

## CHAPTER 4

### RESULTS AND DISCUSSION

As mentioned in the previous chapter, the experimental studies in this work are divided into three parts. Firstly, the property of raw materials and planting materials was studied. Secondly, the adsorption behaviors of inorganic fertilizers ( $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{K}^+$ ) on two types of planting material (FPM and HDB) were evaluated, respectively. The factor affecting adsorption behavior of inorganic fertilizers on both planting materials such as solid/solution ratio was also studied. Finally, the release of some heavy metals from both types of planting materials at various pH was studied using atomic absorption spectrometry. The obtained results are reported and discussed as follows.

#### 4.1 Property of raw materials and planting materials

##### 4.1.1 The chemical and mineral compositions of raw materials

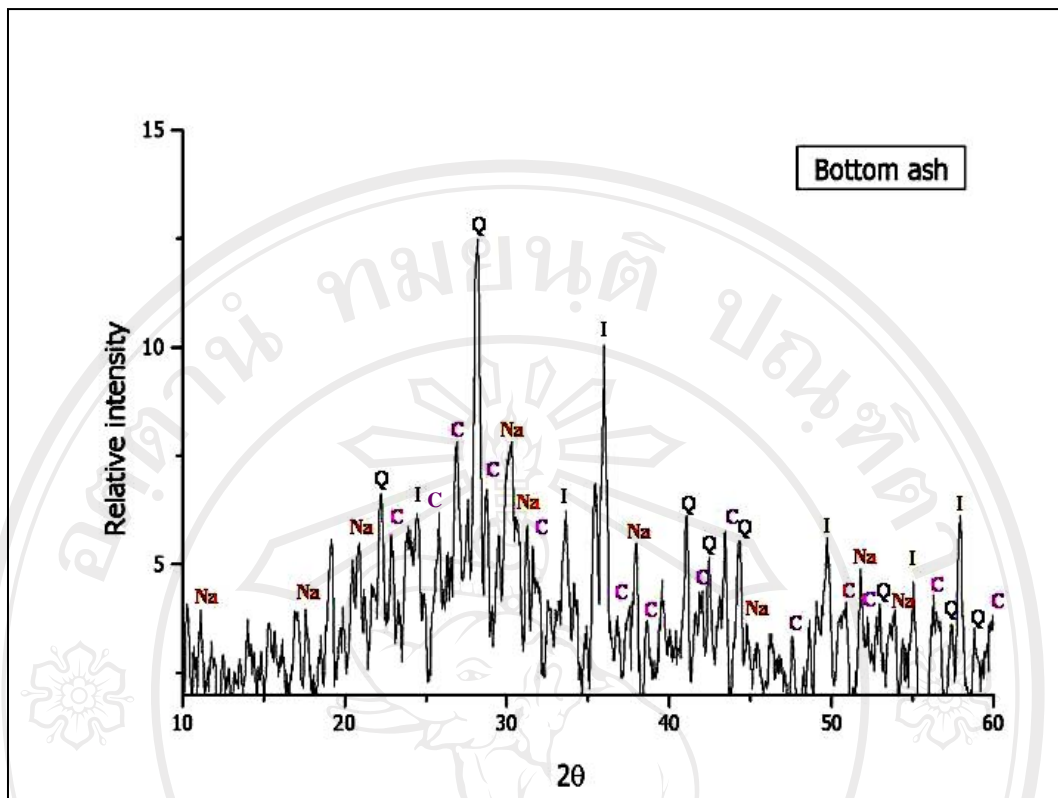
The chemical and mineralogical compositions of the starting materials (BA, FGD gypsum and PC) were measured using XRF and XRD as shown in Table 4.1 and Fig. 4.1, respectively. As shown in Table 4.1, the major chemical components of bottom ash are silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), calcium oxide ( $\text{CaO}$ ) and ferric oxide ( $\text{Fe}_2\text{O}_3$ ). These results correspond with the XRD findings. The mineral components of bottom ash are silicon oxide, sodium aluminum silicate, calcium magnesium carbonate and iron sulfate. FGD gypsum consists of two major components, which are  $\text{CaO}$  23.68 % and  $\text{SO}_3$  64.92 %. Therefore, this raw material consists nearly to 100% of calcium sulfate hydrate. The other raw material, paddy soil, has three major

chemical components, which are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . The XRF results (Table 4.1) were in agreement with the mineralogical compositions as determined by XRD (Fig. 4.1).

**Table 4.1** Chemical composition of solid wastes from Mae Moh power plant and Paradon company.

| Compound                    | Raw materials               |       |       |
|-----------------------------|-----------------------------|-------|-------|
|                             | BA                          | FGDG  | PC    |
|                             | <i>Macro-elements (wt%)</i> |       |       |
| $\text{SiO}_2$              | 37.82                       | 0.87  | 64.13 |
| $\text{Al}_2\text{O}_3$     | 30.83                       | 0.69  | 19.50 |
| $\text{CaO}^{**}$           | 9.44                        | 23.68 | 0.63  |
| $\text{Fe}_2\text{O}_3^*$   | 7.81                        | 0.16  | 6.10  |
| $\text{K}_2\text{O}^{**}$   | 2.07                        | nd    | 2.49  |
| $\text{MgO}^{**}$           | 1.23                        | 0.14  | 1.41  |
| $\text{P}_2\text{O}_5^{**}$ | -                           | -     | 0.09  |
| $\text{MnO}^*$              | 0.06                        | nd    | 0.13  |
| $\text{Na}_2\text{O}$       | 2.71                        | 0.22  | 0.10  |
| $\text{SO}_3^{**}$          | 2.03                        | 64.92 | -     |
| $\text{TiO}_2$              | 0.36                        | nd    | 1.07  |
| LOI.                        | 5.41                        | 9.26  | 4.21  |

BA = bottom ash, FGDG = Flue Gas Desulfurization gypsum, PC = paddy soil, LOI. = loss on ignition, nd = not detectable, - = not detected, \*\* = major nutrient of plant, \* = minor nutrient of plant



Q = quartz

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 4.0054 | 22.176  | 23        |
| 3.1768 | 28.066  | 100       |
| 2.1855 | 41.275  | 16        |

Na = sodium aluminum silicate

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 7.0800 | 12.492  | 86        |
| 4.1000 | 21.658  | 83        |
| 7.0800 | 12.492  | 86        |

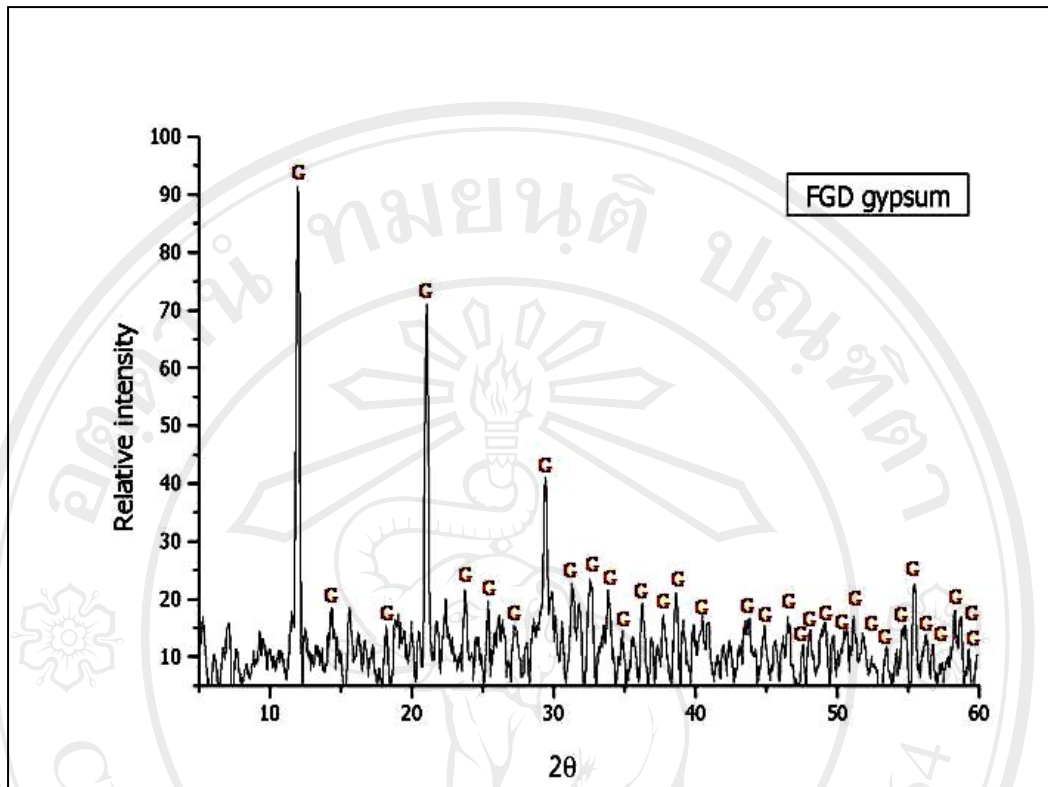
C = calcium sulfate

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 3.4000 | 25.502  | 100       |
| 3.4900 | 25.502  | 100       |
| 2.8446 | 31.423  | 35        |

I = iron sulfate

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 3.6716 | 24.221  | 44        |
| 2.6949 | 33.218  | 100       |
| 2.5077 | 35.778  | 78        |

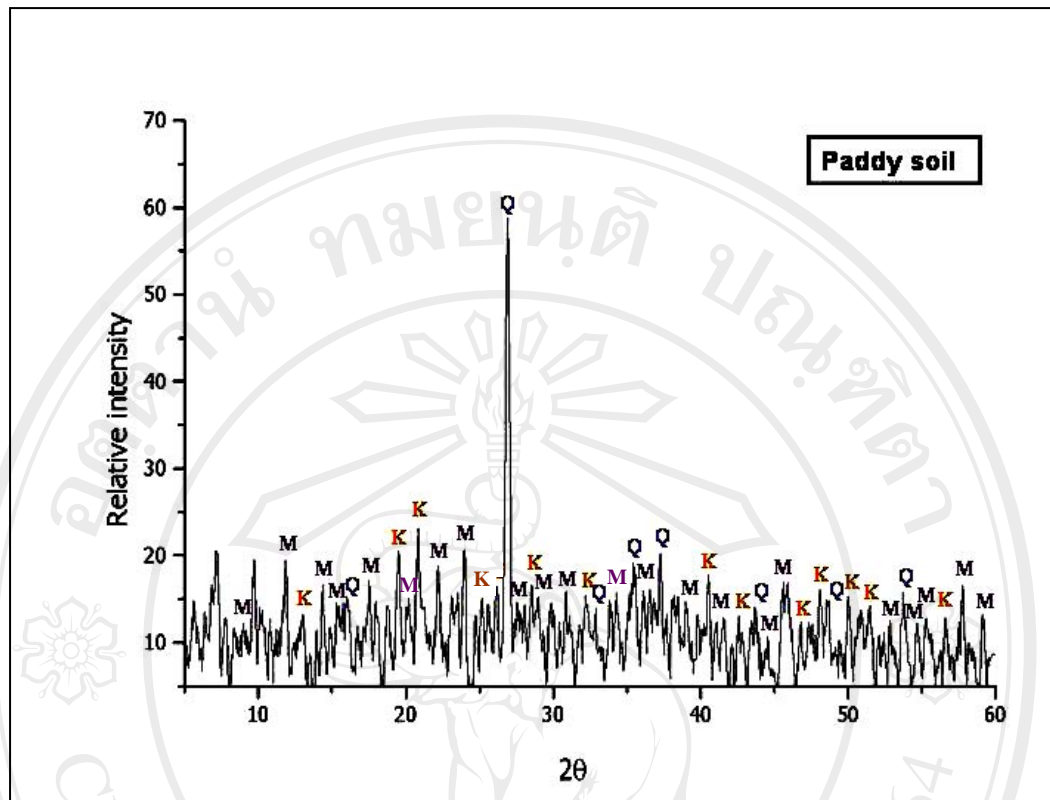
**Figure 4.1** X-ray diffraction of Bottom ash: Q = quartz, Na = sodium aluminum silicate, C = calcium sulfate, I = iron sulfate.



