

CHAPTER 1

INTRODUCTION

At present, planting materials are important for the production of many plants grown in containers. Planting material is used as one kind of soil-less culture which covers all methods and systems of growing plants without soil, such as water culture, soil-less media culture, substrate culture and chemiculture. There is a wide range of waste materials used in the production of planting materials such as peat, bark, rice hulls, coconut fiber, sand, rockwood, perlite, vermiculite and calcined soils. This study focuses on bottom ash (BA) and flue gas desulfurization (FGD) gypsum wastes as novel planting materials for plants to provide economic benefits, as the use of these residues means low cost production of high value products based on solid mixtures.

The Mae Moh power plant in Lampang is a lignite coal fired thermal power plant. The production of power through combustion produces a huge amount of waste. Virtually every economical use of coal is affected by the amount and variety of waste products. The types of wastes which are left over from burning of coal are fly ash (FA), BA, boiler slag and FGD gypsum. Wastes in coal can be the source of deleterious pollutants and corrosive elements, but also a source of useful by-products.

Since 1960 many applications were identified in previous years using BA and FGD gypsum as a substitute for light fill material in construction [1], as engineering material [2], soil amendment [3], improvement of the physical properties of soil [4-6] adsorbents of heavy metals and organic substances [7-10] in previous years. However, its capability to absorb fertilizers [11] is not much exploited so far.

BA - a dark gray, granular material, porous, sand size can be used as a low cost replacement for more expensive sand in ceramic industry [12]. Many elements in BA such as calcium (Ca), iron (Fe), manganese (Mg), potassium (K) and silicon (Si) are essential as plant nutrients [13]. BA still appears to be an acceptable soil amendment which may alter the texture and improve the filth by making soils more friable [14]. Particularly, BA can be applied to be a fertilizer in mixture with FA and sandy soil. Moreover the compost application of BA with wheat straw and inorganic nitrogen has the great benefit to improve soil quality and crop yield. Soil bulk density can be reduced while water-stable aggregates are increased, improving infiltration, and increasing provision of nitrogen, phosphorus, potassium and some micronutrients [15].

Considerable amounts of FGD gypsum are generated when sulfur is recovered from coal burning at electrical generating plants to meet Clean Air standards. FGD gypsum is the solid material resulting from the removal of sulfur dioxide gas from the utility boiler stack gases in the flue gas desulfurization process. The material is produced in the flue gas scrubbers by reacting slurred limestone or lime with the gaseous sulfur dioxide to produce calcium sulfite. Some utility plants further oxidize the calcium sulfite to calcium sulfate (which is the same as natural gypsum). FGD gypsum is 95% pure calcium sulfate and has found to have many applications. Beneficial agricultural uses of FGD gypsum include application as amendment to soil [16]. Gypsum has the ability to improve the physical properties of soil such as water infiltration, increased electrolyte concentration of water at the surface of the soil causing soil flocculation thus reducing sealing, help alleviate soil compaction and improved aggregate stability of soils [17]. BA and FGD gypsum used on land cause

no environmental problems if these products are used appropriately. Based on these characterizations and detail studies, BA and FGD gypsum can be used as low cost substrates in the production of FPM. In this study, they are mixed with paddy soil (PS), to which different amounts of sawdust were added. PC fired gained plasticity and strength with rather high cation exchange capacity (CEC) value after firing. Moreover, soil particles have a charge on their surface. The total charge on the soil is a function of both the surface area and the chemical nature of the particles. While soils have both positive and negative charges, negative surface charges usually exceed by far the positive surface charges. These negative charges allow them to hold cations in a form available to growing plants since many soil nutrients are cations. Firing sawdust can be used to improve the pores in materials and to provide increased porosity and water absorption (WA).

1.1 Types of growing media or planting materials [18]

The various soil-less culture systems in use nowadays may be grouped according to their type and size of the support medium. Due to planting material must be amended to provide the appropriate physical and chemical properties necessary for plant growth. The following is a description of some of the most commonly used amendments for the production of greenhouse crops.

1.1.1 Peat and peat-like materials

Peat moss is formed by the accumulation of plant materials in poorly drained areas. The type of plant material, as shown in Fig. 1.1, and degree of decomposition largely determine its value for use in a growing medium. Although the compositions of different peat deposits vary widely, four distinct categories may be identified: a) Hypnaceous moss b) Reed and Sedge c) Humus or Muck and d) Sphagnum moss. Sphagnum moss is the dehydrated remains of acid-bog plants from the genus *Sphagnum*. It is light in weight and has the ability to absorb 10 to 20 times its weight in water. Sphagnum moss contains specific fungistatic substances which accounts for its ability to inhibit damping-off of seedlings. Sphagnum moss is perhaps the most desirable form of organic matter for the preparation of planting material. Drainage and aeration are improved in heavier soils while moisture and nutrient retention are increased in lighter soils.



Figure 1.1 Peat and peat-like materials.

1.1.2 Wood residues

Wood residues constitute a significant source of soil-less culture. These materials are generally by-products of the lumber industry and are readily available in large quantities (Fig. 1.2). Nitrogen depletion by soil microorganisms during the decomposition process is one of the primary problems associated with these materials.

However, supplemental applications of nitrogen to the growing media can make most wood residues valuable amendments. The high cellulose and lignin content along with insufficient nitrogen supplies creates depletion problems which can severely restrict plant growth. However, supplemental applications of nitrogen can reduce this problem. Different barks are suitable for use in container media. Physical properties obtained from tree barks are similar to those of Sphagnum moss.



Figure 1.2 Wood residues.

1.1.3 Rice hulls

Rice hulls are a by-product of the rice milling industry as shown in Fig. 1.3. Although they are extremely light in weight, rice hulls are very effective at improving drainage. The particle size and resistance to decomposition of rice hulls and sawdust are very similar. However N depletion is not such a serious problem in media amended with rice hulls. Therefore this does not constitute major commercial sources of organic amendments.



