CHAPTER 3

EXPERIMENTAL

3.1 Materials, chemicals and instruments

3.1.1 Materials and chemicals

1) Bottom ash, Mae Moh Power Plant, Lampang, Thailand

2) FGD gypsum, Mae Moh Power Plant, Lampang, Thailand

3) Paddy soil, Paradon company, Thailand

4) Sawdust, Sangwanitwattana company, Thailand

5) Ammonium acetate (CH_3COONH_4), AR, Ajex, Australia

6) Ammonium metavanadate (NH_4VO_3), AR, Carlo Erba. Italy

7) Ammonium molybdate tetrahydrate ($(NH_4)_6MO_7O_{24}.4H_2O$), AR, Carlo Erba. Italy

8) Cadmium nitrate ($Cd(NO_3)_2$), AAS standard, Ajax, Australia

9) Hydrochloric acid (HCl), AR, BDH, England

10) Nitric acid (HNO_3), AR, Carlo Erba. Italy

11) Nickel (II) nitrate ($(Ni(NO_3)_2$, AAS standard, Ajax, Australia

12) Phenol (C_6H_5OH), AR, BDH, England

13) Potassium chloride (KCl), AR, Carlo Erba. Italy

14) Potassium dihydrogenphosphate (KH_2PO_4), AR, Fluka, Switzerland

15) Potassium hydrogen phthalate (KHP), AR, Fisher, England

16) Potassium nitrate (KNO_3), AR, Merck, Germany

17) Sodium chloride (NaCl), AR, APS Finechem, Australia

18) Sodium hydroxide (NaOH), AR, BDH, England

19) Sulfuric acid (H_2SO_4), AR, BDH, England
20) Hydroball (HDB) commercial planting material, purchased at Jatujak Market, Bangkok

3.1.2 Apparatus and instruments

1) Flame atomic absorption spectrophotometer, series AA-275, Varian Company, Australia
2) Flame photometer, model PFP7, Jenway Company, England
3) Hammer mill, model serie 5657, Haan of Retch Company, Germany
4) Oven, model UNE 400, Memmert Company, Germany
5) Particle size analyzer, Mastersizer, Melvern Instrument Ltd
6) pH meter, model pH Scan wp 3+, Eutech Instruments Pte Ltd, Singapore
7) Quantachrome autosorb automated gas sorption system, Mastersizer, Melvern Instrument Ltd
8) Scanning electron microscope, JSM 6335F
9) Shaker, model VRN 480, Gemmy Industrial Company, Taiwan
10) Sieving machine (8-325 mesh), series AS200, Retch Company, Germany
11) UV-VIS spectrophotometer, Genesys^{TM}5, Spectronic Instrument, USA
12) X-ray diffractometer, BrukerD8Advance Diffractometer
13) X-ray fluorescence spectrometry, Phillips MagiX PRO PW 2400 Sequential

3.2 Preparation of raw materials and solution

3.2.1 Preparation of raw materials

As starting materials, BA and FGD gypsum were provided by Mae Moh coal fired power station in Lampang, Thailand. The PS was delivered by Paradon Company, Thailand, and SD was collected from Sangwanitwattana Company, Thailand. Each material (BA, FGD gypsum, PS and SD) was dried sequentially at 110 ^{o}C for 12 hours, 40 ^{o}C for 1 hour, 110 ^{o}C for 12 hours and 40 ^{o}C for 12 hours, in order to reach constant weight. Then the materials were crushed and sieved to different sizes (BA 100 mesh, FGD gypsum 100 mesh, PS 80 mesh and SD 80 mesh) by hammer mill and sieving machine, respectively.

3.2.2 Preparation of solutions

1) Acidified sodium chloride (NaCl) 10% w/w

100 g of ammonia-free sodium chloride were dissolved in 1 L of 0.005 N hydrochloric acid.

2) 100, 3.0, 2.0, 1.5, 1.0, 0.5 and 0.2 mg/L cadmium ion solutions

A 100-mg/L-Cd-solution was prepared by diluting 10 mL of a 1000-mg/L-Cd AAS standard in deionized water to 100 mL in a volumetric flask. From this 100 mg/L solution, 3.0, 2.0, 1.5, 1.0, 0.5 and 0.2 mL were measured into six volumetric flasks and diluted to 100 mL to give 3.0, 2.0, 1.5, 1.0, 0.5 and 0.2 mg Cd/L, respectively.