G = gypsum

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 7.5750 | 11.673  | 75        |
| 4.2709 | 20.782  | 100       |
| 3.0556 | 29.203  | 52        |

**Figure 4.2** X-ray diffraction of FGD gypsum: G = gypsum (calcium sulfate dihydrate).



Q = quartz

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 4.2277 | 20.996  | 17        |
| 3.3230 | 26.807  | 100       |
| 1.8069 | 50.467  | 12        |

K = kaolinite

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 4.6200 | 19.196  | 100       |
| 3.4900 | 25.502  | 80        |
| 3.1000 | 28.776  | 60        |

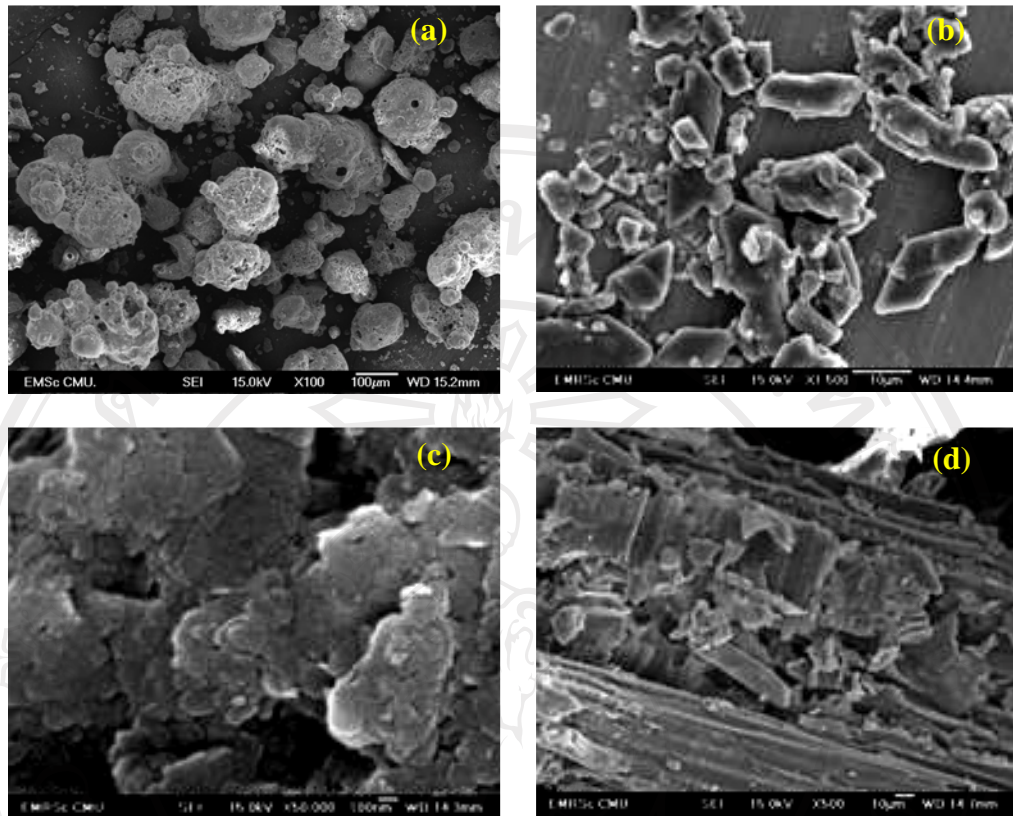
M = muscovite

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 4.4170 | 20.087  | 73        |
| 3.2166 | 27.711  | 59        |
| 2.5348 | 35.383  | 100       |

**Figure 4.3** X-ray diffraction of paddy soil: Q = quartz, K = kaolinite, M = muscovite.

#### 4.1.2 The topology of raw materials (bottom ash, FGD gypsum, paddy soil and sawdust)

According to Fig. 4.4a, the scanning electron microscopy (SEM) images show that the largest fraction of BA consisted of hollow spheres. At higher size ranges, porous sponge-like particles were detected. Therefore, it is suggested that bottom ash could be used as nutrient adsorbent. Gypsum in this study is mostly present as massive crystals (Fig. 4.4b). In the FGD process, lime or calcium oxide is injected into the scrubber at low temperature and low oxygen environment. Sulfur, derived from the coal burning process, is not oxidized to sulfate ( $\text{SO}_4^{2-}$ ) due to the limited amount of oxygen available. The sulfur is instead oxidized to sulfite ( $\text{SO}_3^{2-}$ ) and reacts with the lime to form the mineral of calcium sulfate dihydrate or gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The topology of PC shows more layers (Fig 4.4c). PC has high plasticity and CEC. Sawdust consists of long fibers and has highly irregular structure (see Fig. 4.4a-4.4d). Moreover, after firing, sawdust will be changed to ash leading to high porosity with long pores that allow water and fertilizer solutions pass through the material.

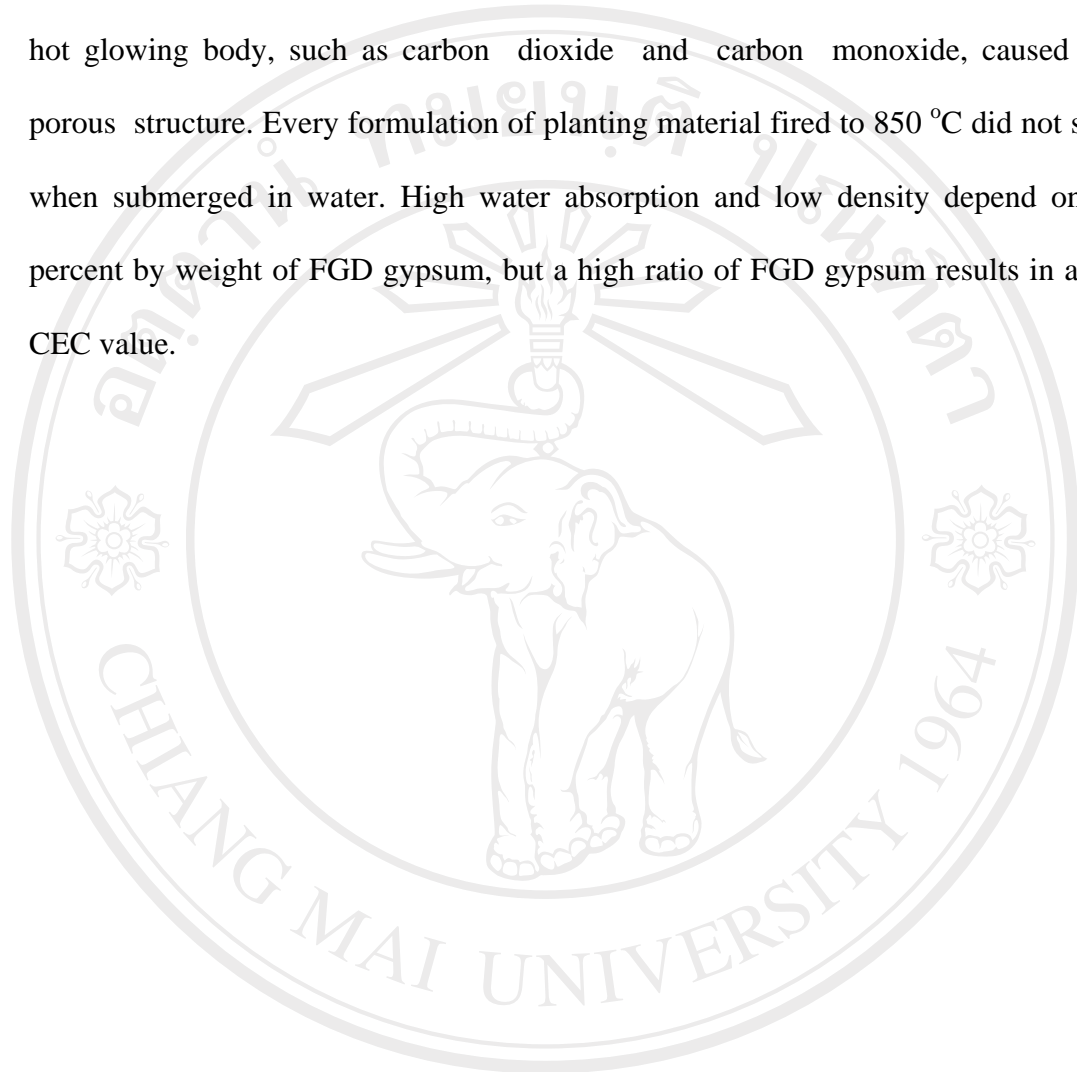


**Figure 4.4** Scanning electron microscopy (SEM) images of raw materials (a) bottom ash, (b) FGD gypsum, (c) paddy soil and (d) sawdust, respectively.

### 4.1.3 The physical and chemical properties of FPM

Table 4.2 shows the physical and chemical properties of bottom ash-FGD gypsum-paddy soil based mixtures with sawdust (materials were fired at 850 °C at a rate of 3°C/minute). Upon heating, the pore structure of planting material changes. When the FGD gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) was heated at temperatures of 150, 200 and 400 °C, it changed from gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) to hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ), to more spacious anhydrite III ( $\text{CaSO}_4$  III), to more spacious anhydrite II ( $\text{CaSO}_4$  II) and to anhydrite I ( $\text{CaSO}_4$  I), respectively [62]. For paddy soil, the following changes were observed: water loss at 100 °C, combustion of organic matters at 200 °C, a

change from  $\alpha$ -quartz to  $\beta$ -quartz at 575 °C and decomposition of sodium carbonate at 600-850 °C [63]. According to the changes above, the generated gases inside the hot glowing body, such as carbon dioxide and carbon monoxide, caused the porous structure. Every formulation of planting material fired to 850 °C did not slake when submerged in water. High water absorption and low density depend on the percent by weight of FGD gypsum, but a high ratio of FGD gypsum results in a low CEC value.



