



CHAPTER IV

ANALYSIS OF RESULTS

This chapter is summarized for experimental results and also categorized into;

- Characteristics of natural clay from Koh Kred Pottery Village
- Characteristics of pillared clay and pillared bentonite
- Characteristics of modified bentonite by mixing with powder activated carbon
- Adsorption capacity of benzene, toluene and xylene
- Regeneration Testing of Modified Bentonite
- Surface area of modified bentonite after thermal testing
- Cost estimation for manufacturing of modified bentonite

4.1 Characteristics of Koh Kred's Clay and Bentonite

Natural clay from Koh Kred Pottery Village and raw bentonite were preliminary tested on particle size distribution, cation exchange capacity, crystal structure, oxide, specific area, and micropore area.

4.1.1 Size distribution

Size distribution of both clay is significant different. Figure 4.1 revealed that clay from Koh Kred source contains larger particle than of bentonite because it mainly combined with quartz, as analysis report in Appendix A. The size distribution of Koh Kred's clay and bentonite are 100 mesh at 35.7% and 140-230 mesh at 45.5 %, respectively. So, it may observe that bentonite may allow the pillaring agent insert to their structure and resulted in higher amount of developed surface area than Koh Kred's clay.

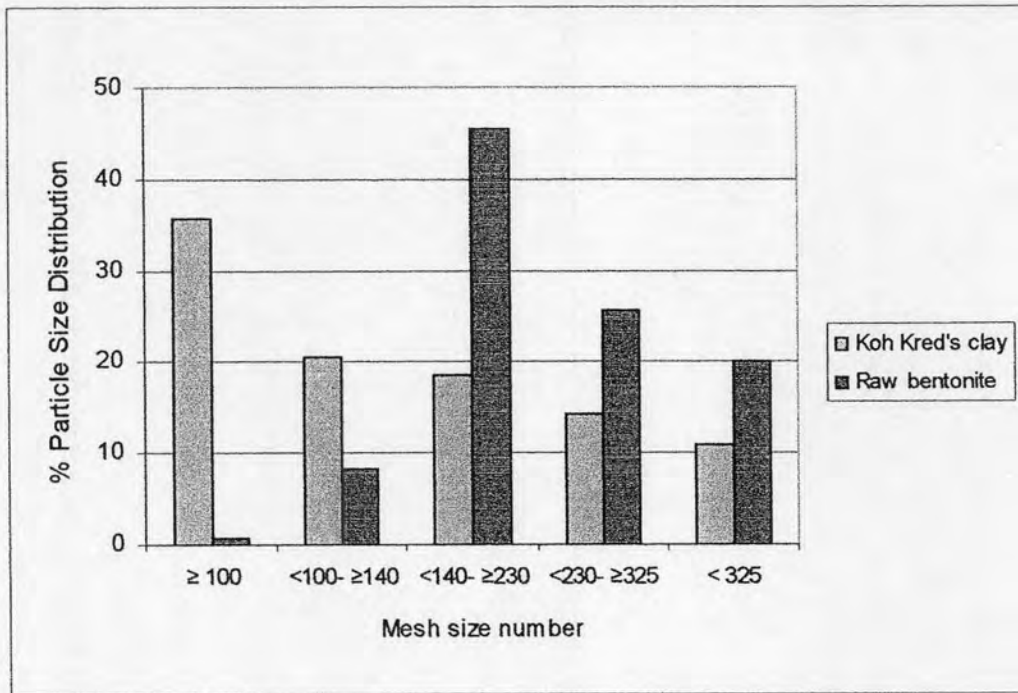


Figure 4.1 Particle size distribution of natural clay from Koh Kred source and raw bentonite

4.1.2 Cation exchange capacity

CEC of clay represented the cation exchange capacity particularly pillaring agent. Table 4.1 indicates that CEC of bentonite is higher than the natural clay from Koh Kred source. 28.8 and 67.5 meq/100 g are the CEC of natural clay from Koh Kred source and bentonite, respectively. By this reason, CEC value results in relative pillaring agent consumption by means of CEC fraction as following equation (1).

$$f = \frac{M_{cation}}{CEC \cdot M_{clay} \cdot GMW_{cation} \cdot X} \dots\dots\dots(1)$$

Where f = fraction cation exchange capacity satisfied by organic cation, M_{cation} = mass organic cation required to achieve required fraction of CEC (mass), CEC = cation exchange capacity of clay (equivalents/mass), M_{clay} = mass clay (mass), GMW_{cation} = gram molecularweight of organic cation (mass/mol), and X = moles of charge per equivalent = 1 mol/eq for the cations used in this study (mol/equivalent).

Table 4.1 Cation exchange capacity of Koh Kred's clay and bentonite

Types of Clay	CEC (meq/100 g)
Koh Kred's clay	28.8
Bentonite	67.5

It may see that bentonite requires amount of pillaring agent in higher quantity than Koh Kred's clay. The calculation for pillaring agent added for pillaring stage, see Appendix D.

4.1.3 Component and mineralization

Consider to XRD and XRF result, crystallization characteristics of Koh Kred's clay are quartz whereas bentonite is more complicated with many types of structures because it is reconditioned by soda ash as shown in Figure 4-2 and 4-3. Besides, cryztobalite is main crystal structure represented in bentonite.

