CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Clay Minerals

Bentonite (BTN) was supplied by Thai Nippon Chemical Industry Co., Ltd.The cation exchange capacity (CEC) ofBTN was55 mmol/100g of clay.

3.1.2 Surfactants

Cetyltrimethylammonium [$C_{16}H_{33}N^{+}(CH_3)_3$] bromide was supplied by Fluka.Dodecylamine, $C_{12}H_{27}N$. (98% purified, MW=185.35)was supplied by Aldrich.

3.1.3 Silica Sources

Tetraehtyl orthosilicate (TEOS), $Si(OC_2H_5)_3$, (MW=208.33)was supplied by Fluka.

3.1.4 Solvents

Methanol (CH_3OH) was supplied by Lab Scan and Hydrochoric acid (HCl) was supplied by Carlo Erba.

3.1.5 Chemicals

Acetic acid gracial (CH_3COOH)were supplied by Carlo Erba.Sodium Hydroxide(NaOH), Ammonium acetate (CH_3COONH_4), Barium chloride ($BaCl_2.2H_2O$) and Potassium sulfate (K_2SO_4)were supplied by Ajax Fine Chem. Potassium phosphate (0-52-34) and urea (46-0-0)were supplied by Viking,and activated carbon was supplied by Fluka.

3.1.6 LiquidSulphur

Liquid sulphurwas supplied byThaioilPlublicCo., Ltd.

3.2 Equipment

3.2.1 X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the d-value of organoclay, PCHsand to investigate the crystal structure of clays. X-ray diffraction patterns were measured on a X-ray diffraction patterns were measured on a Bruker AXS model D8 Discover diffractometer with Ni-filtered Cu K_α radiation operated at 40 kV and 40 mA. The powder samples were observed on the 2θ range of 1-10 degree witha scan speed of 0.5 sec/step and aincrement 0.02 degree/step.

3.2.2 Surface area Analyzer (SAA)

N_2 adsorption-desorption isotherms were obtained at -196°C on a QuantachomeAutosorb-1.Samples were degassed at 150°Cduring12 h in a vacuum furnace prior to analysis. Surface area were calculated using the BET equation. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the nitrogen wasotherm.

3.2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of organoclays, PCHsand Magnetic PCHswere obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000–400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1}. KBr pellet technique was applied in the preparation of powder samples. The incorporation of organic group into silicate network was investigated by using FTIR.

3.2.4 Thermogravimetric Analysis (TGA)

TG-DTA curves were collected on a Perkin-Elmer Pyris Diamond TG/DTA instrument. The clay sample was loaded on the platinum pan and heated from 30°C to 900°C at a heating rate of 10°C/min under N_2 flow of 100 mL/min. For nanocomposites, the sample were heated from 30°C to 500°C at a heating rate of 10°C/min under N_2 flow of 100 mL/min.

3.2.5 Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on Hitachi S-4800 model to observe surface morphology of PCH. The specimens were coated with platinum under vacuumbefore observationto make them electrically conductive.

3.2.6 CHNS Analyzer

CHNS Analyzer was recorded on TruSpec® sulphur Modulefor determination of sulphur content in material. This instrument operated at 1,350 °C, the high heat resistant crucible was required.

3.2.7 UV/Vis Spectrophotometer

UV/VIS Spectrophotometer was recorded on a UV/visspectro-photometer UV-1800 (Shimadzu) scanning in photometric mode at a wavelength of 420 nm at room temperature. Experiments were performed in a liquid cuvette.

3.3 Methodology

3.3.1 Purification and pH Adjustment of Bentonite

Bentonitewas pulverized and sieved though 325 mesh. The 100-g of the passing part wastreated with 1000 ml of 0.5 M-HCl solution at room temperature for 24 h. After that, the solid part was separated by centrifugation and then washed with distilled water until the pH value near 7. The samples was dried in oven overnight and again pulverized in a mortar.

3.3.2 Synthesisof Organoclay

Each purified-bentonite was converted into a quaternary ammonium exchange form by ion exchange withcetyltrimethylammonium bromide. In first container, 100 g of Na-bentonite was swollen in 2 L of water for 24 h, and in second container prepare 0.1 M of CTAB for 2000 ml. The solution was heated at 50°C until it became transparent. Then solutions of two containers were mixed for 24 h at 50°C 400 rpm. The organomodifiedbentonite was filtered and washed with mixture of

methanol and water (1:1 v/v) several times. It was dried in a vacuum oven at 80°C until it dried.

3.3.3Synthesis of Porous Clay Heterostructure (PCH)

The obtaining organoclay was stirred in dodecylamine for 30 min at 50°C following which TEOS was added (at molar ratio of organoclay:dodecyl-amine:TEOS was 1:20:50). The resulting suspension was stirred for further 4 h at room temperature. After the reaction time the solid was separated from solution again by filtration and dried at 80°C until dried. The surfactant was removed from the as-synthesized PCH by calcinations. The as-synthesized PCH was calcined at 600°C for 6 h using a temperature ramp rate of 10°C/min.

