CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization Results

4.1.1 Scanning Electron Microscope (SEM) and Surface Area Analyzer

Figures 4.1 and 4.2 demonstrate the surface morphology of the non-impregnated and 28.57 wt % piperazine-activated carbon (20–40 mesh size) at a magnification of 100,000 times. By comparison, there is only a slight difference in the surface and pore size. The scanning electron microscope was able to observed only the macropore (> 50 nm) and the mesopore (2–50 nm) whereas higher magnifications were needed for the micropore (<2 nm). To understand the surface morphology more precisely, surface area analysis was applied in order to distinguish the changes of non-impregnated and impregnated activated carbon pore volume and pore size distribution. There is a decrease in the surface area and pore volume of the micropore with scarcely change in the mesopore (Table 4.1). The decrease in the surface area could indicate that there was some amount of piperazine blocking in the micropore which resulted in the decrease in pore volume. The result supported the earlier SEM morphology that there was hardly change in the surface morphology for the macro- and mesopore. However, from the result it can be assumed that 28.57 wt % piperazine was not entirely loaded into the pore site of the activated carbon because there was only a slight decrease in the pore volume of the micropore and not even in the mesopore.
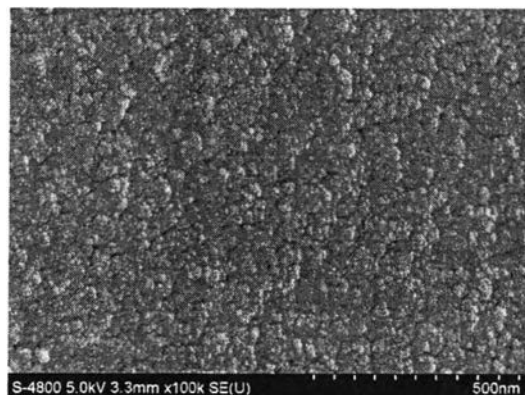

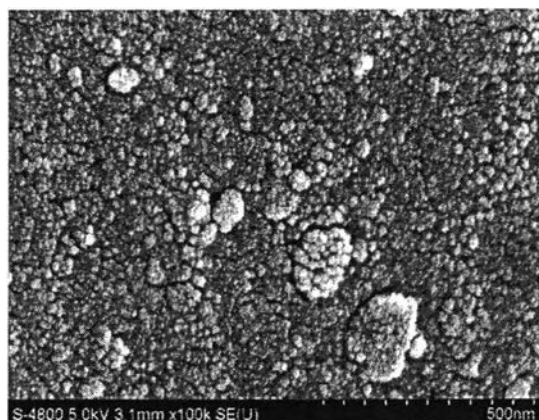**Figure 4.1** Non-impregnated activated carbon 20–40 mesh size magnified 100,000 times.

Figure 4.2 28.57 wt % piperazine loaded on activated carbon 20–40 mesh size magnified 100,000 times.

Table 4.1 The surface area analysis of non-impregnated and impregnated activated carbon

Adsorbing Bed	Total surface area, (m^2/g)	Mesopore surface area, (m^2/g)	Micropore surface (m^2/g)	Total pore volume (cc/g)e-01	Mesopore volume (cc/g) e-01	Micropore volume (cc/g) e-01	Average pore diameter(Å)
Non-impregnated activated carbon	801.9	745.2	764.0	4.43	2.57	3.79	22.10
28.57 wt % piperazine - activated carbon	570.9	734.5	535.3	3.25	2.60	2.65	22.81

4.1.2 Analysis of degree of piperazine loading (wt %)

A calibration curve shown in Figure 4.3 was done to determine the concentration of an unknown sample in the activated carbon by comparing with piperazine standards of known concentration. The plots were then fitted into a straight line, using linear regression which can be described by the linear equation, y = 13771x + 0.8415, where y is the area, 13771 is sensitivity and 0.8415 is the interception and x is the analyte concentration of unknown samples. The piperazine standard of known concentration showed the coefficient of determination, R^2 =0.9989. The result showed the average maximum of 3.12 wt % of piperazine loaded on the activated carbon after loading 28.57 wt %. The unknown concentration had been calculated from the curve. In addition, the CNH analysis showed the actual piperazine loading of 3.54 wt %. However, the result of 3.12 wt % was used instead