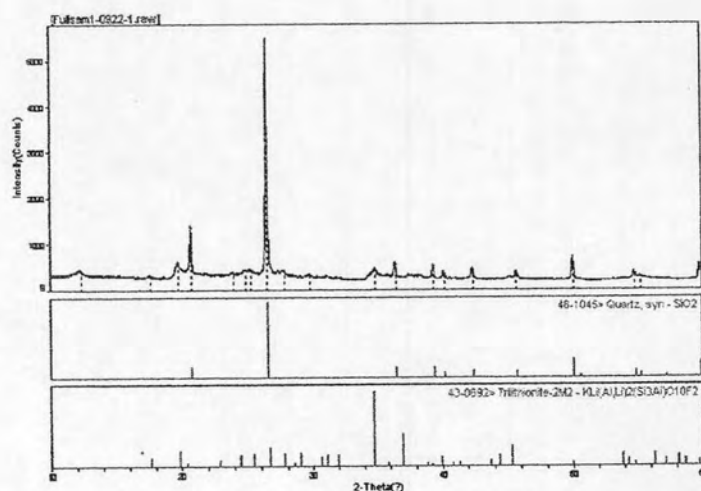


Figure 4-2 XRD analysis result of Koh Kred's clay

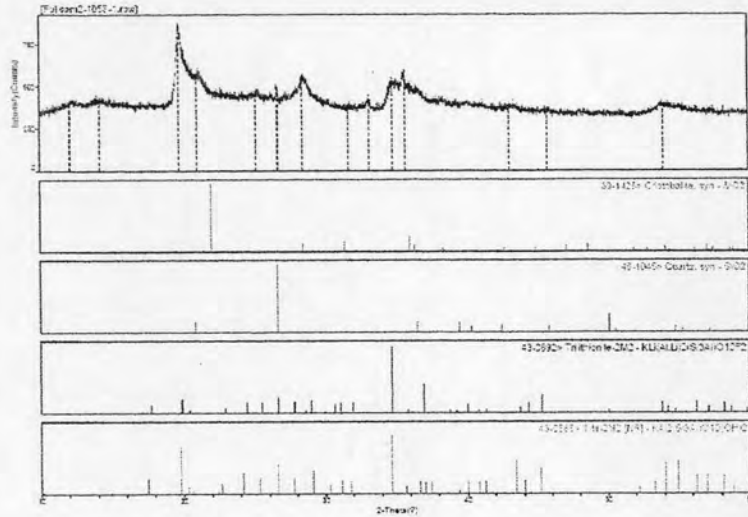


Figure 4-3 XRD analysis result of raw bentonite

4.2 Characteristics of Pillared Clay and Bentonite

4.2.1 Surface area analysis of Koh Kred's clay and raw bentonite

From surface area analysis result by ASAP 2000, it showed that BET and Langmuir surface of raw bentonite are all higher than of natural clay from Koh Kred source with 58% and 59%, respectively. In addition, considering to micropore area, bentonite is quite higher than natural clay at 14% as shown in Figure 4.4.

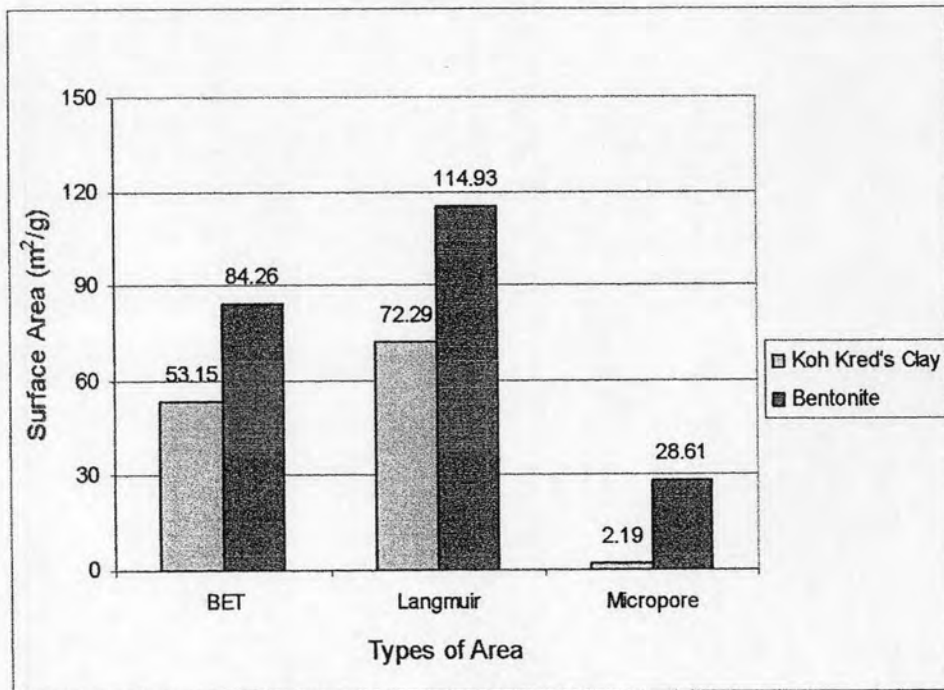


Figure 4.4 Surface areas of Koh Kred's clay and raw bentonite

In addition, when compared with N₂ adsorption at 77 K, it demonstrates that bentonite characterizes higher adsorption capability than natural clay from Koh Kred. Figure 4.5 shows the total volume of bentonite is higher than of natural clay at 11.24%, approximately 1.13 times. Also, micropore volume, which is relative to micropore area, bentonite contains higher volume with 0.0885 cc/g whereas the natural clay represents only 0.0796 cc/g or approximately lowers 6.67 times.

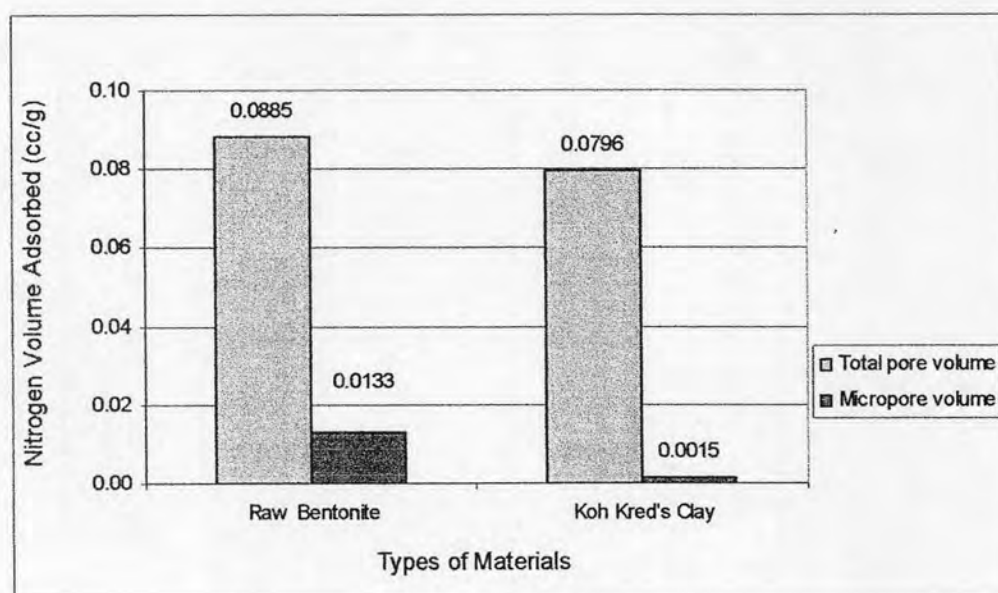


Figure 4.5 Comparison of nitrogen isotherms at 77 K for unpillared Koh Kred's clay and bentonite

As above characteristics, it indicates the feasibility to develop clay surface area by pillaring technique. Due to fine particle of bentonite, it's interesting to conduct for further development in adsorption capacity in terms of Langmuir, BET and micropore area.

