CHAPTER III

METHODOLOGY

This research is a kind of experimental research and conducted at Department of Mine Engineering, Faculty of Engineering, Department of Geology and Marine Science, Faculty of Science, Chulalongkorn University, Thai Parkerizing Company Limited and National Metal and Materials Technology Center.

3.1 Procedure

1) Material and equipment preparation

2) Identify physical and chemical properties of clay

3) Modification of clay by various treatment temperatures

4) Identify clay characteristics after thermal treatment

4) Adsorption testing preparation

5) Examination of adsorption

6) Comparison of efficiency between modified clay and activated carbon

7) Test the strength of modified clay and activated carbon

8) Test properties after regenerations

9) Estimate the cost for manufacturing of modified clay

3.2 Equipments and Chemicals

3.2.1 Equipments for raw materials preparation

1) Oven; Memmert

2) Furnace; Model No. BF 51866C-1 Lindberg/Blue M

3) Closed container for calcination

4) Desiccator; 5 litre

5) Sieve analysis; no. 8 – 325 mesh

6) Ball mill

7) Blender

8) Agitator; with 100 rpm

3.2.2 Equipments in laboratory testing

1) Digital balance;

2) pH meter;

3) Filter paper; Whatman No.5;

4) Glassware

3.2.3 Equipments for clay and activated carbon analysis

1) Scanning Electron Microscope (SEM);

2) BET; ASAP2000

3) X-ray fluorescence spectrometer (XRF); Model D/MAX 2000PC Rigaku

4) X-Ray Diffraction Spectrophotometer (XRD); Model Primus II: Rigaku

5) Sieve analysis machine

3.2.4 Equipments for adsorption testing

1) Test Chamber

2) Thermometer

3) Rota meter

4) Personal pump and charcoal tube

5) PID/VOC gas detector

6) Glass tube

7) Aluminium foil and parafilm

8) Manometer

3.2.5 Reagents

1) Clay from Koh Kred Traditional Village

2) Raw Bentonite; from Volclay Siam Company

3) Activated Carbon; Fitrasorb-300 with mesh size no. 8-30

4) Distilled water

5) Portable water

6) Tetraethylammonium chloride

7) Nitric acid

8) Sulfuric acid

9) Soluble starch

10) Thiosulfate solution ($Na_2S_2O_3.5H_2O$)

11) Iodine solution

12) Potassium iodate solution

13) Sodium carbonate

14) Potassium Iodide

15) Benzene compound

16) Toluene compound

17) Xylene compound

18) CS_2

3.3 Variables

This experiment has 3 types of variables such as fixed, independent, and dependent variables as follows;

3.3.1 Fixed variables

Fixed variables is determined and stable over the period of experiment

Table 3.1 Fixed variables and parameters

Fixed Variables	Data Control
1. Toluene concentration	20-30 ppm
2. Benzene concentration	20-30 ppm
3. Xylene concentration	20-30 ppm
4. Air face velocity	100 ft/min
5. Column diameter, internal diameter	75.0 mm
6. Column Length	20.0 mm
7. Grain size, diameter	8-30 mesh
8. Temperature for adsorption experiment	25 ^{o}C

3.3.2 Independent variables

Table 3.2 Independent variables and parameters

Independent Variables	Parameters
Raw materials	Pillared bentonite
	Activated carbon
Types of VOCs	Benzene
	Toluene
	Xylene
Dehydration temperatures for pillaring	Air room temperature
	300 ^{o}C
	400 ^{o}C
	500 ^{o}C
	600 ^{o}C
Aging times	1 day
	2 days

3.3.3 Dependent variables

1) Specific Surface Area, BET and Langmuir

2) Micropore area

3) Total pore volume

4) Average pore diameter

5) VOCs adsorption capacity

6) Cost of modified clay manufacturing

3.4 Methodology

3.4.1 Koh Kred's clay and raw bentonite characteristics

Natural clay was selected from the traditional pottery source, Koh Kred Traditional Village. After oven drying at 105 ^{o}C for 24 hours, the clay was ground by ball mill. Then, it was conducted for size distribution testing by sieve analysis machine by ranging sieve size number < 325 - >100.

After that, the clays, natural clay and raw bentonite, were prepared by sieving under 100 mesh and tested the characteristics as below.

1) Study on the type of crystal structure by X-Ray Diffraction Spectrophotometer; XRD Model Primus II: Rigaku

2) Study on the oxide component of clay by X-Ray Fluorescence; XRF Model D/MAX 2000PC Rigaku

3) Determine the particle size of clay by sieve analysis machine

4) Determine the specific surface area based on BET and Langmuir by ASAP 2000

5) Determine micropore area of both clays

5) Identify the total pore volume (V_T) by BET

6) Identify micropore Volume by BET

7) Examine Cation Exchange Capacity (CEC)

8) pH

3.4.2 Pillaring clay

1) The prepared clay was ground and dried at 105 ^{o}C for 3 hours. Then, ten grams of sample were suspended in deionized water (10% in weight) and stirred continuously for 16 hours. Afterwards, the contaminant was removed from clay samples.