of 3.54 wt % to all the entire experiment. This comprehends the effect of piperazine loading (wt %) not to be concerned over varying piperazine loading.
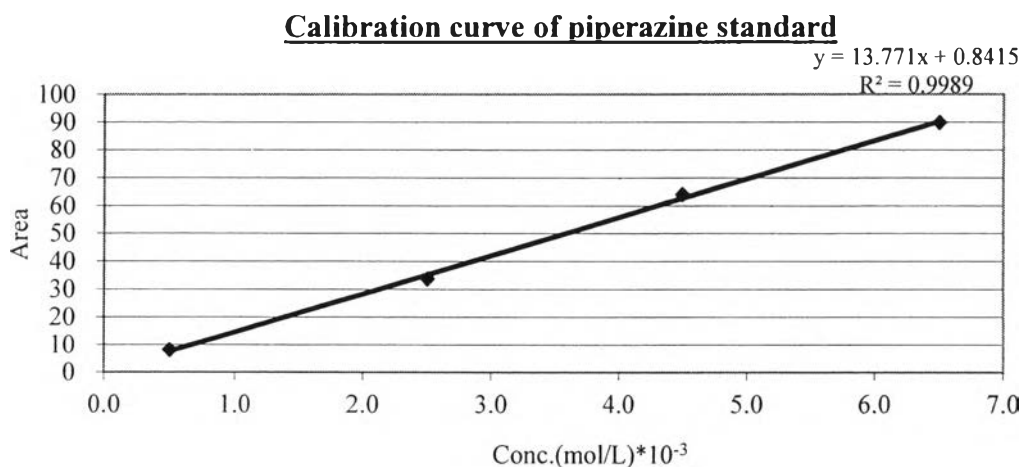
Calibration curve of piperazine standard

$y = 13.771x + 0.8415$
$R^2 = 0.9989$

Figure 4.3 Calibration curve of piperazine standard of known concentration.

