CHAPTER IV
RESULTS AND DISCUSSION

4.1 Characterization

Activated carbon and modified activated carbon were characterized by thermogravimetric (TG) and BET surface area analysis. The surface area and pore volume of the adsorbents are shown in Table 4.1. Activated carbon shows a specific surface area of 1,332 m^2/g and a pore volume of 0.7335 cm^3/g. At the 10% loading, the BET surface area and pore volume of activated carbon are sharply reduced. When the amount of piperazine, MIPA, NMEA, and K_2CO_3 increases, the surface area and pore volume decreases but not as much as at the 30% loading. At the 30% loading, the surface area and pore volume are very low because of the pore filling effect. The reduction of the surface area and pore volume from the three amines show the same trend. These results confirm that the three amines were successfully loaded into the pore of the activated carbon.

Table 4.1 Surface area and pore volume analysis of adsorbents

Adsorbents	BET surface area (m^2/g)	Pore volume (cm^3/g)
Activated carbon	1,332	0.7335
Activated carbon with 10%MIPA	221	0.1335
Activated carbon with 10%NMEA	160	0.0962
Activated carbon with 10%Piparazine	222	0.1315
Activated carbon with 10%K_2CO_3	509	0.2801
Activated carbon with 30%MIPA	21	0.0201
Activated carbon with 30%NMEA	28	0.0210
Activated carbon with 30%Piparazine	29	0.0260
Activated carbon with 30%K_2CO_3	387	0.1789

In Figure 4.1, the TGA profile of the unmodified activated carbon is shown. There is only one step with continuous weight loss from room temperature to 110°C, which can be attributed to the desorption of moisture.

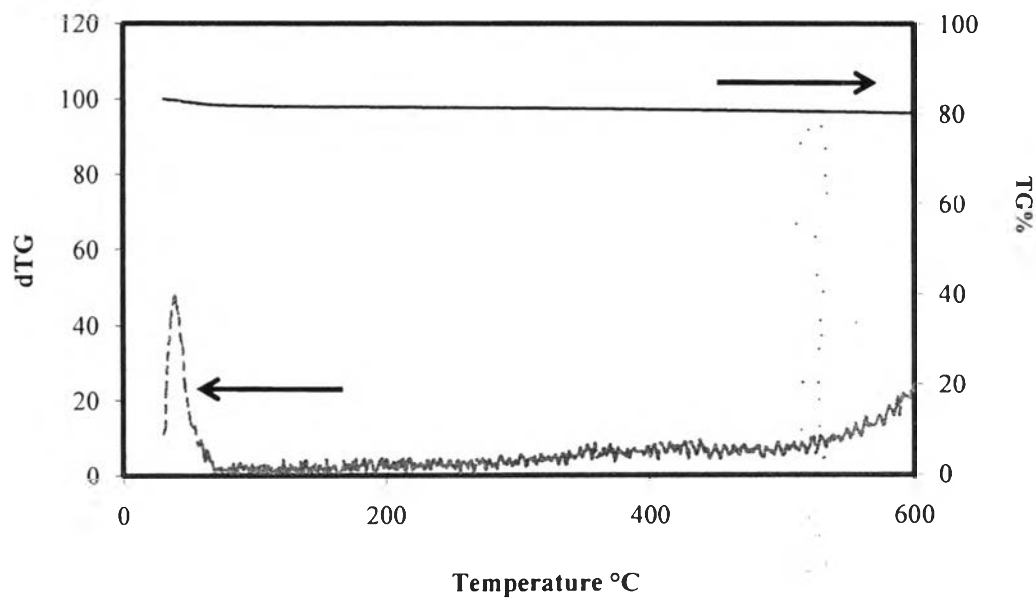


Figure 4.1 TGA profile of activated carbon.

Figures 4.2-4.4 show the TGA data for the activated carbon modified with 10 and 30% of MIPA, NMEA, and piperazine, respectively. In Figure 4.2, there are two steps with distinct weight loss at 120 and 200°C. The maximum weight loss is observed at 200°C. At the temperature below 120°C, the small weight loss can be attributed to the desorption of moisture. At the temperature range from 120 to 480°C, the continuous weight loss can be attributed to the volatilization of amine. As can be seen in Figure 4.2, the degradation of amine species and the weight loss increase with the increase in the amine loading. In Figures 4.3-4.4, the weight loss data from NMEA and piperazine obtained from the TGA show the same trend. The weight loss at room the temperature to 120°C is also related to the desorption from moisture and the mass loss at 120 to 480°C corresponds to the degradation of amine species. In all cases, the degradation of the 30% loading sample is greater than the 10% loading one.

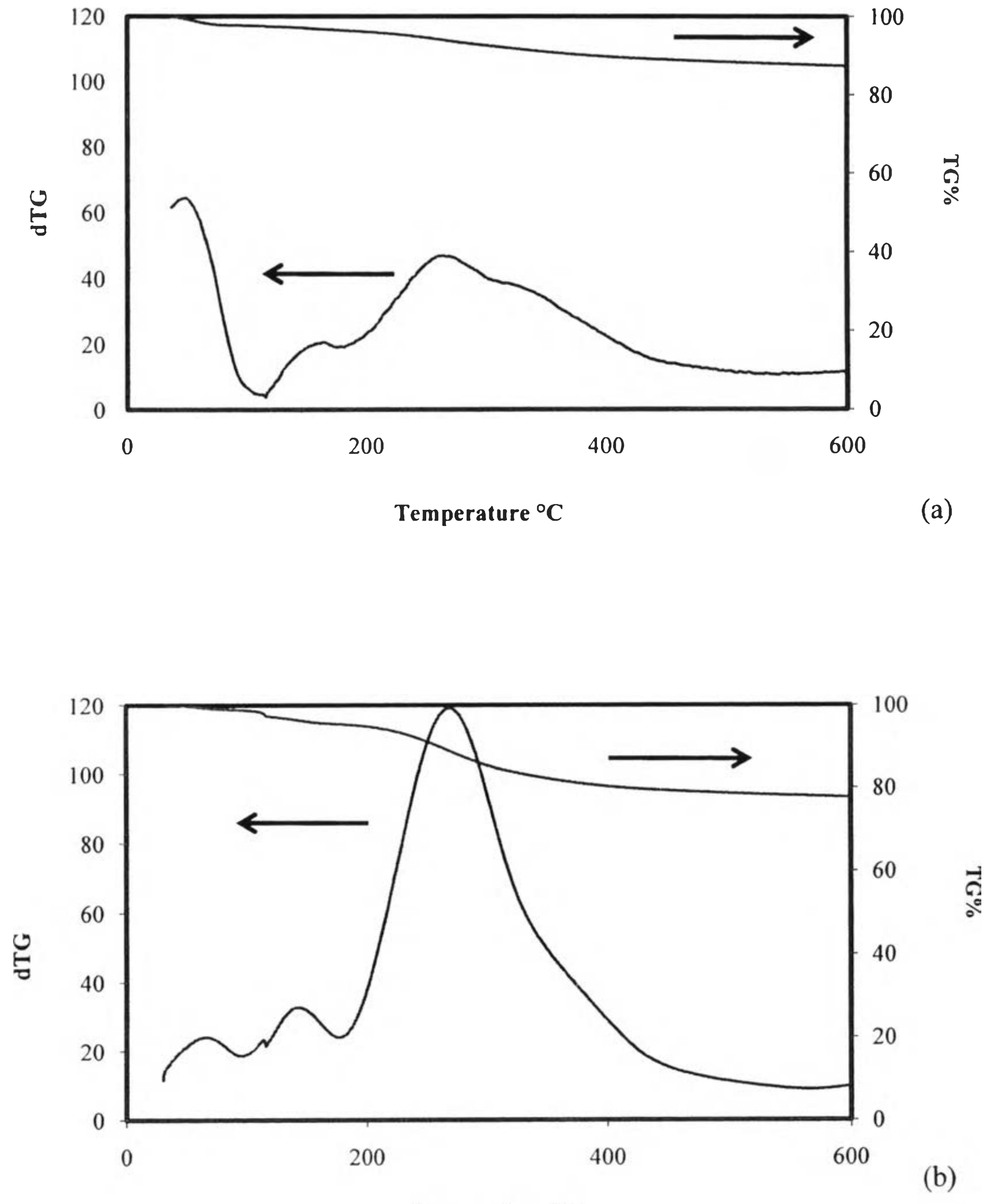


Figure 4.2 TGA profiles of activated carbon modified with MIPA (a) 10% loading (b) 30% loading.

