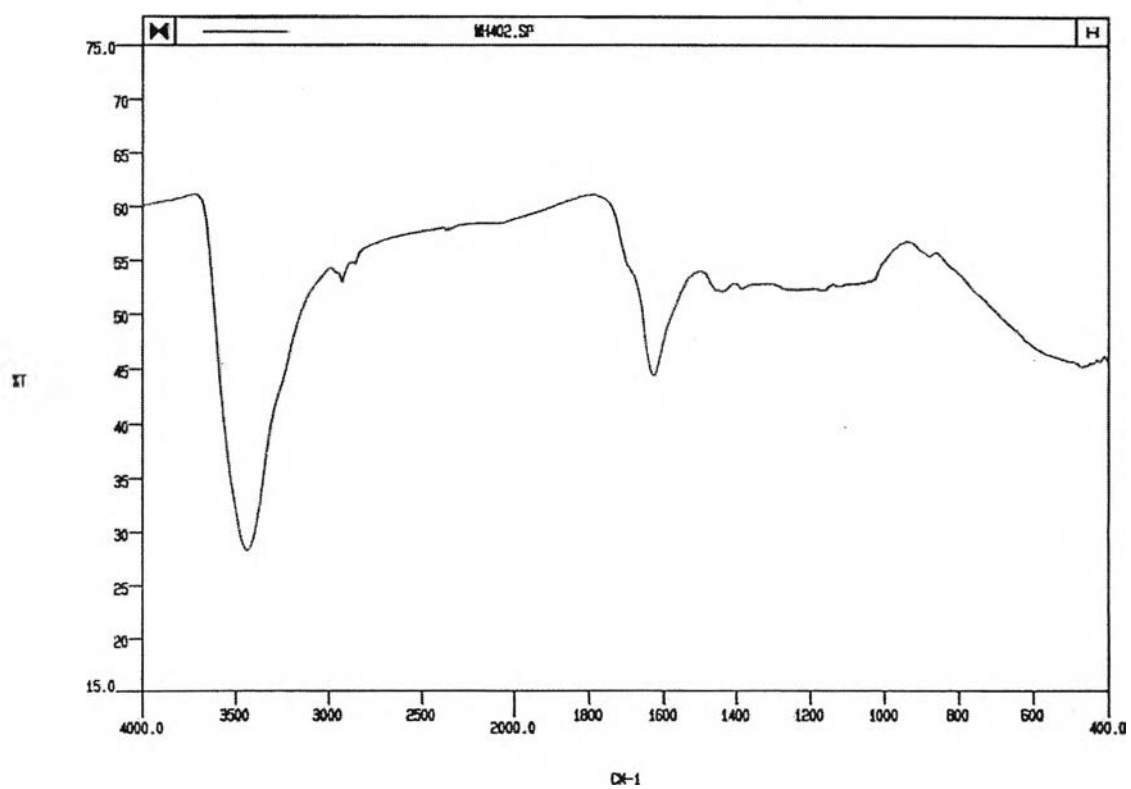


Figure 5.22 IR spectrum of carbon adsorbent WH402

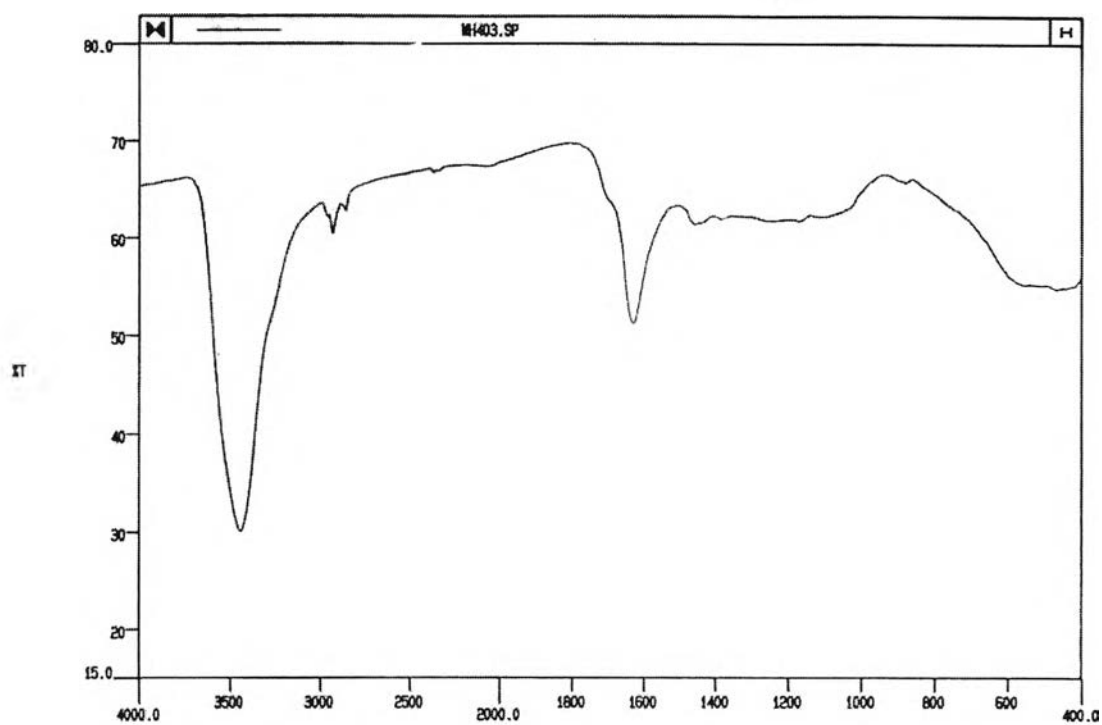


Figure 5.23 IR spectrum of carbon adsorbent WH403

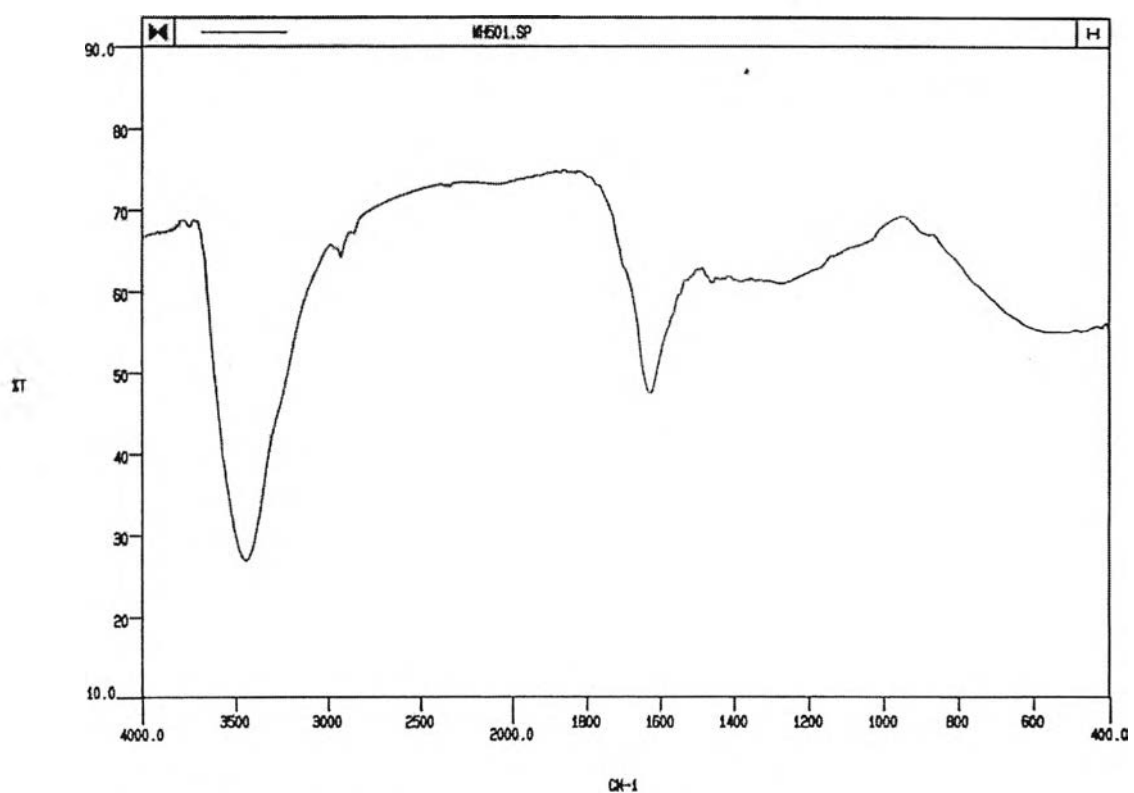


Figure 5.24 IR spectrum of carbon adsorbent WH501



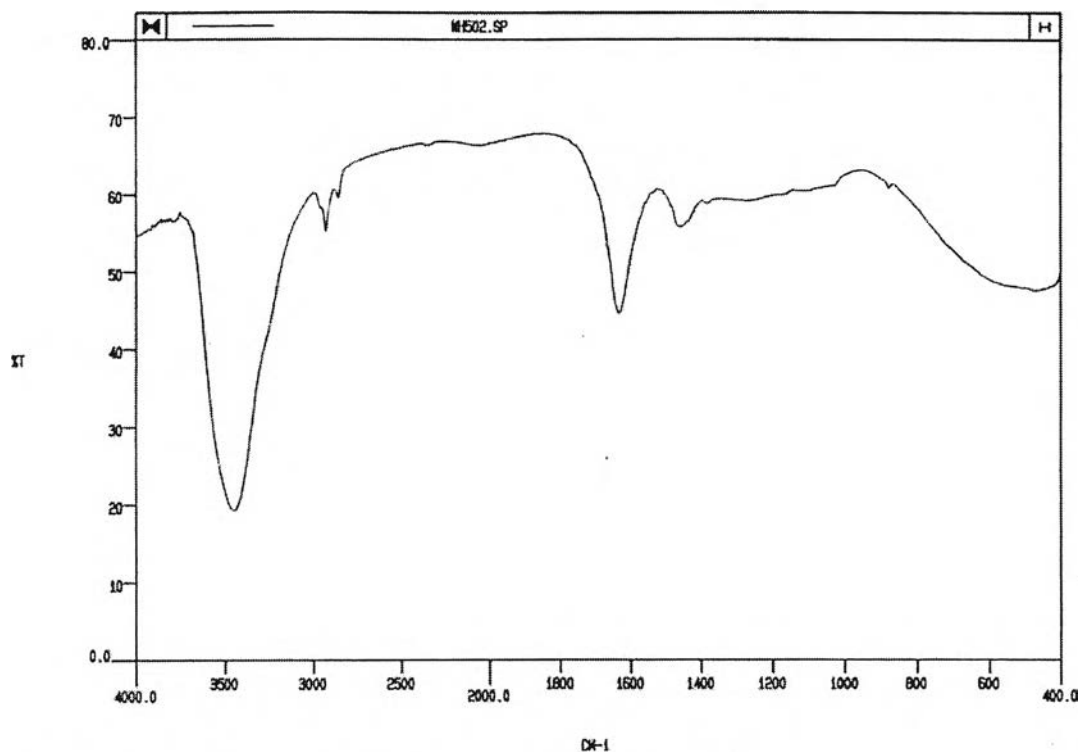


Figure 5.25 IR spectrum of carbon adsorbent WH502

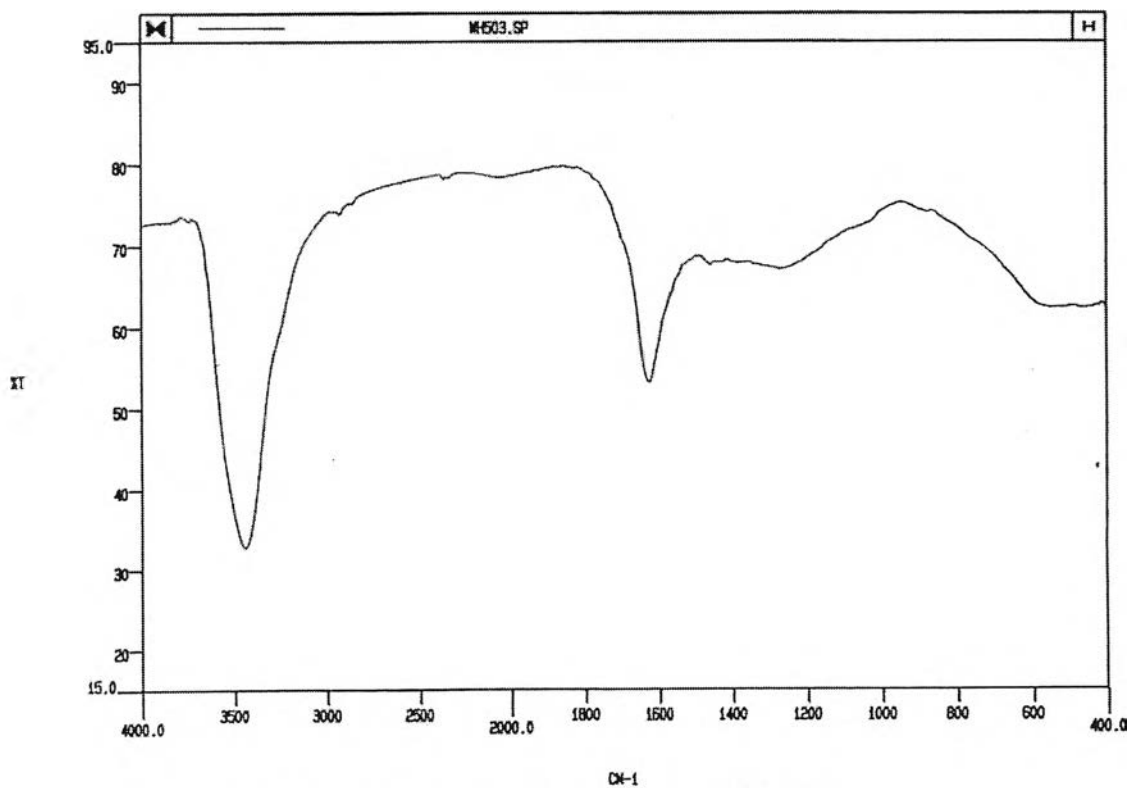


Figure 5.26 IR spectrum of carbon adsorbent WH503