4.1.3 Thermo gravimetric analysis (TG-DTA)

Piperazine, activated carbon and 3.12 wt % piperazine-activated carbon were subjected to pyrolysis in 90 mL/min of nitrogen gas at a heating rate of 5 °C/min to 900 °C to study their thermal stability. Piperazine decomposed at 78.99 °C as shown in Figure 4.4. To evaluate the stability of the impregnation of piperazine and the activated carbon, pure activated carbon and 3.12 wt% piperazine activated carbon were also exposed to heat and their thermal stability shown in Figure 4.5. The impregnated 3.12 wt% piperazine-activated carbon was decomposed at a higher temperature of 82.84 °C.
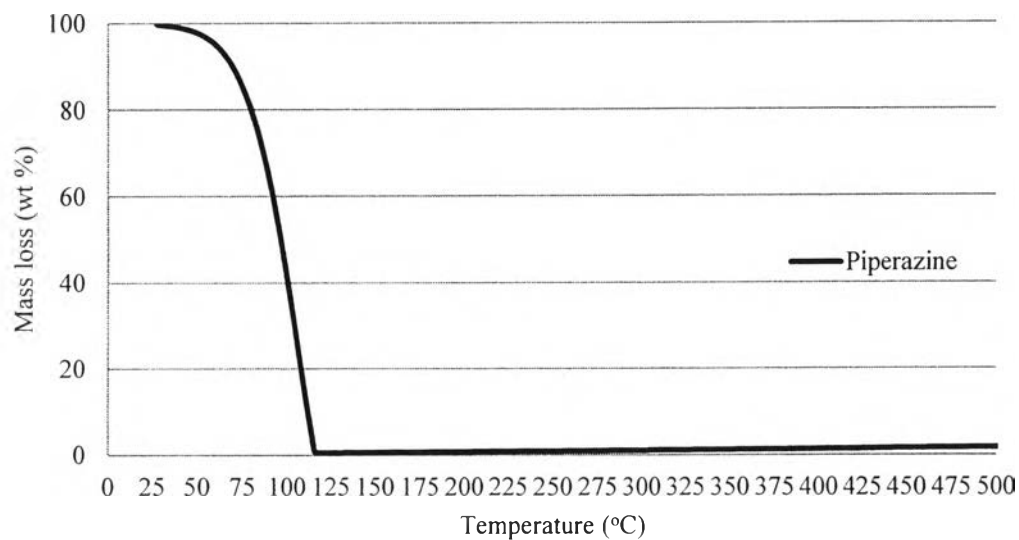
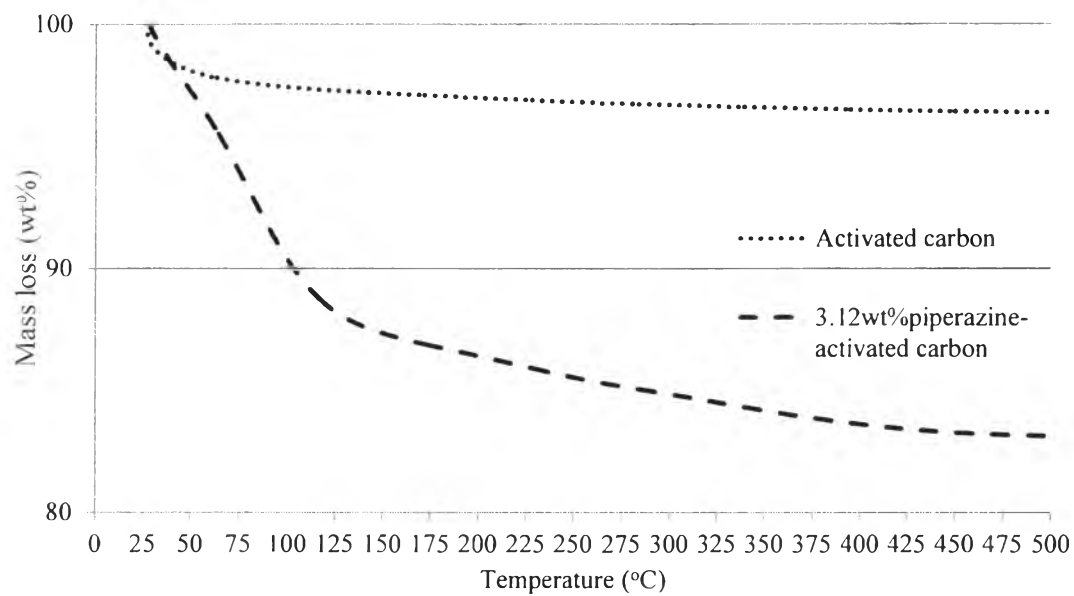**Figure 4.4** Thermal stability of piperazine at room temperature to 500 °C.

Figure 4.5 Thermal stability of acitvated carbon and 3.12 wt % piperazine-activated carbon at room temperature to 500 °C.

4.1.4 Breakthrough curve results

Figure 4.6 illustrates the breakthrough curves of pure activated carbon at different temperature and atmospheric pressure. These curves were obtained using the WiniLab III V4.6 program in the computer connecting to the GC-TCD displaying the amount of CO_2% leaving the adsorber. The monitor displayed 0 % in the beginning of the experiment as the CO_2 molecules were adsorbed by the surface and the pore sites until the saturation stage showing the S-shape and reaches $C/C_0 = 1$ at the equilibrium stage.
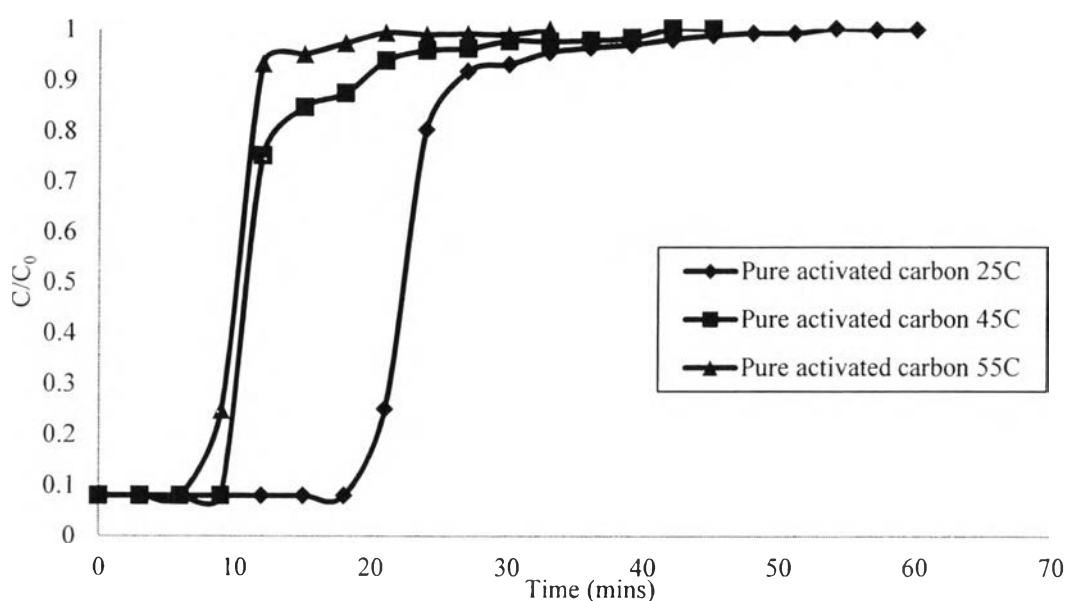