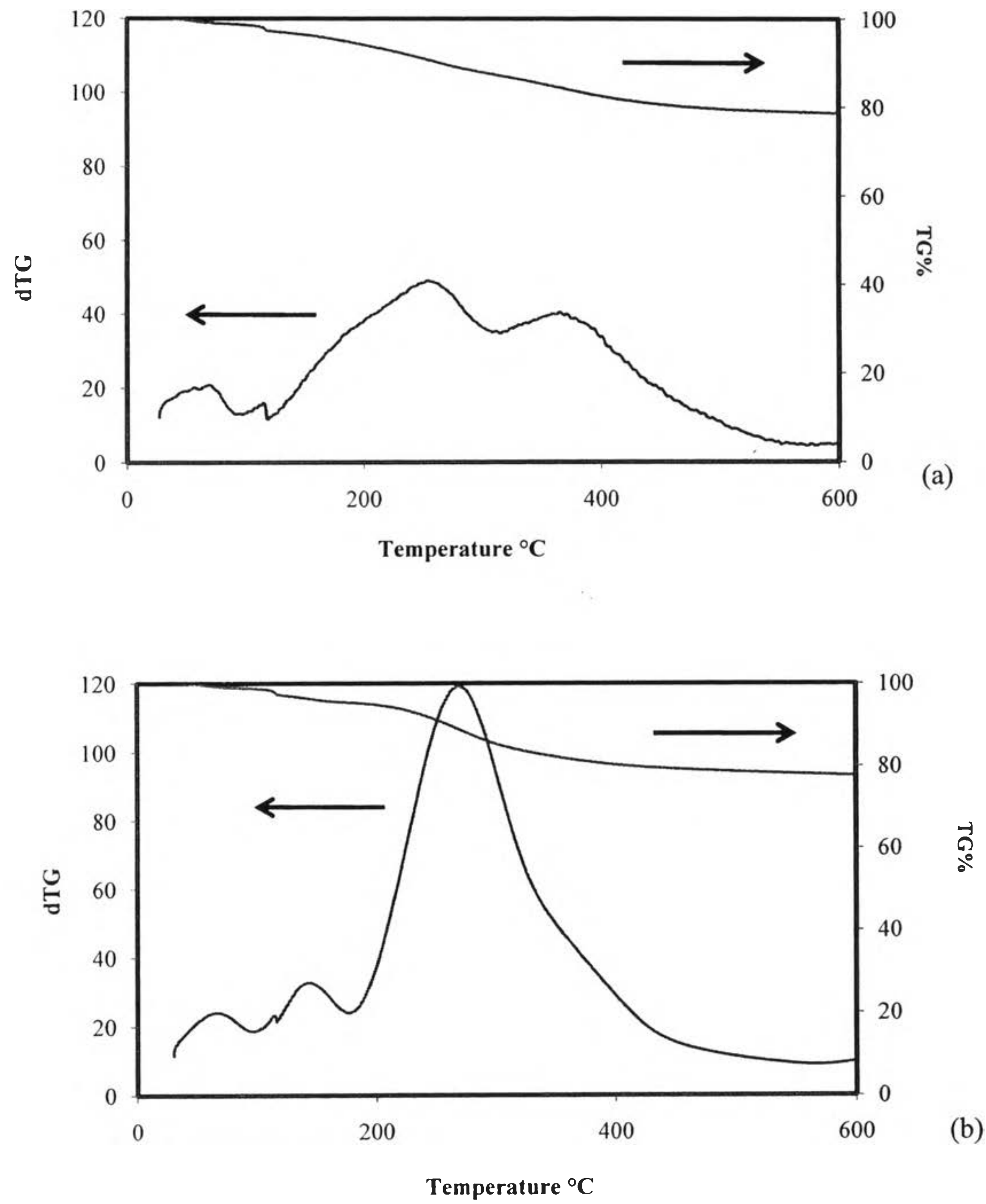


Figure 4.3 TGA profiles of activated carbon modified with NMEA (a) 10% loading (b) 30% loading.

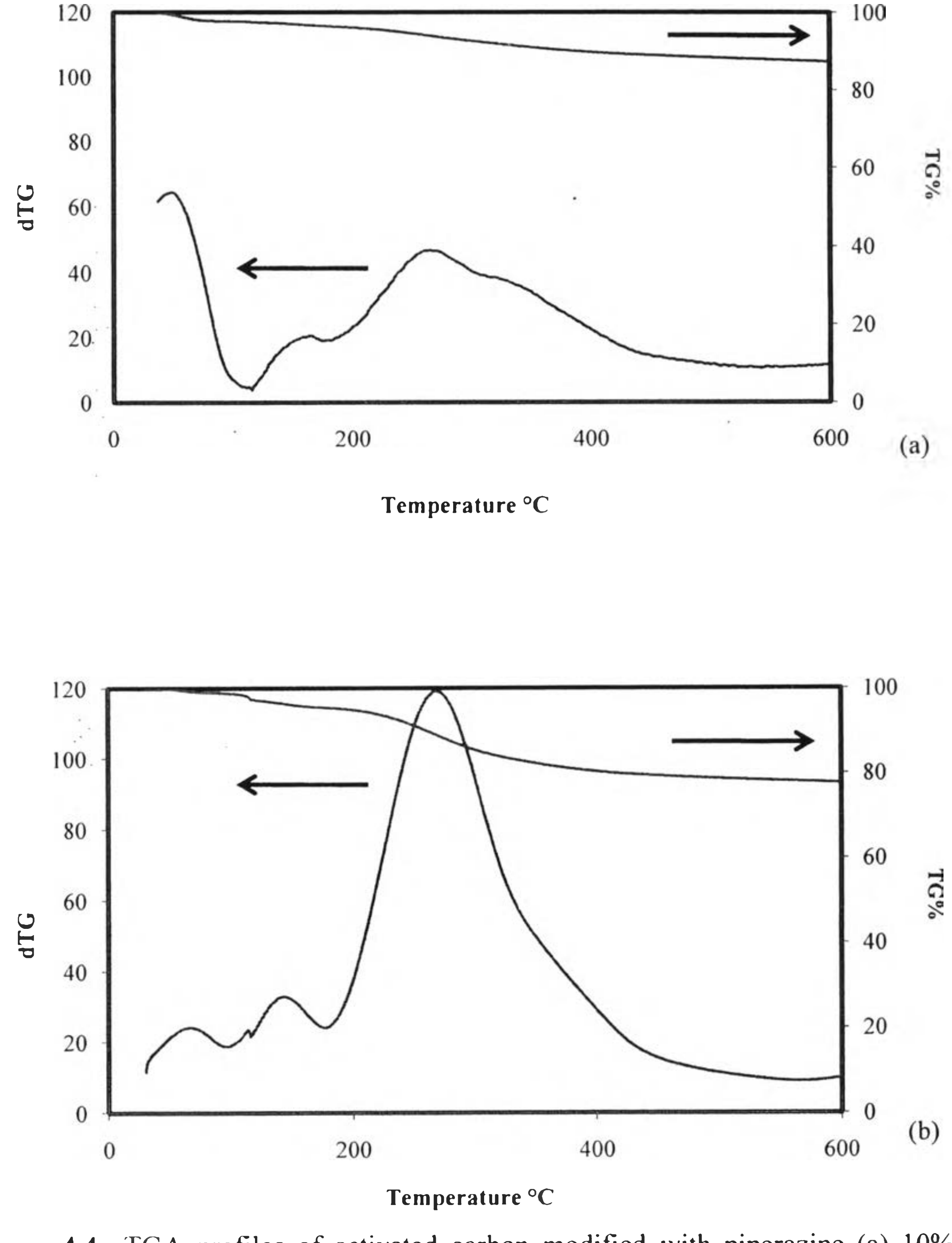
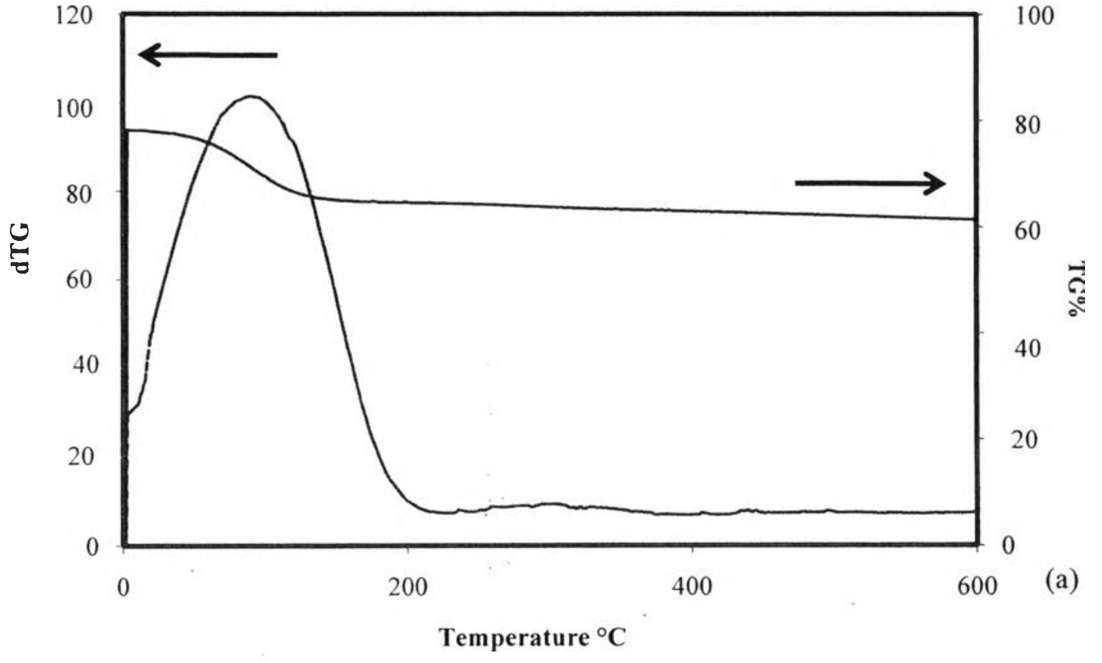