Figure 1.3 Rice hulls.

1.1.4 Coir

Coir is a waste material from coconut production as shown in Fig. 1.4. Coir is the market leader in hydroponic coir media. Coir has been pretreated or washed to eliminate the high level of salts often found in the raw material. Other coconut coir's on the market are often unsuitable for soil-less gardening due to these high salt contents.



Figure 1.4 Coir.

1.1.5 Sand

Sand, a basic component of soil, ranges in particle size from 0.05 mm to 2.0 mm in diameter (Fig. 1.5). Fine sands (0.05 mm - 0.25 mm) do little to improve the physical properties of a growing media and may result in decreasing drainage and aeration. Medium and coarse sand particles are those which provide optimum adjustments in media texture. Although sand is generally the least expensive of all inorganic amendments, it is also the heaviest. This may result in prohibitive transportation costs. Sand is a valuable amendment for both potting and propagation media.



Figure 1.5 Variety of sand.

1.1.6 Rockwool

Rockwool is made from molten basalt rock spun into a candy floss like fiber. It is a popular medium used by hobby gardeners and commercial growers alike. The material is available in small starter cubes for propagating seeds or cuttings, through to large slabs as shown in Fig. 1.6.



Figure 1.6 Rockwool.

1.1.7 Perlite

Perlite is a silicious mineral of volcanic origin. Lightness and uniformity make perlite very useful for increasing aeration and drainage. However, perlite is very dusty when it is dry and has a tendency to float to the top of a container during irrigation. It has also been shown that perlite contains potentially toxic levels of fluorine. Although costs are moderate, perlite is an effective amendment for planting material (Fig. 1.7).



Figure 1.7 Perlite.

1.1.8 Vermiculite

Vermiculite is a micaceous mineral produced by heating to approximately 745°C (Fig. 1.8). The expanded, plate-like particles which are formed have a very high water holding capacity and aid in aeration and drainage. Vermiculite has excellent ex-change and buffering capacities as well as the ability to supply potassium and magnesium. Although vermiculite is less durable than sand and perlite, its chemical and physical properties are very desirable for container media.



Figure 1.8 Vermiculite.

1.1.9 Calcined soils

Calcined soils are formed by heating montmorillonitic soil minerals to approximately 690 °C. The pottery-like particles formed are six times as heavy as perlite. Calcined soils have a relatively high cation exchange as well as water holding capacity. This material is a very durable and a useful amendment. These inorganic soil amendments are generally utilized to increase the number of large pores, decrease water holding capacity and improve drainage and aeration. Other material such as hydroball (HDB) is also suitable for this use.

HDB is a special fired soil based aggregate that is heated and formed into small 'marbles' usually between 4 mm to 16 mm in diameter (Fig. 1.9). The inner core structure is porous, absorbs and releases nutrients and water to the plants as required.

It is not compact, this ensures good aeration for the root zone. HDB is completely reusable. HDB is a suitable medium for pot culture and popular with Orchid growers.



Figure 1.9 Hydroball.

1.2 Advantages and disadvantages of soil-less culture [19]

The advantages of soil-less culture over soil culture may be summarized as follows: a) it is possible clean-indoor cultivation easily, b) digging/weeding is eliminated, c) more plants can grow per given area, d) it can enhance flavor of crops, e) plants grow quicker with increased yield, f) soil borne pests are eliminated, g) it can reduce pesticide use. The main disadvantages of soil-less culture are: a) relatively more expensive in initial investment, especially in gravel and water culture methods, b) environmental problems if (1) used nutrient solution spoils groundwater or (2) used growth material such as a rock-wool is not properly removed.

1.3 The fertilizer of plants [20]

The elements needed by plants are carbon (C), hydrogen (H) and oxygen (O), coming from air and water; nitrogen (N), phosphorous (P), sulfur (S), potassium (K), calcium (Ca) and magnesium (Mg), which exist in solution as macronutrients; iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), boron (B), molybdenum (Mo) and chlorine (Cl), which also have to be given in solution as micronutrients. Plants need

around 16 mineral nutrients for optimal growth. Three major minerals, nitrogen, phosphorus and potassium, are used by plants in large amounts. These nutrients play many different roles in plants. Here are some of their dominant functions: nitrogen promotes development of new leaves, phosphorus aids in root growth and blooming, and potassium is important for disease resistance and aids growth at extreme temperatures. Nutrients like boron, copper, cobalt, iron, manganese, molybdenum, and zinc are only present in minute quantities in plants.

1.4 Background information of heavy metals [21]

The term “heavy metal” is entrenched in the literature of environmental pollution. A heavy metal is a metallic element with a density greater than 5 g/cm^3 . After a new classification of heavy metals by Neibore and Richardson in 1980, Martin and Coughtrey introduced a list of 27 elements, which commonly encountered as environmental pollutants under the heading “heavy metals”. Heavy metal is rarely used while some terms such as trace metals, trace inorganic, microelements and micronutrients have been used as synonym one. Another name that has been used for a term of elements is “toxic metal”. This name is even less appropriate because all trace elements are toxic to living organisms when they present in excess.

The increasing levels of heavy metals or toxic metals in the environment represent a serious threat to human health, living resources and ecological systems. Mobile and soluble heavy metal species are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Heavy metal contamination exists in aqueous waste streams of many industries such as power plant, metal plating facilities, mining operations, and tanneries. The soils surrounding

many military bases are also polluted and pose a risk groundwater and surface water contamination. Some metal ions associated with these activities are cadmium ion (Cd^{2+}), lead (II) ion (Pb^{2+}), nickel (II) ion (Ni^{2+}) and mercury (II) ion (Hg^{2+}). Wastewater discharged by enterprises processing ores and concentrates of nonferrous metals are usually polluted with heavy metal ions such as Cd^{2+} , Pb^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} . Environmental contamination by metals is mainly by the emission of liquid effluents with relatively low. Therefore the removal of heavy metals from wastewaters is required prior to discharge into receiving water [22].