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**Table 4.2** Physical and chemical properties of bottom ash-FGD gypsum-paddy soil based mixtures with sawdust (materials were fired at 850 °C at a rate of 3 °C/minute).

| No. | Weight ratio<br>BA:FGDG:PC:SD | Properties |           |                                 |     |                   |
|-----|-------------------------------|------------|-----------|---------------------------------|-----|-------------------|
|     |                               | Slake      | WA<br>(%) | Density<br>(g/cm <sup>3</sup> ) | pH  | CEC<br>(meq/100g) |
| 1   | 10: 80: 10: 0                 | ns         | 50        | 2.0                             | 7.7 | 2                 |
| 2   | 30: 60: 10: 0                 | ns         | 46        | 2.1                             | 7.8 | 2                 |
| 3   | 10: 60: 30: 0                 | ns         | 40        | 2.3                             | 6.7 | 3                 |
| 4   | 40: 40: 20: 0                 | ns         | 41        | 2.1                             | 7.8 | 4                 |
| 5   | 20: 40: 40: 0                 | ns         | 41        | 2.5                             | 7.1 | 6                 |
| 6   | 60: 30: 10: 0                 | ns         | 40        | 2.3                             | 8.1 | 4                 |
| 7   | 10: 30: 6: 0                  | ns         | 36        | 2.5                             | 6.6 | 7                 |
| 8   | 40: 20: 40: 0                 | ns         | 37        | 2.2                             | 6.7 | 6                 |
| 9   | 80: 10: 10: 0                 | ns         | 31        | 2.2                             | 8.6 | 5                 |
| 10  | 60: 10: 30: 0                 | ns         | 31        | 2.3                             | 7.8 | 6                 |
| 11  | 30: 10: 60: 0                 | ns         | 28        | 2.8                             | 6.9 | 8                 |
| 12  | 10: 10: 80: 0                 | ns         | 28        | 2.8                             | 5.8 | 9                 |
| 13  | 9: 69: 9: 13                  | s          | x         | x                               | x   | x                 |
| 14  | 26: 52: 9: 13                 | s          | x         | x                               | x   | x                 |
| 15  | 9: 52: 26: 13                 | s          | x         | x                               | x   | x                 |
| 16  | 35: 35: 17: 13                | ns         | 45        | 2.1                             | 8.1 | 5                 |
| 17  | 17: 35: 35: 13                | ns         | 42        | 2.1                             | 7.5 | 6                 |
| 18  | 52: 26: 9: 13                 | s          | x         | x                               | x   | x                 |

| No. | Weight ratio<br>BA:FGDG:PC:SD | Properties |           |                                 |     |                   |
|-----|-------------------------------|------------|-----------|---------------------------------|-----|-------------------|
|     |                               | Slake      | WA<br>(%) | Density<br>(g/cm <sup>3</sup> ) | pH  | CEC<br>(meq/100g) |
| 19  | 9: 26: 52: 13                 | ns         | 40        | 2.1                             | 6.0 | 8                 |
| 20  | 35: 17: 35: 13                | ns         | 46        | 2.1                             | 6.6 | 7                 |
| 21  | 69: 9: 9: 13                  | ns         | 36        | 2.2                             | 8.6 | 5                 |
| 22  | 52: 9: 26: 13                 | ns         | 37        | 2.2                             | 8.4 | 7                 |
| 23  | 26: 9: 52: 13                 | ns         | 38        | 2.4                             | 6.0 | 9                 |
| 24  | 9: 9: 69: 13                  | ns         | 37        | 2.4                             | 5.9 | 10                |
| 25  | 8: 64: 8: 20                  | s          | x         | x                               | x   | x                 |
| 26  | 24: 48: 8: 20                 | s          | x         | x                               | x   | x                 |
| 27  | 8: 48: 24: 20                 | s          | x         | x                               | x   | x                 |
| 28  | 32: 32: 16: 20                | s          | x         | x                               | x   | x                 |
| 29  | 16: 32: 32: 20                | ns         | 46        | 1.1                             | 7.7 | 6                 |
| 30  | 48: 24: 8: 20                 | s          | x         | x                               | x   | x                 |
| 31  | 8: 24: 48: 20                 | ns         | 47        | 1.4                             | 6.1 | 8                 |
| 32  | 32: 16: 32: 20                | s          | x         | x                               | x   | x                 |
| 33  | 64: 8: 8: 20                  | s          | x         | x                               | x   | x                 |
| 34  | 48: 8: 24: 20                 | s          | x         | x                               | x   | x                 |
| 35  | 24: 8: 48: 20                 | ns         | 43        | 1.7                             | 6.2 | 9                 |
| 36  | 8: 8: 64: 20                  | ns         | 37        | 1.7                             | 6.1 | 10                |
| 37  | 7: 60: 7: 26                  | s          | x         | x                               | x   | x                 |

| No.       | Weight ratio<br>BA:FGDG:PC:SD | Properties |           |                                 |            |                   |
|-----------|-------------------------------|------------|-----------|---------------------------------|------------|-------------------|
|           |                               | Slake      | WA<br>(%) | Density<br>(g/cm <sup>3</sup> ) | pH         | CEC<br>(meq/100g) |
| 38        | 22: 45: 7: 26                 | s          | x         | x                               | x          | x                 |
| 39        | 7: 45: 22: 26                 | s          | x         | x                               | x          | x                 |
| 40        | 29: 29: 16: 26                | s          | x         | x                               | x          | x                 |
| 41        | 16: 29: 29: 26                | s          | x         | x                               | x          | x                 |
| 42        | 45: 22: 7: 26                 | s          | x         | x                               | x          | x                 |
| 43        | 7: 22: 45: 26                 | s          | x         | x                               | x          | x                 |
| 44        | 29: 16: 29: 26                | s          | x         | x                               | x          | x                 |
| 45        | 60: 7: 7: 26                  | s          | x         | x                               | x          | x                 |
| 46        | 45: 7: 22: 26                 | s          | x         | x                               | x          | x                 |
| <b>47</b> | <b>22: 7: 45: 26</b>          | <b>ns</b>  | <b>50</b> | <b>1.2</b>                      | <b>6.4</b> | <b>9</b>          |
| 48        | 7: 7: 60: 26                  | ns         | 49        | 1.5                             | 6.2        | 10                |

WA = water absorption, CEC = cation exchange capacity, ns = not slake, s = slake,

x = not detectable

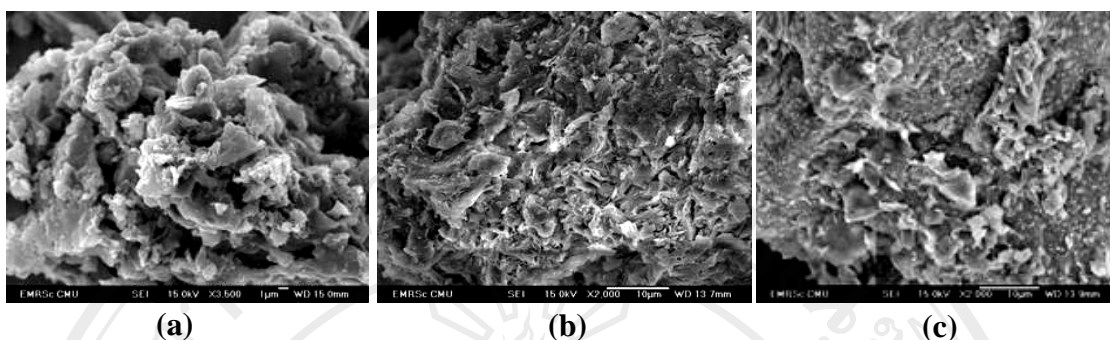
The results in Table 4.2 show that the weight ratio of bottom ash-FGD gypsum-paddy soil at 30:10:60 in formula 11 and firing at 850 °C for 30 minutes with a heating rate of 3 °C/minute, provided the best conditions without sawdust. This planting material has the initial nutrient compositions but the other properties were not in agreement with the commercial ones. However, when 26% by weight of sawdust was added, the properties of water absorption and density were improved and

pores increased. Water absorption was also increased to 50 % in formula 47. The improved planting material (Fig. 4.5) is slightly acidic with a pH of 6.4, has light weight (density = 1.2 g/cm<sup>3</sup>) and rather high CEC value.

The best planting material (Fig 4.5) has the ability to absorb and retain large quantities of water for plant use between irrigations due to its high porosity (Fig 4.6a). When compared with HDB, it has higher porosity (Fig 4.7), so it should be able to absorb more water.



**Figure 4.5** The best fired planting material.



**Figure 4.6** Scanning electron microscopy (SEM) images of the best FPM fired at (a) 850 °C (b) 900 °C and (c) 1000 °C.



**Figure 4.7** Scanning electron microscopy (SEM) images of HDB.

Firing at higher temperatures at 900 °C (Table 4.3) and 1000 °C (Table 4.4) could not improve the properties of the planting materials. The firing FPMs at both 900 and 1000 °C had lower CEC and water absorption than those prepared at 850 °C because at higher temperature the humus was destroyed and the surface of the materials fused so the surface area decreased (Fig 4.6b, 4.6c).