Figure 4.6 Breakthrough curve of pure activated carbon at 25 °C, 45 °C and 55 °C.

From the result obtained, the increase of the adsorption temperature causes an early reach of the saturation stage. Carbon dioxide molecules are attached to the high surface area of the activated carbon by weak van der Waals force, which is a low heat of adsorption; therefore, at an elevating temperature the attractive force between the surface of the activated carbon and the carbon dioxide molecules is reduced. The adsorption capacities of the pure activated carbon at 25 °C, 45 °C and 55 °C are 0.3742, 0.2101 and 0.1737 mmol/g, respectively. For the effect of adsorption temperature on impregnated activated carbon, Figure 4.7 illustrates the breakthrough curve of 3.12 wt % piperazine-activated carbon at different

temperature. The adsorption capacities of 3.12 wt % piperazine-activated carbon at 25 °C, 45 °C and 55 °C is 0.5266, 0.2870 and 0.1990 mmol/g, respectively. The results indicate that piperazine in the activated carbon in fact contributes adsorption which enhances the physisorption of unmodified activated carbon at different temperature. The carbon dioxide adsorption capacity dropped gradually when the temperature is increased, which was assumed physisorption. The chemisorption was not clearly observed due to the limitation of maximum piperazine loading of 3.12 wt % as the chemical adsorption would be expected to happen between the amine group of piperazine and carbon dioxide. By comparing the adsorption capacity of unmodified and modified activated carbon, the enhancements were 40.73 % at 25 °C, 36.60 % at 45 °C and 14.57 % at 55 °C.
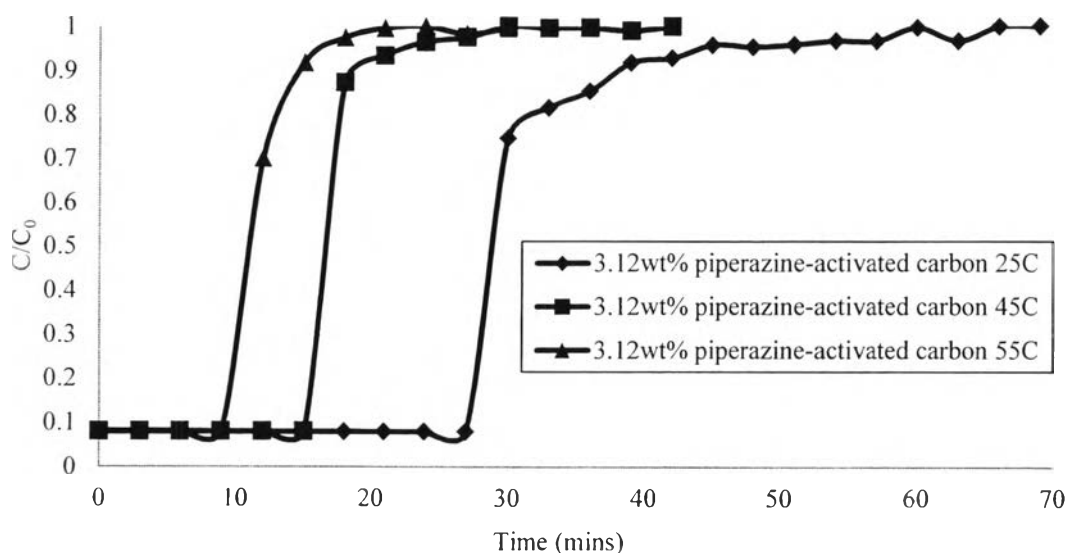

Figure 4.7 Breakthrough curve of 3.12 wt % piperazine-activated carbon at 25 °C, 45 °C and 55 °C.