2) Both Koh Kred's clay and bentonite were pillared with tetraethylammonium chloride, TEA, equivalent to 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00 times of CEC clay. The amount of TEA required to be equal to desired fraction of CEC was calculated by equation (1) and shown in Appendix D

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

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).

The pillaring agent solution, tetraethylammonium chloride (TEA), as calculated was added over clay suspension while stirred vigorously. The result suspension was kept at 80 ^{o}C for three hours and at room temperature for 16 hours.

3) The solid was recovered by vacuum filtration and then repeatedly washed with deionized water at 80 ^{o}C until the wash water conductivity was less than 20 μS/cm by detected with conductivity meter.

4) After the pillared clay was oven dried at 105 ^{o}C, it was ground and mixed with 15% water by weight and left for 30 minutes to swell water throughout the portion.

5) After kneading, the clay was granulated and then validated with sieve size number 8-30.

6) The granular pillared clay and bentonite was divided into 5 sample groups.
The first specimen was dehydrated under dried-air condition and the others were done in furnace with programmable temperature controller at 30 ^{o}C/min up to finalize at 300^{o}C, 400^{o}C, 500 ^{o}C, and 600 ^{o}C respectively and then kept for two hours.

7) After dehydration, the pillared clay and bentonite were investigated the specific surface area.