Figure 4.4 TGA profiles of activated carbon modified with piperazine (a) 10% loading (b) 30% loading.



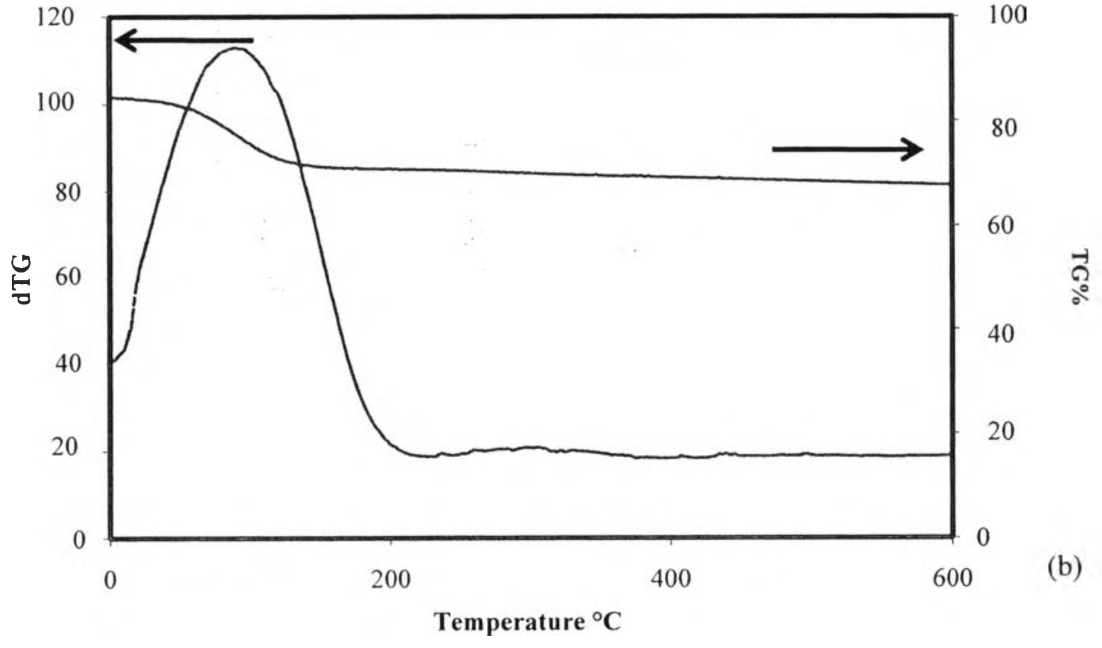


Figure 4.5 TGA profiles of activated carbon modified with K_2CO_3 (a) 30% loading (b) 10% loading.

As can be seen in Figure 4.5, the TGA profiles of the activated carbon modified with K_2CO_3 are different from those modified with the amines. There is only one step with continuous weight loss from 90 to 150°C. After that, the weight stays still. The entire weight loss corresponds to the desorption of moisture and K_2CO_3. The weight loss of 30% K_2CO_3, shown in Figure 4.5(b), is not much different from the one with 10% K_2CO_3.

4.2 CO_2 Adsorption

4.2.1 Effect of Temperature

Figure 4.6 shows the comparison of CO_2 adsorption on various adsorbents at 30°C. The unmodified activated carbon has the highest adsorption capacity at 1 atm because at the ambient temperature, the physical adsorption or physisorption is dominant. The important key to the adsorption process at the ambient temperature is surface area and pore volume of the adsorbent and the unmodified activated carbon has the highest surface area and pore volume. As can be seen in Figure 4.7, the adsorption capacities of 30% loading of the three amines at 1 atm almost unchange compared to the capacities at the low pressure due to the limited surface area and pore volume. However, the capacity with the 30% K_2CO_3 loading is a little higher than that with the 10% loading.

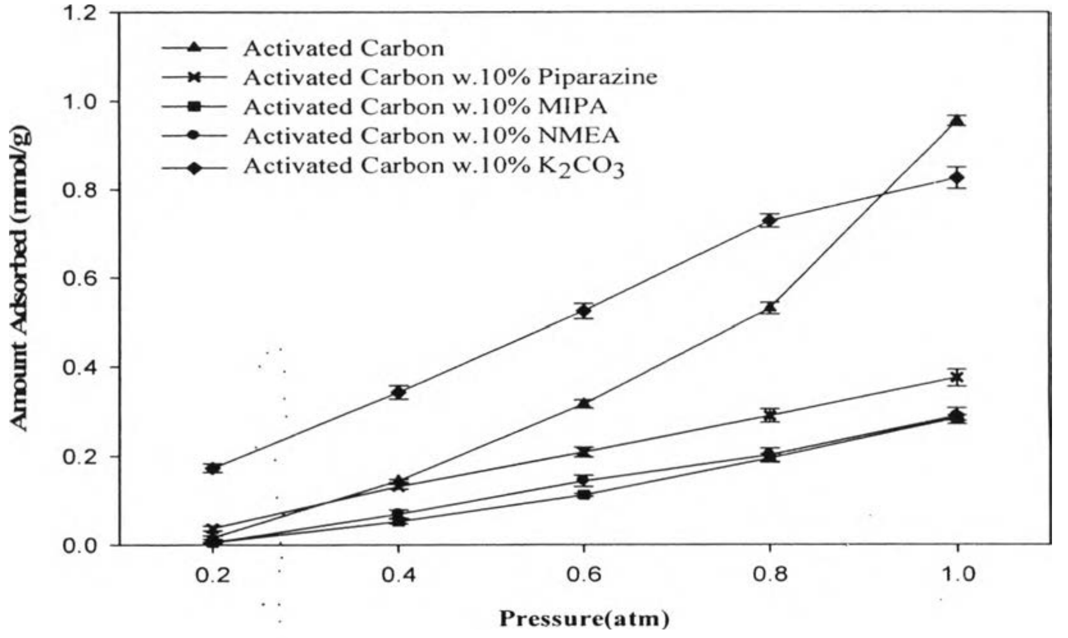


Figure 4.6 CO_2 adsorption isotherms of unmodified activated carbon and activated carbon modified with 10% piperazine, MIPA, NMEA, and K_2CO_3 at 30°C.