1.4.1 Cadmium [23]

Cadmium, an element of atomic mass 112.4 and atomic number 48, is not known to be biological essential or beneficial to human body. Cd at very low concentrations can be toxic to aquatic organisms. Cd, like other heavy metals, may exist in a number of forms in water and other environments. These include free cadmium ion, inorganic and organic complexes and cadmium associated with colloidal and particulate matters. Cadmium ion is toxic to plants, being the strongest phytotoxic element, and is considered 'priority metal' from the standpoint of a potential hazard to human health. The sources of Cd pollution are mainly from industrial origin: smelting operations, electroplating, pigments, plasticizers, batteries, tires, fertilizers, paints, tanneries, mining activities, power plant, etc. The increasing levels of Cd in the environment represent a serious threat to human health, living resources and ecological systems. The normal background levels of Cd are 0.1–1.0 mg/L. Cd can poison man and animals. It interferes with enzymes and other proteins. In livestock, it accumulates in the kidneys, spleen and liver. In humans, Cd interferes

with the metabolism of calcium and phosphorus, causing a painful bone disease. Regular consumption of plants contains 3.0 mg/L. Toxicity level of Cd in soil ranges from 3-8 mg/L.

1.4.2 Nickel [23]

Nickel is a compound that occurs in the environment at low levels. Ni is released into the air by power plants and waste incinerator. It will then deposit or precipitate after reactions with raindrops. Ni can also end up in surface water when it is a part of wastewater streams. The larger part of all Ni compounds that are released to the environment will adsorb to sediment or soil which can damage plants and high Ni concentrations in surface water can diminish the growth rates of algae.

Plants can accumulate Ni from soil. Small amounts of Ni are essential. It can be a danger to human health when the uptake is too high. An uptake of too large quantities of nickel can affect in development of lung cancer, larynx cancer and prostate cancer, birth defects, asthma, chronic bronchitis, heart disorders and skin allergy. For animals, nickel is an essential foodstuff in small amount. However, it can also be dangerous when they take up high amount. This can cause various kinds of cancer on different sites within the bodies of animals, mainly of those that live near refineries.

Ni is a constituent of most meteorites. Background levels of Ni range from 0.5–25 mg/L, and the maximum cumulative loading rate is 420 kg/ha. An average of Ni up to 0.7 mg/L is not toxic. Plants and soils containing more than 100 mg/L nickel develop symptoms of toxicity [23].

1.5 Test procedure for physical and chemical analysis

1.5.1 The pH value [24]

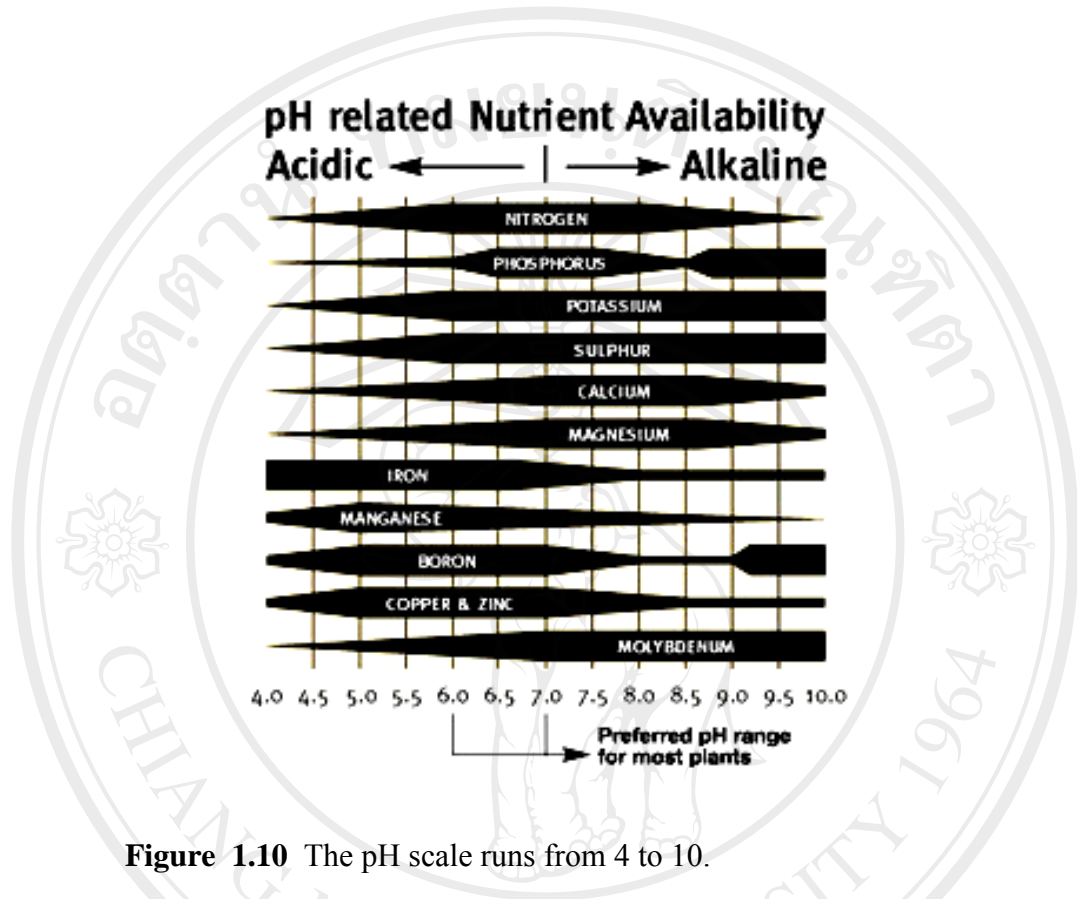


Figure 1.10 The pH scale runs from 4 to 10.