4.2.2 Surface area analysis of pillared clay and bentonite without thermal dehydration

Both clays were prepared by pillaring with tetraethylammonium chloride, TEA, equivalent to 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00 times of clay. The amount of TEA required to be equal to desired fraction of CEC was calculated by equation (1) and shown in Appendix D. Dehydration by air drying resulted that surface areas of natural

clay were not quite different from the original clay. It may imply that pillaring technique was unable to apply for development of natural clay from Koh Kred surface area. Anyhow, surface areas of bentonite were developed after pillaring, but it's not different between fractions of CEC. BET surface areas were ranged from 103.64-109.91 m²/g or averaged 106.50 m²/g. Whereas Langmuir surface area of bentonite were generated to the range of 140.25-150.35 m²/g with average 145.12 m²/g or increasing 26.27%. Micropore areas were also increased by ranging between 36.13- 44.64 m²/g with average 40.78 m²/g and increasing 70.17% as shown in Figure 4.6.

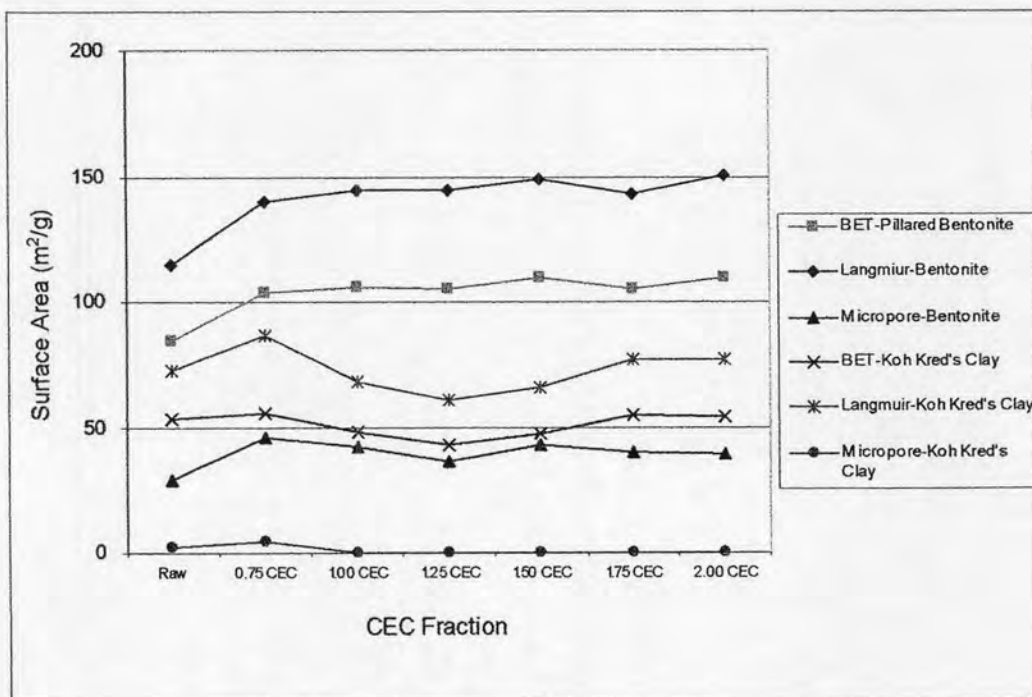


Figure 4.6 Surface areas of both pillared clay and bentonite with air-dried dehydration

Consider to N₂ adsorption by isotherm at 77 K, it was found that pillaring bentonite with TEA equivalent to 0.75 – 2.00 stepwise times the CEC conducted the higher adsorption capacity at the same relative pressure whereas Koh Kred's clay was remained the same as the original clay.

Considering the average pore size as Figure 4.7, both types of clay characterized lower average pore size after pillaring, especially for bentonite that approached to microporous material with 31.73 Å average pore size. As mentioned by

Gregg, S.J. and Sing, K.S.W. 1982, the classification of pores according to their width determine micropores with less than 20 Å. Accordingly, bentonite can be correspondingly enhanced to microporous material whereas Koh Kred's clay can be developed at only 44.58 Å which still quite higher than microporous characteristics.

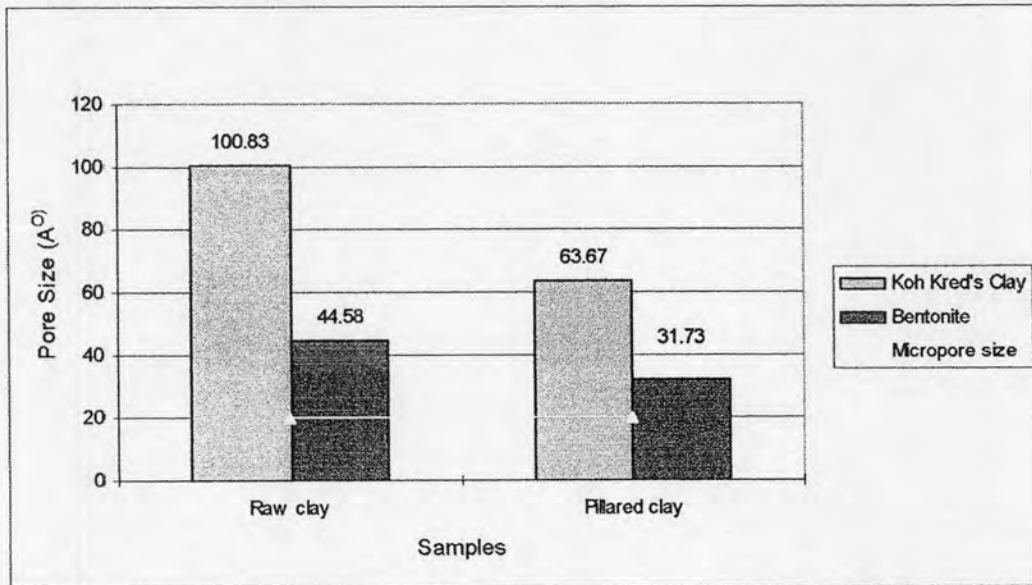


Figure 4.7 Average pore sizes of Koh Kred's clay and raw bentonite

After replacing cation with pillaring agent, TEA, CEC of bentonite was decreased from 67.5 meq/100 g to 37.3 meq/100 g with 44.7% as revealed in Table 4.2 This result was corresponding to Yang, R.T., 2003 which determined that CEC is decreased approximately 10-20% after pillaring. The original CEC is now taken up by the protons. Some or most of these protons migrate into the octahedral sheet of bentonite. It may imply that the pillared bentonite became higher organophilic or hydrophobic characterization.

