CHAPTER IV
RESULT AND DISCUSSION

4.1 Characterization of Adsorbents

The untreated AC and treated AC with several surface treatment techniques were characterized by a number of techniques. The thermal stability was investigated by thermogravimetric analysis. Surface area analyzer was used to determine surface area, pore size and pore volume. SEM was employed to study the morphology of adsorbents. The surface chemistry of adsorbents was employed by CHN/O/S and XPS analyzer.

The oxidized samples were denoted as OX/A/B, where A represents the concentration of nitric acid and B represents the duration of oxidation. And the impregnated samples were denoted as Z/AC or Z/OX/A/B, where Z is the wt% of branched PEI loaded.

4.1.1 BET Surface Area Analysis

Surface area, pore size and pore volume of each adsorbents were shown in Table 4.1. The surface area of an untreated AC has surface area of 1090 m^2/g, pore volume of 0.64 cm^3/g and average pore diameter of 7.36 Å. The surface area of the samples impregnated with branched PEI was dramatically decreased as shown in Table 4.1. These results suggested that branched PEI probably block on the pore of AC as described by Xu *et al.* (2003). The samples oxidized in nitric acid showed a slightly decrease in surface area, pore volume. The main of this reduction is because the embedded oxygen functional groups were presence (Liu *et al.*, 2012) and also partial of the pore walls were collapsed (Plaza *et al.*, 2013).

Table 4.1 Surface area, pore volume and average pore diameter analysis

Adsorbent	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
AC	1090	0.64	7.36
10/AC	678	0.66	7.65
20/AC	326	0.26	8.00
30/AC	4	0.17	-
OX/5/8	953	0.57	8.51
OX/10/1	972	0.58	7.70
OX/10/4	987	0.55	7.64
OX/10/8	913	0.56	8.10
OX/15/8	1000	0.59	7.38
10/OX/5/8	523	0.30	6.47
10/OX/10/8	761	0.69	6.47
10/OX/15/8	417	0.57	8.22

4.1.2 Thermal Stability

The Thermal stability of adsorbents was investigated by thermogravimetric analysis. In these tests, around 10 mg of sample was put on a crucible and placed in TGA. The temperature was increased to 800 °C at 10 °C/min in a nitrogen flow of 100 ml/min. The TG profiles were presented in Figures 4.1 to 4.10. It can be observed that, the untreated AC and oxidized samples, as shown in Figures 4.1 and 4.5 to 4.8, are composed of only 2 steps of weight loss, a removal of moisture and a decomposition of activated carbon. Figure 4.2 shows the thermogram of branched PEI. There is one step of weight loss starting at 176.7 °C and ending at 392.9 °C. For the impregnated samples, as shown in Figures 4.3 to 4.5 and 4.10, there are 3 steps of weight loss. The first step of weight loss was resulting from the removal of moisture. The second step was resulting from a decomposition of PEI and the last step was the weight loss of activated carbon.

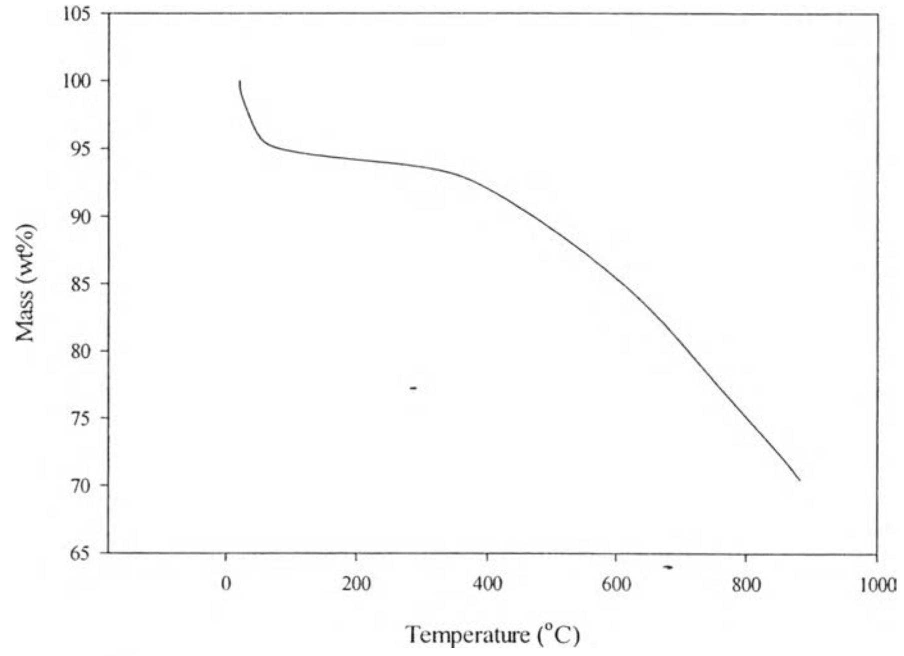


Figure 4.1 TG thermogram of AC in 100 ml/min of N_2 flow at a heating rate of 10 °C/min.

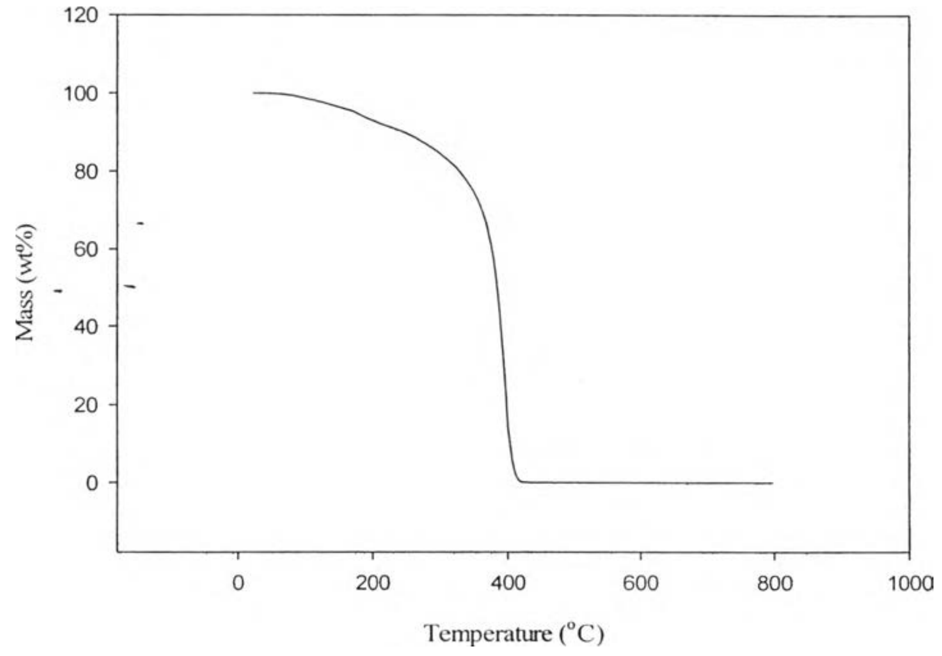


Figure 4.2 TG thermogram of branched PEI in 100 ml/min of N_2 flow at a heating rate of 10 °C/min.

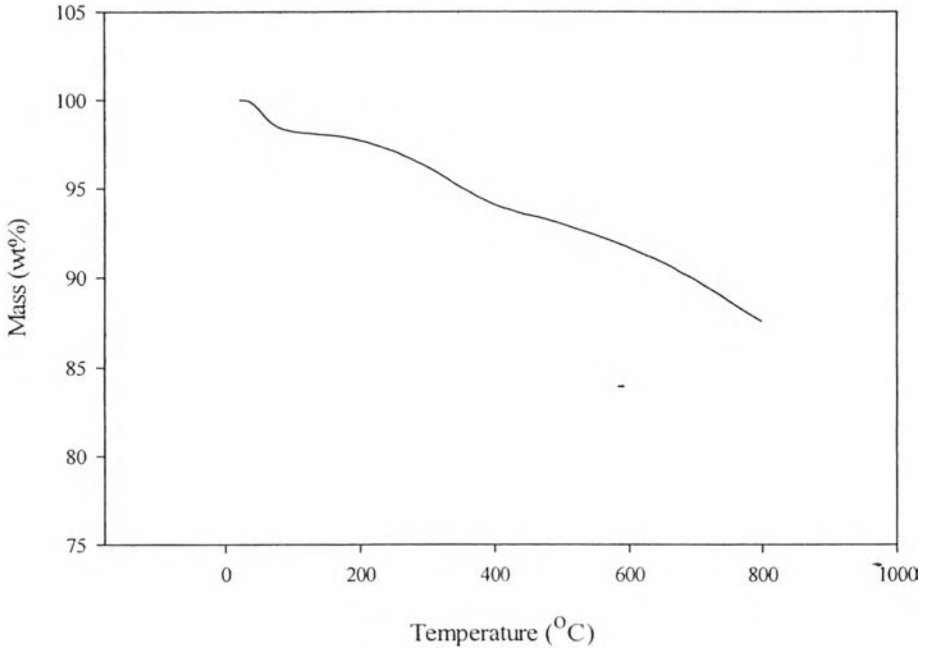


Figure 4.3 TG thermogram of 10/AC in 100 ml/min of N_2 flow at a heating rate of 10 °C/min.