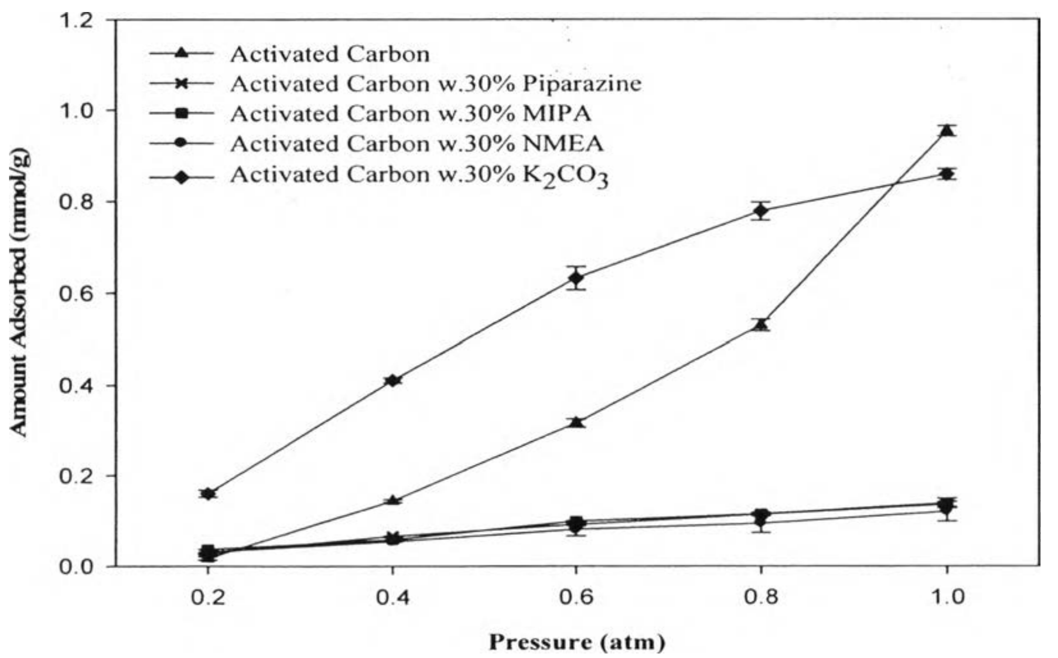


Figure 4.7 CO_2 adsorption isotherms of unmodified activated carbon and activated carbon modified with 30% piperazine, MIPA, NMEA, and K_2CO_3 at 30°C.

However, at the elevated temperatures (50 and 75°C), the modified activated carbon samples show higher adsorption capacities than the unmodified one. In Figures 4.8-4.9, at the beginning, the adsorption capacities of all samples are about the same. When the pressure is increased, the adsorption capacities of the modified activated carbon with 10% piperazine are significantly higher than the rest even though the surface area and pore volume are lower than the unmodified activated carbon. At 50°C and 1 atm, the activated carbon with 10% piperazine gives the highest adsorption capacity because chemisorption plays a major role in the adsorption process, while the capacities of the activated carbon and that with K_2CO_3 decrease with the increase in the temperature. This result confirms the enhancement in the CO_2 adsorption with the introduction of basicity on the activated carbon.

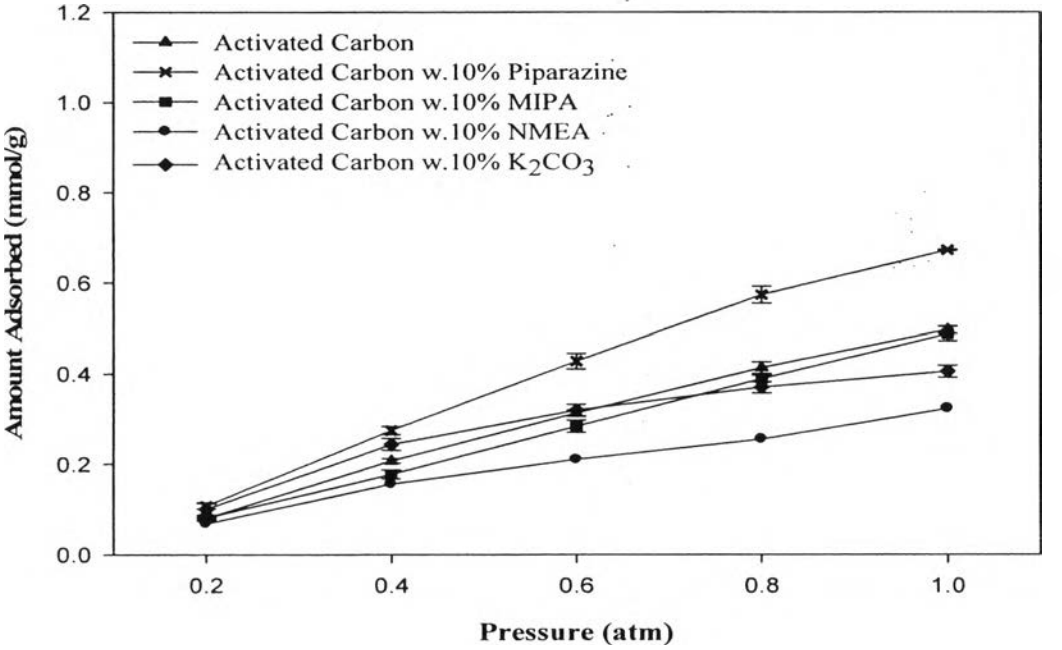


Figure 4.8 CO_2 adsorption isotherms of unmodified activated carbon and activated carbon modified with 10% piperazine, MIPA, NMEA, and K_2CO_3 at 50°C.

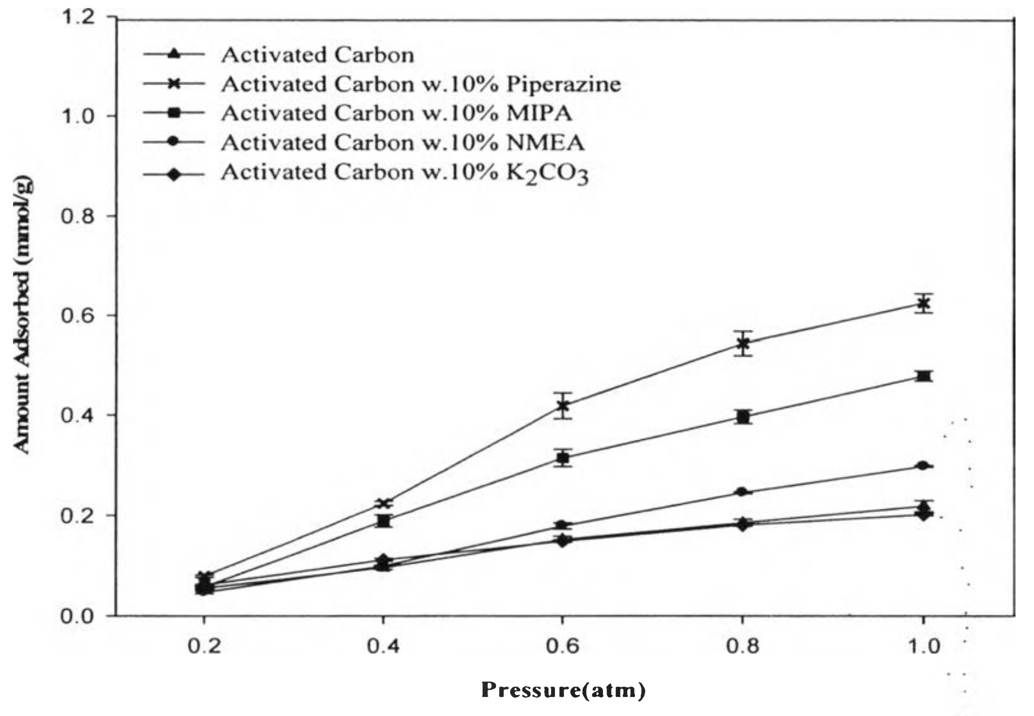


Figure 4.9 CO_2 adsorption isotherms of unmodified activated carbon and activated carbon modified with 10% piperazine, MIPA, NMEA, and K_2CO_3 at 75°C.