**Table 4.3** Physical and chemical properties of bottom ash-FGD gypsum-paddy soil based mixtures with 35% sawdust (materials were fired at 900 °C at a rate of 3 °C/minute).

| No. | Weight ratio<br>BA:FGDG:PC:SD | Properties |           |                                 |     |                   |
|-----|-------------------------------|------------|-----------|---------------------------------|-----|-------------------|
|     |                               | Slake      | WA<br>(%) | Density<br>(g/cm <sup>3</sup> ) | pH  | CEC<br>(meq/100g) |
| 49  | 22: 7: 45: 26                 | ns         | 50        | 1.2                             | 6.5 | 8                 |
| 50  | 7: 7: 60: 26                  | ns         | 47        | 1.5                             | 6.3 | 10                |

WA = water absorption, CEC = cation exchange capacity, ns = not slake

**Table 4.4** Physical and chemical properties of bottom ash-FGD gypsum-paddy soil based mixtures with 35% sawdust (materials were fired at 1000 °C at a rate of 3 °C/minute).

| No. | Weight ratio<br>BA:FGDG:PC:SD | Properties |           |                                 |     |                   |
|-----|-------------------------------|------------|-----------|---------------------------------|-----|-------------------|
|     |                               | Slake      | WA<br>(%) | Density<br>(g/cm <sup>3</sup> ) | pH  | CEC<br>(meq/100g) |
| 51  | 22: 7: 45: 26                 | ns         | 49        | 1.3                             | 6.6 | 7                 |
| 52  | 7: 7: 60: 26                  | ns         | 46        | 1.5                             | 6.5 | 9                 |

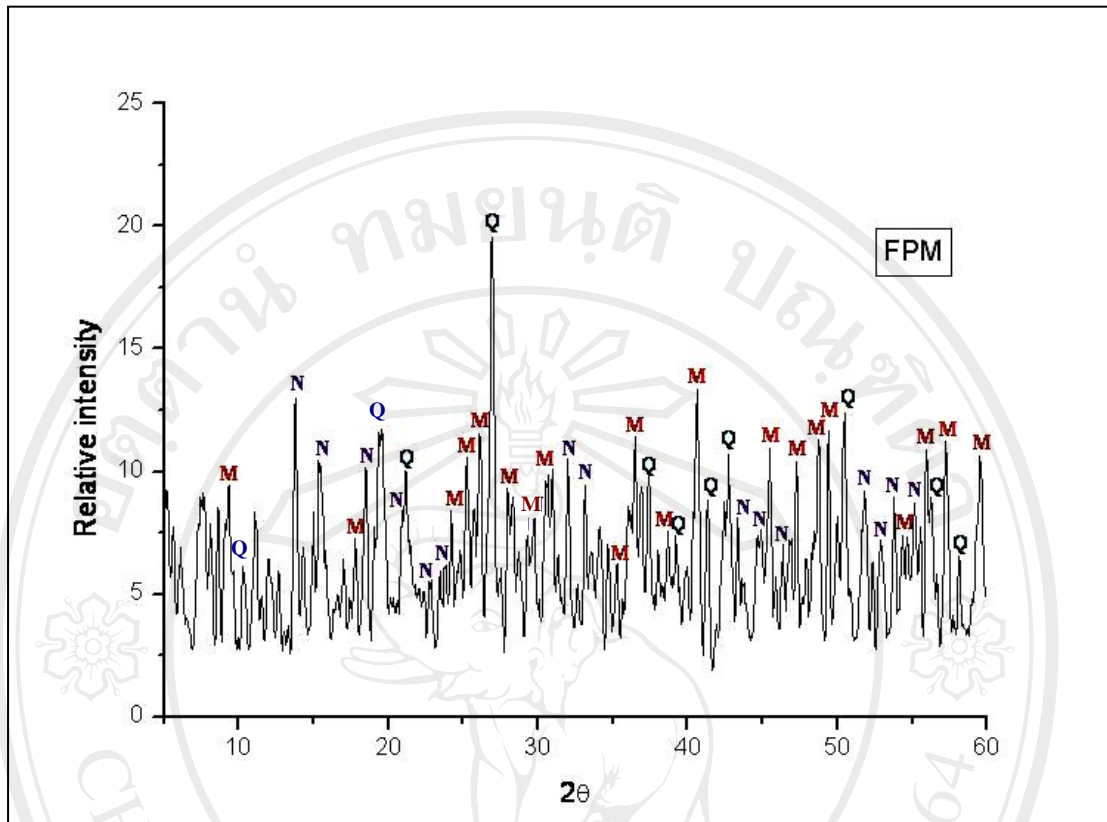
WA = water absorption, CEC = cation exchange capacity, ns = not slake

**Table 4.5** Properties of the best FPM (fired at 850 °C) compared with traditional planting material.

| Property                      | The best FPM<br>BA:FGD gypsum:PC: SC,<br>22:7:45:26 | Traditional planting<br>material |
|-------------------------------|-----------------------------------------------------|----------------------------------|
| Slake                         | not slake                                           | not slake                        |
| Water absorption (%)          | 50                                                  | 45-65                            |
| Density (g.cm <sup>-3</sup> ) | 1.2                                                 | 1.2-1.4                          |
| pH                            | 6.4                                                 | 5.0-6.5                          |
| CEC (meq/100g)                | 9                                                   | 2-15                             |

Planting materials should have a pH range of 5.0-6.5 with a density in the range of 1.2-1.4 g/cm<sup>3</sup> (Table 4.5) because that affect the carefully controlled the pH levels of the nutrient solution. The CEC value of the prepared planting material was 9 meq/100g. It has a higher CEC value than HDB (1.2 meq/100g), and perlite (1.5 meq/100g). The ability of certain media to retain nutrients against leaching losses is related to its CEC. The CEC is the ability of the media to attract and hold various cations such as potassium, calcium, magnesium and iron ions for use by the plant's roots. These positively charged ions are attracted to the negatively charged media particles and therefore aren't leached as quickly from the media. A media with a high CEC will require less frequent applications of nutrients than a media with a low CEC. In other words, a high CEC value correlates with a high nutrient holding capacity and thus retains nutrients for plant uptake between applications of fertilizer.

The mineralogical compositions of the best FPM and HDB are summarized in Fig. 4.8. As shown in Fig. 4.9, the mineral components of the best FPM are quartz, natrolite and muscovite. HDB consists of two major mineral components, are quartz and muscovite. The XRF results in Table 4.6 present the major constituents of traditional planting material are Si, Al, Ca, Fe, K, Mg, P, Mn, Na and Ti. These are typical constituents accounting for about 95% of the mass of the traditional planting material. It has been documented that P, K, Ca and Mg are essential plant nutrients while Fe, and Mn are only minor nutrients for plants.



Q = quartz

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 7.5750 | 11.673  | 75        |
| 4.2709 | 20.782  | 100       |
| 3.0556 | 26.203  | 52        |

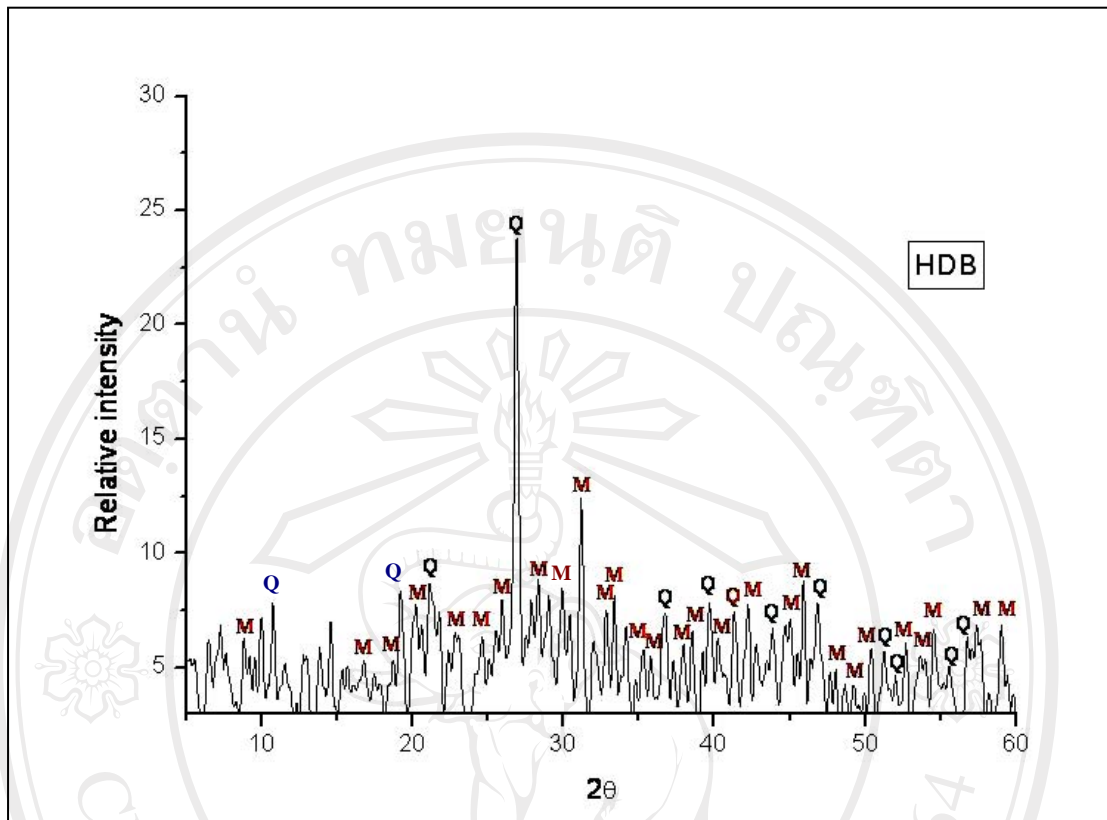
N = natrolite

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 6.3920 | 13.843  | 100       |
| 5.7856 | 15.302  | 79        |
| 2.8224 | 31.676  | 44        |

M = muscovite

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 2.5528 | 35.125  | 100       |
| 4.4476 | 19.947  | 80        |
| 2.9381 | 30.399  | 68        |

**Figure 4.8** X-ray diffraction of the best FPM: Q = quartz, N = natrolite and M = muscovite.



Q = quartz

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 7.5750 | 11.673  | 75        |
| 4.2709 | 20.782  | 100       |
| 3.0556 | 26.203  | 52        |

M = muscovite

| d [Å]  | 2 Theta | Intensity |
|--------|---------|-----------|
| 2.5528 | 35.125  | 100       |
| 4.4476 | 19.947  | 80        |
| 2.9381 | 30.399  | 68        |

**Figure 4.9** X-ray diffraction of the HDB: Q = quartz, M = muscovite.

**Table 4.6** Chemical compositions of the best FPM and HDB.

| Compound                                    | Products                    |       |
|---------------------------------------------|-----------------------------|-------|
|                                             | FPM                         | HDB   |
|                                             | <i>Macro-elements (wt%)</i> |       |
| SiO <sub>2</sub>                            | 49.74                       | 59.68 |
| Al <sub>2</sub> O <sub>3</sub>              | 14.47                       | 17.16 |
| CaO <sup>**</sup>                           | 12.59                       | 3.65  |
| Fe <sub>2</sub> O <sub>3</sub> <sup>*</sup> | 5.84                        | 12.35 |
| K <sub>2</sub> O <sup>**</sup>              | 1.99                        | 2.41  |
| MgO <sup>**</sup>                           | 0.90                        | 1.56  |
| P <sub>2</sub> O <sub>5</sub> <sup>**</sup> | 0.07                        | 0.19  |
| MnO <sup>*</sup>                            | 0.08                        | 0.14  |
| Na <sub>2</sub> O                           | 0.32                        | 0.50  |
| TiO <sub>2</sub>                            | 0.54                        | 1.49  |
| LOI.                                        | 14.03                       | 0.00  |

LOI. = loss on ignition, \*\* = major nutrient of plant, \* = minor nutrient of plant

#### 4.2 The adsorption behavior of NO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and K<sup>+</sup> on two types of planting materials (FPM and HDB)