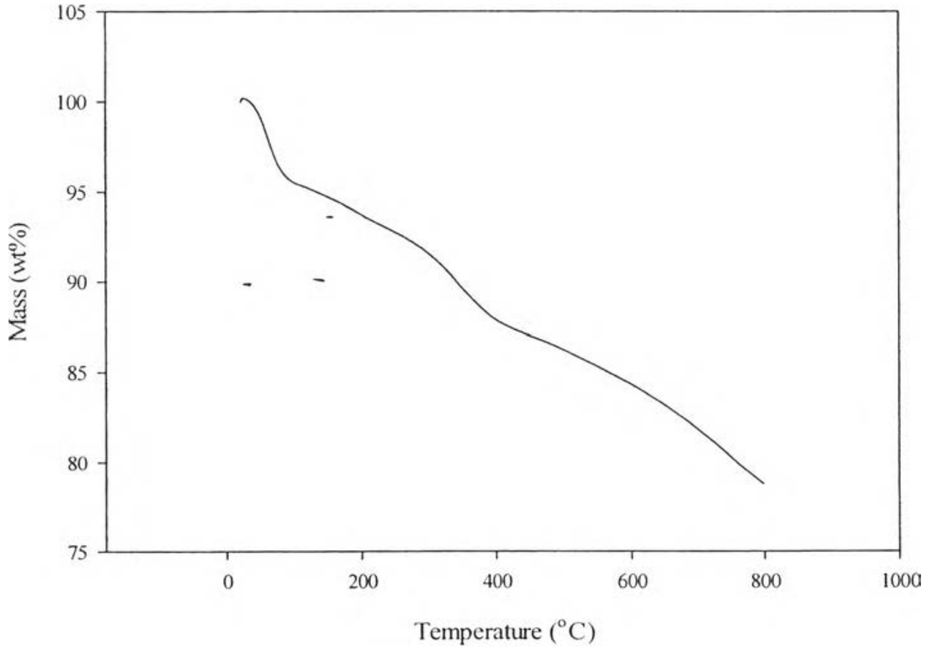


Figure 4.4 TG thermogram of 20/AC in 100 ml/min of N_2 flow at a heating rate of 10 °C/min.

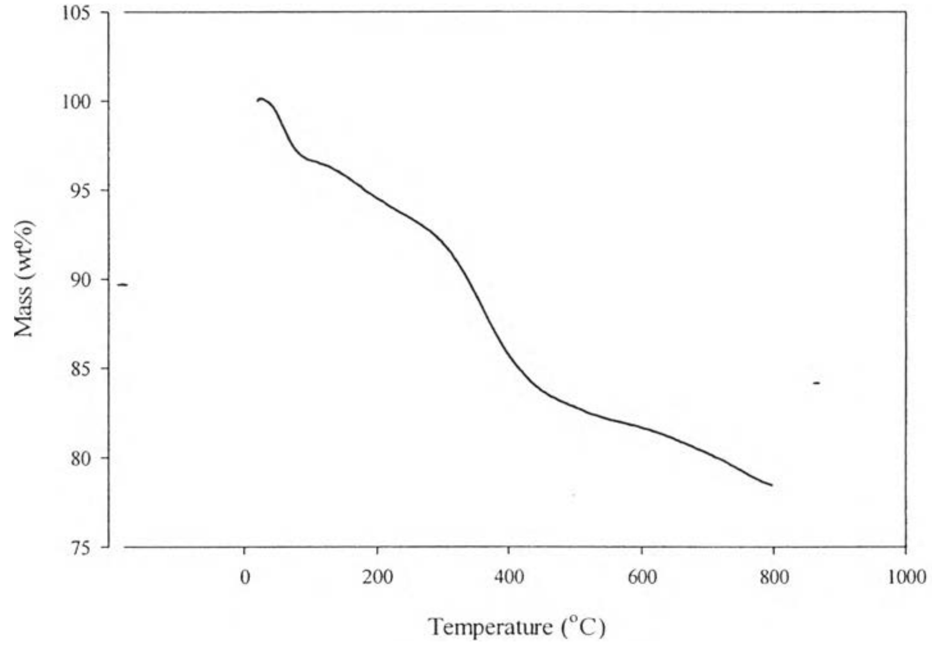


Figure 4.5 TG thermogram of 30/AC in 100 ml/min of N_2 flow at a heating rate of 10 °C/min.

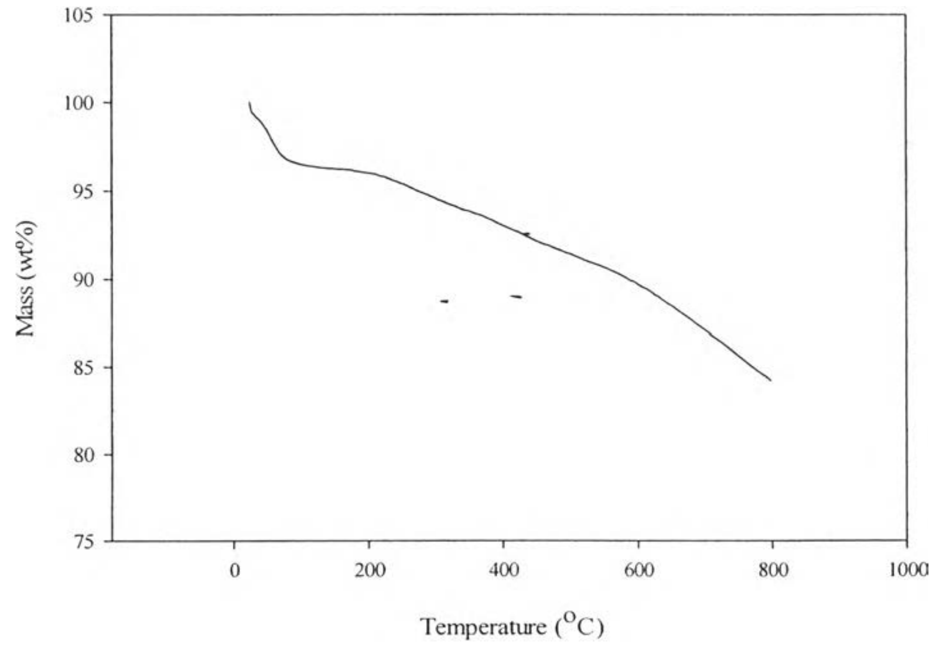


Figure 4.6 TG thermogram of OX/10/1 in 100 ml/min of N_2 flow at a heating rate of 10 °C/min.

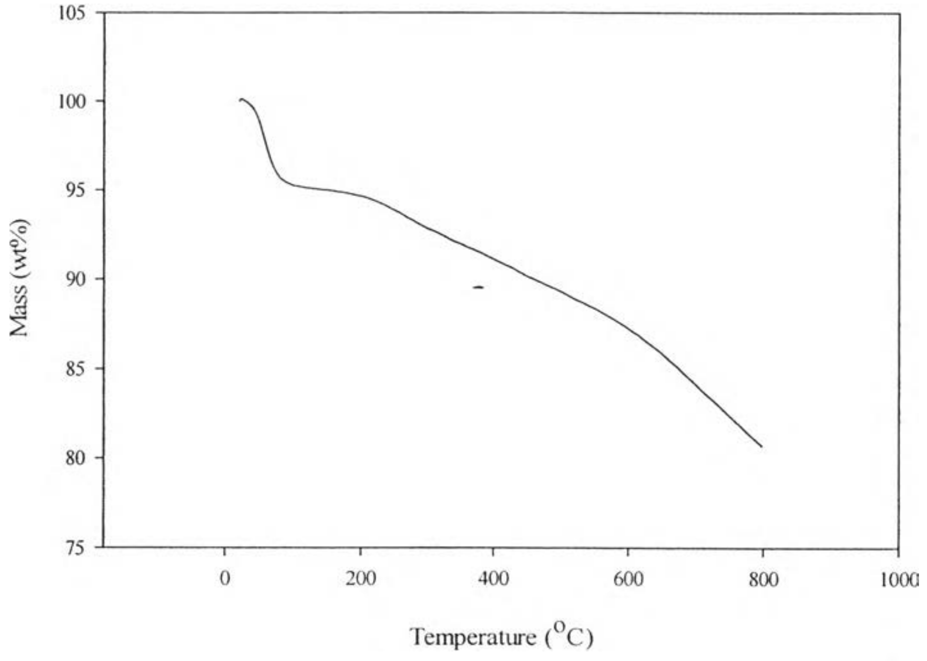


Figure 4.7 TG thermogram of OX/10/4 in 100 ml/min of N_2 flow at a heating rate of 10 °C/min.

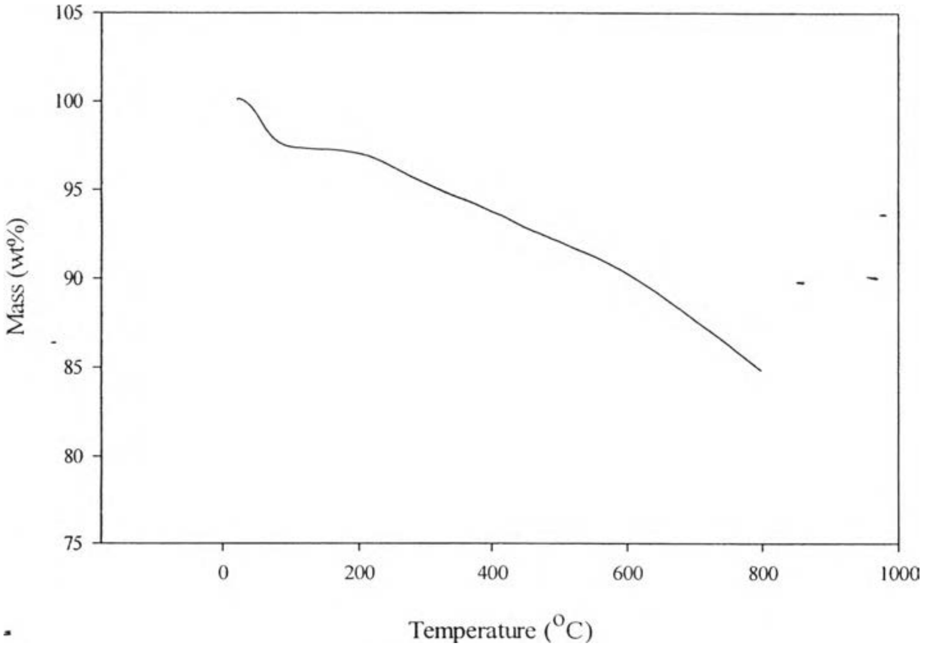


Figure 4.8 TG thermogram of OX/10/8 in 100 ml/min of N_2 flow at a heating rate of 10 °C/min.