The majority of plants prefer a pH between 5.5 and 7.5, beyond this range some nutrient elements will be unavailable to the plants, the optimum pH being between 5.8 and 6.3 (Fig. 1.10). The pH of most tap waters is between 7 and 8. Monitoring the pH can ensure that the plants have the optimum nutrient mix available to them. As shown in Fig. 1.10 some materials are less available to the plant when the pH is out of this optimum range.

1.5.2 Cation exchange capacity [25]

Plant available nutrients are either held on exchange sites on ground particles by adsorption. The capacity to hold nutrients which dissolved in ground water is called the “cation exchange capacity, CEC”. Care needs to be taken that this water does not drain straight out of the container leading to a loss of nutrients and a potential source of water pollution. Such leaching can be minimized by avoiding over-watering, or using additives such as zeolite which allows the media to hold more nutrients in plant-available form (by increasing the CEC). The CEC is also a measure of the plant available nutrient exchange capacity. The CEC varies between different types of media. A high CEC is desirable as this means there will be a more even nutrient supply to the roots and less nutrients will be lost through over-watering.

1.5.3 Moisture content [26]

Moisture-based schedules rely on the accurate determination of the moisture content of drying conditions. Producers and consumers rely on the accurate determination of the final moisture content to ensure a stable product. The easiest method as recognized standards for determining the moisture content of material is the oven-dry method.

1.5.4 Surface area [27]

Adsorption of a gas on a solid surface may happen physically or chemically, depending on the materials in question and the temperature. For surface area determinations, physical adsorption is desirable. Since chemisorption involves activation energy, this is usual to be carried out at very low temperature to ensure only

physical adsorption, and to use a relatively inert gas such as nitrogen. Hence, adsorption of nitrogen, at liquid nitrogen temperatures, is a common technique. The theory of Brunauer, Emmett and Teller (BET) method (section 1.6.3.3) is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. A total surface area (S_{total}) and a specific surface area (S) are evaluated by the following equations 1.1.

$$S_{\text{total}} = \frac{(v_m N s)}{MW} \quad \text{Eq.(1.1)}$$

$$S = \frac{S_{\text{total}}}{W} \quad \text{Eq.(1.2)}$$

where N = Avogadro's number, s = adsorption cross section, MW = molecular weight of adsorbate, W = weight of sample solid, and v_m = the monolayer adsorbed gas quantity.

1.5.5 Density and water absorption [28]

The density of a material has been defined as the relationship between its mass (weight) and its volume; density = (mass/volume).

The water absorption (WA) property is measured by comparing the volume of the pores with the volume or weight of the material itself. Therefore, WA is the ratio of open pore volume to the weight of the test piece.

$$\text{WA \%} = (\text{Open pore volume/Weight})100 \quad \text{Eq.(1.3)}$$

or

$$\text{WA \%} = \{(S-D)/D\}100 \quad \text{Eq.(1.4)}$$

where the dry weight (D) = weight of the dry piece (g) and the soaked weight (S) = weight of the soaked piece (g).

1.5.6 X-ray fluorescence spectrometry [29-30]

The main principle of X-ray fluorescence (XRF) spectrometry is that X-rays of characteristic wavelength (and energy) are emitted from a sample when the sample is ionized by a stream of X-rays. The use of XRF technique for the analysis of minerals has gained since the specification of commercially available equipment has vastly improved. For normal analytical purposes the instrument is set up to determine: 1) the common elements (silicon (Si), aluminum (Al), iron (Fe), titanium (Ti), calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K)) found in most ceramic materials. 2) the trace elements (manganese (Mn), chromium (Cr), phosphorous (P), zirconium (Zr), hafnium (Hf), barium (Ba) and tungsten (W)).

Principles: The XRF principle is depicted in Fig. 1.11. An inner shell electron is excited by an incident photon in the X-ray region. During the de-excitation process, an electron is moving from a higher energy level to fill the vacancy. The energy difference between the two shells appears as an X-ray, emitted by the atom. The X-ray spectrum acquired during the above process reveals a number of characteristic peaks. The energy of the peaks leads to the identification of the elements present in the sample (qualitative analysis), while the peak intensity provides the relevant or

absolute elemental concentration (semi-quantitative or quantitative analysis). A typical XRF spectroscopic arrangement (Fig. 1.11) includes a source of primary radiation (usually a radioisotope or an X-ray tube) and an equipment for detecting the secondary X-rays.