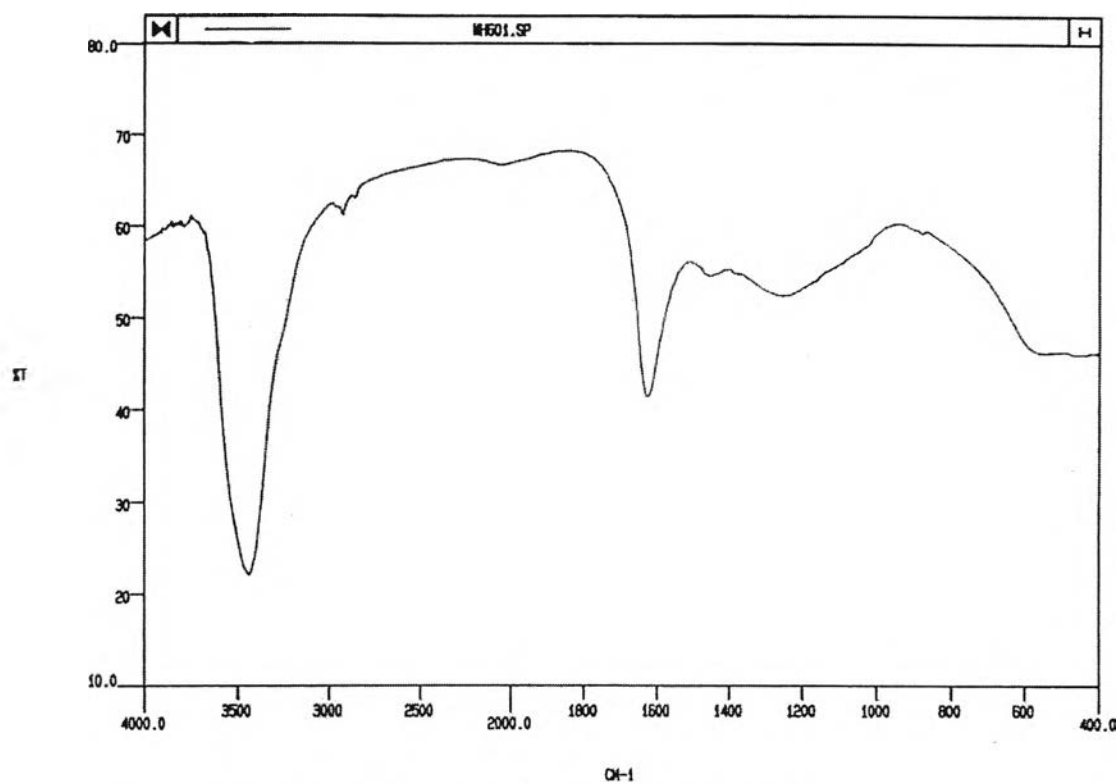


Figure 5.27 IR spectrum of carbon adsorbent WH601

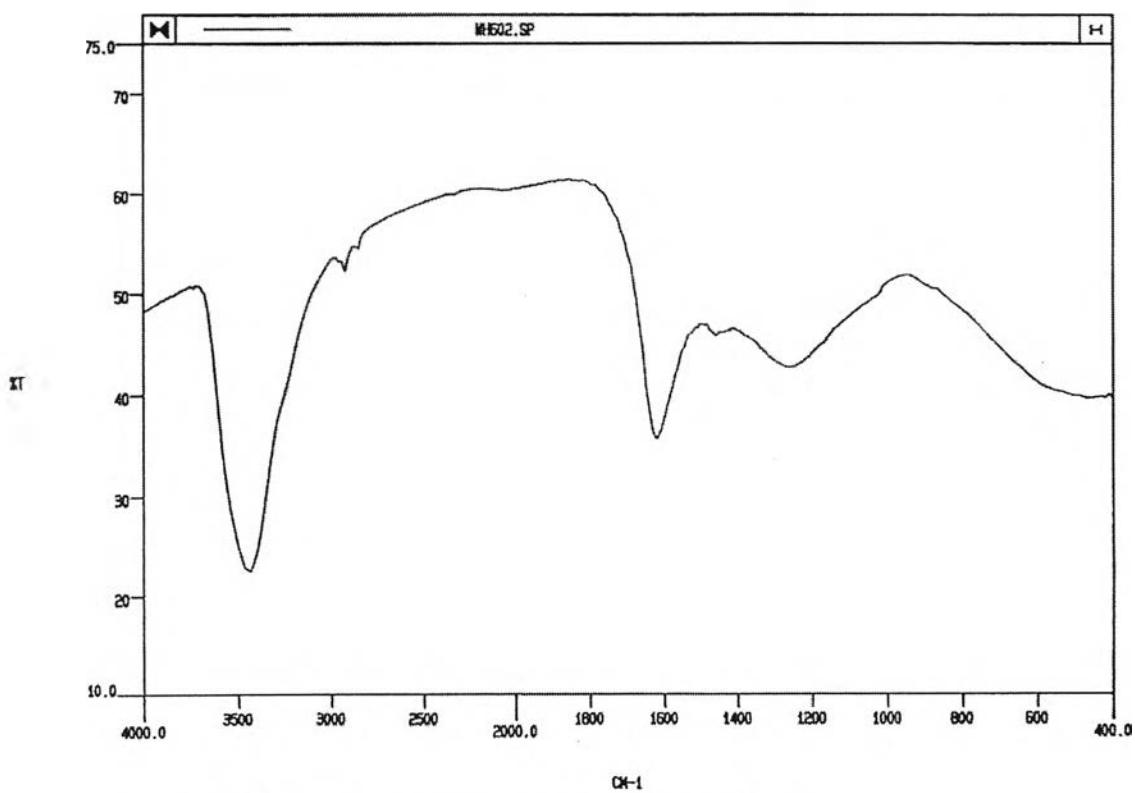


Figure 5.28 IR spectrum of carbon adsorbent WH602

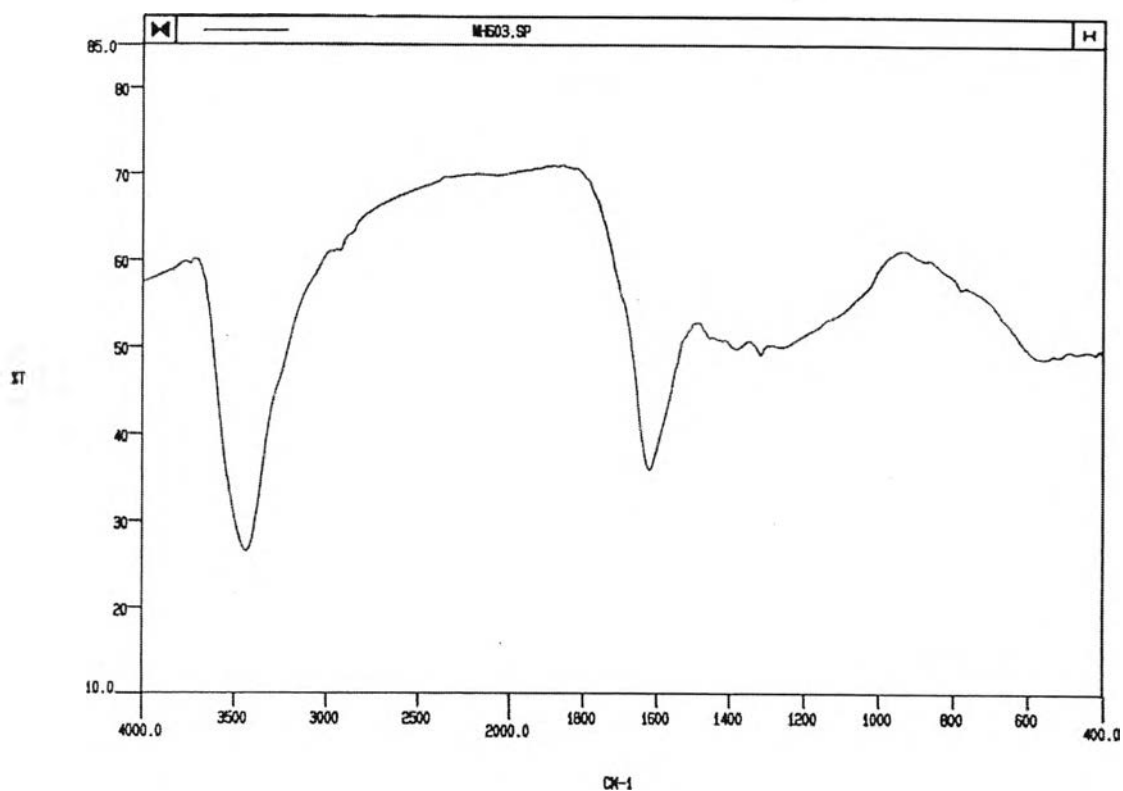


Figure 5.29 IR spectrum of carbon adsorbent WH603

Table 5.3 Peak height of the functional group at 3438 and 1632  $\text{cm}^{-1}$

Carbon adsorbents	Peak location 3438 $\text{cm}^{-1}$	Peak location 1632 $\text{cm}^{-1}$
	Total peak height	Total peak height
WH401	0.7794	0.3709
WH402	0.5487	0.3505
WH403	0.5220	0.2889
WH501	0.5708	0.3219
WH502	0.7163	0.3510
WH503	0.4859	0.2715
WH601	0.6576	0.3787
WH602	0.6487	0.4358
WH603	0.5652	0.4332

So the increasing sequence of quantity of the function group for hydroxyl group was WH503/WH403/WH402/WH603/WH501/WH602/WH601/WH502/WH401

and for the carbonyl group was WH503/WH403/WH501/WH402/WH502/WH401/WH601/WH603/WH602.