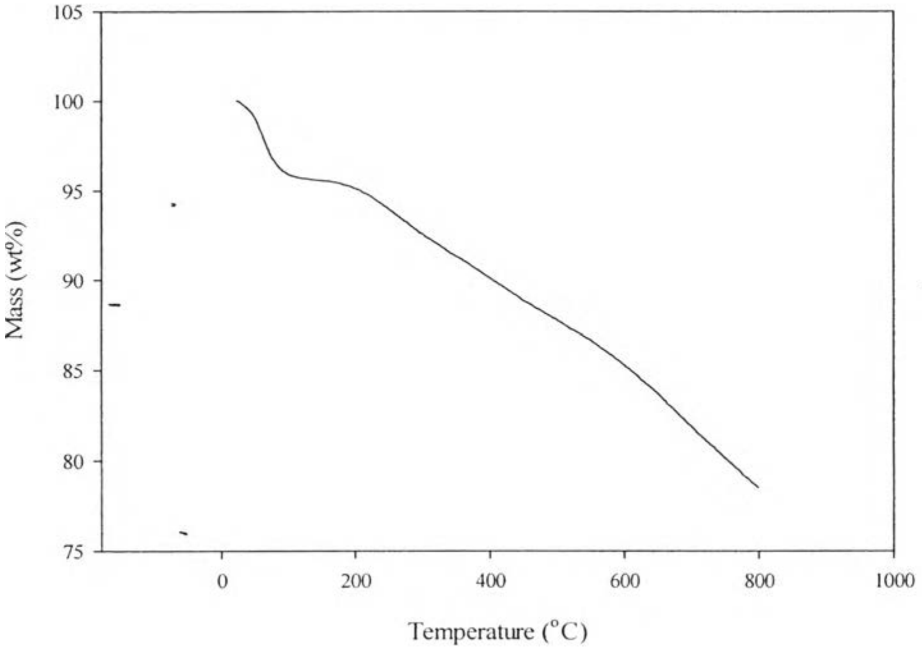


Figure 4.9 TG thermogram of OX/15/8 in 100 ml/min of N_2 flow at a heating rate of 10 °C/min.

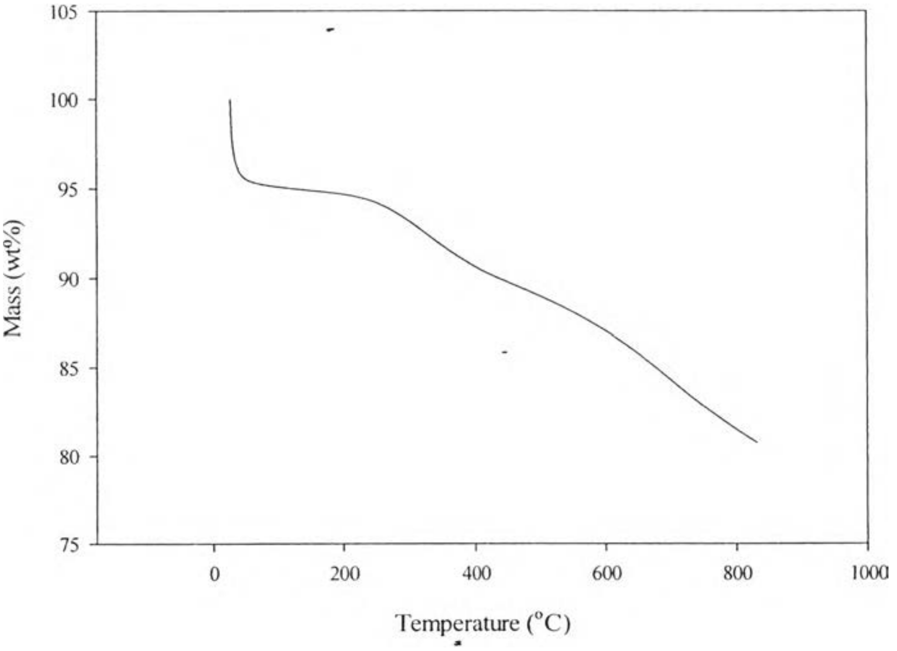


Figure 4.10 TG thermogram of 10/OX/10/8 in 100 ml/min of N_2 flow at a heating rate of 10 °C/min.

4.1.3 Surface Chemistry Analysis

4.1.3.1 Ultimate Analysis

The ultimate analysis of each adsorbent was presented in Table 4.2. In order to determine the best impregnation method, three types of the apparatus, namely magnetic stirrer, shaker and sonic bath, were used to achieve the wet impregnation. The amount of nitrogen from the elemental analysis was used to determine the best preparation techniques, i.e. the higher the nitrogen content, the higher amount of impregnating compounds incorporated into the adsorbent. Table 4.2 shows the nitrogen content increases when the wt% of PEI loaded on the activated carbon increases for all three impregnating methods.

Table 4.2 Ultimate analysis

Sample	Ultimate analysis (wt%)				
	C	H	N	O	S
AC	84.28	0.65	0.04	15.00	0.03
PEI	57.31	14.06	22.27	6.36	0.00
10/AC-stirrer	72.82	1.27	2.82	23.06	0.03
20/AC-stirrer	71.86	2.38	5.22	20.50	0.04
30/AC-stirrer	70.24	2.73	6.50	20.50	0.03
10/AC-shaker	70.56	1.36	2.68	25.36	0.03
20/AC-shaker	71.58	1.84	4.47	22.08	0.04
30/AC-shaker	69.38	2.41	5.98	22.19	0.04
10/AC-sonic bath	69.08	1.39	2.60	26.90	0.04
20/AC-sonic bath	64.34	2.00	4.27	29.36	0.03
30/AC-sonic bath	62.54	2.64	6.29	28.49	0.04
OX/5/8	82.53	0.17	0.50	16.77	0.03
OX/10/1	81.54	0.13	1.52	16.77	0.04
OX/10/4	82.19	0.33	1.53	15.91	0.04
OX/10/8	81.67	0.34	1.13	16.83	0.03
OX/15/8	79.94	0.20	0.50	19.34	0.03

Table 4.2 Ultimate analysis (cont'd)

Sample	Ultimate analysis (wt%)				
	C	H	N	O	S
10/OX/5/8	80.67	0.59	3.05	15.65	0.04
10/OX/10/8	79.05	0.84	3.31	16.77	0.04
10/OX/15/8	78.13	0.62	3.11	18.11	0.03

Figure 4.11 plots between nitrogen content and wt% of PEI loaded on the activated carbon from the three apparatus; magnetic stirrer, shaker and sonic bath. All of apparatus can introduce nitrogen into the activated carbon but magnetic stirrer provide the highest nitrogen content up to 6.50 wt% at 30 wt% of PEI loading as compared to 5.90 and 6.30 wt% obtained from shaker and sonic bath, respectively. Therefore, magnetic stirrer was chosen as to incorporate PEI into activated carbon by wet impregnation method.

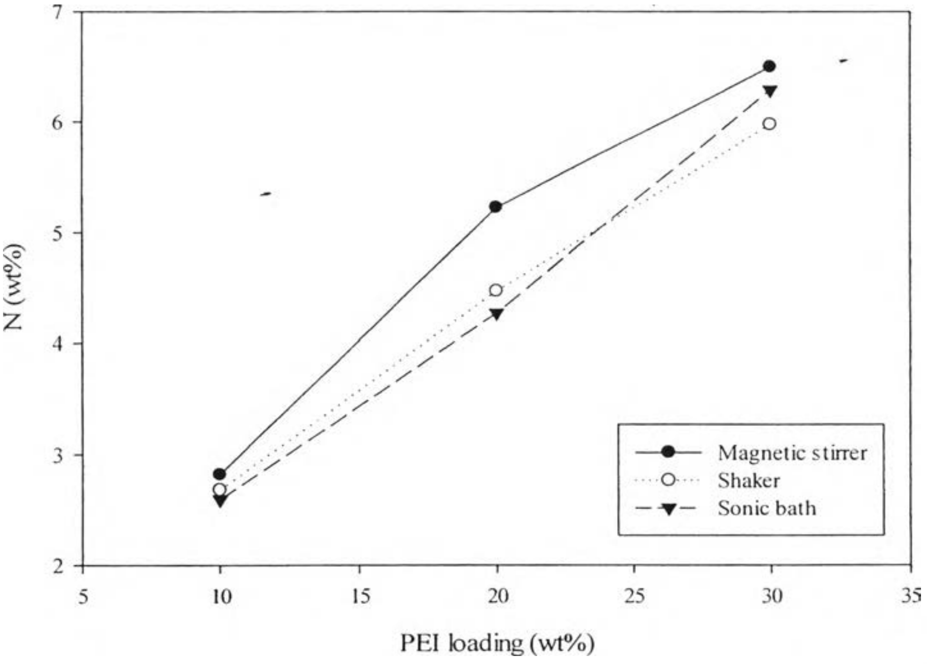


Figure 4.11 Effect of impregnating methods employed for nitrogen introduction on adsorbent.

For the oxidized samples, the amount of oxygen content increased when the concentration and duration of oxidation increase, from 15.00 % of an untreated AC to 19.34 % of OX/15/8. Moreover, there was a small increase in nitrogen content of the oxidized samples from 0.04 % of an untreated AC to 1.53 % of OX/10/4 due to the formation of nitric and nitrate groups (Moreno-Castilla *et al.*, 1995).

4.1.3.2 Fourier Transform Infrared Spectroscopy

To confirm that polyethylenimine used in this work is a high purity grade, Fourier Transform Infrared Spectroscopy (FTIR) was performed. The spectra were collected with 16 scans accumulated at a resolution of 4 cm^{-1} in the range of 400-4000 cm^{-1}. The FTIR spectra of polyethylenimine, as shown in Figure 4.12, represent to the spectra of pure polyethylenimine, thus the purification process of polyethylenimine did not require.