Table 4.2 Cation exchange capacity of bentonite

Items	Raw bentonite	Pillared bentonite	% Reduction
CEC (meq/100 g)	67.5	37.3	44.7

4.2.3 Surface area analysis of pillared bentonite with thermal dehydration

After adding with TEA with various fractions of CEC, pillared bentonite was conducted for dehydration at temperatures from 300 – 600 °C. It was found that surface areas were lower than dehydration with air drying. Additionally, as amount of TEA increased from 0.75 to 2.00 times the CEC, BET and Langmuir surface areas were not significant different between these ratios. The average BET and Langmuir were 81.59 and 111.62 m²/g, respectively, which were lower than those of air drying 30.53% and 30.02%. Consider to micropore area, Figure 4.8 – 4.10 demonstrated that it tended to decrease at higher temperature dehydration by approximately average 58.90%. Therefore, to develop surface area of pillared bentonite, the proper condition should be done under air-drying dehydration and 0.75 times CEC pillaring to consume lowest energy and amount of pillaring agent.

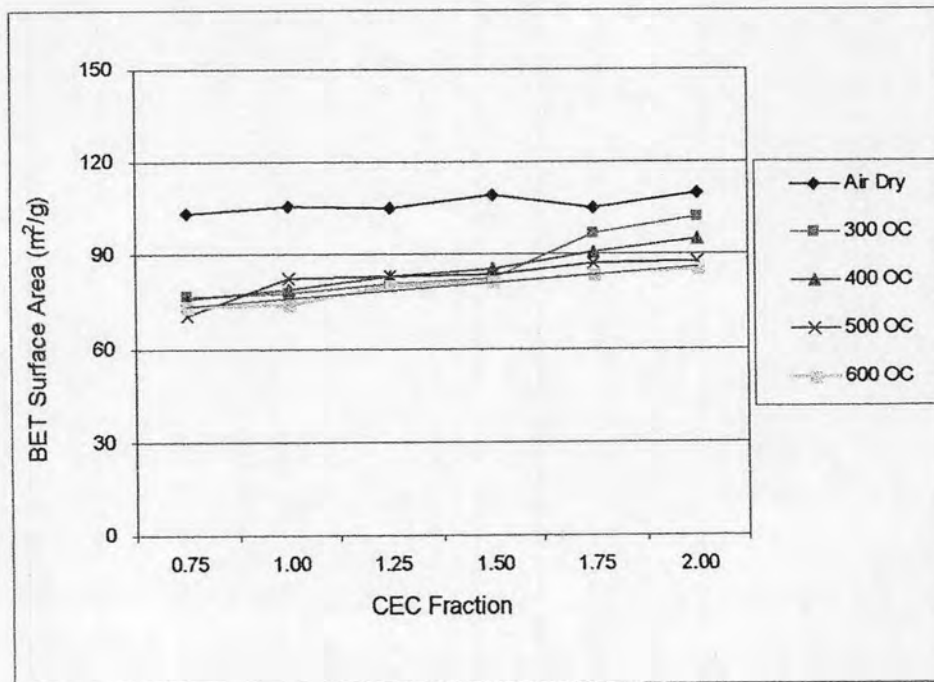


Figure 4.8 BET surface area of pillared bentonite at various dehydration temperatures

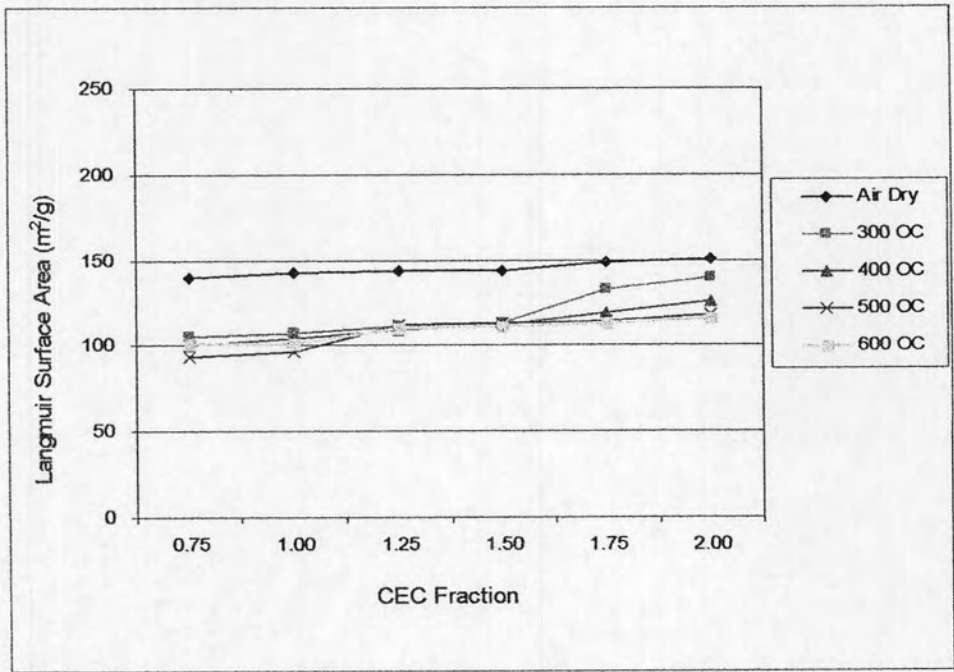


Figure 4.9 Langmuir surface area of pillared bentonite at various dehydration temperatures