3) Neutral normal ammonium acetate (CH_3COONH_4)

70 mL of ammonium hydroxide (sp. gr. 0.90) and 58 mL of acetic acid (99.5 %) were mixed. After cooling, the pH was adjusted to 7.0 and the mixture was diluted to 1 L with deionized water

4) 100, 3.0, 2.0, 1.5, 1.0, 0.5 and 0.2 mg/L nickel ion solutions

A 100-mg/L-Ni-solution was prepared by diluting 10 mL of a 1000-mg/L-Ni AAS standard in deionized water to 100 mL in a volumetric flask. Then 3.0, 2.0, 1.5, 1.0, 0.5 and 0.2 mL of this solution were transferred into six volumetric flasks and diluted to 100 mL to give 3.0, 2.0, 1.5, 1.0, 0.5 and 0.2 mg Ni/L, respectively.

5) 1% v/v nitric acid

1% HNO_3 was prepared by adding 11 mL of conc.HNO_3 to deionized water and diluted to 1000 mL in a volumetric flask.

6) pH 2.0

100 mL of pH 2 solution was prepared by mixing 25 mL 0.2 M KCl with 6.5 mL of 0.2 M HCl in a volumetric flask and diluted to 100 mL with deionized water.

7) pH buffer 5.0

100 mL buffer was prepared by mixing 50 mL 0.1 M KHP with 22.6 mL of 0.1 M NaOH in a volumetric flask and the volume was adjusted to 100 mL with deionized water.

8) pH buffer 6.5

100 mL buffer was prepared by mixing 50 mL 0.1 M KH_2PO_4 with 14.0 mL of 0.1 M NaOH in a volumetric flask and the volume was adjusted to 100 mL with deionized water.

9) Phenoldisulfonic acid reagent

25 g of pure white phenol was dissolved in 150 mL of concentrated sulfuric acid (H_2SO_4). 75 mL of fuming sulfuric acid (13 to 15% sulfur trioxide (SO_3)) was added, mixed thoroughly, and heated in a boiling bath for 2 hours. It was stored in a glass-stoppered brown bottle.

10) 1000, 500, 400, 300, 200, 100 and 50 mg/L potassium ion solutions

One liter of a 1000 mg/L solution of potassium ion was prepared by dissolving 1.9069 g of potassium chloride in deionized water and diluted to 1 L in a volumetric flask. 500, 400, 300, 200, 100 and 50 mL of this solution were transferred into six volumetric flasks and diluted to 1 L to get potassium ion concentrations of 500, 400, 300, 200, 100 and 50 mg/L.

11) 1000, 500, 400, 300, 200, 100 and 50 mg/L dihydrogenphosphate ion solutions

One liter of a 1000 mg/L solution of dihydrogenphosphate ion was prepared by dissolving 1.4173 g of potassium dihydrogenphosphate in deionized water and diluted to 1 L in a volumetric flask. 500, 400, 300, 200, 100 and 50 mL of this solution were transferred into six volumetric flasks and diluted to 1 L to get dihydrogenphosphate ion concentrations of 500, 400, 300, 200, 100 and 50 mg/L.

12) 1000, 500, 400, 300, 200, 100 and 50 mg/L nitrate ion solutions

One liter of a 1000 mg/L solution of nitrate ion was prepared by dissolving 1.6306 g of potassium nitrate in deionized water and diluted to 1 L in a volumetric flask. 500, 400, 300, 200, 100 and 50 mL of this solution were measured into six volumetric flasks and diluted to 1 L to get nitrate ion concentrations of 500, 400, 300, 200, 100 and 50 mg/L.

13) 5 N sulfuric acid

5 N H_2SO_4 was prepared by adding 85 mL of conc. H_2SO_4 in deionized water and diluted to 500 mL in a volumetric flask.

14) Vanadate-molybdate reagent

Solution A: 25 g of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) was dissolved in 200 mL deionized water.

Solution B: 1.25 g of ammonium metavanadate (NH_4VO_3) was dissolved in 150 mL deionized water, and 330 mL of 70% conc. hydrochloric acid (HCl) was added.

Solutions A and B were mixed and gradually the molybdate solution was added gradually under stirring to the vanadate solution at room temperature, under stirring, and diluted to 1 L with deionized water.