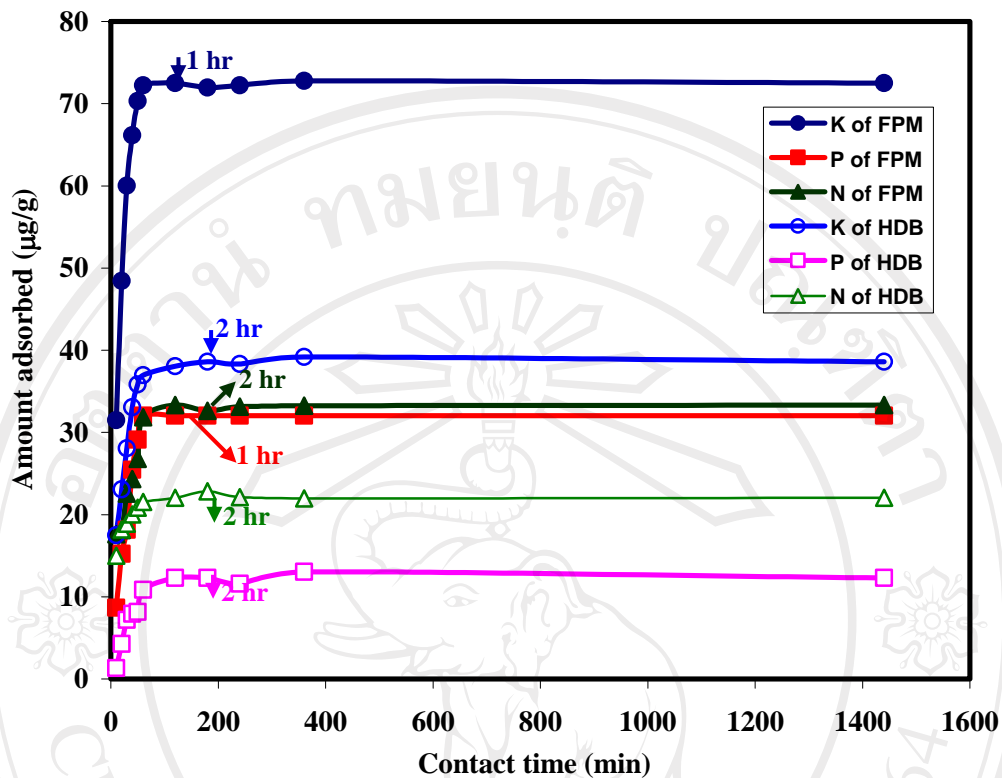
The adsorption behavior of ions on two planting materials, i.e. FPM and HDB using the batch-type techniques is expressed in the form of equilibrium concentration, C<sub>e</sub>, versus adsorbed concentration, q<sub>e</sub>, of the solute. The adsorbed amount, q<sub>e</sub>, was calculated using the equation (Eq. (1.4)).

To predict the relationship between the adsorbed and equilibrium concentrations obtained from batch-type tests, the Langmuir and Freundlich isotherm

equation was adopted in this study as expressed by equations (Eq. (1.8)) and (Eq. (1.10)).

#### 4.2.1 Effect of contact time

In order to study the time required for equilibrating  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  or  $\text{K}^+$  solutions with the planting materials, equilibration times were selected at 10, 20, 30, 40, 50, 60, 120, 180, 240, 360, and 1440 minutes, respectively. The sorption experiments were conducted by shaking 10 g sample of planting material in 50 mL of 500 mg/L  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  or  $\text{Cl}^-$  solution at 150 rpm at room temperature. At the end of the shaking period, the suspension was filtered and the nitrate or dihydrogenphosphate concentration was measured by UV-visible spectrophotometer. The potassium concentration was measured by flame photometry (FLM).



**Figure 4.10** Effect of contact time on adsorption behavior of  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{K}^+$  on the FPM and HDB.

Fig. 4.10 shows the contact time versus adsorbed concentration. It can be seen that  $\text{H}_2\text{PO}_4^-$  and potassium ion on FPM reaches equilibrium faster than HDB. FPM needed one hour to reach equilibrium time while HDB needed two hours.  $\text{NO}_3^-$  on FPM reached equilibrium as fast as on HDB, two hours in both cases. In addition, the amounts of adsorbed  $\text{H}_2\text{PO}_4^-$  and  $\text{K}^+$  on FPM are two times higher than that on HDB. It was also confirmed by BET measurements that the FPM prepared from this work had double surface area compared to HDB. The longer period for HDB to achieve the steady state may be partly due to its less specific surface area relative to the FPM (Table 4.7). During the test, the initial concentration of each ion, the mass of planting

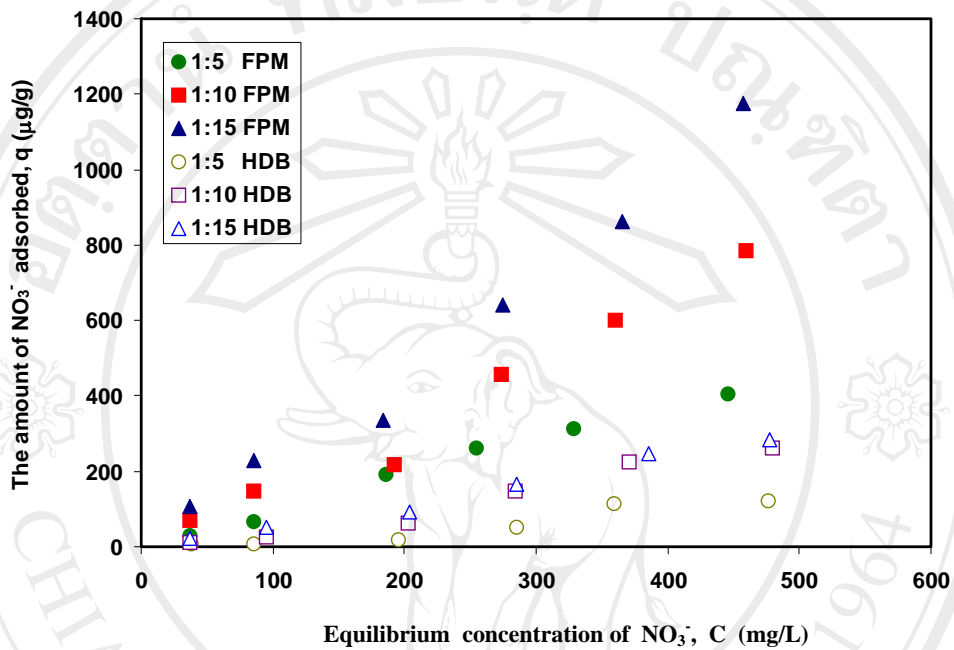
material and other test conditions (temperature and pressure, etc.) remained the same. Therefore the larger the available surface area for adsorption is the more adsorption sites should be available and subsequently the faster the equilibrium condition could be reached.

**Table 4.7** Physico-chemical properties of both planting materials.

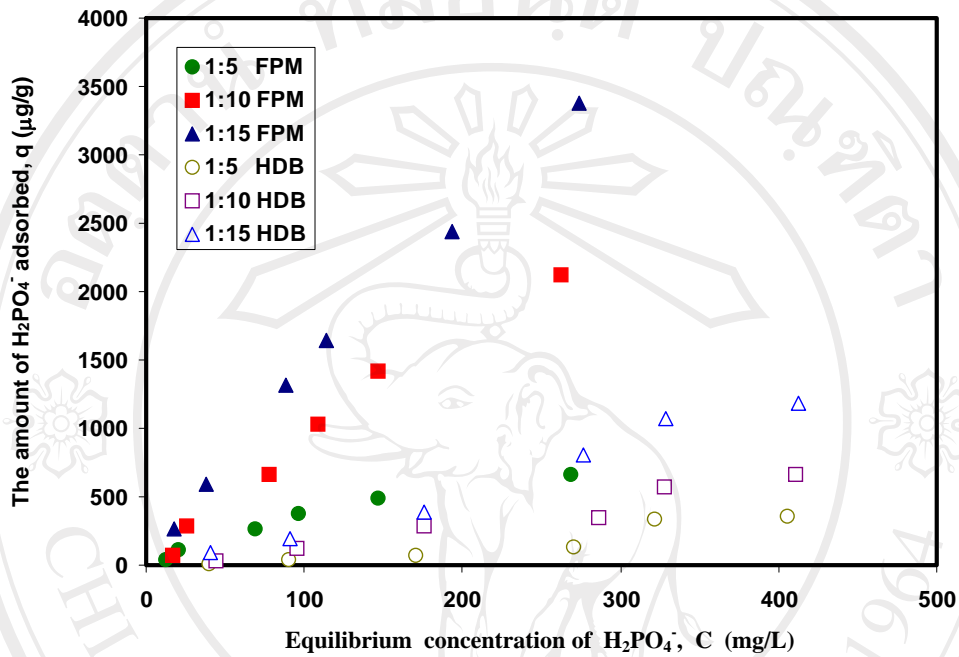
| Physico-chemical properties                 | Type of planting materials |      |
|---------------------------------------------|----------------------------|------|
|                                             | FPM                        | HDB  |
| Cation exchange capacity (meq/100 g)        | 8.90                       | 1.20 |
| pH at 1:3 planting materials/solution ratio | 6.43                       | 7.10 |
| Moisture content (%)                        | 0.30                       | 0.10 |
| Specific surface area (m <sup>2</sup> /g)   | 23.8                       | 11.8 |

#### 4.2.2 Effect of planting material/solution ratio

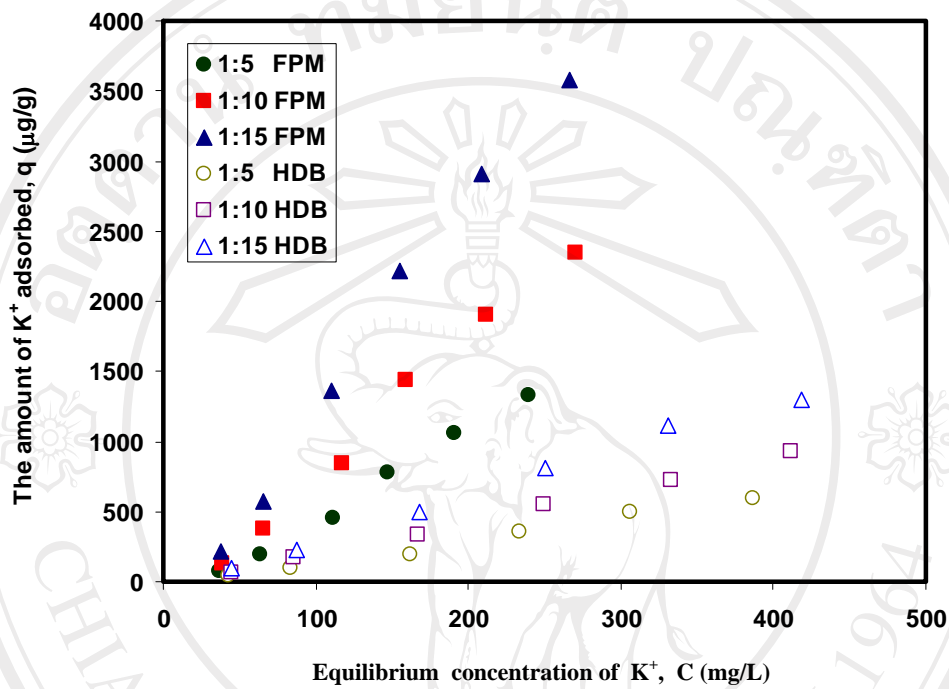
In order to understand the nature of adsorption occurring on the surface of the two types of planting materials, adsorption isotherms at different planting material/solution ratios were measured. In this experiment, three different planting material/solution ratios, 1:5, 1:10 and 1:15 (weight by volume) were selected for the isotherm study of nitrate, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and K<sup>+</sup> on both types of planting materials.