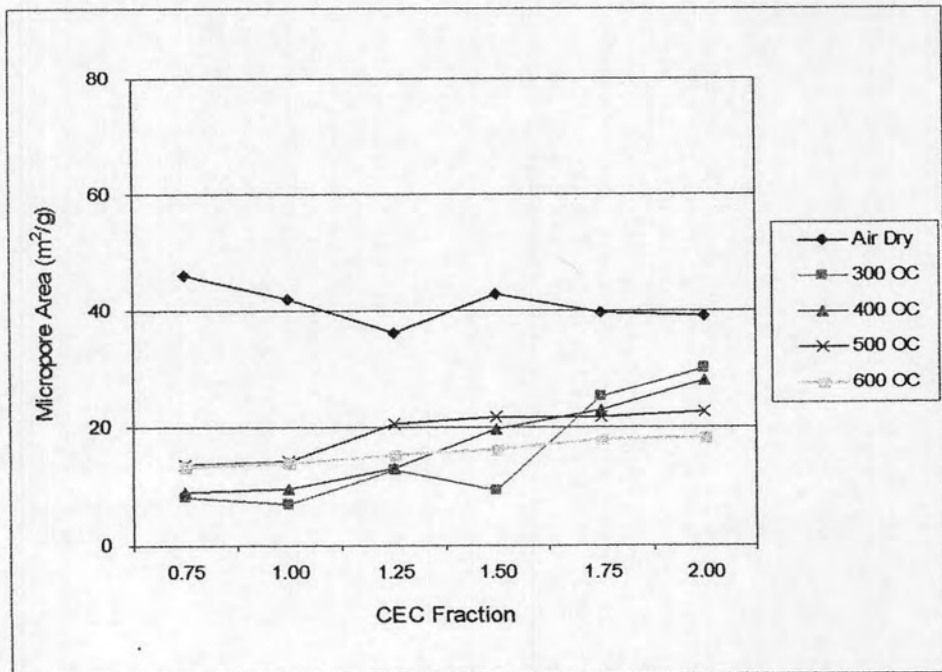


Figure 4.10 Micropore area of pillared bentonite at various dehydration temperatures

After aging the bentonite sample with TEA for 2-days, it's found that not only both surface areas were not different from 1-day aging time but also micropore area characterized in the same practice as shown in Figure 4.11.

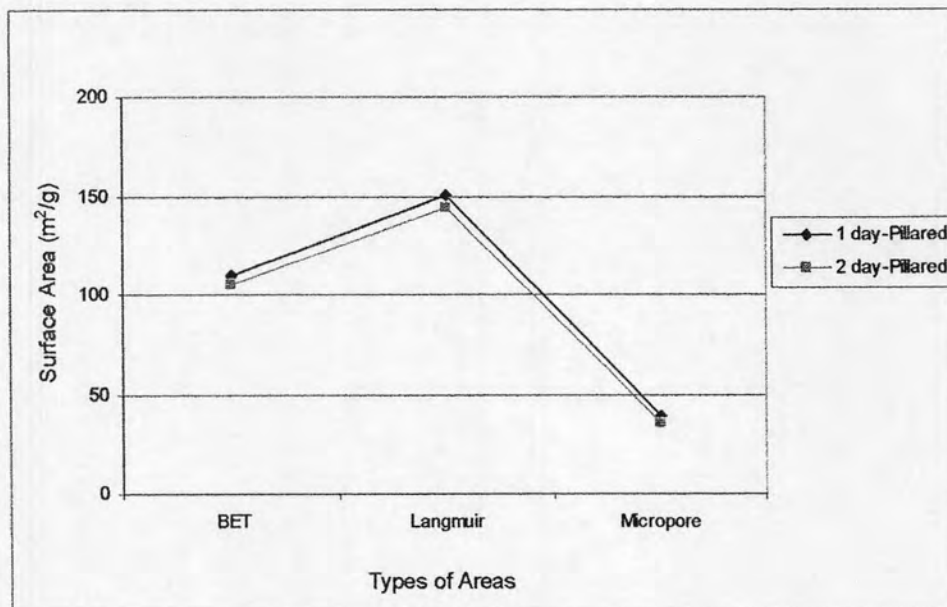


Figure 4.11 Surface areas of pillared bentonite with various aging times

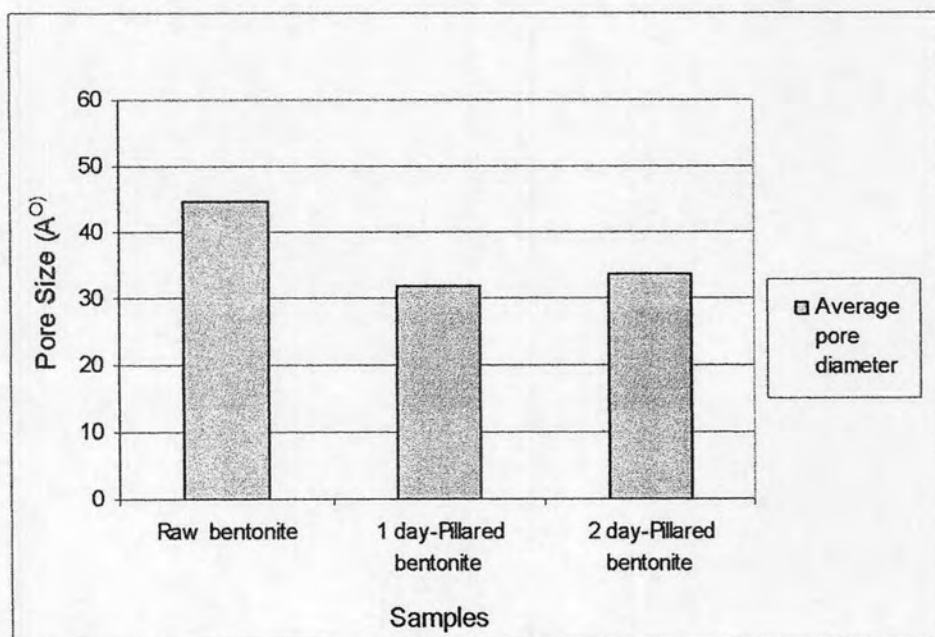


Figure 4.12 Average pore size of pillared bentonite with various aging times

For this reason, even though the pillared bentonite was prepared with tetraethylammonium chloride in the longer time, all types of surface areas were not developed. In addition, the average pore diameter as revealed in Figure 4.12 was still the same as 1-day pillared bentonite. It may imply that the aging time does not effect on surface area development and pore size characteristics. So, the further study of modified bentonite by mixing with activated carbon, only 1-day aged pillared bentonite was conducted for experiment by then.