3.3 Determination of the chemical and mineral composition of BA, FGD gypsum and PS

3.3.1 Chemical composition determination

The starting materials (BA, FGD gypsum and PS) were sieved through a 325 μm sieve and analyzed for their chemical composition. The chemical compositions were obtained by X-ray fluorescence spectrometry (XRF). Material compositions were analyzed on a Phillips MagiX PRO PW 2400 Sequential X-ray Spectrometer (wavelength dispersive spectrometer) using Rhodium (Rh) tube.

3.3.2 Mineral composition determination

The mineralogical compositions of the three starting materials were obtained by XRD patterns from randomly oriented powder mounts using Cu Kα radiation. X-ray XRD was performed on powder samples using a BrukerD8 Advance diffractometer equipped with a copper anode at the Department of Geological Sciences, Faculty of Science, Chiang Mai University. Diffraction patterns were recorded from 2 to 80^o 2θ with a step interval of 0.04^o 2θ and counting time of 1 s per step.

3.4 Fired planting material production

The three raw materials (BA, FGD gypsum and PS) were mixed in different proportions to produce mixtures whose compositions correspond to the numbered circles of the ternary diagram (Fig. 3.1). These samples were combined with different percentages of SD (sieved at 80 mesh). From each mixture a wet powder was produced by adding 10% of distilled water. The wet powders were compressed into metallic moulds to form granules (diameter 0.8 mm and height 1 mm). These granules were fired in a half cubic meter furnace, using liquid petroleum gas (LPG) as a fuel. Initially, all samples were dried at 100 °C, then fired at various temperatures (600, 700, 800, 850, 900 and 1000 °C) with a heating rate of 3 °C/minute.

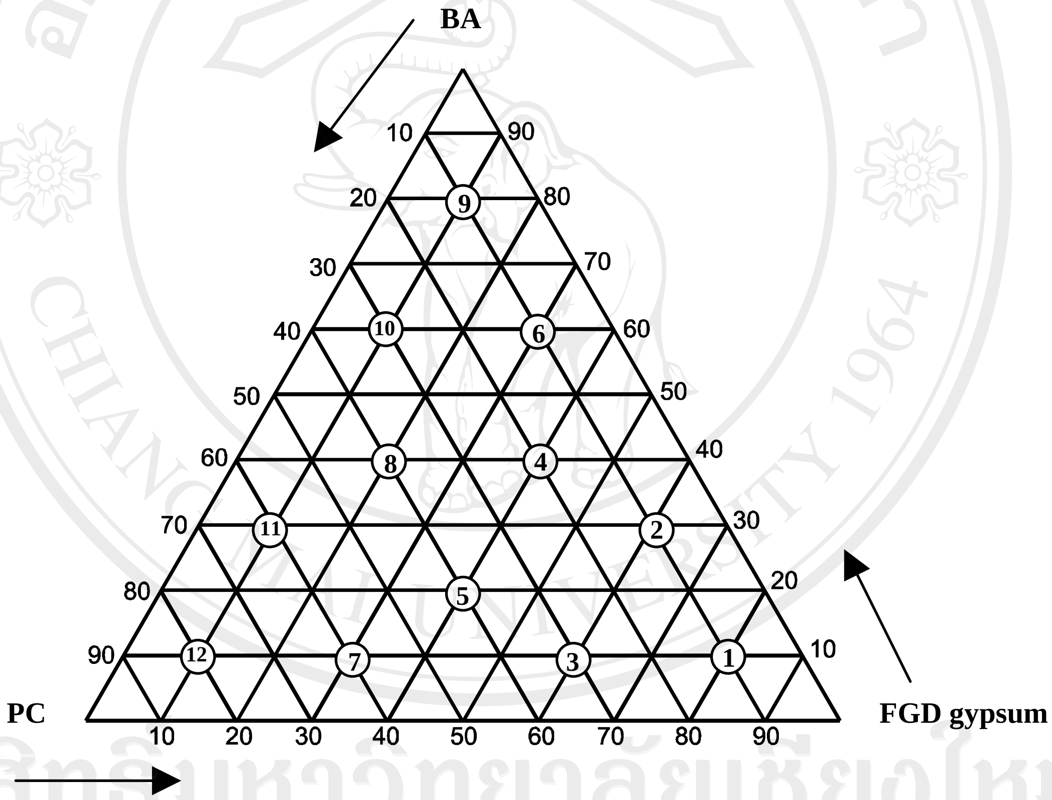

Figure 3.1 Three-dimensional diagram for generate the formulas of planting materials.