It is believed that the functional groups on the surface of carbon adsorbent were active sites of the carbon adsorbents because they could exchange the electron or ion [Hassler, 1974]. According to these assumption, it could be assumed that the more the quantity of active site, the more the power of adsorption.

Consider the IR spectrum data from the peak height, this data could be utilized in the adsorption part. This will be discussed later.

### 5.2.3 Particle Density

Particle density of each carbon adsorbent was measured indirectly by measuring the pressure drop across the packed bed at various flowrates of carrier gas. The results corresponded with equation 4.2. The porosity of the bed was determined from the bulk density as summarized in Table 5.4.

Table 5.4 Particle density of prepared carbon adsorbents

Carbon adsorbents	Weight (g)	Volume of bed (cm <sup>3</sup> )	<i>L</i> (cm)	$\rho_b$ (g/cm <sup>3</sup> )	$\rho_p$ (g/cm <sup>3</sup> )	$\epsilon$
WH401B	0.1469	0.6336	2.0	0.2318	0.3639	0.3631
WH402B	0.1207	0.6336	2.0	0.1905	0.3314	0.4252
WH403B	0.0654	0.3168	1.0	0.2064	0.2999	0.3118
WH501B	0.0237	0.3168	1.0	0.0748	0.1211	0.3822
WH502B	0.0555	0.6336	2.0	0.0876	0.1292	0.3219
WH503B	0.0464	0.4752	1.5	0.0976	0.1464	0.3334
WH601B	0.0304	0.3168	1.0	0.0959	0.1262	0.2402
WH602B	0.0274	0.3168	1.0	0.0865	0.1211	0.2860
WH603B	0.0213	0.3168	1.0	0.0672	0.1030	0.3477

### 5.3 FIRST MOMENT ANALYSIS

For the chromatographic method, a necessary condition of the mathematical description of the adsorption process was that the adsorption was linear. The adsorption measurements were made at sufficiently low concentrations. Injected amount had to be varied in order to achieve the appropriate chromatograms which could be analyzed precisely.

The sample gas for adsorption experiments contained benzene vapour, toluene vapour, and o-xylene vapour about 15.9, 4.8, and 1.2% by volume, respectively.

#### 5.3.1 Adsorption Equilibrium Constants

Figure 5.30 illustrated the plots of weighted mean retention time ( $t_R$ ) versus  $L/v$  for toluene vapour. All results were straight line of which the adsorption equilibrium constants ( $K$ ) were able to be determined from the slope of corresponding line according to equation 2.11. The adsorption equilibrium constants of toluene, benzene, and o-xylene were summarized in Table D.1–9.

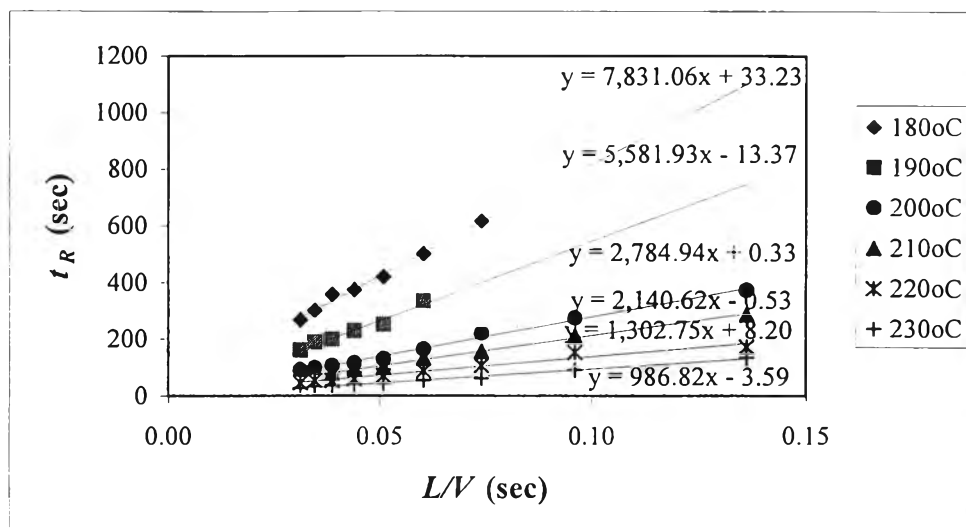


Figure 5.30 The retention time of toluene vapour on WH401 as a function of  $L/v$

The retention time of each chromatogram was affected by two parameters, i.e. the adsorption equilibrium constant and the carrier gas velocity. In principle, the retention time became longer with a large value of the equilibrium constant than a small one for a given gas velocity. In contrast, it became shorter with a high flowrate than the slow one for a given adsorption equilibrium constant.

As the effects of temperatures, the retention time decreased as an increase in temperature for a given flowrate. In other words, the adsorption equilibrium constant became smaller at high temperature than at low temperature. The results corresponded to exothermic process.

According to equation 2.11, the straight line should pass the origin; but for some systems, the intercepts clearly deviate from the origin. This is the effect of the deviation from isobaric condition within the bed [Carleton, 1978]. The extrapolations

of the asymptotic linearity to infinite flowrate led to first moment are equal to zero on the negative axis. It depends only on the parameters of the packed bed and the viscosity of the carrier gas but it is independent of the nature of the adsorbed species.

The correlation between the adsorption equilibrium constant and the column temperature obeyed van't Hoff equation. In other words, the logarithmic of equilibrium constant was proportionate to the reciprocal temperature. Then the heat of adsorption was able to be obtained from the slope of the linear plot. In addition, the resulted heat of adsorption was independent of temperature.

For a given adsorbate, the heat of adsorption on each type of adsorbents, as summarized in Table 5.5 was different from others owing to their surface chemistry. Heat of adsorption is about twofold value of heat of condensation (see Table E.5).

Table 5.5 Summary of heat of adsorption

Adsorbent	Heat of Adsorption (kJ/mole)		
	Benzene	Toluene	o-Xylene
WH401	-73.44	-81.27	-104.37
WH402	-71.22	-86.03	-96.58
WH403	-59.64	-90.30	-109.88
WH501	-53.92	-58.26	-102.45
WH502	-69.00	-83.61	-96.01
WH503	-95.64	-70.57	-36.91
WH601	-84.79	-93.08	-69.25
WH602	-69.83	-75.55	-89.57
WH603	-70.48	-88.47	-56.17
Corncob [Supaporn, 1998]	-96.40	-55.48	-151.15
Coconut shell [Ratchada, 1997]		-65.05	
MSC [Kawazoe, 1974]	-91.56		
Activated carbon [Grajek, 1997]	-81.90		

In comparison with the others' works, the heat of adsorptions of toluene, benzene and o-xylene vapours on the carbon adsorbent prepared from water hyacinth reacted with zinc chloride were closed to those results

#### 5.3.1.1 Effects of Reaction Temperatures and Periods

The carbon adsorbents were prepared from water hyacinth and the products were characterized with nitrogen adsorption surface area and iodine adsorption. All data were summarized in Table 5.6. From Figure 5.31, it is found that the WH602 adsorbent gave the highest value of the adsorption equilibrium constants, but it had the surface area about 1,268 m<sup>2</sup>/g. While the WH503 had the highest surface area, but it could adsorb the lowest amount of toluene. However, the iodine number was not corresponded with the adsorption equilibrium constant. The results demonstrated that the equilibrium constant did not correspond with the specific surface area. They may be because the carbon adsorbent did not have the adsorptive power at active site in all positions of surface. Thus, the total surface area did not necessarily mirror the utility of a carbon adsorbent. Frequently for a given situation, a type of carbon adsorbent having relatively small area of surface will be more effective than another carbon adsorbent with much greater total surface. In many applications, only part of the surface participates in the adsorption and the rest of the surface is not occupied by the substance being adsorbed [Hassler, 1974].