In addition, the adsorption capacities of all adsorbents at 75°C have the same trend and close to the adsorption capacities at 50°C. Figure 4.10 represents adsorption isotherms of the activated carbon at different temperatures. Again, the figure reiterates the effect of temperature on the CO_2 adsorption on the activated carbon that is the higher the temperature, the lower the CO_2 adsorption. In Figure 4.11, K_2CO_3 becomes less effective at the elevated temperature resulting in the decrease in the adsorption capacities. In contrast, with the unmodified activated carbon and modified activated carbon with 10% K_2CO_3, Figures 4.12-4.13 show the adsorption isotherms of the modified activated carbon with 10% piperazine and 10% MIPA at various temperatures. In both figures, the adsorption capacities at the beginning are almost the same. At 0.4 atm, the adsorption capacities at 50 and 75°C are getting higher than those at 30°C. A 1 atm, the capacities at the high temperature are obviously higher than those at 30°C. This is because chemisorption plays the major role in the adsorption process.

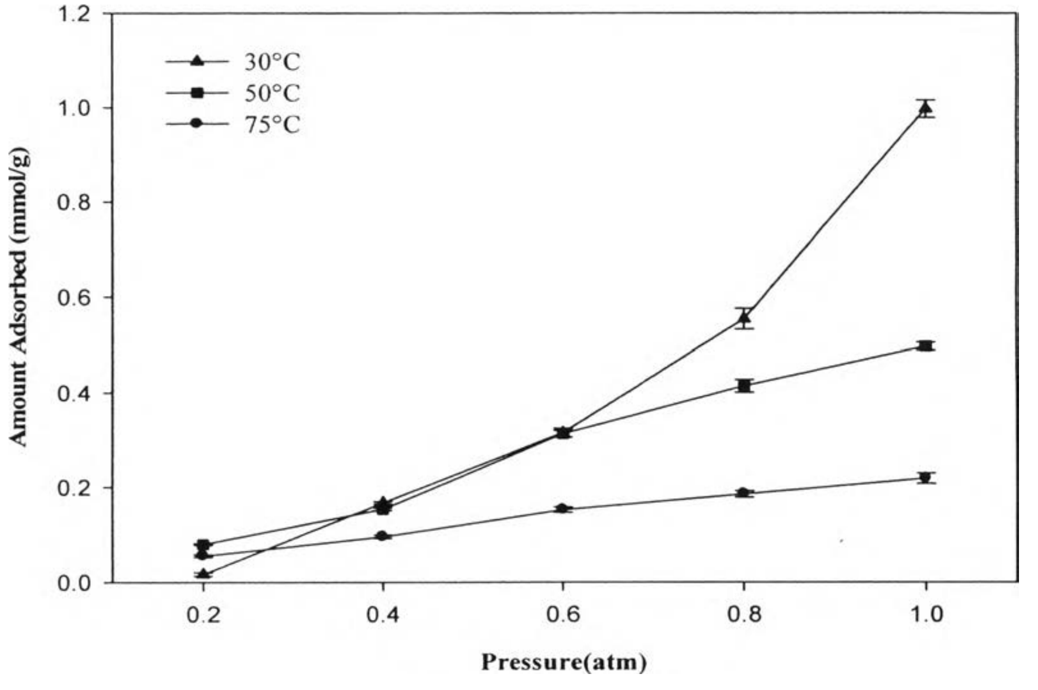


Figure 4.10 CO_2 adsorption isotherms of unmodified activated carbon at 30, 50, and 75°C.

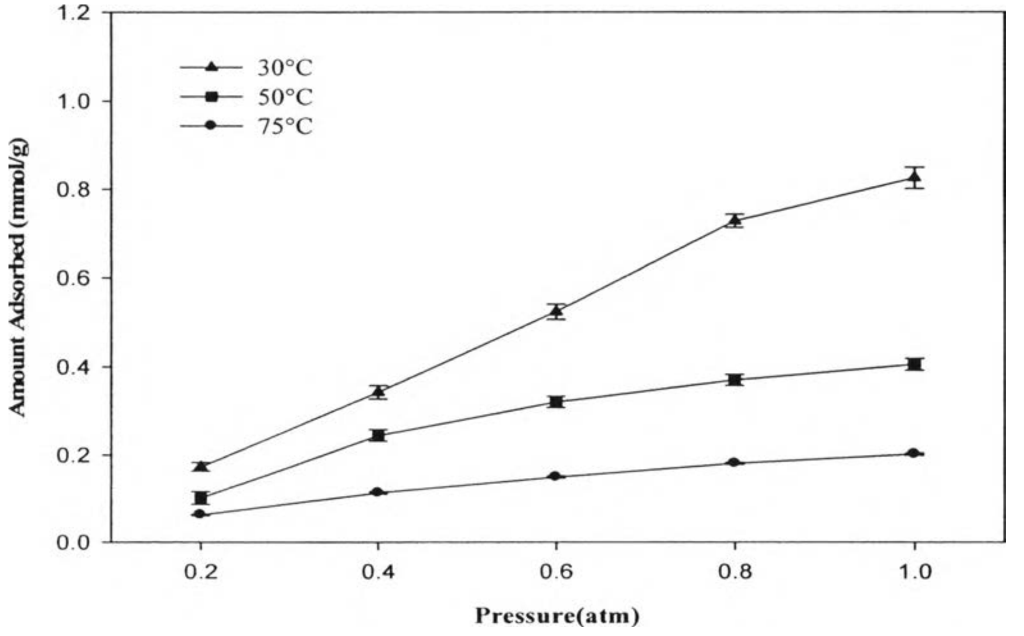


Figure 4.11 CO_2 adsorption isotherms of modified activated carbon with 10% K_2CO_3 at 30, 50, and 75°C.

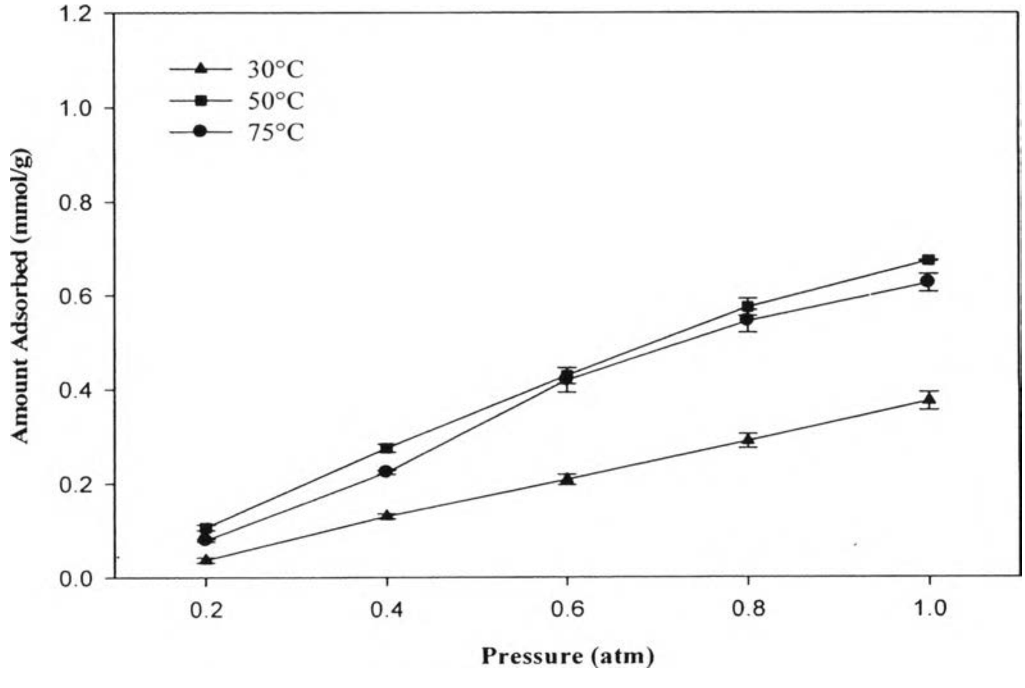


Figure 4.12 CO_2 adsorption isotherms of modified activated carbon with 10% piperazine at 30, 50, and 75°C.