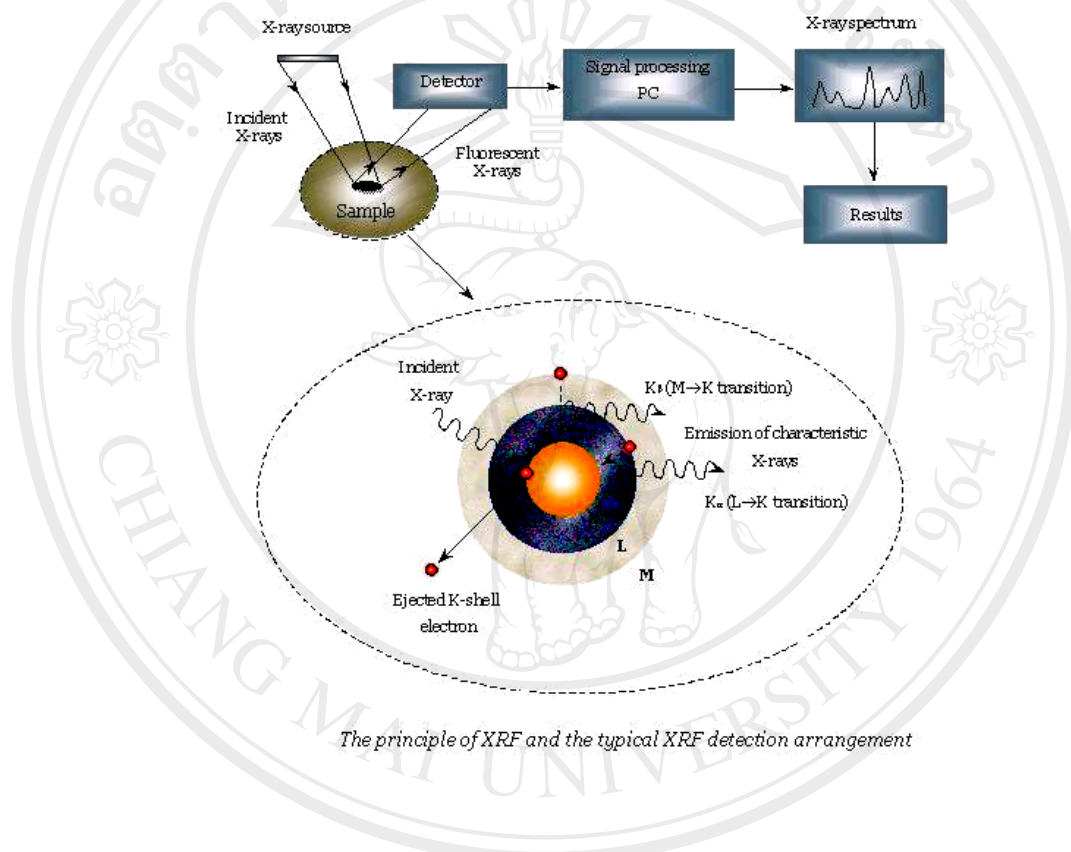


Figure 1.11 Schematic diagram of XRF and the typical XRF detection arrangement.

The instrumentation consists of a source for primary X-rays, collimators, analyzing crystal and detector.

Applications: It is one of the non-destructive methods in the elemental analysis of solid or liquid samples for major and minor constituents. Most of the elements in the periodic table, both metals and nonmetals, respond to this technique. Detection limit is between 10 to 100 mg/L.

Disadvantages: The sensitivity is affected for elements with lower atomic numbers, particularly elements with atomic number lower than 15 are difficult to analyze. The sensitivity is also limited by matrix absorption, secondary fluorescence and scattering of the particles. Instruments are often large, complicated and costly.

1.5.7 X-ray diffractometry [28]

Principles: X-ray diffraction (XRD) analysis is a nondestructive method for the structure analysis of crystals. The sample is irradiated with monochromatic X-ray light and the scattered radiation is recorded. An important field of application is the identification of crystalline fractions in powders. XRD analysis uses the property of crystal lattices to diffract monochromatic X-ray light (Fig. 1.12). This involves the occurrence of interferences of the waves scattered at successive crystal planes, which are described by Bragg's equation from the characteristic diffraction pattern that is obtained:

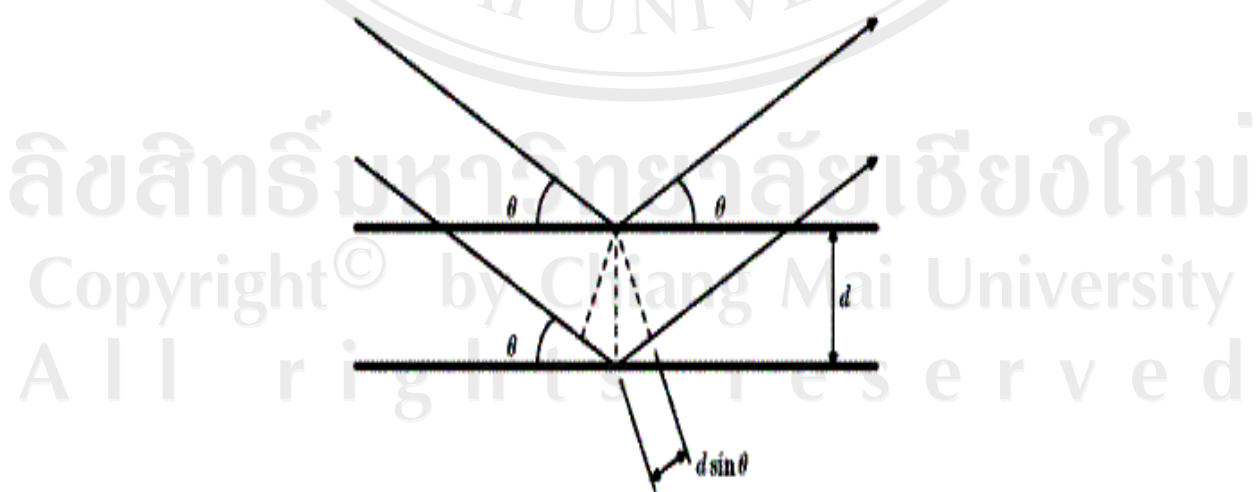


Figure 1.12 Reflection of X-ray from a crystal.

Bragg's equation; $n\lambda = 2d \sin \alpha$ ($n=1, 2, 3, \dots$) Eq. (1.5)

where λ is the wavelength, d is the lattice plane distance and α is half the diffraction angle. This relation can be used for the structure analysis of crystals. In diffractograms of powders not free from phase shift, several diffraction patterns of different crystalline fractions can be superimposed. The detector is a position-sensitive proportional counter for high-speed recording or a scintillation counter for better angular resolution. Instruments that work on this principle are called diffractometers.