However, the moisturized activated carbon results a rapid saturation stage with a dramatically decrease in the carbon dioxide adsorption capacity. As shown in Figure 4.8, the adsorption capacities are 0.2802, 0.1511 and 0.1136 mmol/g at 25 °C, 45 °C and 55 °C, respectively. This indicated that the moisture could deactivate the active sites of the activated carbon. However, similar effect is shown in Figure 4.9 for moisturized 3.12 wt % piperazine-activated carbon at different temperature which

suggests that the carbon dioxide adsorption capacities of the loaded activated carbon is negatively affected by the moisture. The adsorption capacities are 0.2802, 0.1511 and 0.1136 mmol/g at 25 °C, 45 °C and 55 °C, respectively.
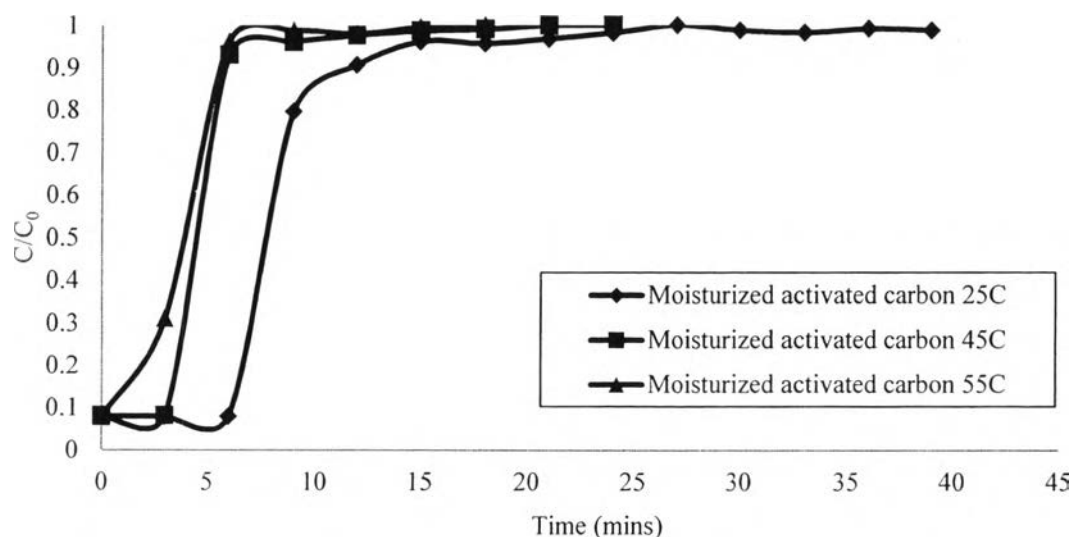

Figure 4.8 Breakthrough curve of moisturized activated carbon at 25 °C, 45 °C and 55 °C.
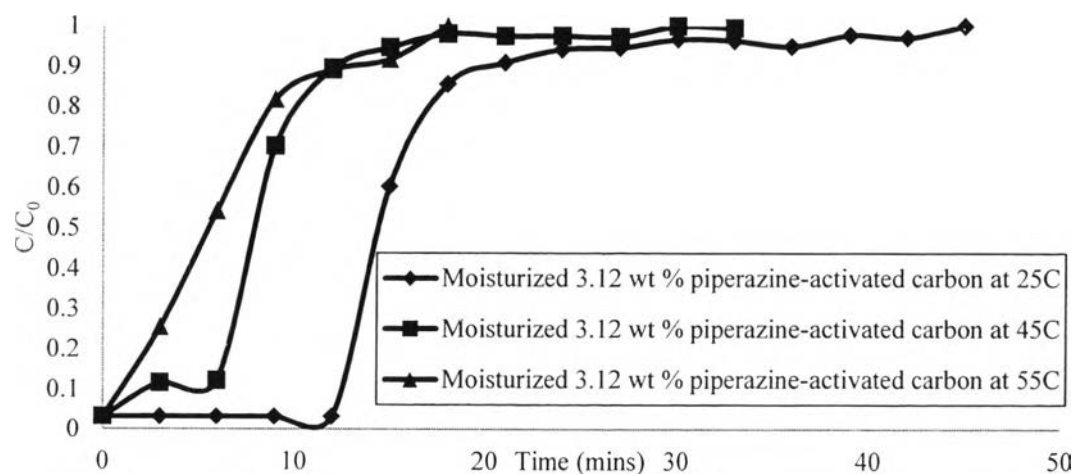

Figure 4.9 Breakthrough curve of moisturized 3.12 wt % piperazine-activated carbon at 25 °C, 45 °C and 55 °C.