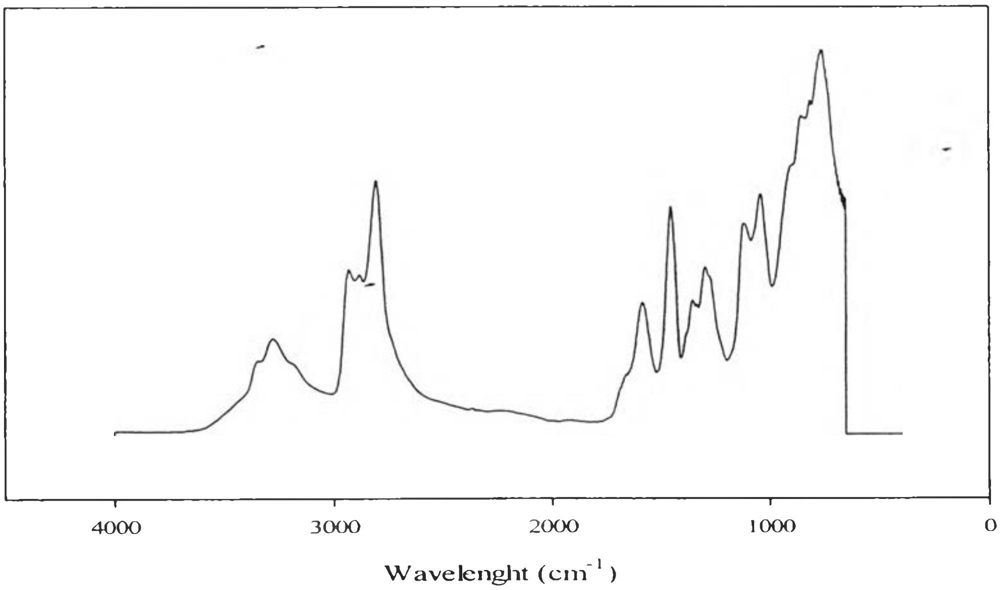


Figure 4.12 FTIR spectra of polyethylenimine.

4.1.3.3 X-Ray Photoelectron Spectroscope

The surface chemistry of adsorbents was determined by X-ray Photoelectron Spectroscope (XPS) on a Kratos Axis Ultra DLD. The narrow scans were corrected for charging of the samples by calibration to the main C1s peak at binding energy of 284.6 eV, with pass energy of 20 eV. The results of XPS are summarized in Table 4.3. It can be concluded that the appropriate concentration of nitric acid and duration of oxidation play a significant role. The sample OX/10/8 gave the highest carbonyl and carboxyl groups (48.1%) at binding energy of 531.52 eV. These acid functionalities could help improve the adsorption performance especially for carboxyl group because it presents not only carbonyl group (C=O) that can act as a Lewis base towards the carbon atom (Lewis acid) of CO_2 molecule, but also acidic proton (H^+) that can act as Lewis acid towards the oxygen atoms (Lewis bases) of the CO_2 molecule (Plaza *et al.*, 2013). Whereas the impregnation with PEI gives rise to the nitrogen functional groups mainly amine on the surface of the samples at binding energy of 399.76 eV.

Table 4.3 Results of the XPS spectra

Region	Position (eV)	Intensity (%)						Assignment
		AC	10/AC	20/AC	30/AC	OX/5/8	OX/10/1	
C1s	284.58±0.1	65.2	56.9	34.5	31.5	61.1	52.6	Hydrocarbon
	285.53±0.1	8.4	11.2	10.4	20.5	14.3	8.4	Hydroxyl, Ether
	286.43±0.2	7.0	10.9	30.0	25.9	8.7	5.9	C-N, Carbonyl
	288.59+0.2	4.0	8.2	11.2	11.2	9.8	6.2	Carboxyl, Ester
Total		84.6	87.2	86.1	89.1	93.9	73.1	
O1s	531.52±0.2	68.1	75.7	84.6	63.2	69.4	88.0	Carbonyl, Carboxyl
	533.27±0.2	31.9	24.3	15.4	36.8	30.6	12.0	Hydroxyl, Carboxyl
Total		100.0	100.0	100.0	100.0	100.0	100.0	
N1s	399.76±0.2	0.0	90.2	94.6	85.2	0.0	0.0	Amine
	401.94±0.2	0.0	9.8	5.4	14.8	0.0	0.0	Protonated Lactam
Total		0.0	100.0	100.0	100.0	0.0	0.0	

Table 4.3 Results of the XPS spectra (cont'd)

Region	Position (eV)	Intensity (%)						Assignment
		OX/10/4	OX/10/8	OX/15/8	10/OX/5/8	10/OX/10/8	10/OX/15/8	
C1s	284.58±0.1	58.0	48.2	58.2	34.2	36.0	44.3	Hydrocarbon
	285.53±0.1	14.0	16.2	10.9	16.9	17.4	9.2	Hydroxyl, Ether
	286.43±0.2	6.3	12.6	8.1	20.9	20.1	17.5	C-N, Carbonyl
	288.59+0.2	8.0	8.9	11.1	12.8	10.7	11.6	Carboxyl, Ester
Total		86.3	85.9	88.3	84.8	84.2	82.6	
O1s	531.52±0.2	48.1	14.7	46.1	75.2	53.3	82.0	Carbonyl, Carboxyl
	533.27±0.2	51.9	85.3	53.9	24.8	46.7	18.0	Hydroxyl, Carboxyl
Total		100.0	100.0	100.0	100.0	100.0	100.0	
N1s	399.76±0.2	0.0	0.0	0.0	91.4	97.5	90.8	Amine
	401.94±0.2	0.0	0.0	0.0	8.6	2.5	9.2	Protonated Lactam
Total		0.0	0.0	0.0	100.0	100.0	100.0	

4.1.3.4 Scanning Electron Microscope

The morphology of adsorbents was investigated by Scanning Electron Microscope (SEM) TM3000 at 9,000 magnifications. Untreated activated carbon, impregnated activated carbon with 30 wt% PEI and oxidized activated carbon in 10 M nitric acid were shown in Figures 4.13 to 4.15, respectively. The surface morphology of an untreated activated carbon and oxidized activated carbon show a similar character. There are heterogeneous and rough on their surface. For the impregnated sample, Figure 4.14 shows some foreign substances blocking the pores. This might be the evidence of the pore blockage of PEI in the impregnated activated carbon. However, the magnification used in this research was not enough and there was no tool to pin point what were the foreign substances. To evidence through the nano scale, the instrument requires a higher magnification to be able to observe the micro- to mesoporous ranges.

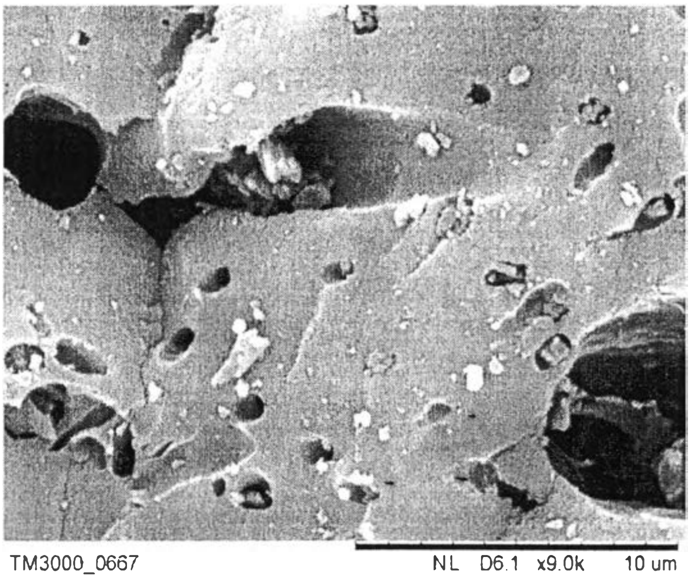


Figure 4.13 SEM micrograph of activated carbon.

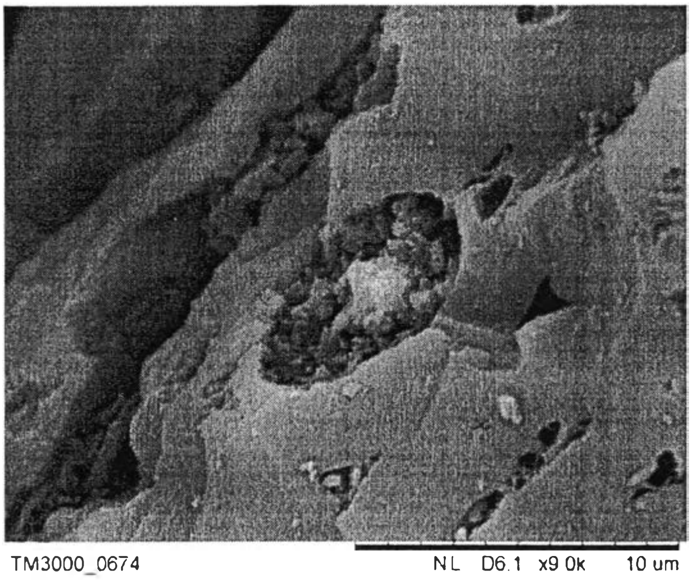


Figure 4.14 SEM micrograph of sample 30/AC.

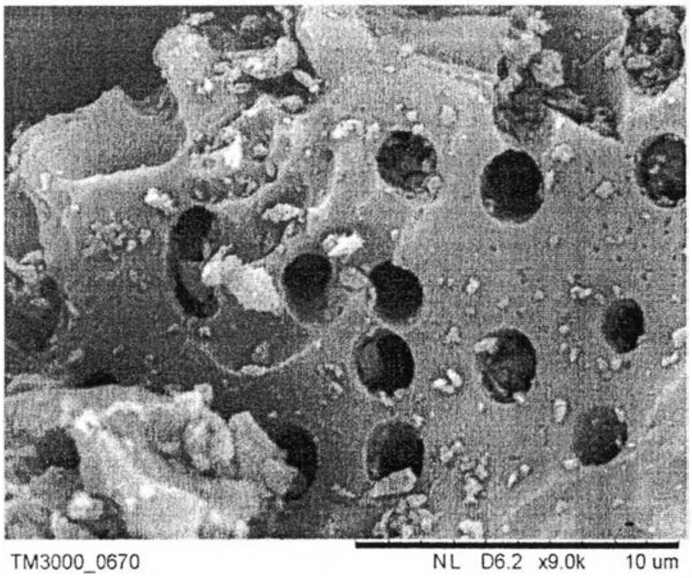


Figure 4.15 SEM micrograph of sample OX/10/8.

4.2 Effect of PEI Loading on CO_2 Adsorption Performance

Figures 4.16 to 4.18 show the CO_2 adsorption/desorption profile of the different impregnated samples measured at 40, 75 and 110°C for 1 atm. The CO_2 adsorption capacity of the untreated AC sample was 6.88, 3.72 and 2.03 wt% (1.56, 0.85 and 0.46 mmol/g sorbent) at 40, 75 and 110 °C, respectively. The CO_2 adsorption capacity of the samples impregnated with branched PEI, as shown in Table 4.4, lead to a decrease in adsorption capacity. The sample impregnated with 30 wt% of branched PEI (30/AC) gave the adsorption capacity of 0.93, 1.10 and 1.36 wt% (0.21, 0.31 and 0.25 mmol/g sorbent) measured at 40, 75 and 110 °C, respectively. The adsorption capacity increased with increasing in the temperature due to the chemisorption. But for other samples, including AC, 10/AC and 20/AC, the adsorption capacity decreased when the temperatures increased due to the lower effect of physisorption at high temperature. Furthermore, the CO_2 adsorption for all of the samples impregnated with branched PEI occurred slowly and did not reach a steady state even after 60 min.