Instrumentation: It consists of an X-ray tube for the source, monochromator and a rotating detector.

Applications: The diffraction of X-rays is a good tool to study the nature of crystalline substances. In crystals the ions or molecules are arranged in a well-defined position in planes in three dimensions. The impinging X-rays are reflected by each crystal plane. Since the spacing between the atoms and hence the planes can not be the same or identical for any two chemical substances, this technique provides vital information regarding the arrangement of atoms and the spacing in between them.

Sample can be of either a thin layer of crystal or in a powder form. Since, the power of a diffracted beam is dependent on the quantity of the corresponding crystalline substance, it is also possible to carry out quantitative determinations.

1.5.8 Analysis through spectroscopy at the atomic level

1.5.8.1 Atomic absorption spectroscopy [31]

Absorption: The process by which the energy of the light (in the form of photons) is transferred to atoms raising the electrons from the ground state to an excited state.

Principles: The sample is vaporized by aspiration of solution into a flame or evaporation from an electrically heated surface. At this condition where the individual atoms coexist, a beam of light is passed through them. The atoms will absorb in the visible and ultraviolet region resulting in changes in electronic structure (excited state). So the resultant light beam coming out of the sample will be missing the light in the corresponding wavelength, which is a measure of the characteristics of the sample.

Instrumentation: Sources emitting radiation characteristic of element of interest are hollow cathode lamp, flame or electrically heated furnace, monochromator, detector (photomultiplier) and recorder. The following in Fig. 1.13 is the simplified outline of the instrumentation.

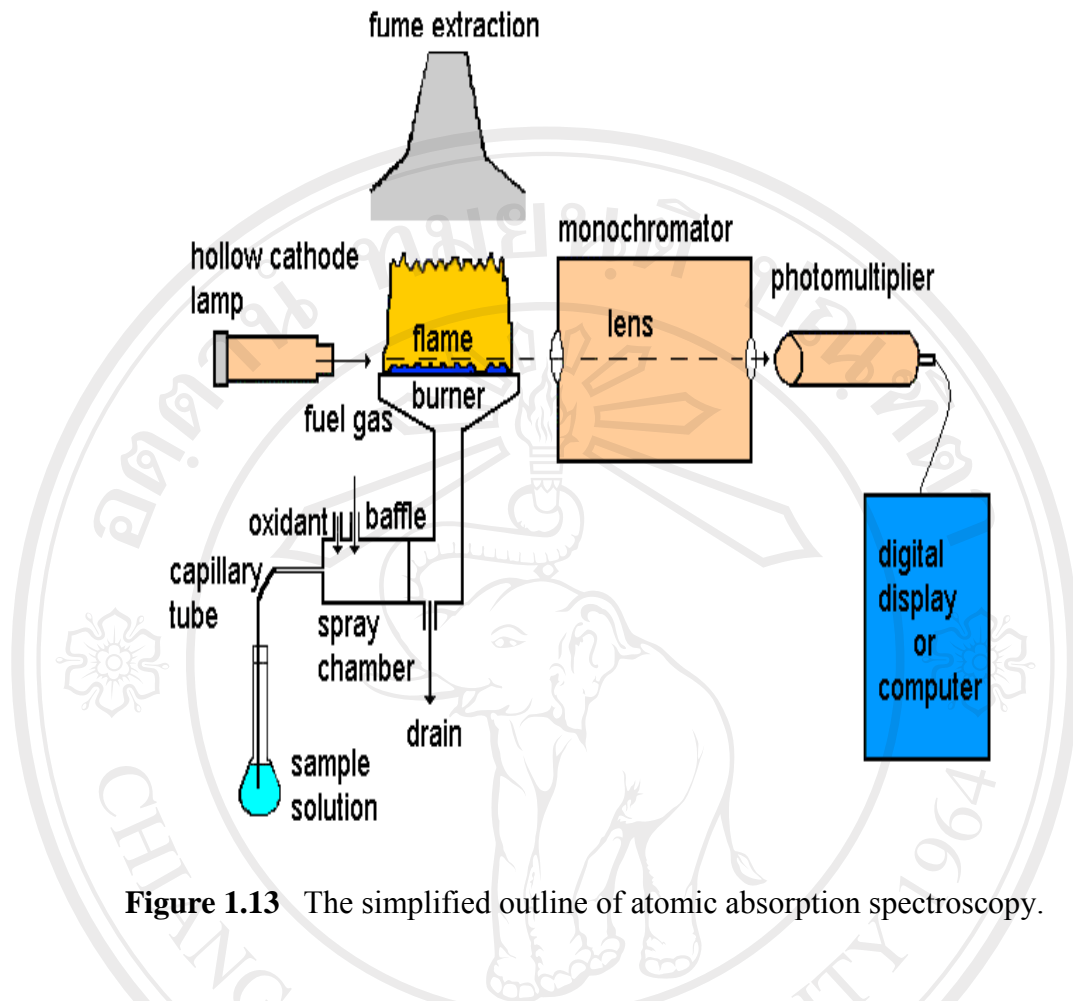


Figure 1.13 The simplified outline of atomic absorption spectroscopy.

Applications: This is the most widely used technique for the quantitative determination of metals at trace levels (0.1 to 100 mg/L). It is based on the Beer - Lambert Law using a standard curve by plotting absorbance vs. concentration of the samples taken. The usual procedure is to prepare a series of standard solutions over a concentration range suitable for the sample to be analysed. Then, the standards and the samples are separately aspirated into the flame, and the absorbances read from the instrument. The plot will give the useful linear range and the concentrations of the samples can be found out from the plot.

Disadvantages: Sample must be in solution. Individual source lamp and filters are needed for each element, since each metal has its own characteristic absorption.