4.3 Characteristics of Modified Bentonite Combined with Activated Charcoal

After testing the pillaring of benotnite by TEA, the best condition, which was adding with 0.75 times of CEC fraction and air-drying dehydration, was conducted for further surface area development with mixing with high surface area material. For this experiment, commercial activated charcoal, Filtrasorb-300 with 1,034 m²/g surface area, was brought for mixing material. The mixing ratio between pillared bentonite and activated carbon were 4:1 and 3:2 by weight. When mixed material as ratios, these modified material were analyzed surface areas, porous structure and also scanning electron microscope afterwards as presented in Figure 4.13.

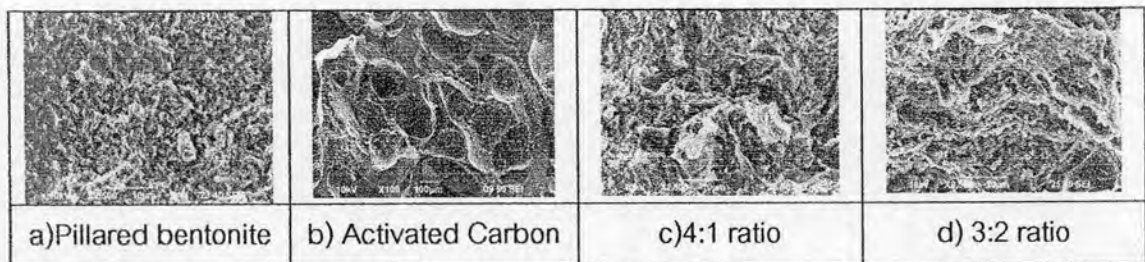


Figure 4.13 Scanning Electron Microscope of a) pillared bentonite, b) activated carbon c,d) combined materials between pillared bentonite

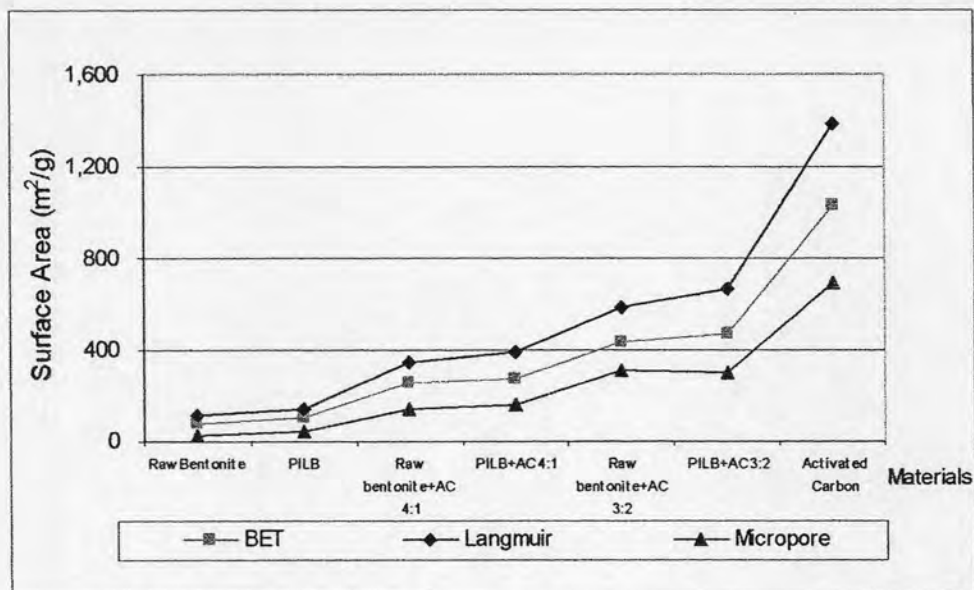


Figure 4.14 Surface areas of modified bentonite after mixing with activated charcoal by 4:1 and 3:2 ratios

From the experimental result in Figure 4.14, it's found that mixing materials between pillared bentonite and activated carbon with 3:2 ratio generate highest BET and Langmuir surface areas which are 471.36 and 667.65 m²/g, respectively. Moreover, when comparing with activated carbon, mixing material between pillared bentonite and activated carbon with 3:2 ratios can be developed surface area but it's still outstanding lower than activated carbon approximately at 35.5%.

4.4 Benzene, Toluene and Xylene Adsorption on Modified Bentonite

After modifying adsorbent by combination of pillared bentonite and activated carbon, it was conducted for testing adsorption of benzene, toluene and xylene. The batch experiment was modeled by air exhaust system recommended by ACGIH guideline. It was determined the face velocity at 100-200 f/min and duct velocity at least 2,000 f/min. Benzene, toluene, and xylene were experimented separately in batch type and investigated the breakthrough time by PID and also capacity was determined by then. Table 4.3 summarized the VOC adsorption capacity by loading of VOC per weight of adsorbents. The adsorption capacity of benzene, toluene, and xylene, PILB 32 was practically 1/7 times lower than activated carbon.

Table 4.3 VOC adsorption capacity of activated carbon and PILB 32

VOCs	Replicate	Weight ,g		Vface ,fpm		Inlet, ppm		Breakthrough time, min		Capacity, mg/g	
		PILB 32	AC	PILB32	AC	PILB 32	AC	PILB 32	AC	PILB 32	AC
Benzene	1	36.5882	19.2524	140	143	27	27	12	41	2.2004	14.59
	2	37.9563	21.1258	145	140	28	29	14	39	2.6579	13.30
Toluene	1	35.1452	20.2309	140	144	27	30	15	37	2.4277	14.02
	2	36.8851	19.3856	147	147	29	27	12	42	2.0870	15.26
Xylene	1	35.0896	19.4176	143	140	30	28	15	45	2.3951	16.12
	2	36.4979	20.6231	144	145	28	30	16	47	2.3085	17.60

4.5 Physical Characteristics of Modified Bentonite after Thermal Testing

This experiment is to investigate existing properties of modified bentonite from remain surface area after thermal testing 3 times. The conditions for testing are various temperatures at 80, 90 and 100 °C with various times for 30, 45, and 60 minutes. It found that each testing times may effect on surface area.

In spite of this, decreasing rate was fit to linear term eventually all temperature conditions as shown in Figure 4.15.