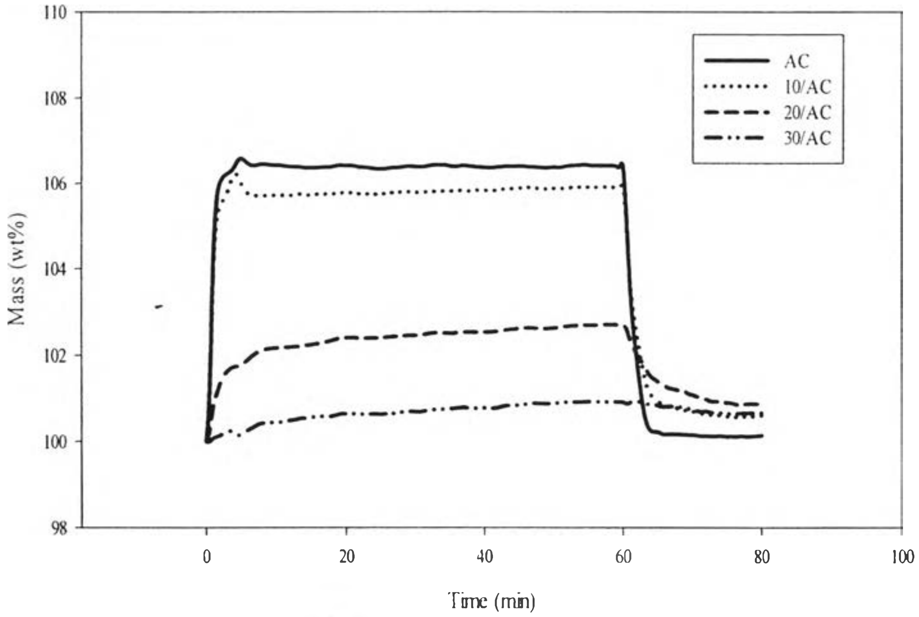


Figure 4.16 Isotherms (40 °C) adsorption/desorption profile of the series of samples by impregnation with various wt% of PEI.

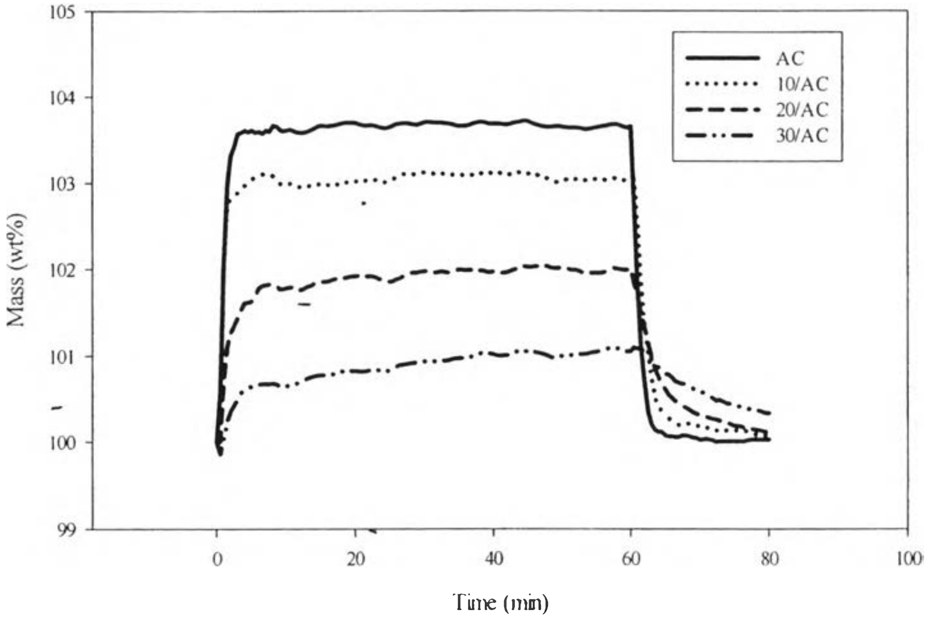


Figure 4.17 Isotherms (75 °C) adsorption/desorption profile of the series of samples by impregnation with various wt% of PEI.

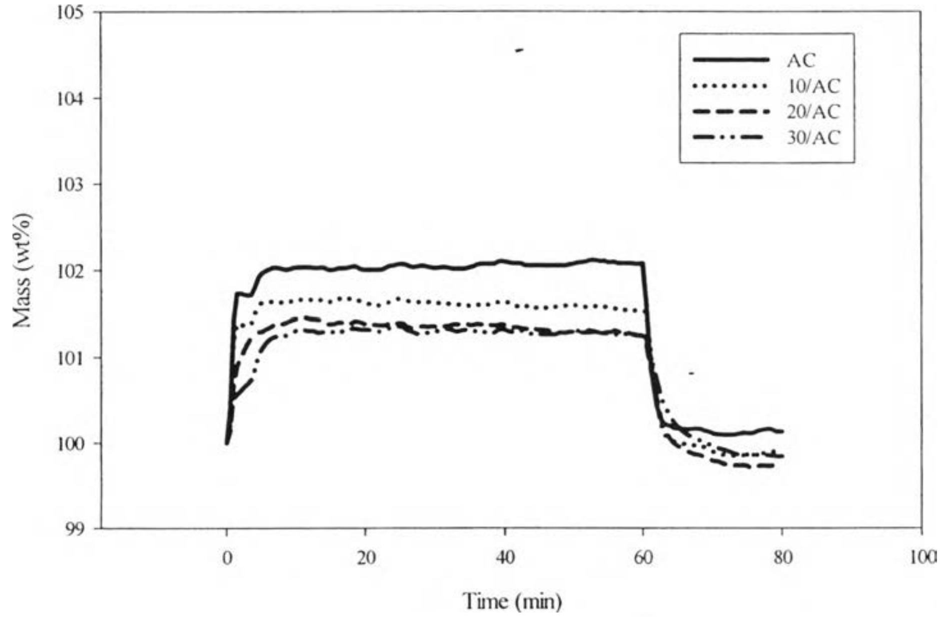
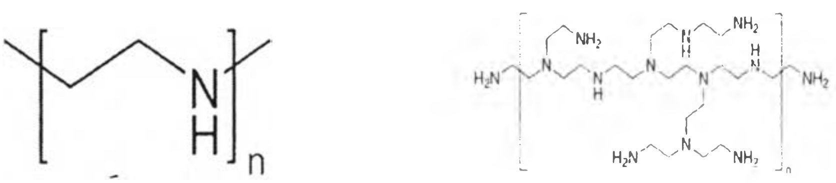


Figure 4.18 Isotherms (110 °C) adsorption/desorption profile of the series of samples by impregnation with various wt% of PEI.

A decrease in adsorption capacity of the impregnated samples resulting from the pore blocking effect occurring after the impregnation of branched PEI. The molecular structure of branched PEI, as shown in Figure 4.19b, is more bulky as compared to linear PEI (Figure 4.19a). Another possible reason is because the pore volume and pore size of the starting AC used in this study are too low. Table 4.3 illustrates the surface area, pore volume and pore size of the starting materials. The pore volume and pore size used in this study are lower than other studies. Therefore, branched PEI has a chance to block the pore of activated carbon. As described from Xu *et al.* (2003), when the pore of activated carbon excessively filled with PEI the synergic adsorption gain between chemisorption and physisorption is small. The extensive of PEI would be coated only on the external surface. Hence, the types of PEI and wt% of the impregnation loaded on the adsorbent become the important factors.



(a) (b)

Figure 4.19 Molecular structure of polyethylenimine; (a) linear, (b) branched.

Table 4.4 The comparison of surface area, pore volume and pore size of the starting materials

Adsorbent	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)	Reference
AC	1090	0.64	7.36	This study
AC-850-3	928	0.44	19.10	Maroto-Valer *et al.* (2005)
MCM-41	1486	1.00	27.50	Xu *et al.* (2003)
MCM-41	1042	0.85	28.00	Son *et al.* (2007)
SBA-15	753	0.94	55.00	Son *et al.* (2007)
Carbon black	1486	2.93	-	Wang *et al.* (2011)

4.3 Effect of Duration of an Oxidative Treatment on CO_2 Adsorption Performance

Figures 4.20 to 4.22 show the effect of duration of an oxidative treatment on activated carbon measured at 40, 75 and 110°C, respectively, at 1 atm. The summary of adsorption capacities were shown in Table 4.4. The duration of oxidation is significantly effect on the adsorption capacity. The results of the oxidized sample in 10 M of nitric acid for 1 and 4 h (OX/10/1 and OX/10/4) show similarly adsorption capacity as compared to an untreated AC for both 75 and 110°C. Only at 40°C the oxidized samples gave the adsorption capacity higher than the adsorption capacity of the untreated AC. The samples oxidized in 10 M of nitric acid for 8 h (OX/10/8) gave the adsorption capacity of 7.58, 4.19 and 2.16 wt% (1.72, 0.95 and 0.49 mmol/g sorbent), which are higher than 6.88, 3.72 and 2.03 wt% (1.56, 0.85 and 0.46 mmol/g sorbent) of an untreated AC measured at 40, 75 and 110°C, respectively

The oxidative treatment in liquid phase can give rise to the amount of oxygen functional groups, for instance carboxylic acids; carboxylic anhydrides and lactones. These oxygen functional groups present a strong Lewis acid-Lewis base with CO_2 molecules by electrostatic interaction especially for carboxylic acids. Therefore, the oxidative treatment in an adequate duration introduces the appropriate oxygen functional groups on the surface of adsorbent which help enhance the CO_2 affinity.