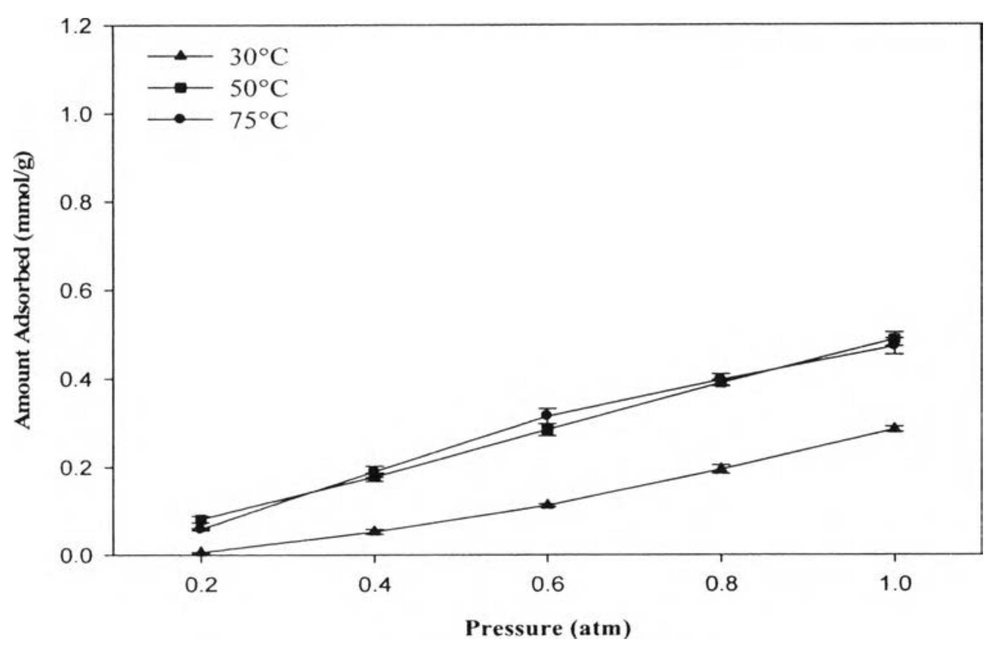


Figure 4.13 CO_2 adsorption isotherms of modified activated carbon with 10% MIPA at 30, 50, and 75°C.

Figure 4.14 shows the adsorption capacities of the modified activated carbon with 10% NMEA. Three adsorption temperatures were studied in order to find the optimum condition. The results show that the adsorption capacities of all the pressure ranges at the elevated temperatures are slightly higher than those at 30°C because the basicity of NMEA is lower than MIPA and piperazine. Accordingly, NMEA does not help enhancing the CO_2 adsorption.

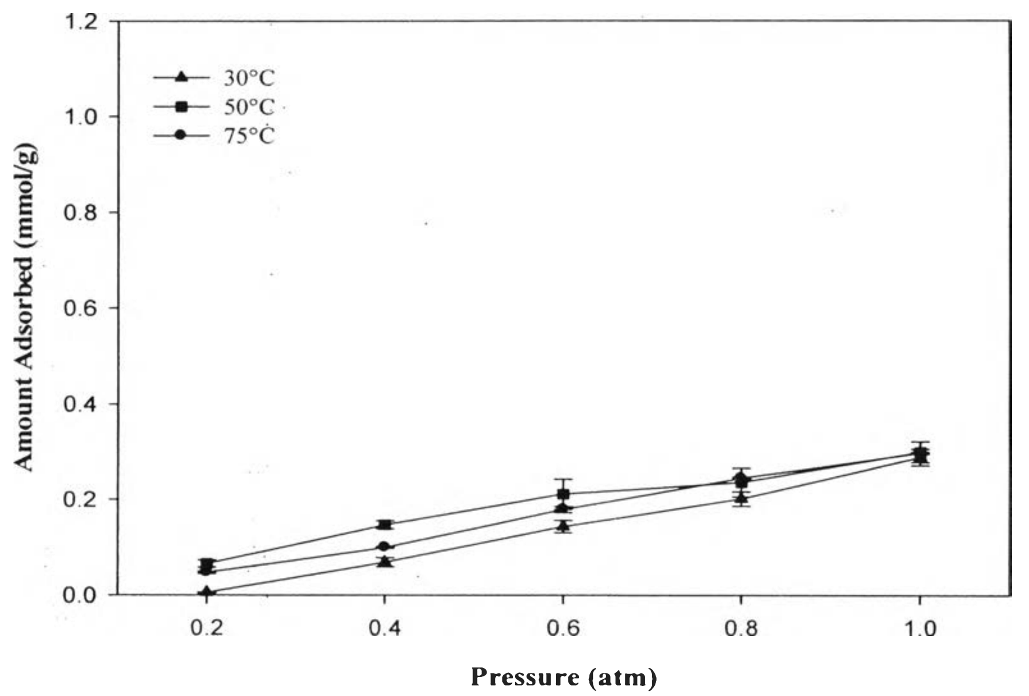


Figure 4.14 CO_2 adsorption isotherms of modified activated carbon with 10% NMEA at 30, 50, and 75°C.

4.2.2 Effect of Loading

The adsorption isotherms at 50°C of the activated carbon modified with piperazine are shown in Figure 4.15. At the beginning, the capacities of all adsorbents are almost the same. With the increase in the pressure, the capacities of the sample with 10% loading are significantly higher than the unmodified and the one with 30% loading. The 10% loading gives the highest adsorption capacity at 50°C and 1 atm. while the adsorption capacity of 30% loading is lower than the adsorption capacity of the unmodified activated carbon. This can be attributed to the pore filling effect. CO_2 molecules cannot diffuse into the pore of the adsorbent because of amines blocking the pores of the adsorbent (Jadhav *et al.*, 2007). According to that, the adsorption process may take place only the surface of the adsorbent.

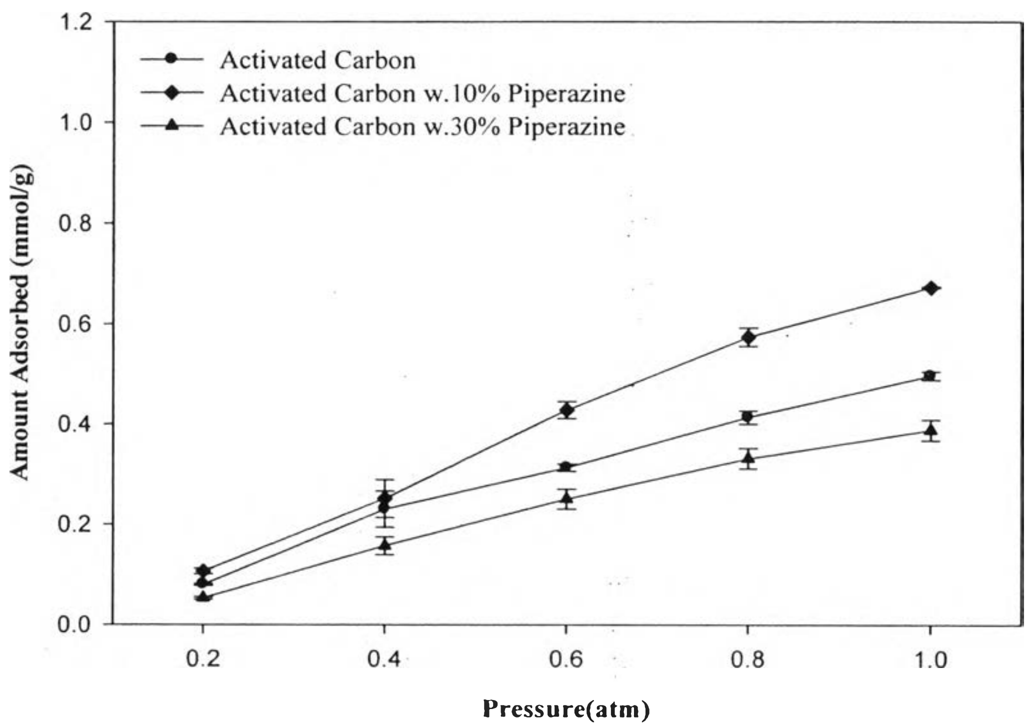


Figure 4.15 CO_2 adsorption isotherms of unmodified activated carbon and activated carbon modified with 10 and 30% piperazine at 50°C.