**Figure 4.11** Effect of planting material/solution ratios (1:5, 1:10 and 1:15 w/v) on the adsorption behavior of  $\text{NO}_3^-$  on FPM and HDB.



**Figure 4.12** Effect of planting material/solution ratios (1:5, 1:10 and 1:15 w/v) on the adsorption behavior of  $H_2PO_4^-$  on FPM and HDB.



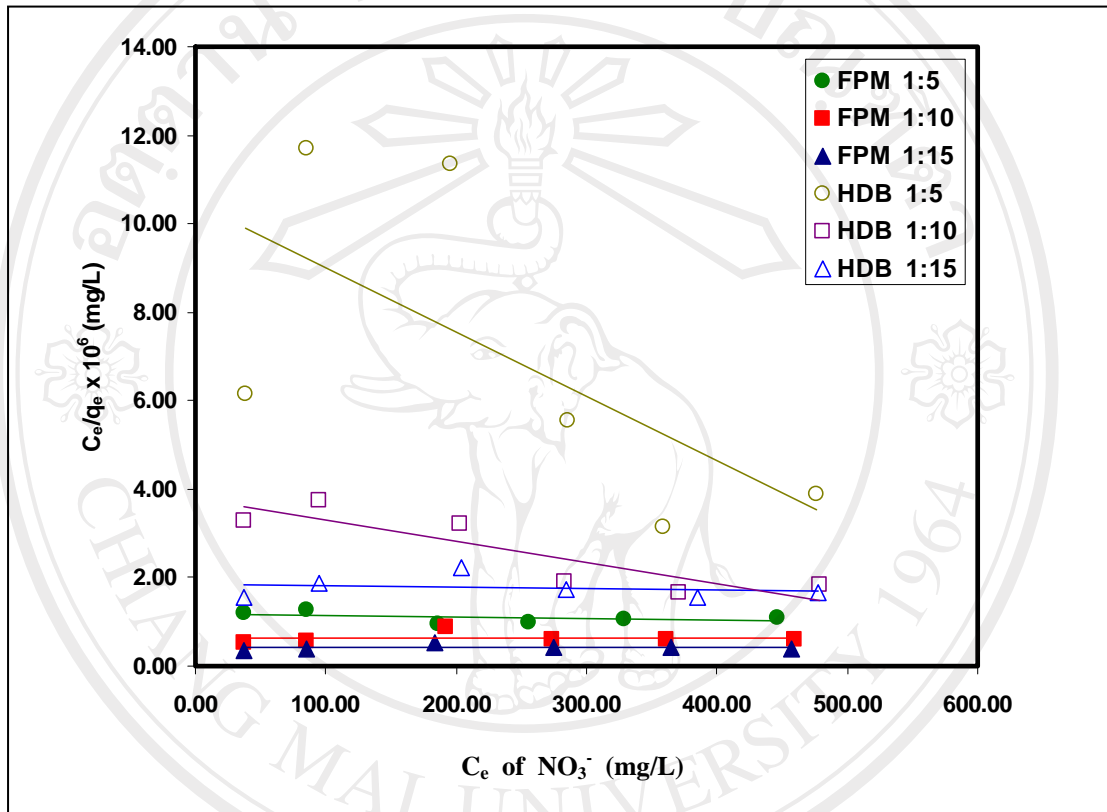
**Figure 4.13** Effect of planting material/solution ratios (1:5, 1:10 and 1:15 w/v) on the adsorption behavior of  $K^+$  on FPM and HDB.

The adsorption isotherm of  $NO_3^-$ ,  $H_2PO_4^-$  and  $K^+$  on FPM and HDB at three different planting material/solution ratios (1:5, 1:10 and 1:15 w/v), respectively, are shown in Figs. 4.11-4.13. At the same planting material/solution ratio, the FPM adsorbed much larger amount of each ion than HDB in every case, which is mainly due to its larger CEC (Table 4.7).

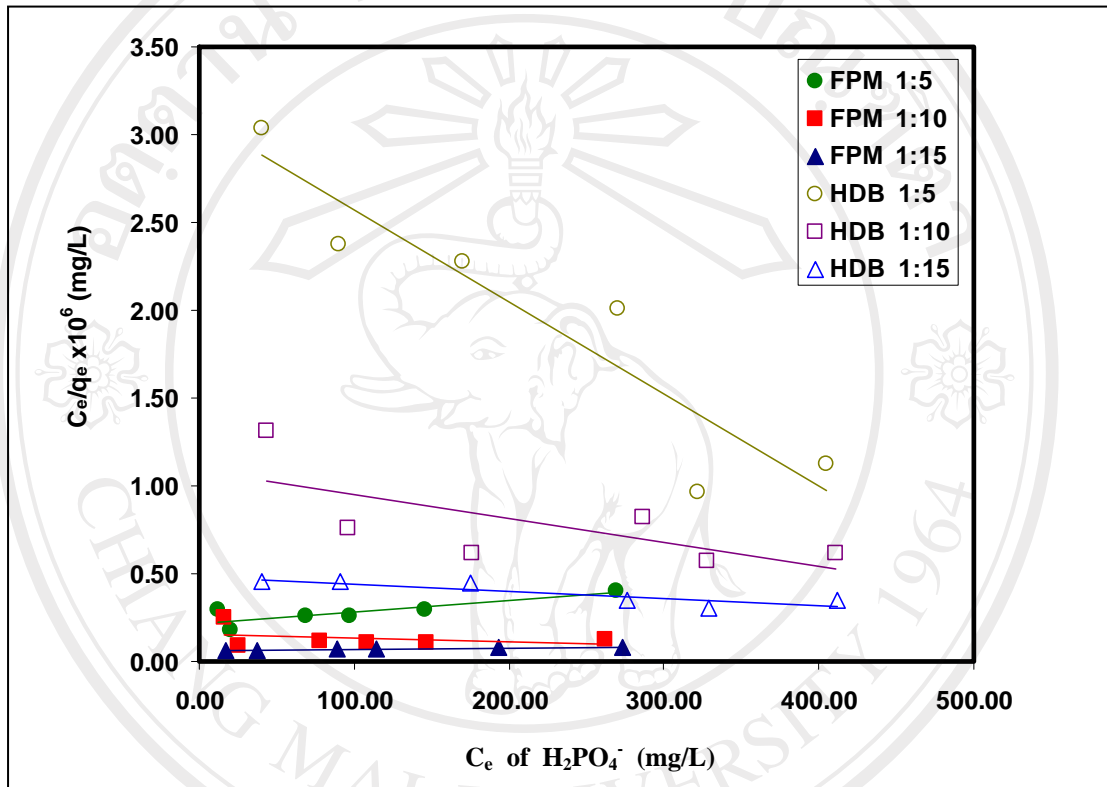
In order to interpret the effect of  $NO_3^-$  from  $KNO_3$ ,  $H_2PO_4^-$  from  $KH_2PO_4$  and  $K^+$  from  $KCl$  adsorption onto the planting materials, the adsorption behavior of each ion on both planting materials was studied at various ratios of planting

material/solution shown in Figs. 4.11-4.13. The effect of the planting material/solution ratio on the adsorbed concentration is more significant for FPM than for HDB. The amount of  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{K}^+$  adsorbed on FPM and HDB increased with the increase of solid/solution ratio from 1:5 to 1:10 and 1:15 (w/v) resulted in a higher ion adsorption by FPM and HDB. The largest amount of  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{K}^+$  adsorbed was observed when the planting material/solution ratio was 1:15.

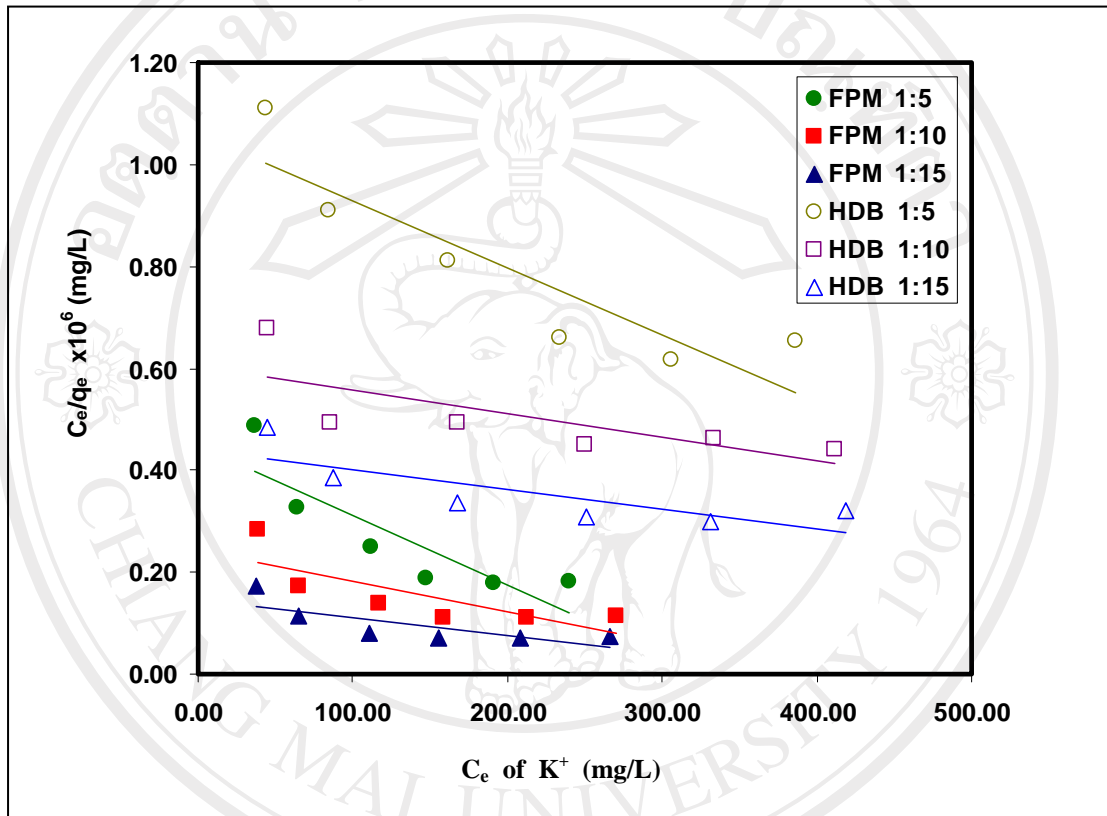
From the Langmuir plots in Figs. 4.14-4.16 the adsorption behavior on the two types of planting materials showed non-linear lines. Therefore the type of adsorption behavior of  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{K}^+$  on both planting materials does not correspond with the Langmuir isotherm.