1.5.8.2 Flame photometry [32]

Emission: If the substances (atoms) are heated to high temperatures (in a flame or in an electric discharge) the electrons are excited to higher energy levels. Later, they relax to the ground state with the emission of radiation, the magnitude of which is more or less equivalent to the absorbed energy.

Principles: Flame Photometry is the technique which measures the atoms excited by a flame and not by light source as in the atomic absorption case. After excitation, atoms will readily lose the gained energy and revert back to the ground state and the emission occurs. The emission light is measured. The wavelengths of the emitted light will almost be similar as those that were absorbed in the atomic absorption, since exactly the same energy transitions occur.

Instrumentation: A simple flame photometer consists of burner, nebulizer, monochromator, detector and recorder.

Applications: It is used exclusively in the quantitative determination of metals in solution, especially alkali and alkaline earth in the given samples. The principle is like that described for atomic absorption. Qualitative determination is also possible as each element emits its own characteristic line spectrum.

Disadvantages: Intensity of emission is very sensitive to changes in flame temperature.

1.5.9 Ultra violet - visible spectroscopy [33]

Principles: It involves the absorption of electromagnetic radiation by the substances in the visible and ultraviolet regions of the spectrum. This will result in changes in the electronic structure of ions and molecules.

Instrumentation: It consists of a dual light source (tungsten lamp for visual range measurements and deuterium lamp for measurements at ultra-violet regions), a grating monochromator, photo detector, mirrors and glass or quartz cells. For measurements to be made under visible region, both glass and quartz cells can be used. For the measurements under ultra-violet region, only quartz cell should be used, since, glass cells absorb ultra-violet rays. There are two types of instruments for this technique as single beam and double beam spectrophotometers. However, nowadays, double beam spectrophotometers are widely used.

Applications: It is the most widely used technique for quantitative trace analysis, for the Beer-Lambert law is applied. Sometimes it is used in conjunction with other techniques in the identification and structural analysis of organic materials. For qualitative analysis the so-called “molecular absorption spectrum” is obtained, which exactly tells the nature of the compound-since no two compounds can have the same absorption and hence the same spectrum.

Disadvantages: Samples should be in solution. Mixture of substances poses difficulties to analyse and requires prior separation. Interference sometime makes the measurement difficult, but these disturbances are quite common with these types of techniques.

1.5.10 Scanning electron microscopy [34]

The techniques described here are not for the simple, ordinary optical microscopes. Optical microscopes are used for the examination and characterization of matter at enhanced magnification using visible light. The information is obtained by light transmitted or reflected from matter. The methods explained below are about

the advanced microanalysis of surfaces to nano-scale levels through specialised techniques of the kind of their own.

Principles: In this technique, an electron beam is focused onto the sample surface kept in a vacuum by electro-magnetic lenses. The scattered electron from the sample is then fed to the detector and then to a cathode ray tube through an amplifier, where the images are formed, which gives the information on the surface of the sample.

Instrumentation: The instrumentation is very large and comprises of heated filament as source of electron beam, condenser lenses, aperture, evacuated chamber for placing the sample, electron detector, amplifier, etc.

Applications: Scanning electron microscopy (SEM) has been applied to the surface studies of metals, ceramics, polymers, composites and biological materials for both topography as well as compositional analysis. An extension (or sometimes conjunction to SEM) of this technique is Electron Probe Micro Analysis (EPMA), where the emission of X-rays, from the sample surface, is studied upon exposure to a beam of high energy electrons. Depending on the type of detectors used this method is classified into two as: Energy Dispersive Spectrometry (EDS) and Wavelength Dispersive Spectrometry (WDS). This technique is used extensively in the analysis of metallic and ceramic inclusions, inclusions in polymeric materials, and diffusion profiles in electronic components.

Disadvantages: The instrumentation is complicated, expensive and needs high vacuum for the optimum performance.

1.6 Absorption and adsorption [35]

Sorption reactions generally occur over a short period of time, however if the adsorbed contaminant begins to be incorporated into the structure of the sorbent, a slow occurring reaction, known as absorption, begins to take place. To be more precise, the difference between adsorption and absorption is that adsorption is the attraction between the outer surface of a solid particle and a contaminant, whereas absorption is the uptake of the contaminant into the physical structure of the solid. Figure 1.14 shows the primary differences between intraparticle absorption versus surface adsorption. The main difference is that some contaminant particles are attracted to the outer surface of the soil particle, while another has been actually incorporated into the particle's structure.

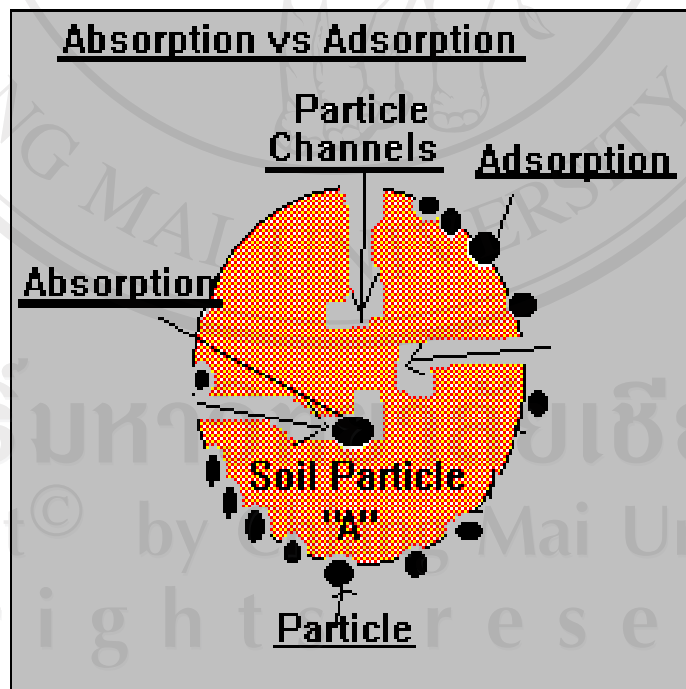


Figure 1.14 Absorption and adsorption.