Figure 4.16 presents the isotherms at 75°C of the activated carbon modified with piperazine. The results are quite similar to the adsorption capacities of the sample modified with piperazine at 50°C. In Figures 4.17-4.18, the adsorption capacities of the modified activated carbon with 10 and 30 wt% of MIPA at 50 and 75°C are shown. The results of the samples modified with MIPA show the same trend with the results of the samples modified with piperazine. Accordingly, both piperazine and MIPA are potential modifiers to increase CO_2 adsorption of the activated carbon from 50 to 75°C.

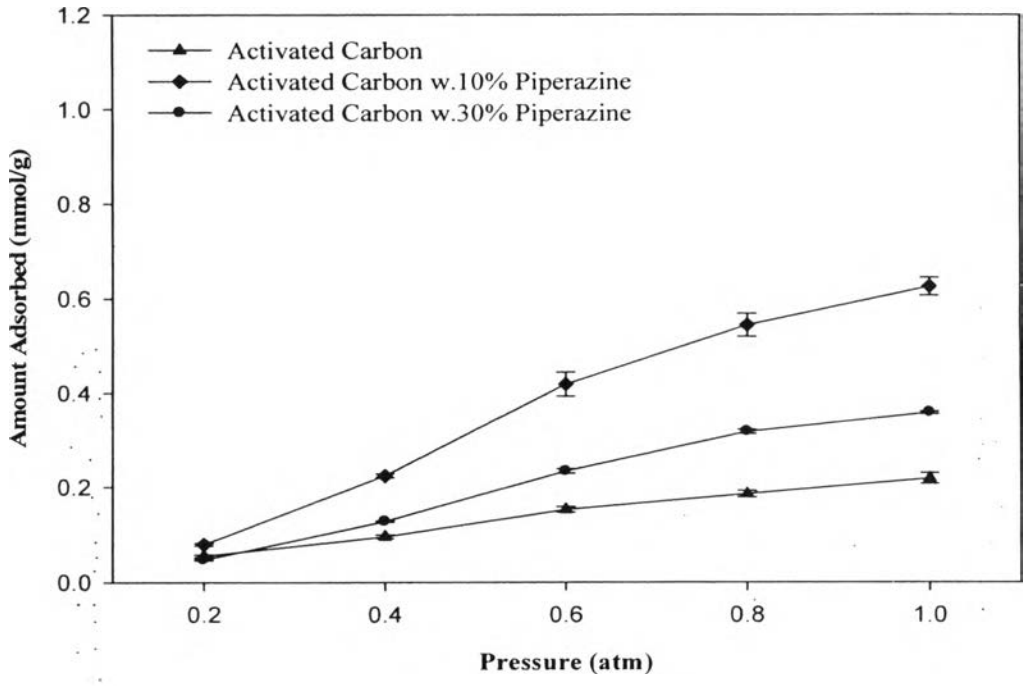


Figure 4.16 CO_2 adsorption isotherms of unmodified activated carbon and activated carbon modified with 10 and 30% piperazine at 75°C.

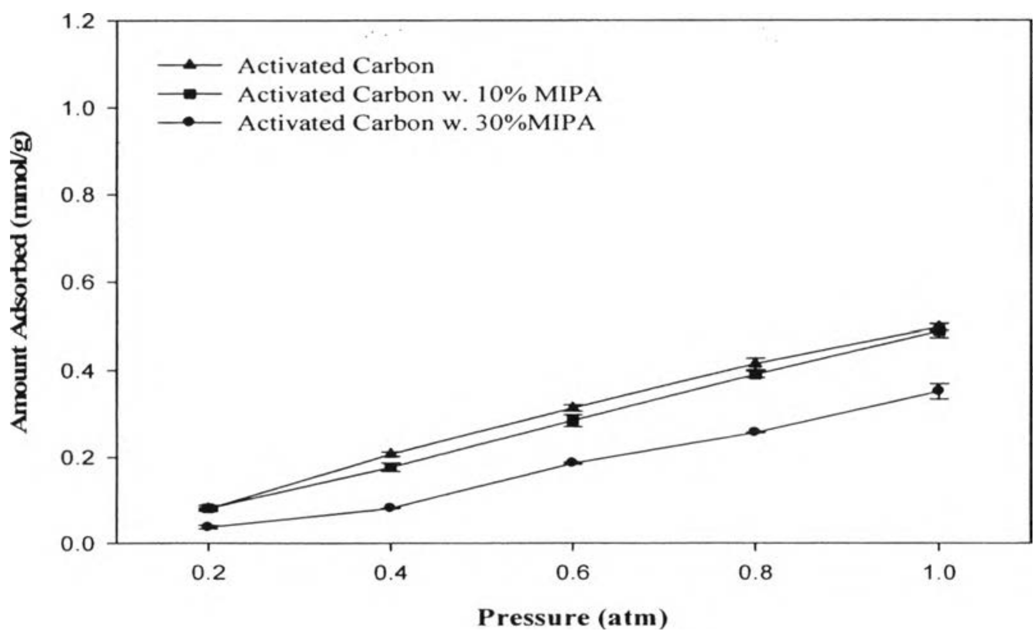


Figure 4.17 CO_2 adsorption isotherms of unmodified activated carbon and activated carbon modified with 10 and 30% MIPA at 50°C.

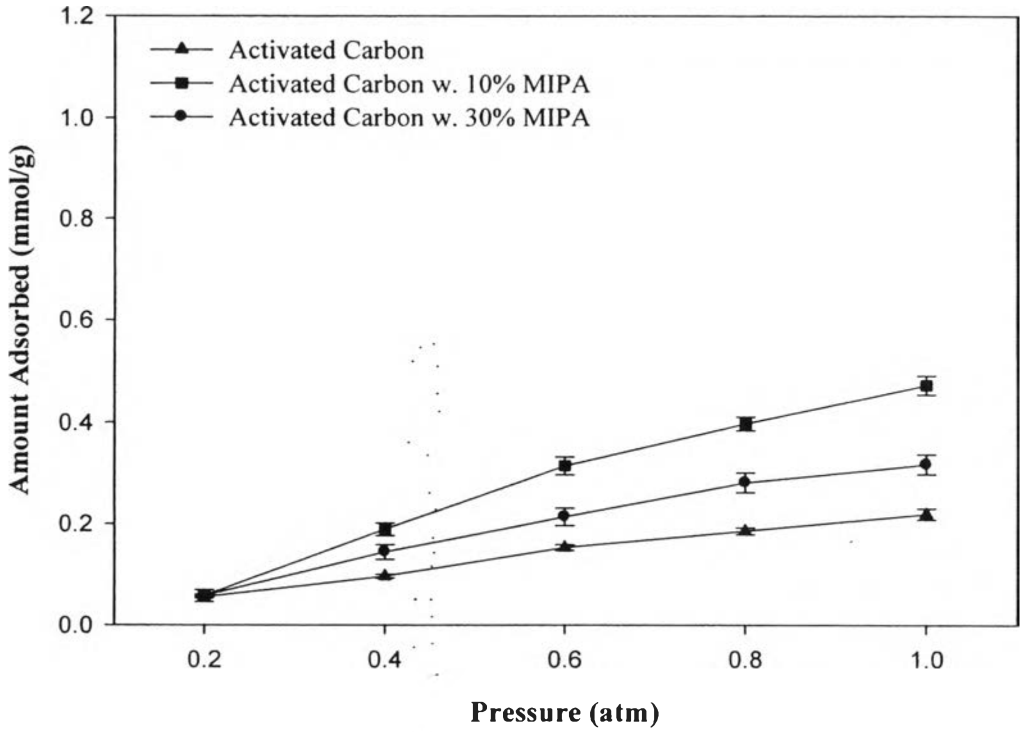


Figure 4.18 CO_2 adsorption isotherms of unmodified activated carbon and activated carbon modified with 10 and 30% MIPA at 75°C.