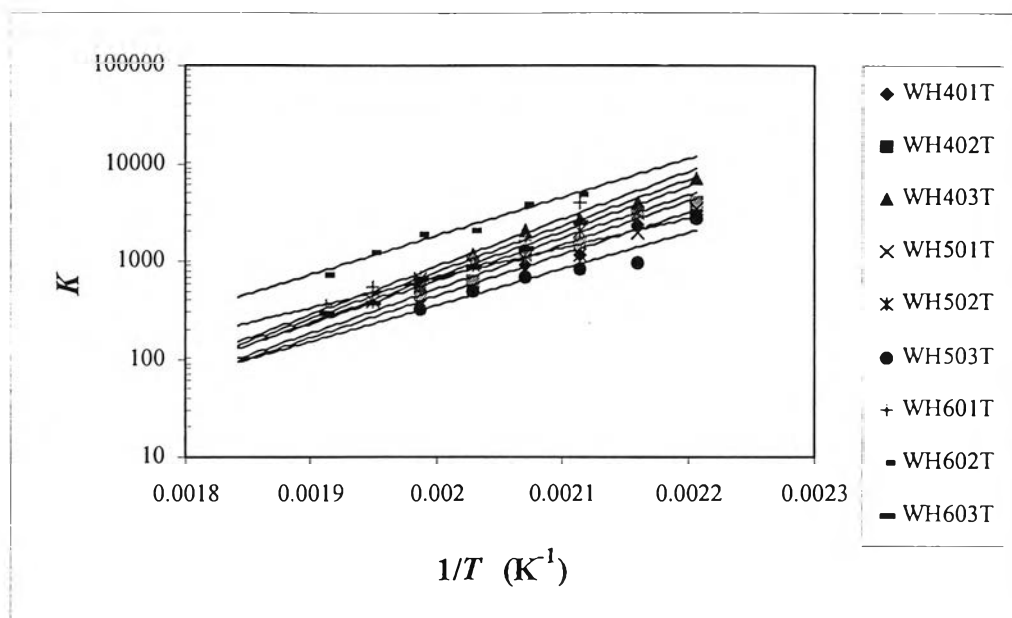


Figure 5.31 The adsorption equilibrium constants of toluene vapour on various adsorbents

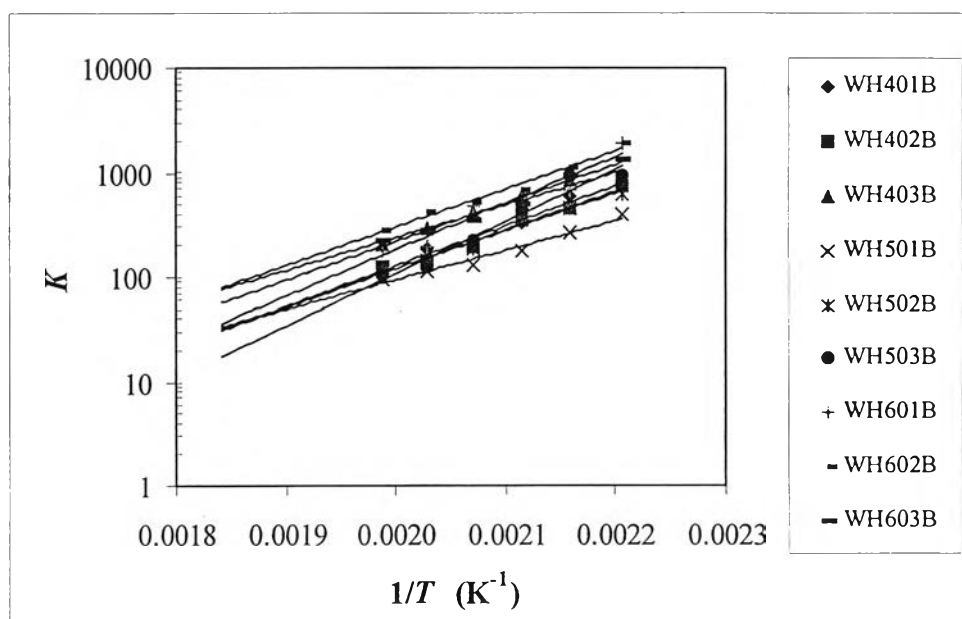


Figure 5.32 The adsorption equilibrium constants of benzene vapour on various adsorbents

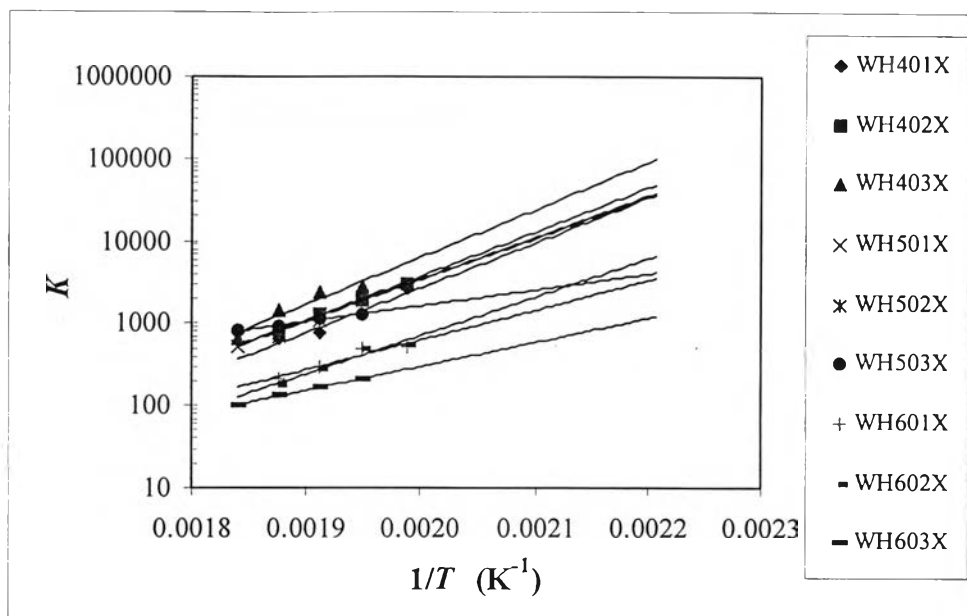


Figure 5.33 The adsorption equilibrium constants of o-xylene vapour on various adsorbents

For the IR spectrum results, it is found that the highest peak height at the wave number of  $1600\text{ cm}^{-1}$  (carbonyl group) is corresponded to the highest adsorption capacity of WH602 for toluene vapour, and also the lowest peak height at the wave number  $1600\text{ cm}^{-1}$  is corresponded to the lowest adsorption capacity of WH503 (see Table 5.3 and Figure 5.31). From this result, it suggests that the active site on the carbon adsorbent surface influences the adsorption capacity of carbon adsorbents more than the BET surface area or iodine number.

Table 5.6 Characteristic of carbon adsorbents from water hyacinth

Properties of Adsorbents	BET surface area (m <sup>2</sup> /g)	Average pore size (Å)	Iodine number (mg/g)	Yield <sup>§</sup> (%)
WH401	786.04	16.62	703	32.77
WH402	907.65	24.32	747	31.56
WH403	982.59	24.77	764	31.31
WH501	1293.44	40.48	794	29.25
WH502	1352.41	54.96	821	27.83
WH503	1323.75	55.14	820	26.99
WH601	1152.03	61.54	749	24.90
WH602	1268.53	63.25	795	24.02
WH603	1231.24	60.27	816	24.05

<sup>§</sup> % yield is referred to the ratio of carbon adsorbent weight after washing and drying to the weight of water hyacinth after drying at 100°C, 1–2 hours multiply with 100.