Table 4.2 summarized the overall CO_2 adsorption capacity of activated carbon and piperazine-activated carbon
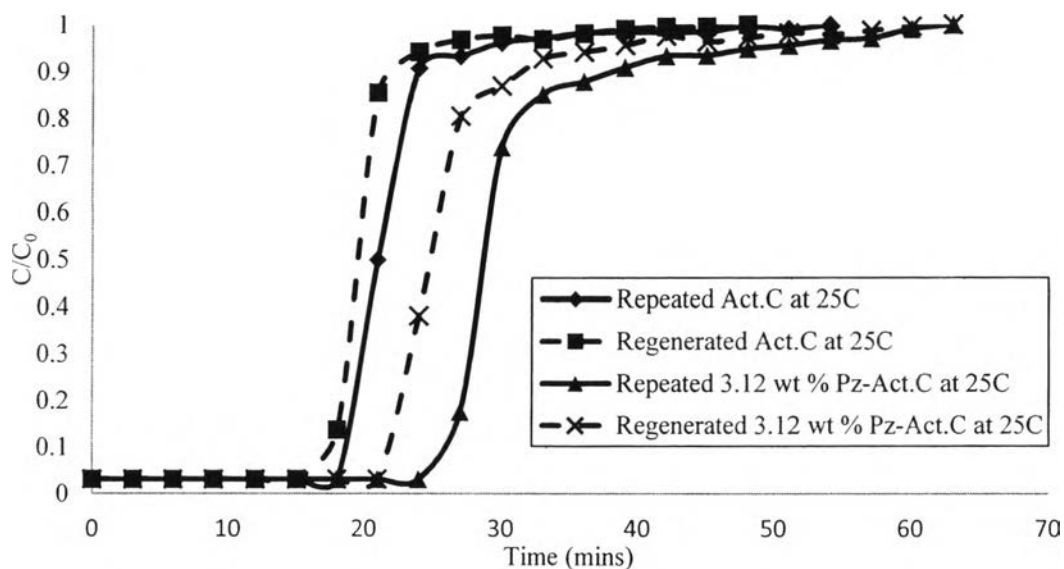

Figure 4.10 Breakthrough curve of repeated activated carbon, repeated piperazine-activated carbon, regenerated activated carbon and regenerated piperazine-activated carbon at 25 °C.

The average adsorption capacities of activated carbon and piperazine-activated carbon are 0.3799 ± 0.0080 and 0.5322 ± 0.0078 mmol/g at 25 °C as the adsorption shown in Figure 4.10. The regeneration was run after the adsorption cycle and the adsorption capacity was calculated. The results show that adsorption capacities were 0.4532 and 0.3566 mmole/g corresponding to the adsorption efficiency of 93.87 % and 85.16 % for Act.C and 3.12 wt % PZ-Act.C, respectively. This indicated that some of the carbon dioxide molecules could be attached to the amine of 3.12 wt % PZ-Act.C surface better than the pure activated carbon.

Table 4.2 Summary of CO_2 adsorption with activated carbon and piperazine-activated carbon

	Q_{ads} (mmol/g)					
	Dry Condition		Moisture effect		Regeneration	
Adsorption Temp (°C)	Pure Act. C (Aver. 2 runs)	3.12wt%Pz-Ac (Aver 2 runs)	Act.C	3.12 wt % Pz-Act. C	Act.C	3.12 wt % Pz-Act.C
25	0.3799 ± 0.0146	0.5322 ± 0.0078	0.1390	0.2802	0.3566	0.4532
45	0.2101	0.2870	0.0826	0.1511		
55	0.1737	0.1990	0.0670	0.1136		

Act.C= activated carbon, Pz= piperazine