3.5 Study of physical and chemical properties of FPM

3.5.1 Slake investigation [28]

FPM or HDB was soaked in a 50 mL beaker with 25 mL water covering the material. Afterwards the sample shape of the materials was investigated visually.

3.5.2 Water absorption determination [28]

1) The weighed dried planting material was put into a 50 mL beaker and 20 mL of water was added and allowed to stand for 24 hours.

2) The water was decanted and the beaker was placed in an oven at 105 ^{o}C for 24 hours. Afterwards the beaker was immediately placed into a desiccator. After cooling, the beaker was removed from the desiccator and weighed immediately.

3) The water absorption was calculated according to:

$$\text{Water absorption (WA)} = \{(m_2 - m_1) / m_1) \times 100 \ (\%)$$

where m_1 is the dry mass (g) and m_2 the soaked mass (g).

3.5.3 Density determination [28]

1) The dried planting material (FPM or HDB) was weighed.

2) 25 mL of water was added into a 50 mL cylinder and the weighed-dried planting material was added into cylinder for volume measurement.

3) The density was determined as the mass (weight) per unit volume of the solid material.

3.5.4 The pH determination [57]

The pH value was measured by a pH meter using the ratio of material to distilled water at 1:3.

1) 5 g of the sample was put into a beaker.

2) 15 mL of deionized water was added into the beaker.

3) The mixture in the beaker was stirred with a glass rod for 10 minutes.

4) The material was allowed to stand for 15 minutes.

5) The pH value was measured by pH meter.

3.5.5 Cation exchange capacity determination [57]

The Cation exchange capacity (CEC) was measured to evaluate the adsorption capacity by the ammonium acetate method.

1) Material with mesh size < 2 mm of the dried planting material (FPM or HDB) was used. 25 g was weighed into 500 mL erlenmeyer flask and 250 mL of a 1N ammonium acetate solution (pH 7.0) was added. This mixture was stirred and left overnight.

2) The clear supernatant liquid was filtered off using a Buchner filtration apparatus and a filter paper number 42 with suction flask and vacuum pump.

3) The suspended solid was washed while filtering on the filter pad using 50-mL-portions of 99% isopropyl alcohol until the washings were free from ammonium ions (washing may take ½ to 1 hour and involves up to 200 mL of alcohol).

4) When the washings were free from ammonium, the sample solid was sucked dry on the filter and then the filtered flask was emptied and cleaned for step 5) (discard the filtrate).

5) The suspended solid was filtered with 225 mL of 10% acidified sodium chloride solution (in 5 to 6 portions), the filtrate was collected in a clean 500 mL flask.

6) 60 mL of the filtrate in step 5) was transferred into a 800 mL microkjeldahl flask and 25 mL of 1 N solution of sodium hydroxide was added. The mixture was distilled into about 50 mL of 2% boric acid indicator (bromcresol green) solution until the color changed from apple green to blue.

7) Finally, the boric acid solution containing the distilled ammonia, now as ammonium borate, was titrated with standard sulfuric acid solution to the end point of bromocresol green (blue to apple green).

8) The milliequivalent value of ammonium ion in a 100 g sample was calculated by the formula:

CEC (meq/100g) = {volume of acid used (mL) x (normality of acid used) x 100} / weight of sample used (g)

3.5.6 Moisture content determination [57]

1) The dried planting material (FPM or HDB) on an aluminum dish was weighed.

2) The aluminum dish was put into an oven at 105 °C for 24 hours and placed immediately into a desiccator to cool and weighed again.

3) The moisture content was calculated by the formula:

moisture content (M.C.) = {[wt. of air-dry sample (g)] - [wt. of oven-dry sample (g)]}

3.5.7 The topology determination

After grounding, the materials (BA, FGD gypsum, PS, SD, FPM and HDB) were put on a copper plate. SEM was used to determine the topology of the materials.

3.5.8 Surface area determination

After passing through a 325 µm sieve, the raw materials were used for analysis of surface area. The specific surface area (m^2/g) was measured by a Quantachrome Autosorb automate with nitrogen gas (version 2.46).