3.3.4 Preparation ofSulphur bentonite Fertilizers

Thee formulas of sulphur bentonite were synthesized; (1) bentonite+sulphur (BS°), (2) organoclay+sulphur (OS°), (3) PCH+sulphur (PCHS°). Each formula was divided into 3 compositions of clay: 10, 20, 30, % of clay (w/w). A process to produced pills of clays and sulphur mixture was mixed by mixing stirrer in a mixing chamber at 140°C for 2 h. Then forming droplets of the mixtureimmediately, the droplets of mixture was dipped on stainless steel plate to obtained sulphur bentonite fertilizer.

3.3.5 Determination of Sulphur Content in Sulphur bentonite Fertilizer

The sulphur content was determined by loss on ignition. Sulphur bentonite fertilizer was weight approximately 200 mg on the known weight crucible. The sample was placed into TruSpec® sulphur module furnace at 1350 °C. After 5 minutes, sulphur was completely burn up. After that the crucible was removed from the oven and then the crucible was cooled at room temperature for 10 minutes or until the temperature of crucible was equal to the room temperature. The sample in the crucible was reweighted again. The lost weight was the weight of sulphur.

3.3.6 Dispersion of Sulphur bentonitePrill in Water

Small colander of approximately 10 cm diameter and 7 cm height were made from stainless steel mesh of about 1 mm aperture. For prills of each sulphur/bentonite ratio dispersion tests were carried out simultaneously in 12 colanders (3 replicates, 4 time intervals). One gram of prills was weighed into each oven dried colander and the cells were placed in a tray of water at 25°C at 2 minutesintervals. After time interval 1, the first colander was removed and the material carefully and quickly washed with 100 ml of water to flush from the colander those particles dispersed to dimensions less than 1 mm. The other two replicates for the time interval were similarly removed and rinsed at 2 minutes intervals. After washing, the cells and the retained particles were oven-dried for 5h at 85°C and reweighed. The time intervals chosen ranged widely from 2 minutes up to 35 minutes depending on the bentonite content; but for each mixture the four times used covered a wide dispersal range

3.3.7 Purification and pH Adjustment of Soil

Sandy-soil was sieved pass 1 mm sieves, after that it was washed with distilled water many times until soil pH approximately 6.5 by neutralizing soil using 0.1 N HCl or 0.1 N NaOH. The soil was determined sulphur content in soil by using TruSpec® sulphur Module before and after washed with distilled water. Treated soil was dried in air for 5 days or until it completely dried.

3.3.8 Oxidation of Sulphur Fertilizers

The equivalent of 2.5 kg air-dried soil was weighed and placed in a 3-litre black plastic bag with drainage holes. There were 8 treatments of sulphur fertilizer: (1) control (no sulphur), (2) elemental sulphur, (3-5) sulphur bentonite 10, 20, 30 wt% of bentonite content, respectively, (6-8) sulphur-PCH 7, 10, 12wt% of PCH content, respectively.The quantities of sulphur fertilizer were weighed base on 500 mg of sulphur content. Each sulphur fertilizer was put on the surface of soil, and each pot was watered 250 ml per day until day 45. 20 grams of soil sample was collected by digging down 2 inches deep, after that soil samples were oven-dried at 60°C for 24 h.The water soluble sulfate in soil was determined by the extraction of

sulfate from soil. After that the extracted sulfate solution was determined the concentration of sulfate by using UV/Vis spectroscopy technique.

3.3.9 Soybean Plantation

The equivalent of 2.5 kg air-dried soil was weighed and placed in a 3-litre black plastic bag with drainage holes.There were 9 treatments of sulphur fertilizers: (1) control (non nutrient), (2) NPK fertilizer only, (3) NPK plus Ammonium sulfate, (4–6) NPK plus sulphur bentonite 10, 20, 30 wt% of bentonite content, respectively, (7–9) NPK plus sulphur-PCH 7, 10, 12wt% of PCH content, respectively. Each treatment was planted 3 pods per treatment. The quantities of sulphur fertilizer were weighed base on 200 mg of sulphurcontent, the sulphur fertilizer was put on the soil surface. Each pot excepted control treatment (non nutrient) received a NPK fertilizer dressing of 240 mg potassium phosphate (KH_2PO_4) and 162 mg of urea ($(NH_2)_2CO$).Each pod, 3 seeds of soybean were buried under soil surface depth 1 cm. Pots were arranged orderly on benches in a mosquito net with controlled environmental conditions. The pots were watered with water to the soil surface to allow the fertilizers to percolate though the soil. Height, amount of leaves and seeds data were collected every 10 days. The plants were harvested at maturity (60 days after planting) by removing sand and washing with deionised water until roots completely clean. Soybeans (shoot and root) were separated into leaves, stem, root, and seeds. All soybean parts were oven dried at 80°C for 72 h to remove moisture, after that each dried part were weighed and collected dry weight data.

3.3.10Sulphur Uptake of Soybean

Each part of soybean including of leaves, root, stem, and seeds were oven dried. After that analyzed samples were cut, pulverized and, ground to pass a No. 100 (150 micron) sieve, respectively. The prepared samples were determined sulphur content by using TruSpec® sulphur Module. The sulphur uptake of each part calculated by the product sulphur content of each part and dried weight.