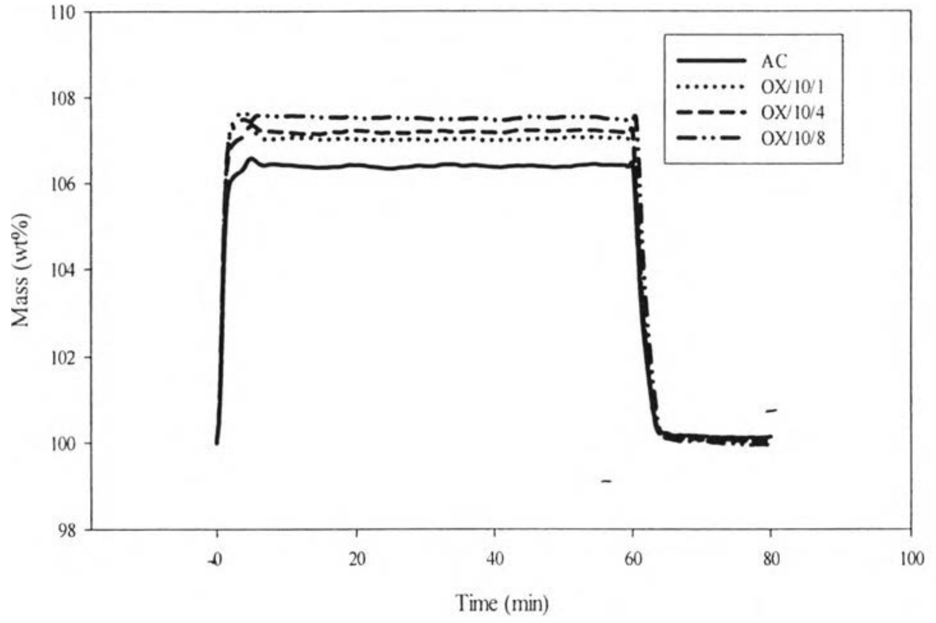


Figure 4.20 Isotherms (40 °C) adsorption/desorption profile of the samples by oxidative treatment in 10 M nitric acid.

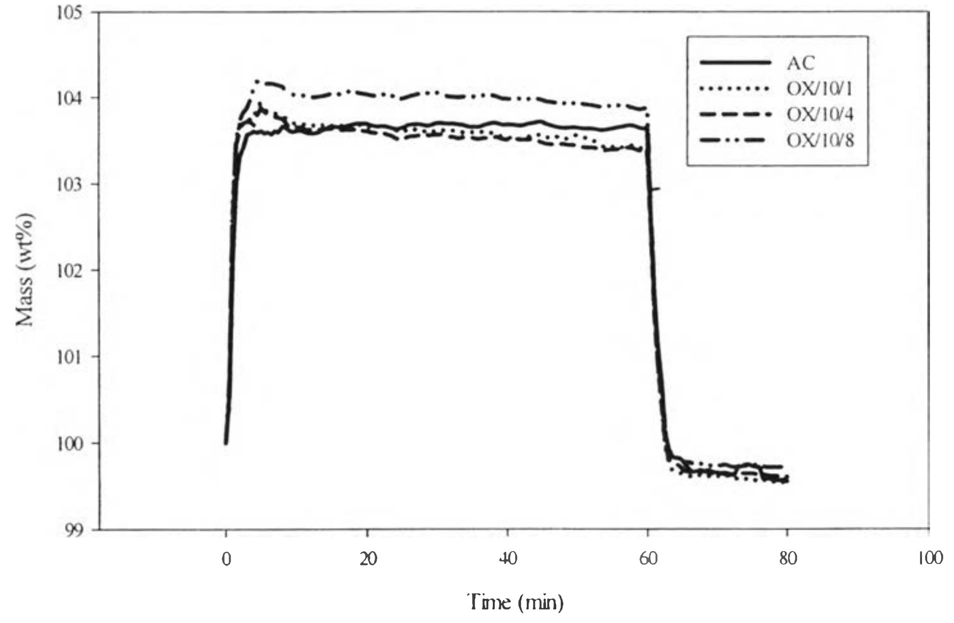


Figure 4.21 Isotherms (75 °C) adsorption/desorption profile of the samples by oxidative treatment in 10 M nitric acid.

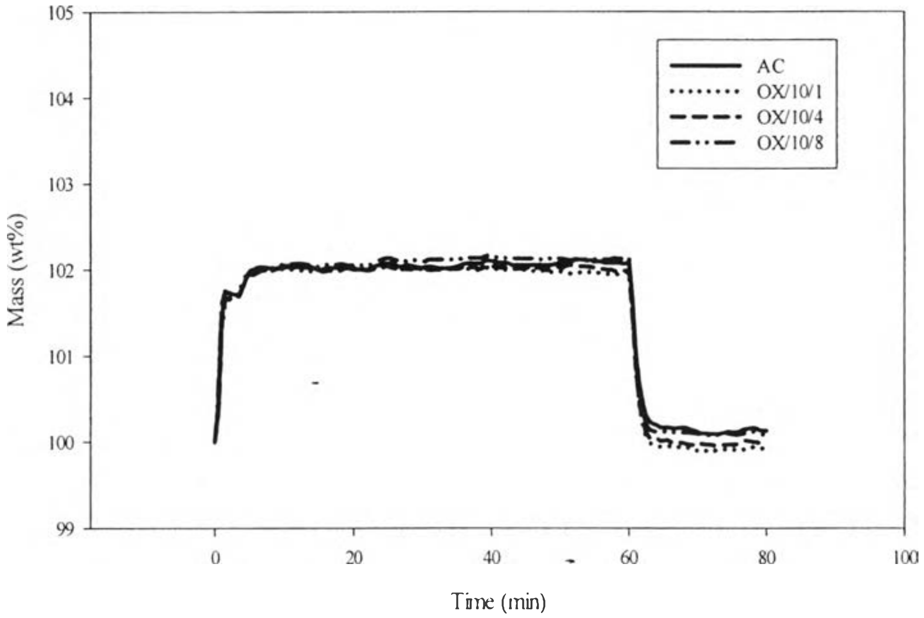


Figure 4.22 Isotherms (110 °C) adsorption/desorption profile of the samples by oxidative treatment in 10 M nitric acid.

4.4 Effect of Concentration of Oxidative Treatment on CO_2 Adsorption Performance

An effect of concentration of nitric acid used to oxidize the activated carbon is a significant factor. Figures 4.23 to 4.25 show the adsorption isotherms of the oxidized samples, with various concentrations at the same duration (8 h), measured at 40, 75 and 110 °C, respectively, for 1 atm. The sample oxidized in 10 M nitric acid (OX/10/8) gave an adsorption capacity of 7.58, 4.19 and 2.16 wt% (1.72, 0.95 and 0.49 mmol/g sorbent) at 40 °C, which are the highest adsorption capacity for all samples studied in this work. These results can explain by analyzing the surface chemistry by XPS as described in 4.1.3.3. The surface of the sample OX/10/8 has more acid functionalities, mainly carbonyl, carboxyl and hydroxyl. Therefore, oxidized sample in 10 M nitric acid gave higher adsorption capacity than those samples treated with 5 M and 15 M nitric acid.

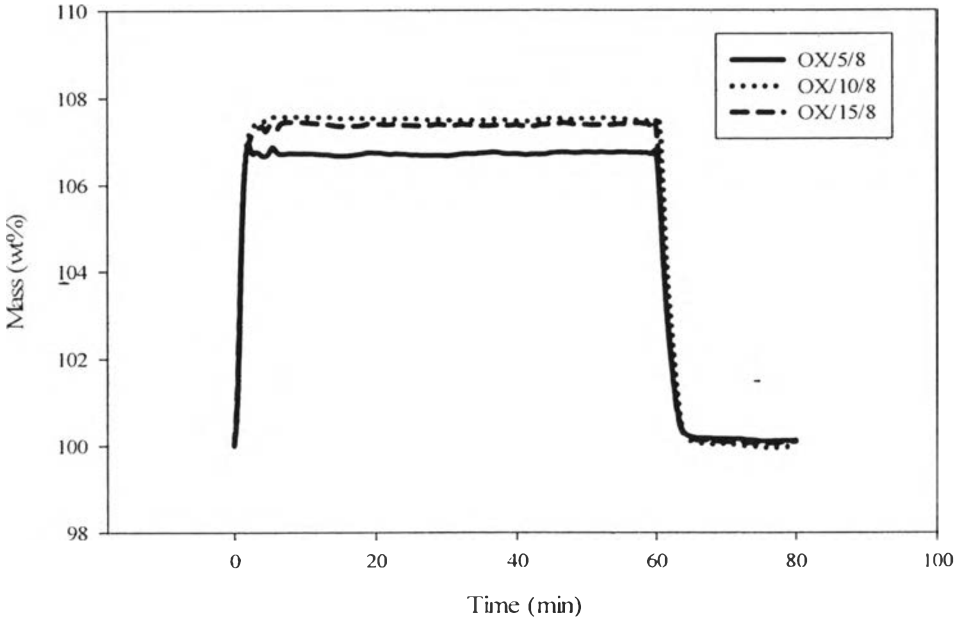


Figure 4.23 Isotherms (40 °C) adsorption/desorption profile of the samples by oxidative treatment in various concentration.

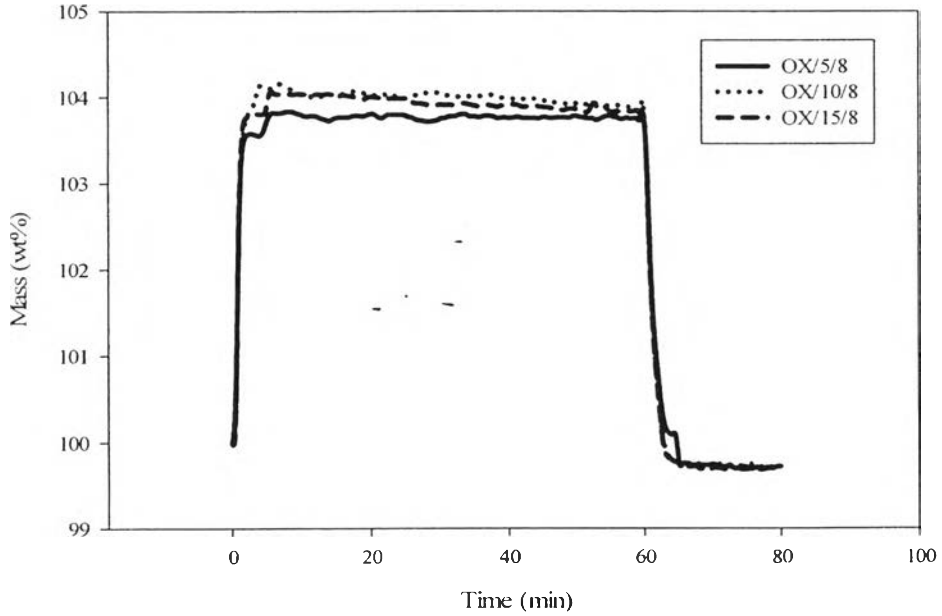


Figure 4.24 Isotherms (75 °C) adsorption/desorption profile of the samples by oxidative treatment in various concentration.