The adsorption of benzene vapour and o-xylene vapour did not agree with the quantity of the functional group of carbonyl or hydroxyl group, as the result of toluene vapour adsorption. It might be that there are many active sites which can adsorb the benzene and o-xylene vapours, so the dominant active site could not be distinguished by using the two active sites, i.e. carbonyl group and hydroxyl group. The adsorption equilibrium constants of benzene and o-xylene vapours were shown in Figure 5.32–5.33, respectively.

Some samples of the experimental results about the adsorption equilibrium constant that did not agree with the characteristics of carbon adsorbents (BET surface area and iodine number) were shown in Figure 5.34–5.36.

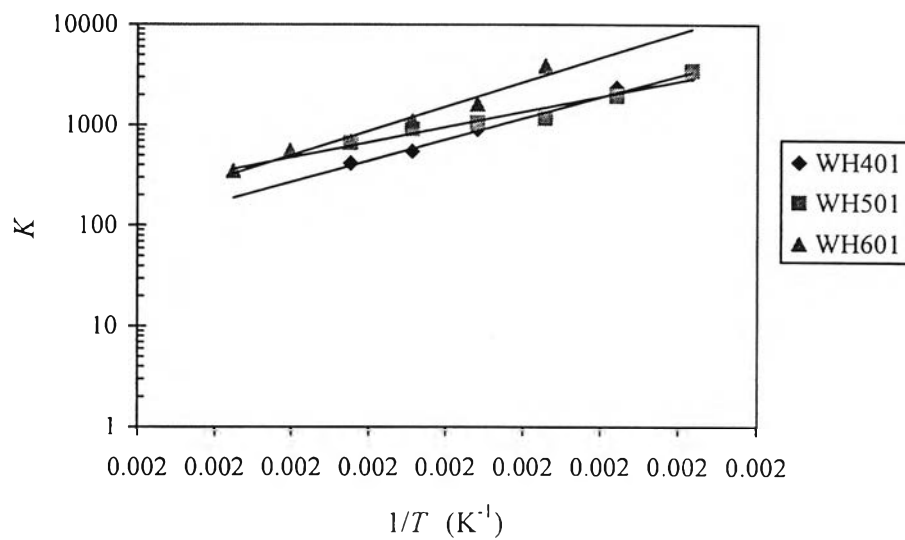


Figure 5.34 The adsorption equilibrium constants of toluene vapour on WH401, 501, and 601

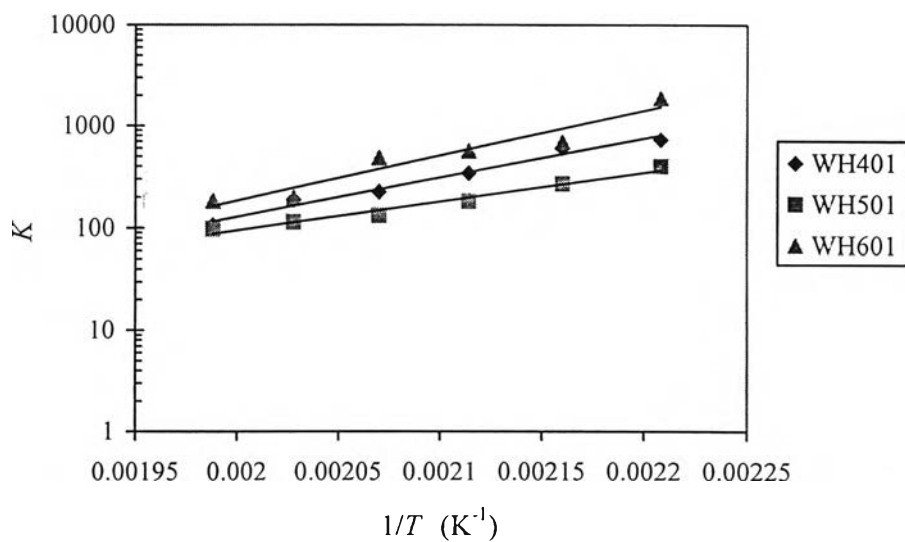


Figure 5.35 The adsorption equilibrium constants of benzene vapour on WH401, 501, and 601

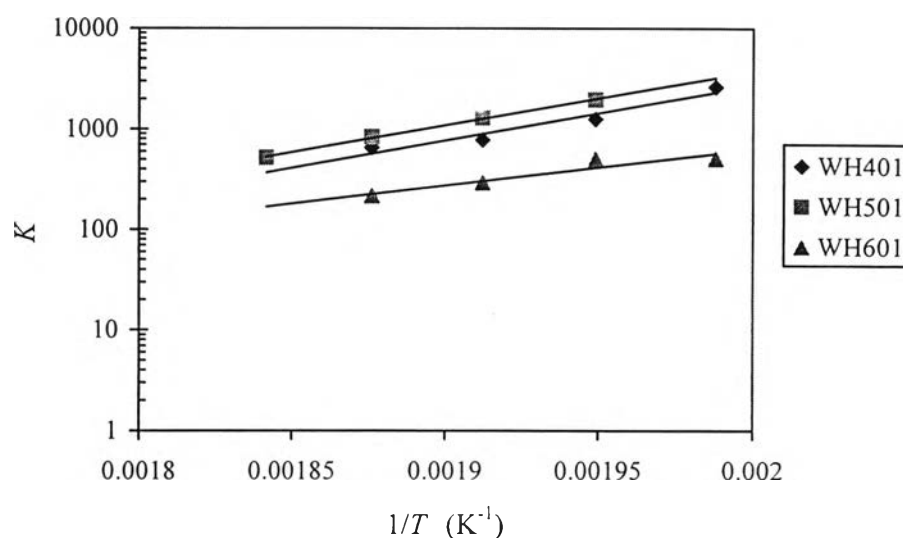


Figure 5.36 The adsorption equilibrium constants of o-xylene vapour on WH401, 501, and 601

In comparison among the adsorbates, the adsorption equilibrium constant of o-xylene on each carbon adsorbent was the highest. While that of toluene was higher than that of benzene on the same adsorbent. The results demonstrated that the adsorbents produced from zinc chloride contained polar surface and preferred adsorbing polar molecules to non-polar molecules (See Table E.5 – dipole moment) as shown in Figure 5.37–5.42.