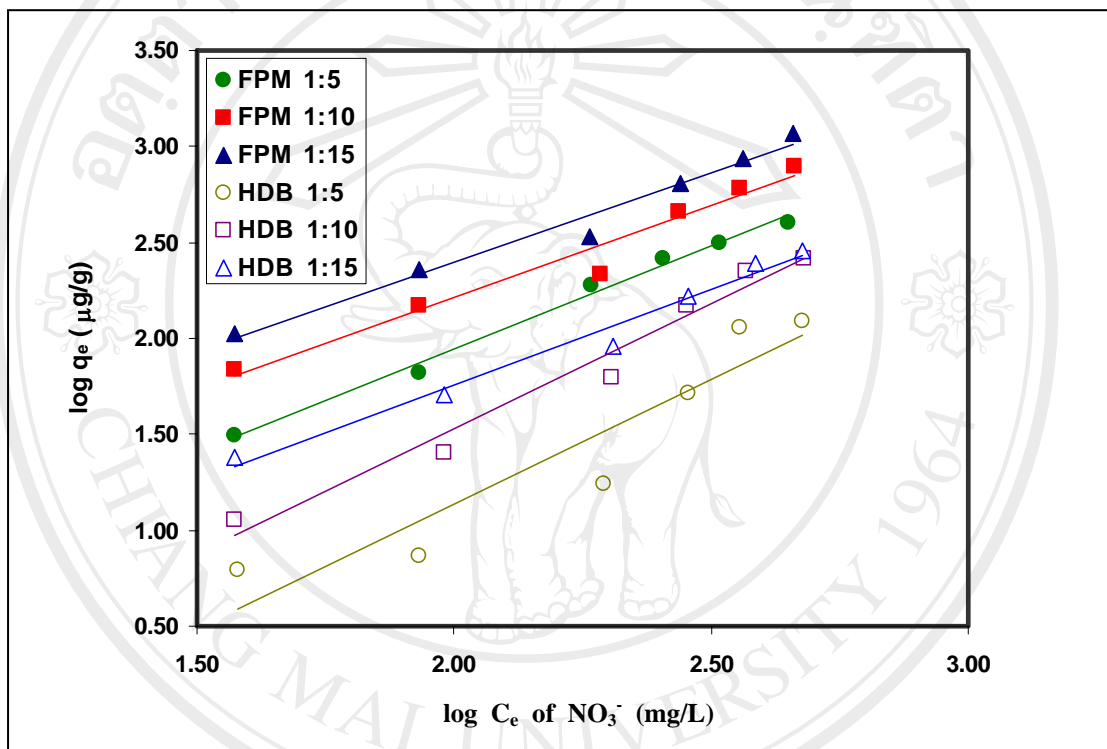
**Figure 4.14** Langmuir expression of  $\text{NO}_3^-$  on FPM and HDB at solid/solution ratios of 1:5, 1:10 and 1:15 w/v.



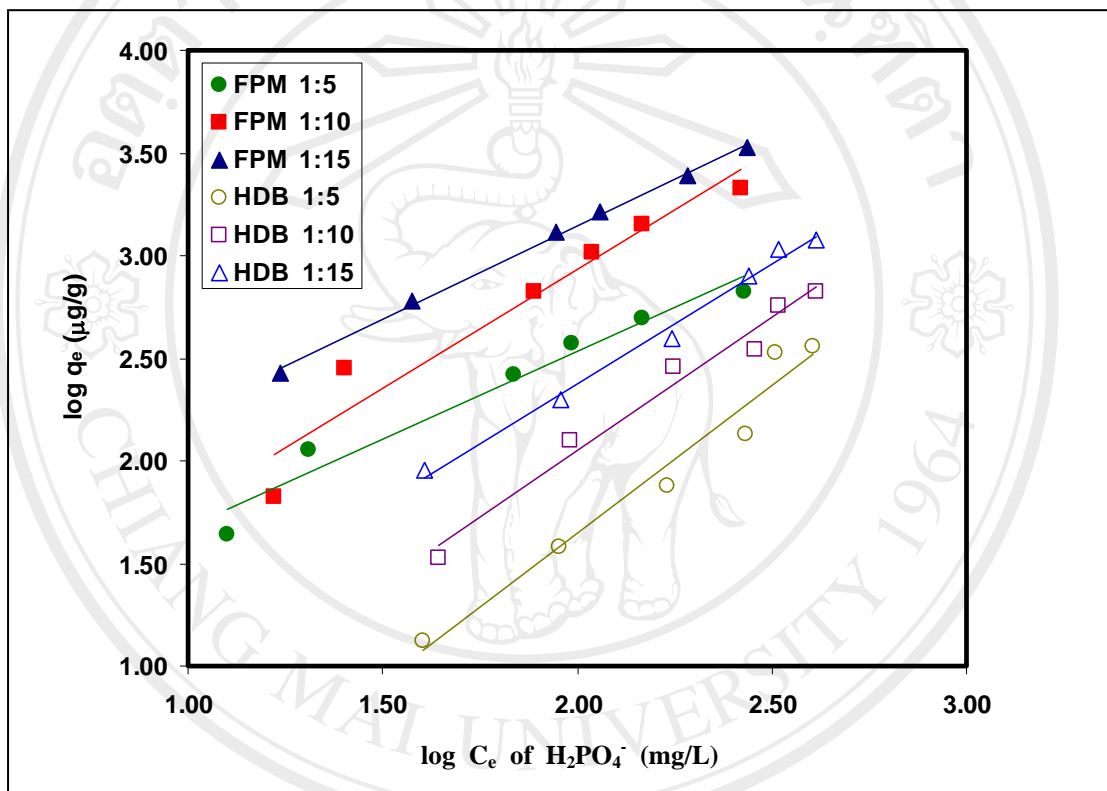
**Figure 4.15** Langmuir expression of  $H_2PO_4^-$  on FPM and HDB at solid/solution ratios of 1:5, 1:10 and 1:15 w/v.



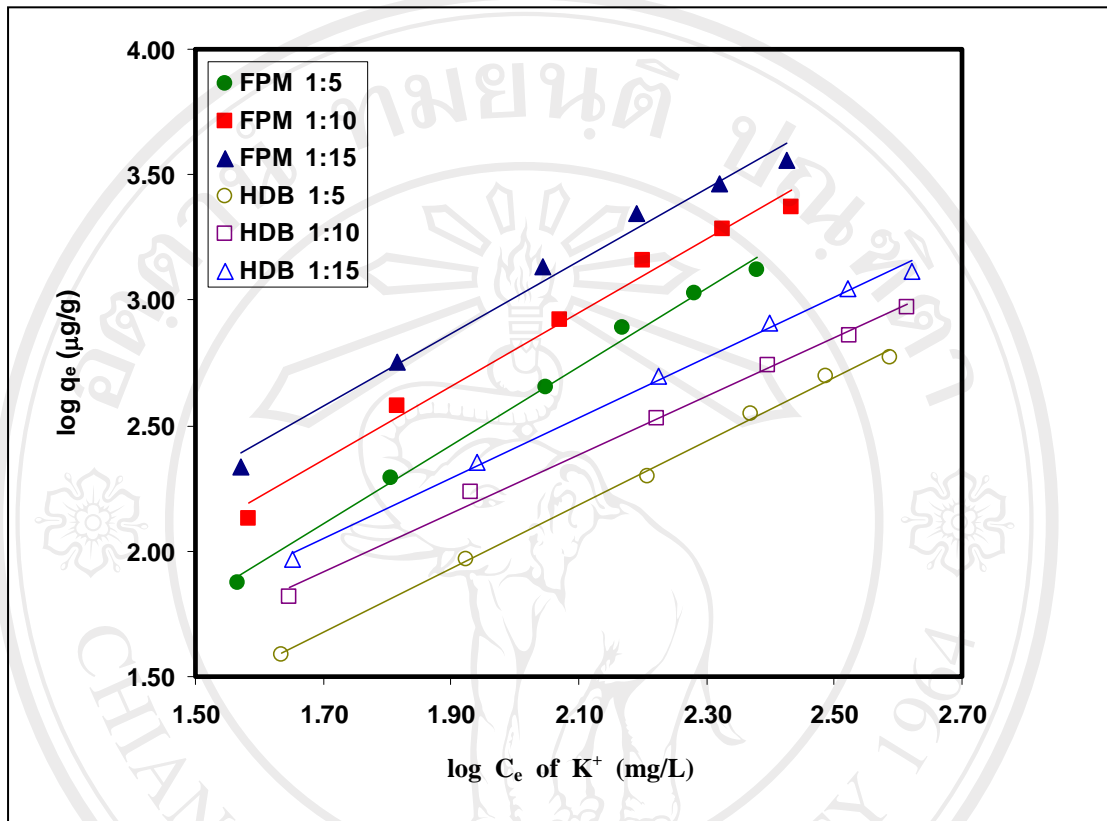
**Figure 4.16** Langmuir expression of  $K^+$  on FPM and HDB at solid/solution ratios of 1:5, 1:10 and 1:15 w/v.



**Figure 4.17** Freundlich expression of  $\text{NO}_3^-$  on FPM and HDB at solid/solution ratios of 1:5, 1:10 and 1:15 w/v.