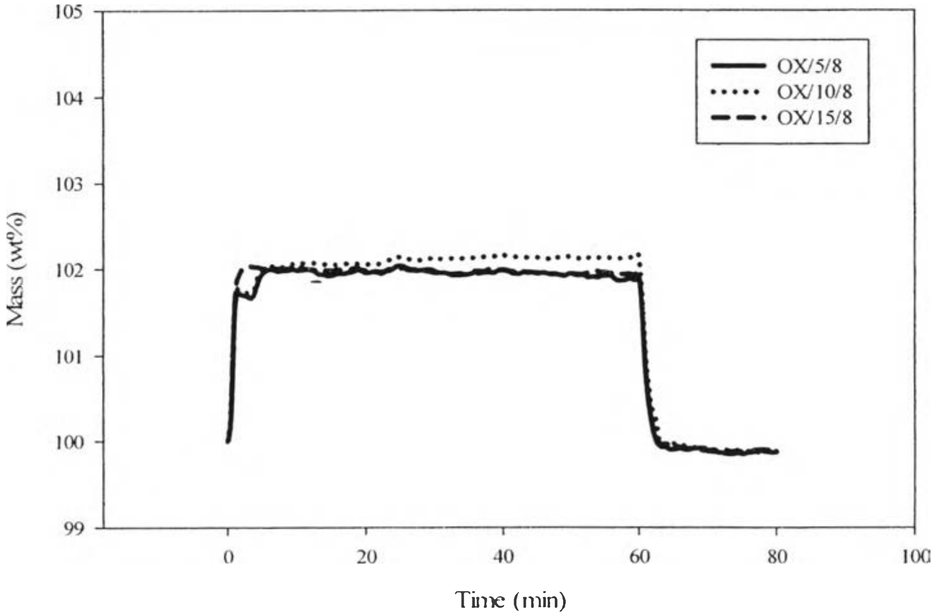


Figure 4.25 Isotherms (110 °C) adsorption/desorption profile of the samples by oxidative treatment in various concentration.

4.5 Effect of Oxidation before Impregnation

Figure 4.26 shows the adsorption performance of the impregnated samples on the untreated activated carbon (10/AC) and treated by oxidation in 10 M nitric acid for 8 h (10/OX/10/8). The adsorption isotherm of the untreated AC was also plotted as a reference. The adsorption capacity of sample 10/OX/10/8 is slightly higher than sample 10/AC (3.23 wt% or 0.73 mmol/g sorbent vs 3.12 wt% or 0.71 mmol/g sorbent) because the oxidized activated carbon has more proper acid functionalities as described in 4.1.3.3. The presence of acids can help improve the interaction between the adsorbate (CO_2) and adsorbent. However both of the impregnated samples gave lower adsorption capacity as compared to the untreated activated carbon due to the pore blocking effect.

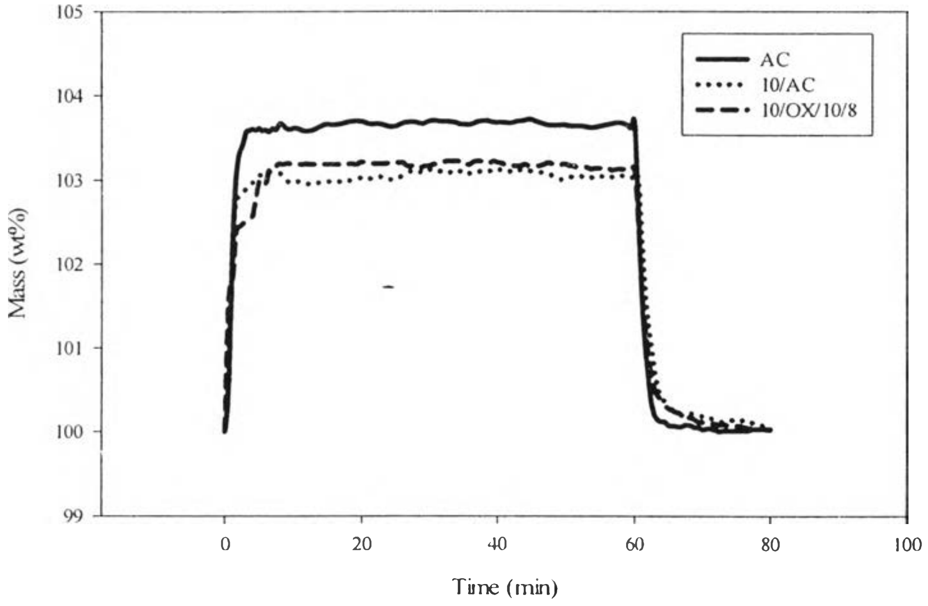


Figure 4.26 Isotherms (75 °C) adsorption/desorption profile of the impregnated samples with and without oxidation.

Table 4.5 The summarization of CO_2 adsorption capacity wt% (mmol/g sorbent) of each adsorbents

Sample	Temperature (°C)		
	40	75	110
AC	6.88 (1.56)	3.72 (0.85)	2.03 (0.46)
10/AC	6.20 (1.41)	3.12 (0.71)	1.68 (0.38)
20/AC	2.72 (0.62)	2.04 (0.46)	1.46 (0.33)
30/AC	0.93 (0.21)	1.10 (0.25)	1.36 (0.31)
OX/5/8	7.25 (1.65)	3.83 (0.87)	2.04 (0.46)
OX/10/1	7.08 (1.61)	3.81 (0.87)	2.02 (0.46)
OX/10/4	7.35 (1.67)	3.88 (0.88)	2.05 (0.47)
OX/10/8	7.58(1.72)	4.19(0.95)	2.16(0.49)
OX/15/8	7.45 (1.69)	4.12 (0.94)	2.05 (0.47)
10/OX/10/8	-	3.23 (0.73)	-

4.6 Effect of Treated Methods to the Regeneration Process

The regeneration of all samples was employed for 20 min at the same temperature of the adsorption process under 100 ml/min of N_2 flow. The desorption process of the impregnated samples as shown in Figures 4.27 to 4.29 are relatively slower than the untreated AC due to the chemisorption between CO_2 and amine groups and CO_2 seem to remain adsorbed after 20 min of desorption process at 40 and 75 °C. The 30/AC sample, the highest amine loading, can obtain only 34.37 % and 65.50 % regeneration at 40 and 75 °C, respectively. The 10/AC and 20/AC samples that contain lower amine compound can be regenerated at 92.57 % and 71.49 % at 40 °C and 97.82 % and 94.95 % at 75 °C, respectively. A desorption process was also employed with the sample that was oxidized before impregnation with 10 wt% PEI (10/OX/10/8). The 10/OX/10/8 sample (98.21 % regeneration) performed a similar desorption performance with the 10/AC sample (98.21 % regeneration). At 110 °C of the desorption process, there are no CO_2 remain adsorbed on adsorbents because the higher temperature has less physisorption interacting between adsorbent and adsorbate. Table 4.6 tabulates the percentage of regeneration process of each adsorbent. For the series of samples by oxidative treatment, the tendency of desorption performance of AC and oxidized samples were similar, moreover, there are no CO_2 remain adsorbed on adsorbents as shown in Figures 4.30 to 4.32.

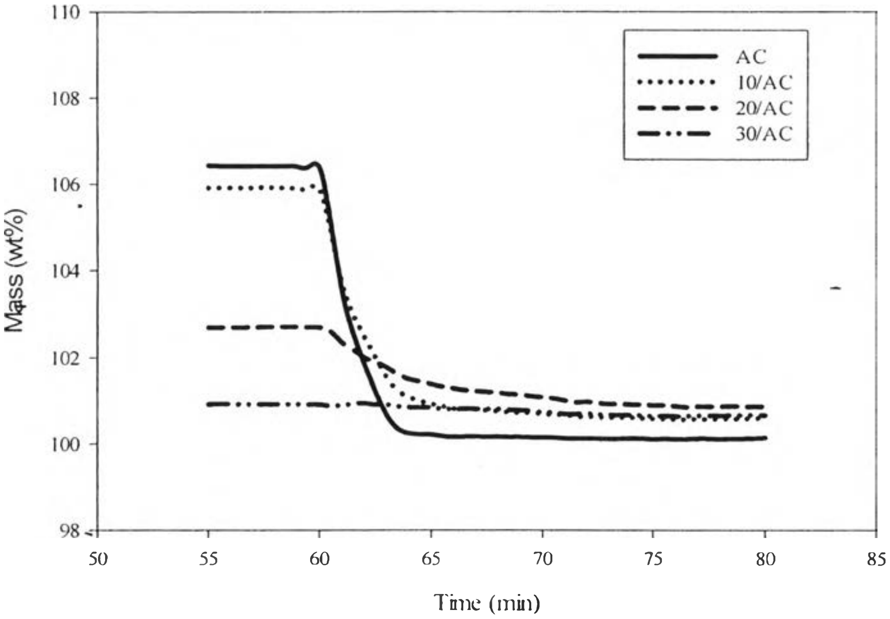


Figure 4.27 Desorption profiles of the series of samples by impregnation with various wt% of PEI measured at 40 °C.