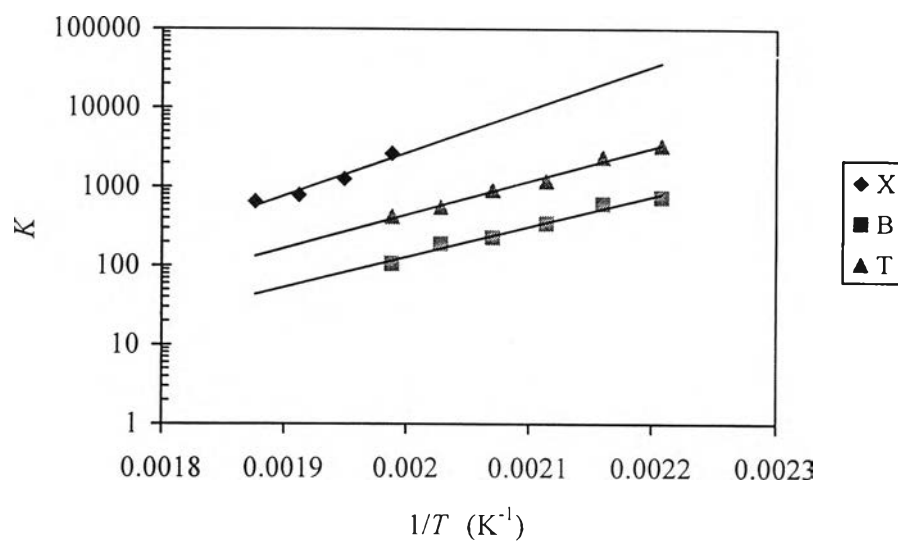


Figure 5.37 The adsorption equilibrium constants of BTX vapours on WH401

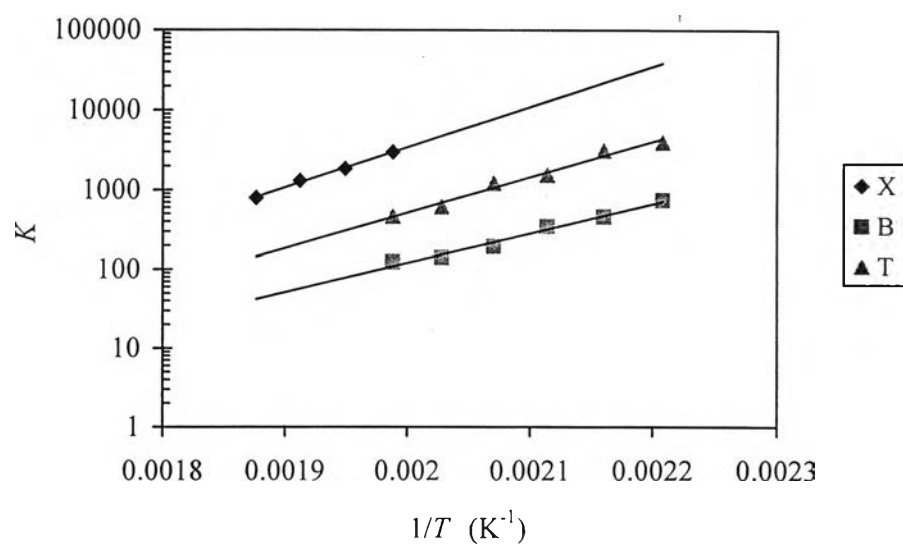


Figure 5.38 The adsorption equilibrium constants of BTX vapours on WH402

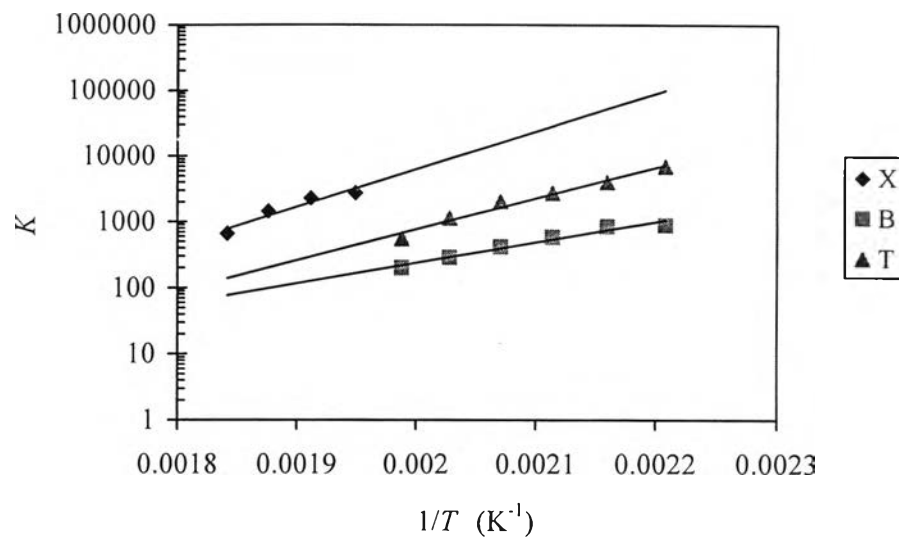


Figure 5.39 The adsorption equilibrium constants of BTX vapours on WH403

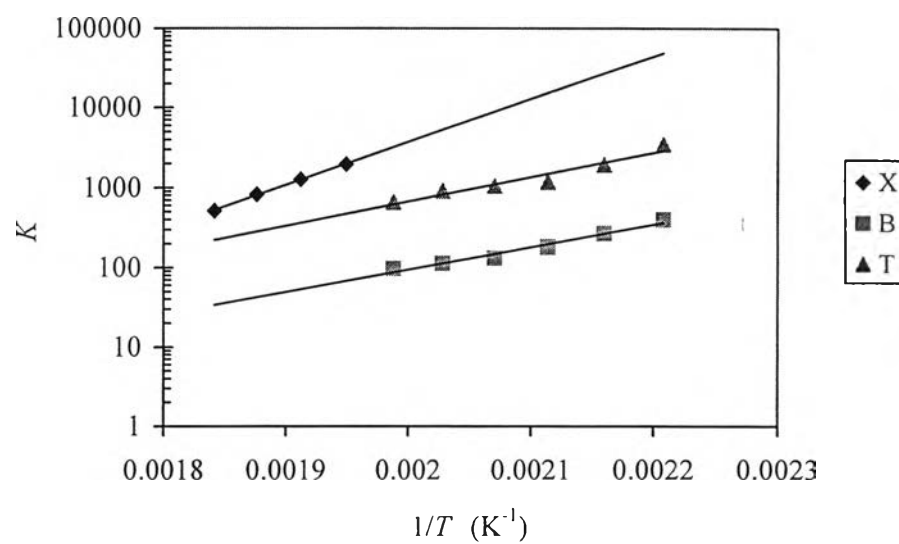


Figure 5.40 The adsorption equilibrium constants of BTX vapours on WH501

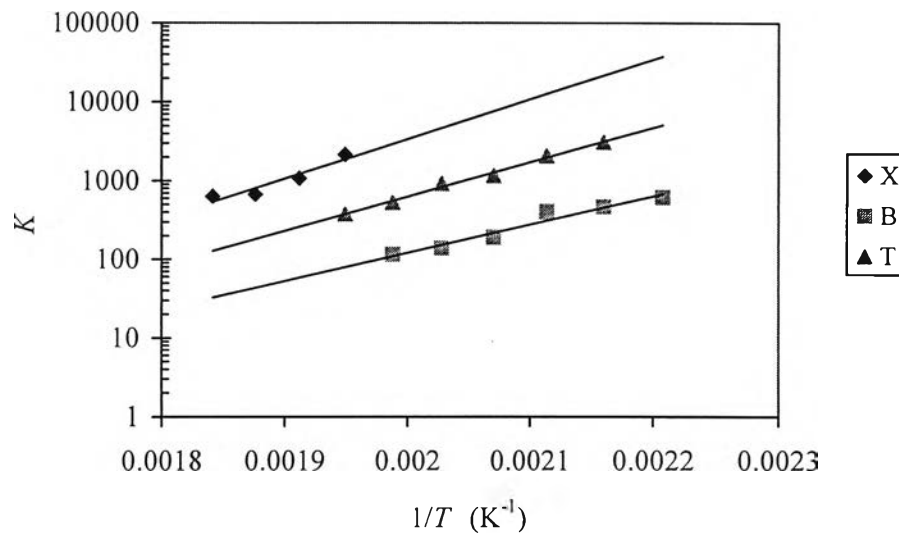


Figure 5.41 The adsorption equilibrium constants of BTX vapours on WH502

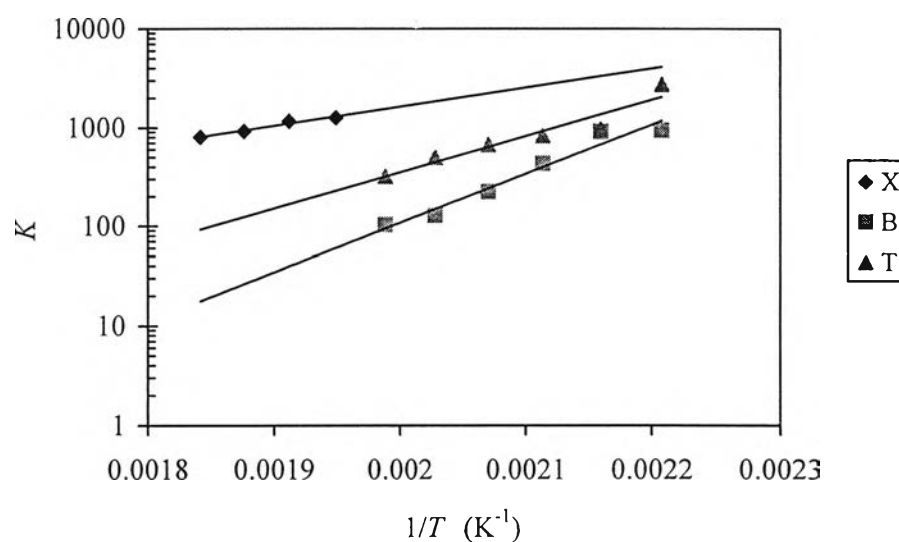


Figure 5.42 The adsorption equilibrium constants of BTX vapours on WH503

The results correspond with Supaporn's experiments [Supaporn, 1998]. The results for WH401, WH402, WH501, WH502, WH503 were the same as WH401 as mentioned above. But for the adsorption results of WH601, WH602 and WH603, the adsorption sequence is  $T > X > B$ . It might be the active sites of carbon



were decreased due to the high activation temperature, and so affected the amount of active sites.