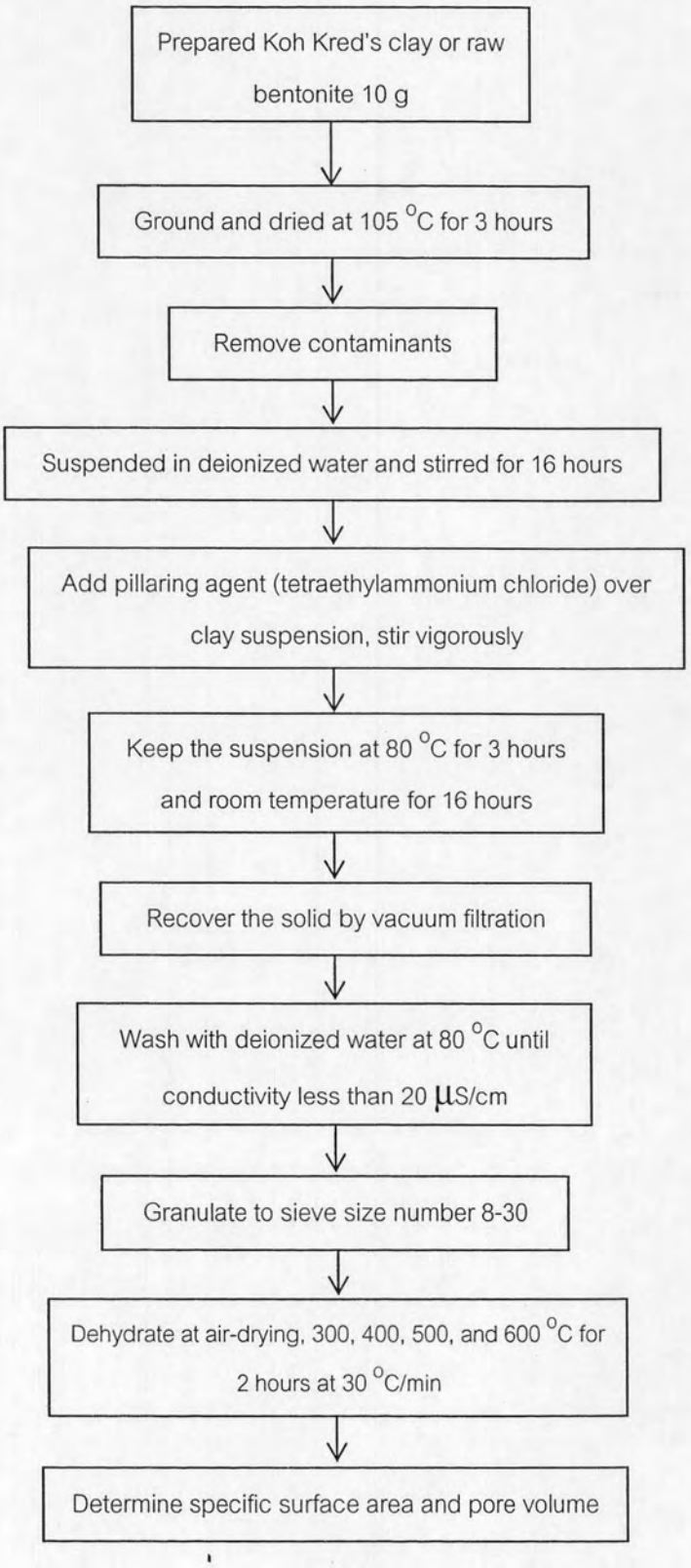


Figure 3.1 Flow diagram of pillaring clay

Figure 3.2 Pillared Koh Kred's clay pellet

Figure 3.3 Pillared bentonite pellet

3.4.3 Develop more porosity

1) To develop more porosity, the pillared benonite slurry was mixed with activated charcoal by following ratio;

Table 3.3 Composite ratio between pillared clay and activated carbon Filtrasorb-300

Bentonite:Activated Charcoal Filtrasorb-300
5:0
4:1
3:2

2) After mixing and kneading, the mixture was dehydrated with air-drying and under high temperature in furnace with programmable temperature controller at 30 ^{o}C/min up to 300 ^{o}C and then kept at 300 ^{o}C for two hours (for other thermal treatments, the final temperatures were 400, 500, and 600 ^{o}C).

3) Afterwards, sample was investigated the specific surface area and further identified BTX adsorption capacity.

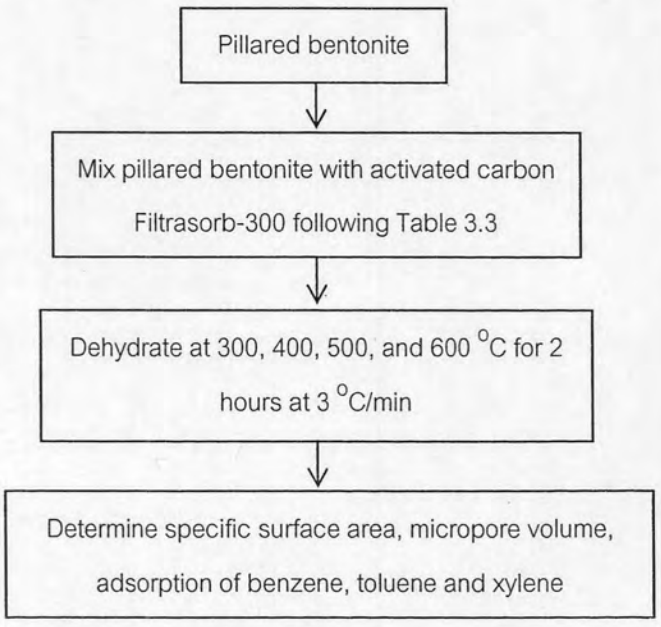
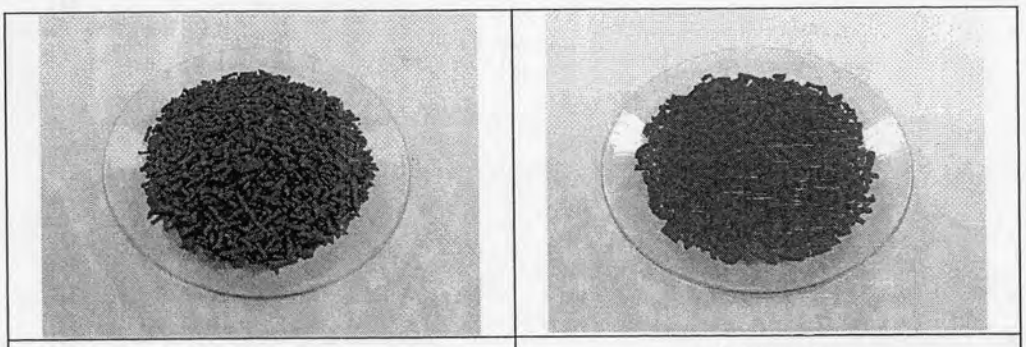


Figure 3.4 Flow diagram of pore development



a) 4:1 ratio | b) 3:2 ratio

Figure 3.5 Composite materials between pillared bentonite with powder activated carbon a) 4:1 ratio b) 3:2 ratio

3.4.4 Benzene, toluene and xylene adsorption experiments

1) Weigh the adsorbent sample 25-30 g and contain into testing bed with diameter 7.5 cm and 2 cm in depth.