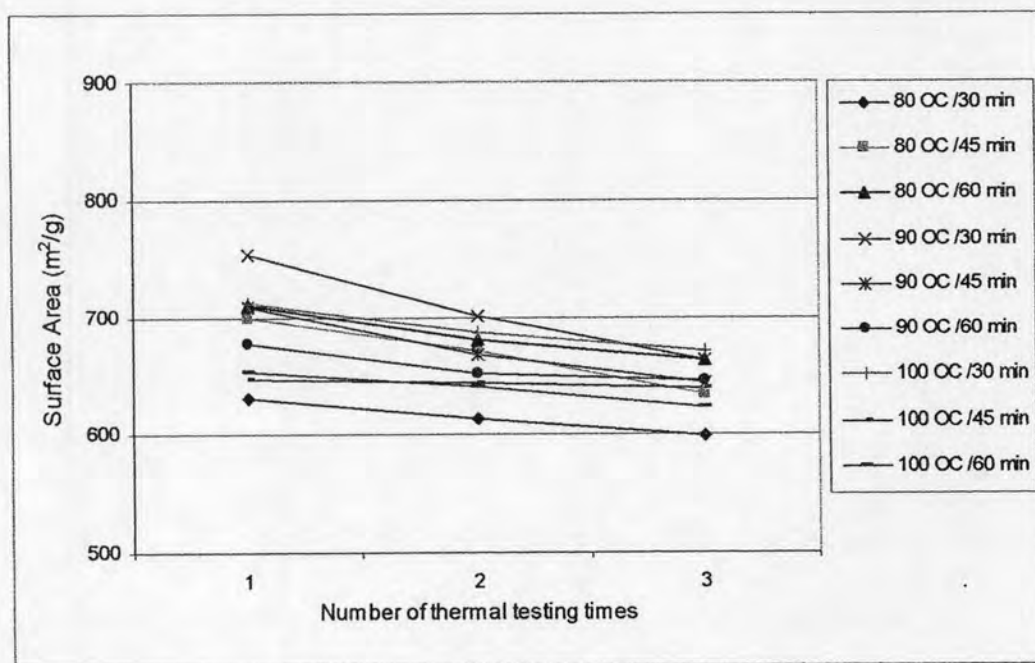


Figure 4.15 Surface areas of combined PILB 32 and activated carbon with 3:2 ratios after thermal testing

Furthermore, the thermal testing of activated carbon conducted the result in the same practice which surface area reduced when number of testing increased. By the way, eventually activated carbon loss their surface area in higher number than PILB32

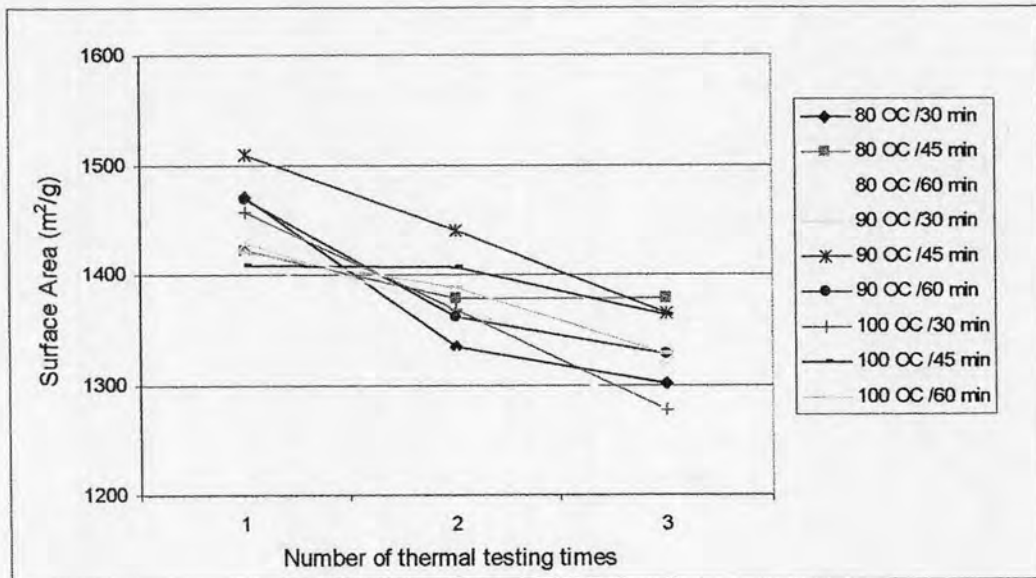


Figure 4.16 Surface areas of activated carbon after thermal testing

Considering to the comparison of thermal testing condition between two samples, it may be considered that at 80 °C and 30 minutes was the appropriate condition and practical for further application because both surface area and yield represented the lowest decreasing rate when compared with other conditions.

4.6 Regeneration Testing of Modified Bentonite

Afterwards, both samples were conducted for testing adsorption of benzene, toluene and xylene and testing regeneration under 80 °C for 30 minutes, the result was presented in Table 4.4 and 4.5.

Table 4.4 Adsorption capacity and surface area retention of PILB 32

VOCs	Regen 1st		Regen 2nd		Regen 3rd		Regen 4th		Regen 5th	
	Capacity (mg/g)	Langmuir (m2/g)	Capacity (mg/g)	Langmuir (m2/g)	Capacity (mg/g)	Langmuir (m2/g)	Capacity (mg/g)	Langmuir (m2/g)	Capacity (mg/g)	Langmuir (m2/g)
Benzene	2.13	710.98	2.08	690.34	1.98	650.46	1.82	630.56	1.78	613.43
Toluene	2.20	708.34	2.11	689.04	2.03	645.98	1.96	624.96	1.84	605.63
Xylene	2.15	713.45	2.09	698.76	2.01	667.12	1.93	634.64	1.81	616.49

Table 4.5 Adsorption capacity and surface area retention of activated carbon

VOCs	Regen 1st		Regen 2nd		Regen 3rd		Regen 4th		Regen 5th	
	Capacity (mg/g)	Langmuir (m ² /g)	Capacity (mg/g)	Langmuir (m ² /g)	Capacity (mg/g)	Langmuir (m ² /g)	Capacity (mg/g)	Langmuir (m ² /g)	Capacity (mg/g)	Langmuir (m ² /g)
Benzene	13.76	1432.65	12.12	1382.67	11.98	1293.25	10.88	1182.13	9.18	1076.34
Toluene	14.87	1465.34	12.98	1412.56	12.34	1301.67	11.41	1190.56	9.29	1085.07
Xylene	15.75	1428.12	13.21	1378.06	12.63	1288.42	11.65	1161.50	9.32	1069.23

After regeneration 5 times, both of adsorbent decrease their surface areas and capacity. Anyhow, activated carbon still possessed their better characteristics than PILB 32. After 5th regeneration times, activated carbon obtained higher benzene, toluene and xylene adsorption capacity with 9.18, 9.29 and 9.32 mg/g, respectively. In the other hand, PILB 32 represented the lower capacity with 1.78, 1.84 and 1.81 mg/g.