## 5.4 SECOND MOMENT ANALYSIS

### 5.4.1 Overall Mass-Transfer Coefficients

According to equation 2.20, overall mass-transfer coefficients for adsorption of benzene, toluene, and o-xylene on various adsorbents were obtained from the intercept of the corresponding of the linear plot.

In addition, the mass-transfer coefficient (the adsorption rate constant) increased with an increase in the temperature of system quite strongly as shown in Figure 5.43 which is similar to chemical reaction characteristics.

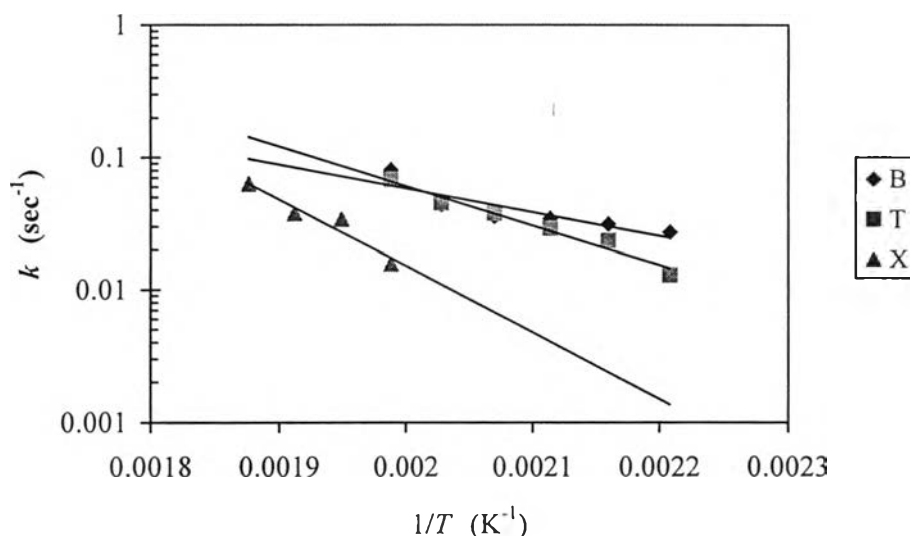


Figure 5.43 The overall mass-transfer coefficients of BTX vapours on WH401

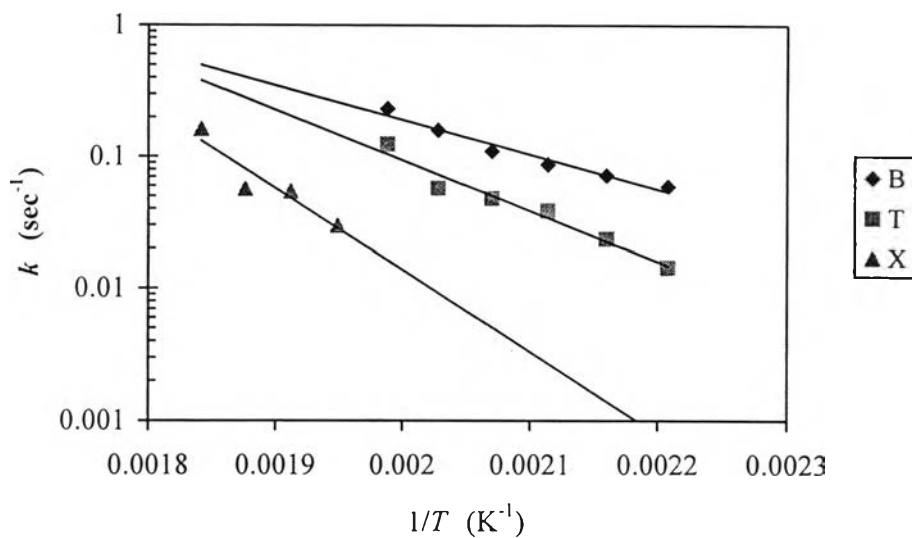


Figure 5.44 The overall mass-transfer coefficients of BTX vapours on WH403

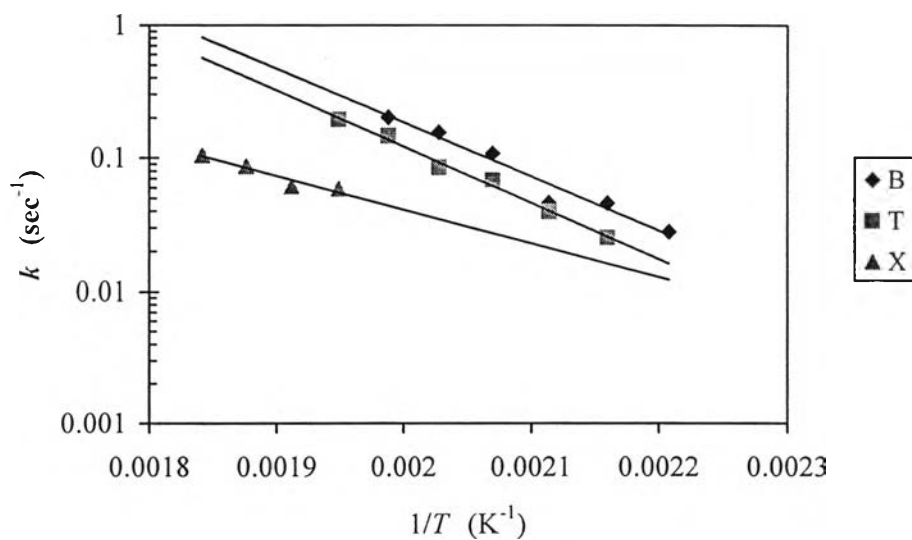


Figure 5.45 The overall mass-transfer coefficients of BTX vapours on WH502

In comparison among the adsorbates, the overall mass-transfer coefficient or adsorption rate constant of benzene on each carbon adsorbent was the highest. While that of toluene was higher than that of o-xylene on the same adsorbent. The results demonstrated that the rate of adsorption depended on the shape of the adsorbate molecule. Benzene had symmetry of the molecule, and toluene and o-xylene had the unsymmetry molecules, whereas o-xylene was more unsymmetric than toluene. So, when the adsorbate molecule moved to attach the adsorbent, o-xylene had the most difficulty in moving because of the obstruction of its molecules more than that of toluene and benzene molecules.

Consider the mean free path and the molecular size of the 3 adsorbates (Table E.5), the benzene molecule has a longer mean free path than the others, so it has an opportunity to be adsorbed more rapidly than the toluene and o-xylene molecules, which agree with the experimental results as shown in Figure 5.43–5.45.

The resulted overall mass-transfer coefficient included the external film mass-transfer coefficient and pore mass transfer whereas the controlling step of each system was not verified.

The external film mass-transfer coefficients calculated from Sherwood number in equation 2.13 were much higher than the overall mass-transfer coefficients from the experimental results. Thus, the controlling step of mass transfer should be pore-diffusion step [Supaporn, 1998; Ratchada, 1997].