Figure 4.19 presents the adsorption isotherms of the modified activated carbon with 10 and 30% of K_2CO_3 at 30°C. The capacities of the unmodified samples are lower than the modified activated carbon at low pressure. At 1 atm, the adsorption capacity of the unmodified activated carbon surpasses the sample modified with K_2CO_3. Figure 4.20 shows the adsorption capacities at 50°C. The 30% K_2CO_3 loading gives the lowest adsorption capacities over the studied pressure range. The unmodified activated carbon also provides higher adsorption capacities. The results imply that K_2CO_3 may not be suitable for the CO_2 adsorption at the elevated temperatures.

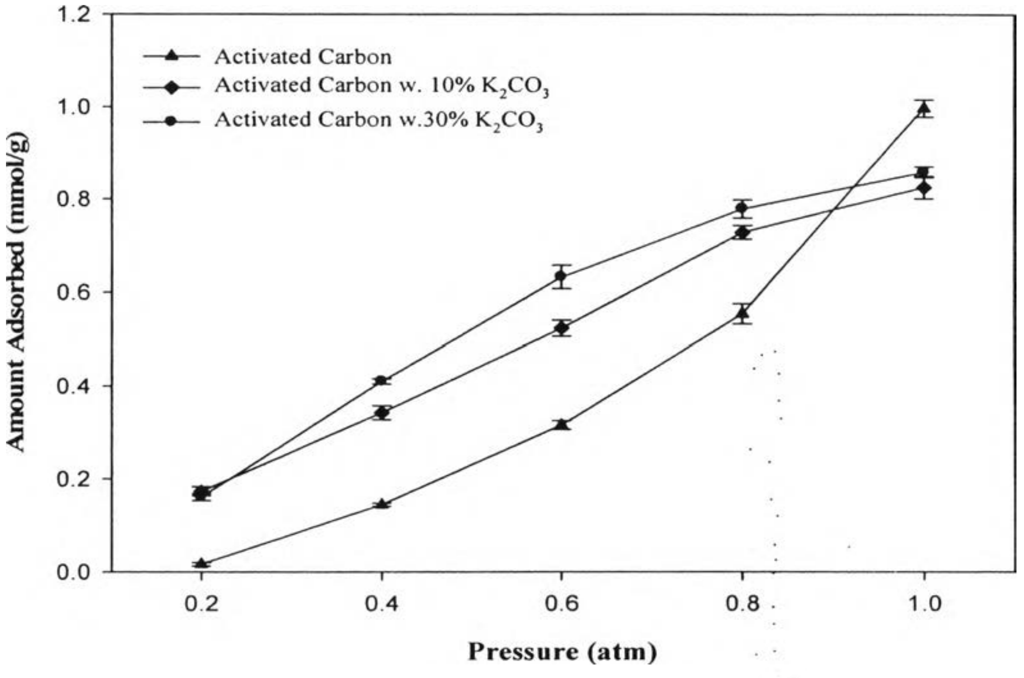


Figure 4.19 CO_2 adsorption isotherms of unmodified activated carbon and activated carbon modified with 10 and 30% K_2CO_3 at 30°C.

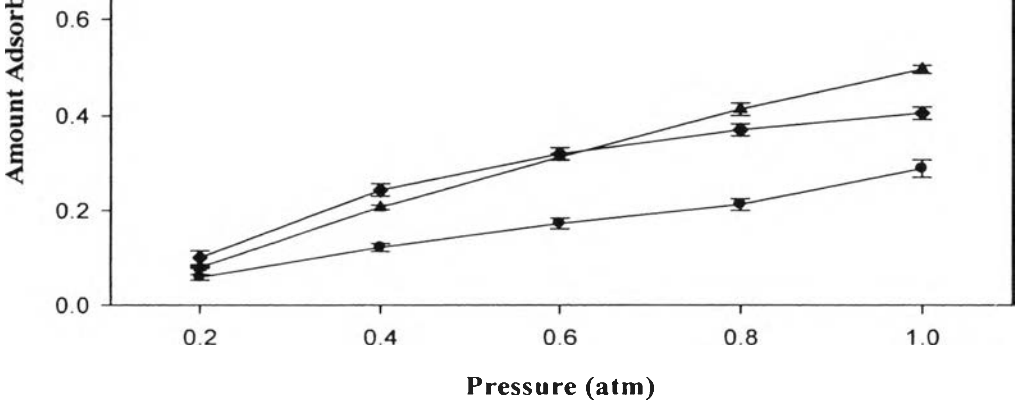


Figure 4.20 CO_2 adsorption isotherms of unmodified activated carbon and activated carbon modified with 10 and 30% K_2CO_3 at 50°C.

4.2.3 Regeneration

Figure 4.21 presents the CO_2 adsorption isotherms of the activated carbon with 10% piperazine and the regenerated activated carbon with 10% piperazine by heating the adsorbents at 110°C for 3 hr. The results show that the adsorption capacities of regenerated adsorbent are significantly lower than the adsorption capacities of the fresh adsorbent which means that heating may not be the suitable technique for regenerated the adsorbent.

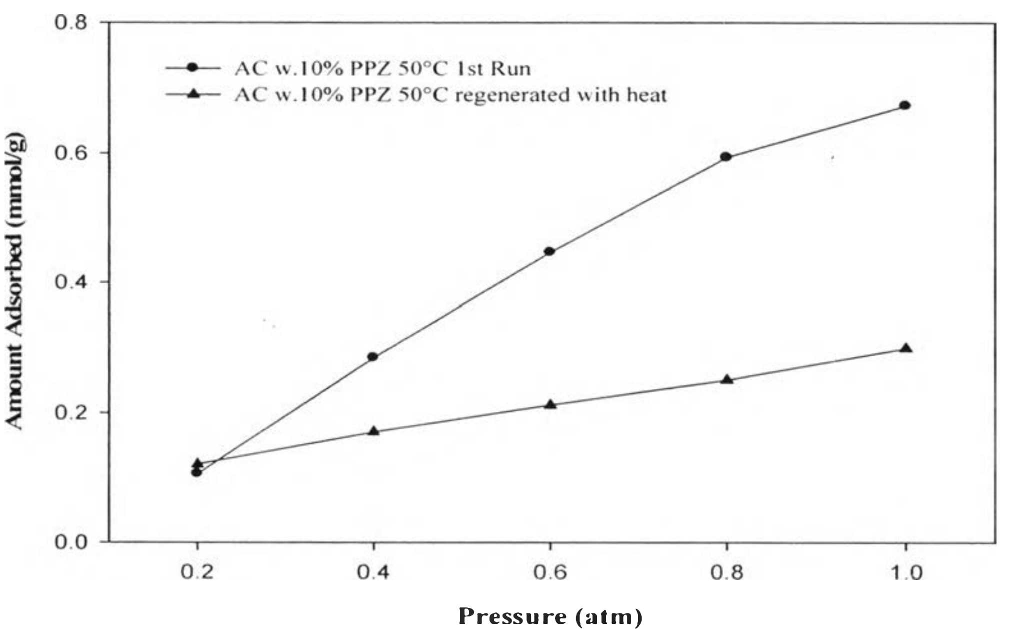


Figure 4.21 CO_2 adsorption isotherms of the modified activated carbon with 10% piperazine and the regenerated activated carbon modified with 10% piperazine at 50°C.