Considering surface area, PILB 32 habited lower reduction rate than activated carbon and practically retained it even pass many regeneration times.

Additionally, their physical characteristics were further tested under higher thermal condition at 800 °C and 30 minutes. Figure 4.17 revealed % yield reduction of activated carbon and PILB32. The graph characterized that activated carbon tended to decrease their yield higher than PILB 32.

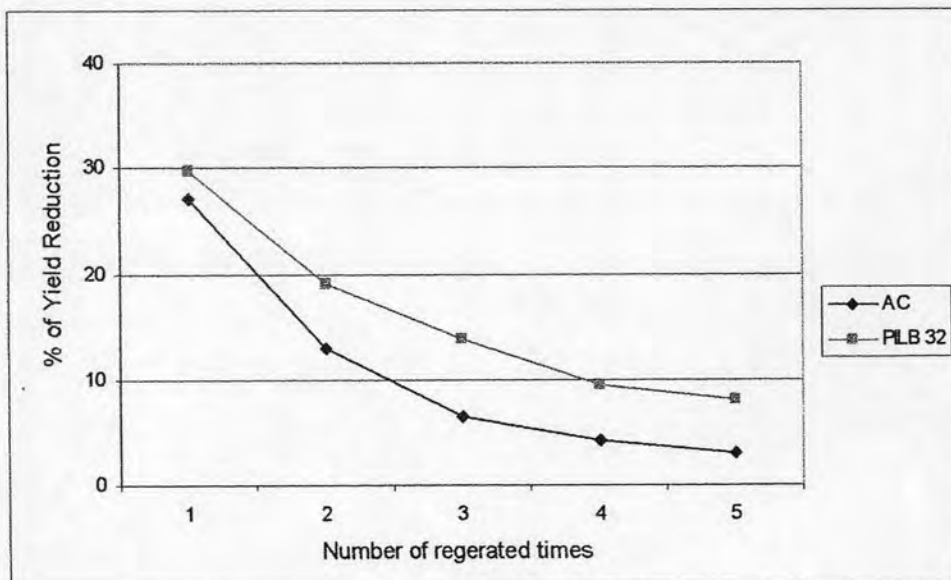


Figure 4.17 Effect of thermal testing at 800 °C for 30 minutes on % yield reduction

In the same practice as surface area, activated carbon tended to decrease with higher rate than PILB 32 as shown in Figure 4.18.

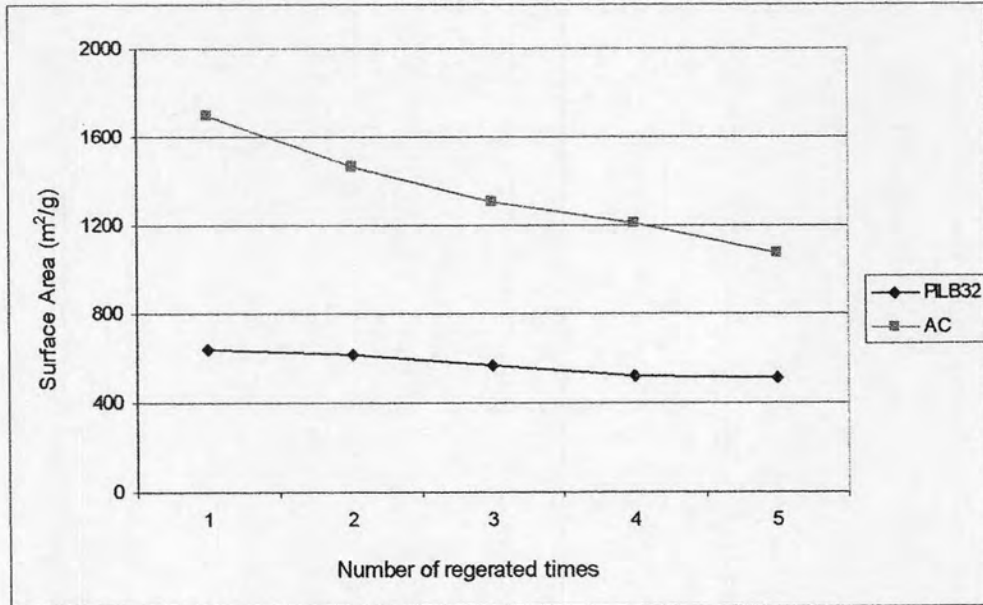


Figure 4.18 Effect of thermal testing at 800 °C for 30 minutes on Langmuir surface area

From the both result of yield reduction surface area retaining, it may conclude that PILB 32 was superior to activated carbon due to specific structural characteristics of high thermal resistance at 800 °C.

4.7 Cost Estimation

Because Koh Kred's clay could not be enhanced their surface area by pillaring method, so the cost of manufacturing was conducted for calculating for modified bentonite from chemicals used for pillaring, water, and electricity. The following items were based on product 1 kg, so the total cost would be approximately cost 1,546 Baht/kg as shown in Table 4.6.

Table 4.6 Cost estimation

Items	Price per unit	Consumed quantity for 1 batch manufacturing (kg of product)	Expense (Baht)
Raw Bentonite	700 Baht/50 kgs	1 kg	14.00
Activated Carbon, F-300	200 Baht/kg	378 g	76.50
Portable water	5 Baht/m ³	60.25 Litre	3.01
DI water	5 Baht/m ³	602.5 litre	3.01
Tetraethylammonium Chloride	7,149 B/250 g	50.6 g	1,447.00
Electricity charge (furnace for dehydration)	5 Baht/Kw.hr	1.0 Kw X 0.50 hr	2.50
Total			1,546

Whereas commercial activated carbon, Filtrasorb-300 is 300 Baht/kg.

It may conclude that modified bentonite has been still high cost for manufacturing, when compared with commercial activated carbon. Nevertheless, it can be further development for higher surface area and also applied for other hazardous organic compounds adsorption in future.