2) Install the adsorption testing set by modeling from enclosure paint booth from workplace in painting factory as following Table 3.4

Table 3.4 Data control for adsorption experiment

Fixed Variables	Data Control
1. Toluene concentration	20-30 ppm
2. Benzene concentration	20-30 ppm
3. Xylene concentration	20-30 ppm
4. Air face velocity	100 ft/min [1)]
5. Opening area	9/144 ft^2
6. Column diameter, internal diameter	75.0 mm
7. Column Length	20.0 mm
8. Grain size, diameter	8-30 mesh
9. Contact time	0-50 minutes
10. Grain size, diameter	8-30 mesh
11. Temperature for adsorption experiment	25 ^{o}C

[1)] Source: Nimmon, 2005

3) Install testing model as shown in Figure 3.6

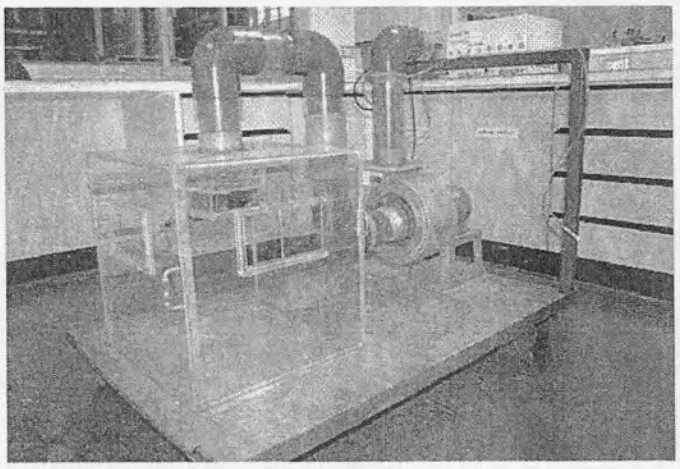


Figure 3.6 Model of adsorption determination

4) Set up VOC vapor in system

4.1) Prepare amount of benzene, toluene, and xylene separately with 25 ml per each in 50 ml beaker, and cover by aluminium foil to prevent vapor dispersion to atmosphere.

4.2) Provide nanometer, personal pump with charcoal tube, and VOC portable gas detector, rotameter.

4.3) Weigh control specimen to set up stable vapor and air flow rate in system approximately at 25-30 g and put on the testing chamber.

4.4) Switch on the air blower to pull air directly through testing duct and specimen. Then, control air face velocity at 100 f/m approximately and inspect pressure drop within the adsorption testing system.

4.5) Open aluminium foil of prepared sample as 4.4) in proper opening size, so that it practically releases VOC about 40 ppm.

4.6) Sampling VOC vapor with PID portable gas detector and verified with NIOSH method 1501 in result with acceptable range $\pm$ 5 ppm.

5) Start experiment of adsorption

5.1) Replace the control specimen with the testing sample such as PILB 32 or activated carbon to adsorb benzene, toluene and xylene separately.

5.2) Start adsorption of each adsorbent and adsorbate so that the adsorption approach the breakthrough time.

5.3) Record the breakthrough time of each samples and conduct for capacity calculation

5.4) Vent the exhaust gas to outside by purging about 5 minutes prior to next experiment.

6) Calculate adsorption capacity of sample by following equation (2)

$$\text{Adsorption Capacity} = \frac{\text{MW X ppm of adsorbate X Qair X breakthrough time}}{\text{24.45 X mass of adsorbent}} \quad \text{.....(2)}$$

Where

ppm of adsorbate = concentration of VOC detected by PID gas detector (ppm) Under $25^{\circ}C$ temperature at 1 atmosphere

MW = molecularweight of VOCs (mass/mol)

Qair = Volume of air contaminated with benzene or toluene or xylene pass through testing specimen (cfm), or = face velocity X opening area (cfm)

mass of adsorbent = mass of modified clay or bentonite and activated carbon(g)

Adsorption Capacity = mg of adsorbate adsorbed on adsorbent (mg/g)

7) Duplicate the experiments for each sample as above items

3.4.5 Test the strength of adsorbent 3 times and test BET

This experiment is to investigate existing properties of modified Koh Kred's clay and modified bentonite from remain surface area after baking 3 times. The conditions for testing are various temperatures at 80, 90 and 100 ^{o}C with various times for 30, 45, and 60 minute. After that, all samples were investigated the surfaced area, micropore area, pore volumn, and average micropore by ASAP 2000. The result will be raised as the trend of surface area and yield reduction.

3.4.6 Test properties after regenerations

This test is to determine properties of both materials by identifying the retaining of surface areas, BTX adsorption capacity and yield reduction after 5th regeneration times by following the experiment as 3.4.4. Afterwards, comparison of their characteristics was further conducted.

3.4.7 Estimate cost of modified Koh Kred's clay and modified bentonite manufacturing

Cost of pillaring and modified bentonite/clay was calculated from raw bentonite and clay, chemical for pillaring, energy consumption, and water. The comparison of cost for manufacturing between modified bentonite/clay and commercial activated carbon is estimated to determine possibility for large scale field application.