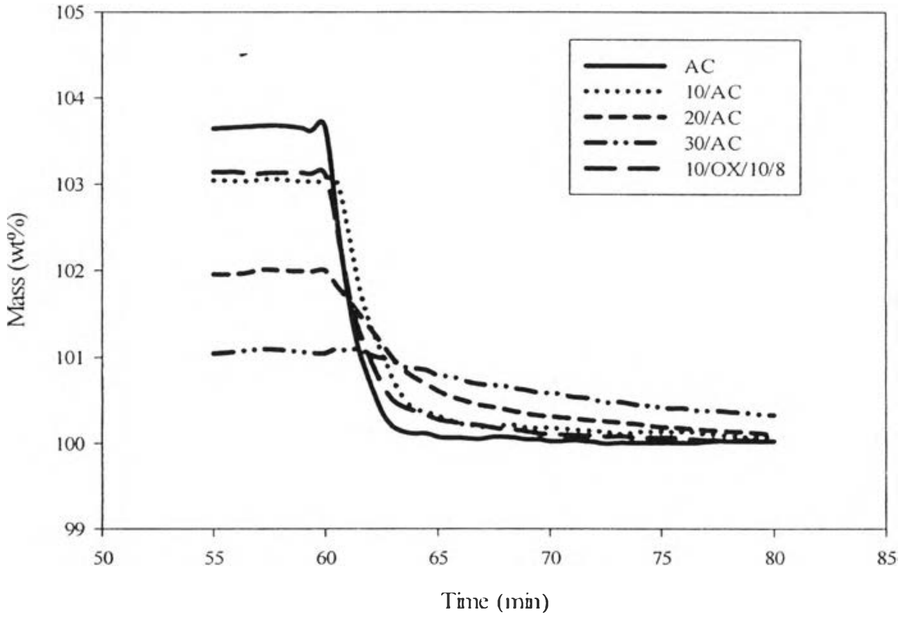


Figure 4.28 Desorption profiles of the series of samples by impregnation with various wt% of PEI measured at 75 °C.

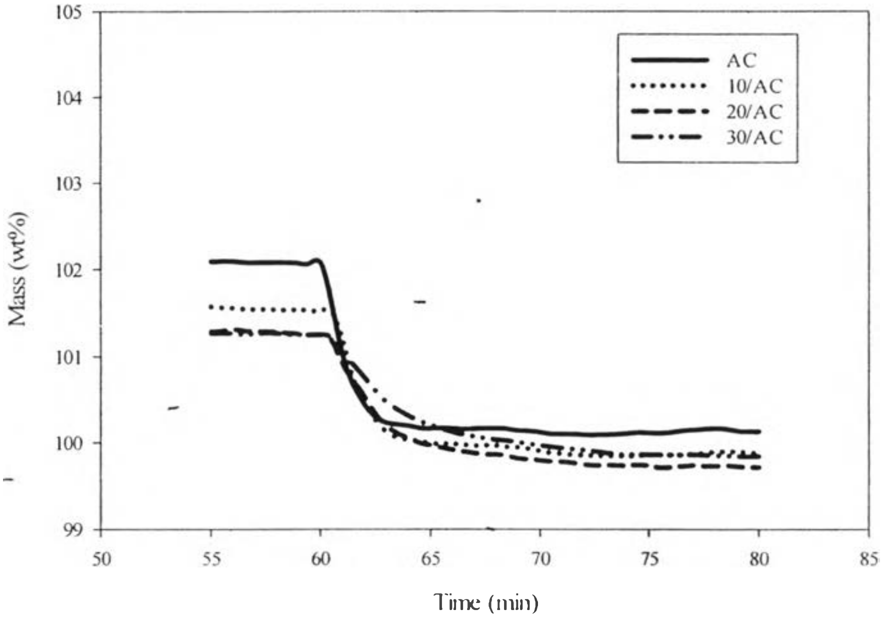


Figure 4.29 Desorption profiles of the series of samples by impregnation with various wt% of PEI measured at 110 °C.

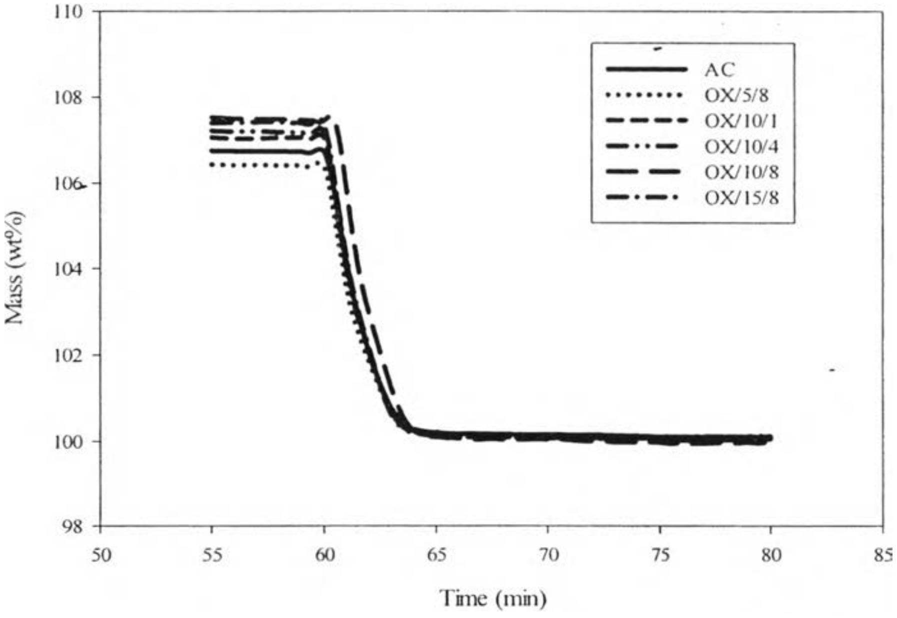


Figure 4.30 Desorption profiles of the samples by oxidative treatment measured at 40 °C.

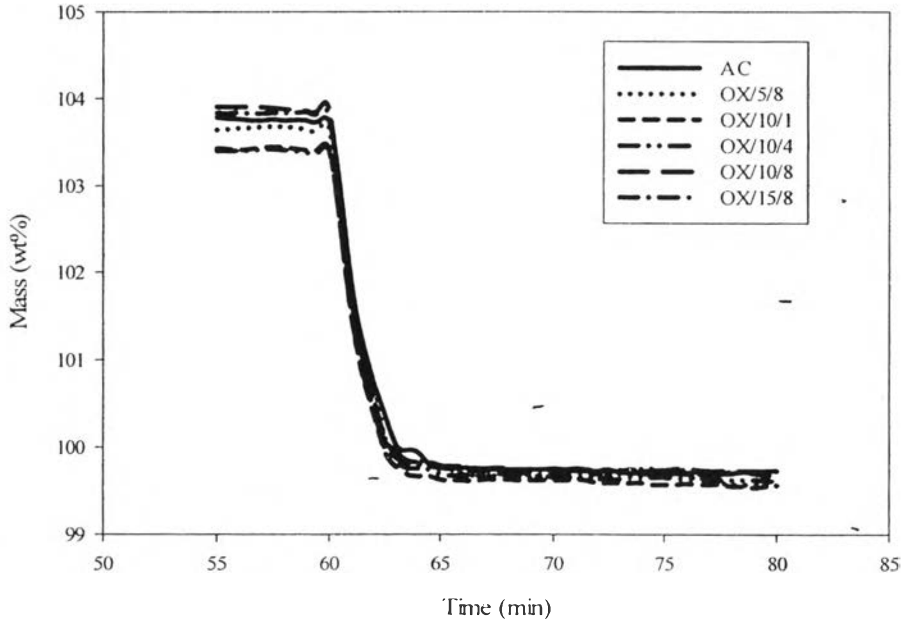


Figure 4.31 Desorption profiles of the samples by oxidative treatment measured at 75 °C.

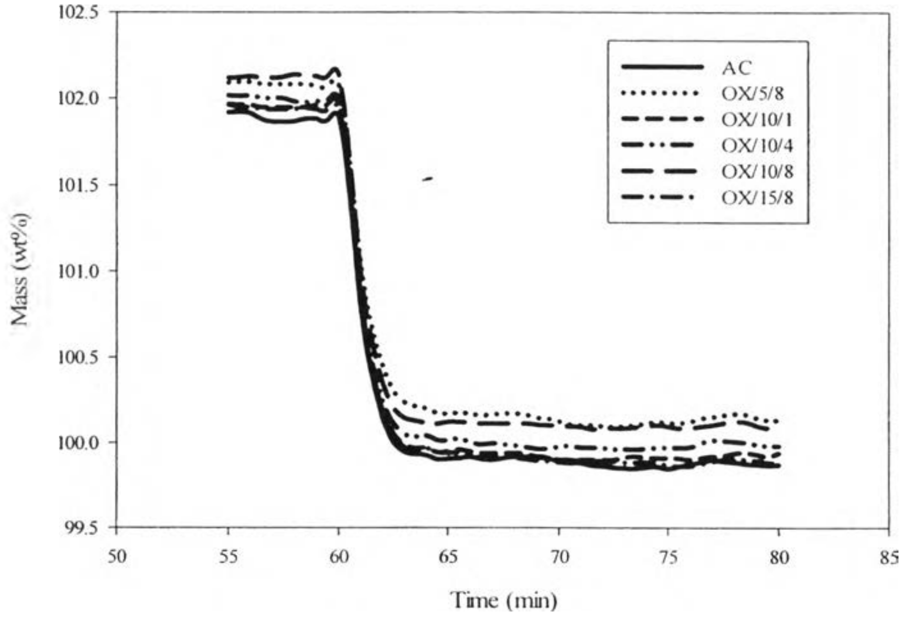


Figure 4.32 Desorption profiles of the samples by oxidative treatment measured at 110 °C.

Table 4.6 The percentage of regeneration process

Temperature (°C)	Sample	% of regeneration
40	AC	100
	10/AC	92.57
	20/AC	71.49
	30/AC	34.37
	OX/5/8	100
	OX/10/1	100
	OX/10/4	100
	OX/10/8	100
	OX/15/8	100
75	AC	100
	10/AC	97.82
	20/AC	94.95
	30/AC	69.50
	OX/5/8	100
	OX/10/1	100
	OX/10/4	100
	OX/10/8	100
	OX/15/8	100
	10/OX/10/8	98.21
110	AC	100
	10/AC	100
	20/AC	100
	30/AC	100
	OX/5/8	100
	OX/10/1	100
	OX/10/4	100
	OX/10/8	100
	OX/15/8	100