3.6 Adsorption study of inorganic fertilizer (nitrogen, phosphorus and potassium) on planting materials

3.6.1 The effect of the contact time between planting materials and solutions [58-59]

1) The planting materials (FPM and HDB) with size 8-10 mesh were used to prepare for adsorption study.

2) 10 g of planting materials were put into flasks and 50 mL of 500 mg/L fertilizer was added.

3) After that, each flask was closed with parafilm and shaken at 150 rpm for different time intervals upto 24 hours.

4) The solution concentration at different time intervals (10, 20, 30, 40, 50, 60, 120, 180, 240, 360, 1440 minutes) was filtered and measured.

3.6.2 Effect of solid/solution ratio on the adsorption on both types of planting materials

1) 10 g of planting materials were put into flasks and 50 mL of fertilizer with different concentrations (50, 100, 200, 300, 400 and 500 mg/L) were added.

2) Each flask was shaken at 150 rpm at room temperature.

3) The remaining solutions at different concentrations (50, 100, 200, 300, 400 and 500 mg/L) were measured at equilibrium time.

4) The solid/solution ratio was changed from 1:5 to 1:10 and 1:15, by changing the amount of solutions from 50 mL to 100 and 150 mL.

3.6.3 Determination of nitrate ion by UV-VIS spectrometry [57]

3.6.3.1 Preparation of standard and sample solutions

1) 50 mL of each standard nitrate ion (0, 1, 2, 3, 4, 5 mg/L) and sample solutions was put in a 150 mL beaker and evaporated to dryness on a steam bath.

2) After cooling, 1 mL of phenoldisulfonic acid solution was added and mixed, using a glass stirring rod.

3) 25 mL of deionized water was added and mixed together.

4) 4 mL conc. ammonia diluted with 25 mL deionized water was added slowly with stirring, until the yellow nitrophenoldisulfonic acid color developed.

3.6.3.2 Measurement of nitrate ion concentration

A blank reagent was run through the entire procedure and wavelength at 430 nm was used for UV absorption.

3.6.4 Determination of dihydrogenphosphate ion by UV-VIS spectrometry [60]

3.6.4.1 Preparation of standard solutions

1) Standard stock solution of potassium dihydrogenphosphate containing 200 mg HPO_4^- per L was prepared.

2) Portions of 0, 0.2, 0.4, 0.6, 0.8, 1.0 mL of the stock potassium dihydrogenphosphate standard solution were transferred into a series of six calibrated 50 mL volumetric flasks.

3) 2 mL of vanadomolybdate solution and deionized water to dilute to the mark were added, mixed thoroughly, and let stand for 10 minutes for the color development. These solutions contained respectively 0.0, 0.8, 1.6, 2.4, 3.2 and 4.0 mg HPO_4^- /L.

3.6.4.2 Preparation of sample solutions

1) 20 mL of sample solutions were transferred into 50 mL volumetric flasks.

2) 2 mL of molybdovanadate reagent were added to all the solutions within a 5-minute period.

3) Deionized water was added to dilute to the mark, mixed thoroughly, and let stand for 10 minutes for color development.

3.6.4.3 Measurement of dihydrogenphosphate ion concentration

A blank reagent was run through the entire procedure and wavelength at 420 nm was used for UV absorption.

3.6.5 Measurement of potassium ion concentration by flame photometry [57]

1) For the study of the effect of the contact time between planting materials and solutions, 20 mL of the solution at each time interval was drawn and filtered through a Whatman filter paper number 6.

2) For the study of the effect of the solid/solution ratios, the solutions were filtered after equilibrium.

3) The potassium concentrations in the solutions were measured by FLM model PFP 7.

3.7 Determination of some heavy metals (cadmium and nickel) released from both types of planting materials at various pH (6.5, 5.0 and 2.0) by atomic absorption spectrophotometer [57, 61]

1) 1 g of planting material was put into a flask.

2) 100 mL buffer solution (pH 6.5, 5.0 or 2.0) was added.

3) The mixture was shaken at 150 rpm for 24 hours.

4) 50 mL of the solution was drawn and filtered through a Whatman filter paper number 6.

5) The filtrate was diluted with 1 % nitric acid.

6) The concentration of cadmium or nickel released from each FPM and HDB was measured by atomic absorption spectrophotometer (AAS).