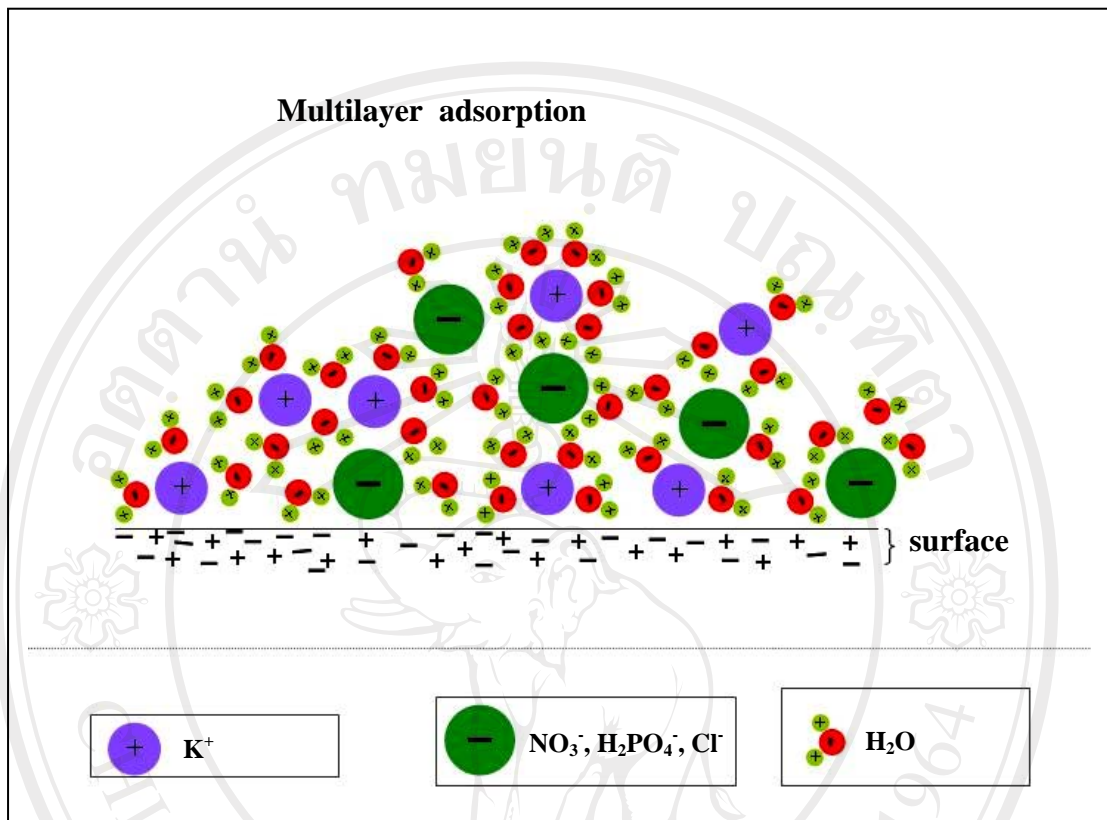
**Figure 4.18** Freundlich expression of  $H_2PO_4^-$  on FPM and HDB at solid/solution ratios of 1:5 and 1:10, 1:15 w/v.



**Figure 4.19** Freundlich expression of  $K^+$  on FPM and HDB at solid/solution ratios of 1:5, 1:10 and 1:15 w/v.

The graphs in Figs. 4.17-4.19 show the relationship between adsorbed amount of the three ions (nitrate, dihydrogenphosphate and potassium) and their equilibrium concentration in solution. These results confirmed that the adsorption behavior of all these three ions on both planting materials correspond with the Freundlich isotherm from the linear lines with high  $R^2$  values. All  $R^2$  values in Table 4.8 are higher than 0.900.

The experimental results in Table 4.8 show that practical parameters  $1/n$  (or slopes) are more than one. This indicates that the adsorbed ability of ions is increased at high solution concentrations and decreased gradually at low solution concentrations. The determined values of the Freundlich adsorption equation parameters,  $K_F$  and  $n$ , are summarized in Table 4.8. According to the Freundlich isotherm equation,  $(\log q_e = \log K_F + (1/n) \log C_e)$  the  $q_e$  values depend on equilibrium solution concentration. Since the amounts of adsorption increase when the solution concentration increases, therefore, the adsorption behavior of all three ions on both planting materials tend to be of multilayer type confirmed by the Freundlich plots. The schematic for multilayer adsorption of ions on both type of planting materials is shown in Fig. 4.20



**Figure 4.20** Scheme of the adsorption behavior of some ions.

**Table 4.8** Langmuir adsorption parameters on the FPM and HDB in the case of  $KNO_3$ ,  $KH_2PO_4$  and  $KCl$  solutions.

| Parameter                                           | FPM                               |            |            | HDB                               |            |            |
|-----------------------------------------------------|-----------------------------------|------------|------------|-----------------------------------|------------|------------|
|                                                     | Planting materials/solution ratio |            |            | Planting materials/solution ratio |            |            |
|                                                     | 1:5                               | 1:10       | 1:15       | 1:5                               | 1:10       | 1:15       |
| <b><i>KNO<sub>3</sub> solution</i></b>              |                                   |            |            |                                   |            |            |
| 1/q <sub>0</sub>                                    | -0.000398                         | -0.0000116 | 0.0000585  | -0.0145                           | -0.00477   | -0.000316  |
| 1/q <sub>0</sub> b                                  | 1.19                              | 0.635      | 0.406      | 10.4                              | 3.77       | 1.85       |
| q <sub>0</sub>                                      | -2514                             | -86196     | 17084      | -69.07                            | -209.7     | -3165      |
| b                                                   | -0.000335                         | -0.0000183 | 0.000144   | -0.00139                          | -0.00126   | -0.000171  |
| R <sup>2</sup>                                      | 0.241                             | 0.0002     | 0.019      | 0.4262                            | 0.7734     | 0.0412     |
| <b><i>KH<sub>2</sub>PO<sub>4</sub> solution</i></b> |                                   |            |            |                                   |            |            |
| 1/q <sub>0</sub>                                    | 0.000647                          | -0.000224  | 0.0000753  | -0.00523                          | -0.00135   | -0.000411  |
| 1/q <sub>0</sub> b                                  | 0.216                             | 0.155      | 0.0616     | 3.09                              | 1.08       | 0.484      |
| q <sub>0</sub>                                      | 1546                              | -4459      | 13283      | -191.2                            | -743.0     | -2431.6    |
| b                                                   | 0.00300                           | -0.00144   | 0.00122    | -0.00169                          | -0.00124   | -0.000850  |
| R <sup>2</sup>                                      | 0.7151                            | 0.1193     | 0.9427     | 0.8659                            | 0.4744     | 0.7669     |
| <b><i>KCl solution</i></b>                          |                                   |            |            |                                   |            |            |
| 1/q <sub>0</sub>                                    | -0.001371                         | -0.0005980 | -0.0003573 | -0.001309                         | -0.0004592 | -0.0003861 |
| 1/q <sub>0</sub> b                                  | 0.4497                            | 0.2415     | 0.1474     | 1.059                             | 0.6021     | 0.4392     |
| q <sub>0</sub>                                      | -729.3                            | -1672      | -2798      | -763.8                            | -2178      | -2590      |
| b                                                   | -0.003049                         | -0.002476  | -0.002425  | -0.001236                         | -0.000763  | -0.000879  |
| R <sup>2</sup>                                      | 0.7479                            | 0.6143     | 0.6014     | 0.8078                            | 0.5532     | 0.6276     |

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**Table 4.9** Freundlich adsorption parameters on the FPM and HDB in the case of  $KNO_3$ ,  $KH_2PO_4$  and  $KCl$  solutions.

| Parameter                                           | FPM                               |        |        | HDB                               |         |         |
|-----------------------------------------------------|-----------------------------------|--------|--------|-----------------------------------|---------|---------|
|                                                     | Planting materials/solution ratio |        |        | Planting materials/solution ratio |         |         |
|                                                     | 1:5                               | 1:10   | 1:15   | 1:5                               | 1:10    | 1:15    |
| <b><i>KNO<sub>3</sub></i> solution</b>              |                                   |        |        |                                   |         |         |
| log K                                               | -0.204                            | 0.297  | 0.532  | -1.47                             | -1.08   | -0.231  |
| 1/n                                                 | 1.07                              | 0.959  | 0.933  | 1.30                              | 1.30    | 0.994   |
| K                                                   | 0.625                             | 1.98   | 3.40   | 0.0341                            | 0.0832  | 0.587   |
| n                                                   | 0.931                             | 1.04   | 1.07   | 0.769                             | 0.768   | 1.01    |
| R <sup>2</sup>                                      | 0.9924                            | 0.9658 | 0.9924 | 0.8820                            | 0.9722  | 0.9795  |
| <b><i>KH<sub>2</sub>PO<sub>4</sub></i> solution</b> |                                   |        |        |                                   |         |         |
| log K                                               | 0.818                             | 0.610  | 1.33   | -1.23                             | -0.540  | 0.0521  |
| 1/n                                                 | 0.858                             | 1.16   | 0.909  | 1.44                              | 1.30    | 1.16    |
| K                                                   | 6.57                              | 4.08   | 21.2   | 0.0590                            | 0.288   | 1.13    |
| n                                                   | 1.16                              | 0.862  | 1.10   | 0.696                             | 0.771   | 0.861   |
| R <sup>2</sup>                                      | 0.9616                            | 0.9364 | 0.9975 | 0.9646                            | 0.9752  | 0.9901  |
| <b><i>KCl</i> solution</b>                          |                                   |        |        |                                   |         |         |
| log K                                               | -0.541                            | -0.139 | 0.110  | -0.483                            | -0.0630 | 0.00828 |
| 1/n                                                 | 1.56                              | 1.47   | 1.45   | 1.27                              | 1.16    | 1.20    |
| K                                                   | 0.288                             | 0.727  | 1.29   | 0.329                             | 0.865   | 1.02    |
| n                                                   | 0.64                              | 0.68   | 0.69   | 0.79                              | 0.86    | 0.83    |
| R <sup>2</sup>                                      | 0.995                             | 0.987  | 0.986  | 0.998                             | 0.995   | 0.996   |

### 4.3 Some heavy metals released from FPM and HDB at various pH by atomic absorption spectrometry

The released of cadmium and nickel ions from FPM and HDB at various pH was studied using atomic absorption spectrometry. It was observed in Table 4.9 that both planting materials released the lower amount of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  in rather neutral solution (pH 6.5) than in the case of low acidic solution (pH 5.0 and 2.0). This indicated that the pH is an important factor governing the release of these two heavy metals. Therefore, it might be concluded that the release of cadmium ion and nickel ion decreased with increasing the pH value of the solution.

**Table 4.10** Heavy metal release from FPM and HDB.

| Sample | Heavy metal (mg/mL) |         |
|--------|---------------------|---------|
|        | Cadmium             | Nickel  |
| pH 6.5 |                     |         |
| FPM    | < 0.002             | < 0.005 |
| HDB    | < 0.002             | < 0.005 |
| pH 5.0 |                     |         |
| FPM    | 0.013               | < 0.005 |
| HDB    | < 0.002             | 0.250   |
| pH 2.0 |                     |         |
| FPM    | 0.533               | 0.167   |
| HDB    | 0.078               | 0.500   |

*Notice: Toxicity level in plant of cadmium 4-200 mg/L and nickel 8-200 mg/L.*