Adsorption is a term used to describe the process by which material accumulates at the interface between two phases. These phases can be liquid-liquid, liquid-solid, gas-liquid, and gas-solid. In this process, the adsorbing phase is termed adsorbent, whereas the substance being adsorbed is called adsorbate. Adsorption can be applied in both gaseous and liquid separations. Adsorption of a material occurs at the surface since it reduces the imbalance of attractive forces, and, therefore, the surface free energy of the heterogeneous system. The adsorption using the batch-type techniques is expressed in the form of equilibrium concentration, C_e , versus adsorbed concentration, q_e , of the solute. The adsorbed amount, q_e , was calculated using the following equation (1.6):

$$q_e = \{(C_0 - C_e)V_e\} / W \quad \text{Eq. (1.6)}$$

where C_0 = initial concentration of the solute (mg/L), C_e = equilibrium concentration or final concentration of the solute (mg/L), V = volume of solution (mL) and W = mass of planting materials expressed on an oven-dried basis (g).

1.6.1 Physical adsorption and chemical adsorption [36]

Adsorption is divided into the two sub-categories of physical adsorption (physisorption) or van der Waals adsorption and chemical adsorption (chemisorption). The adsorption process can be determined whether chemical bonds are formed during the process. Physisorption is applicable to all adsorbate-adsorbent systems under the suitable conditions of pressure and temperature whereas chemisorption may only occur if the system is capable of making a chemical bond.

1.6.1.1 Physical adsorption

The process is a dynamic one where an equilibrium state exists with molecules and the interaction between the adsorbate and adsorbent. No chemical bonds are formed during physical adsorption; attraction between the adsorbate and adsorbent exists by the formation of intermolecular electrostatic, such as London dispersion forces, or van der Waals forces from induced dipole-dipole interactions, or may be dependent on the physical configuration of the adsorbent such as the porosity of activated carbons. Dispersion forces are the result of rapid fluctuations in the electronic density of one adsorbent molecule inducing an electrical moment in a second atom. If the adsorbate possesses a permanent dipole, or even a multipole, then additional interactions may occur, as charge distributions are induced in the adsorbent and interactions of these moments with any permanent field of the solid. The process is a very general one and is analogous with that of condensation. Physisorption occurs to varying extents for all adsorbates, gases and vapors, with all adsorbing solids and the effect increases with decreasing temperature or increasing pressure. Physical adsorption is based on certain basic considerations and adsorption on a heterogeneous surface, that is a surface on which the sites are different, occurs at the sites of highest adsorption potential. The process of physical adsorption into the microporous structure of activated carbon follows the theory of Dubinin. The mechanism of adsorption is dependent upon the size of the admolecule in comparison with the pore width due to the energetic interactions between the chosen adsorbate and the pores. Admolecules initially adsorb into the pores with the highest energy, ignoring activated diffusion effects, then adsorption proceeds via filling of progressively larger, or decreasing energy, porosity. Some pores are capable of accommodating two or three

ad molecules and, therefore, may undergo co-operative adsorption effects by reducing the volume element thus increasing the energy and adsorptive potential of the pore. The process of adsorption is always exothermic due to the increased ordering of the adsorbate on the adsorbent surface, reducing the entropy, as: $\Delta G = \Delta H - T\Delta S$. Thus the amount adsorbed should decrease with increasing temperature as a reduction in the thermal energy supplied to the process, by Le Chatelier's principle, favors the exothermic process of adsorption increasing the equilibrium uptake, except in the case of activated diffusion. It has been proposed by Lamond and Marsh, by the interpretation of data for physical adsorption of nitrogen on both polar and non-polar surfaces that physical adsorption is independent of the surface chemistry of the adsorbent.

1.6.1.2 Chemical adsorption

Chemisorption involves the transfer of electrons between the adsorbent and the adsorbate with the formation of chemical bonds, by chemical reaction, between the two species causing adhesion of the adsorbate molecules. Chemical adsorption is far less common than physical adsorption and due to the chemical bonds formed regeneration of the adsorbent for subsequent re-use is often difficult or impossible. Due to the fact that chemical bonds are formed during the adsorption process, desorption of the adsorbed phase may yield products which are chemically different to the original adsorbate. Two phenomena are observed; physical adsorption and chemical adsorption. Nevertheless, physical adsorption differs from chemisorption according to the parameters listed in the Table 1.1.

Table 1.1 Parameters of physical adsorption and chemical adsorption.

Parameter	Physical adsorption	Chemical adsorption
Heat of adsorption / kJ mol^{-1}	20 - 40 heats of liquefaction	> 80 bulk-phase chemical reactions
Rate of adsorption (at 273K)	Fast	Slow
Temperature dependence of uptake (with Increasing T)	Decrease	Increase
Desorption	Easy- by reduced pressure or increased temperature	Difficult - high temperature required to break bonds
Desorbed species	Adsorbate unchanged	May be different to original adsorptive
Specificity	Non-specific	Very Specific
Monolayer coverage	Mono or multilayer condition dependent	Monolayer

1.6.2 Classification of adsorption isotherm

Adsorption isotherms should conventionally be plotted on the basis of relative pressure, (x-axis) versus amount adsorbed expressed as a molar quantity (y-axis) in mmol g^{-1} , to allow comparisons to be made. The six IUPAC standard adsorption isotherms are shown in Fig. 1.15 because the systems demonstrate different gas/solid interactions.

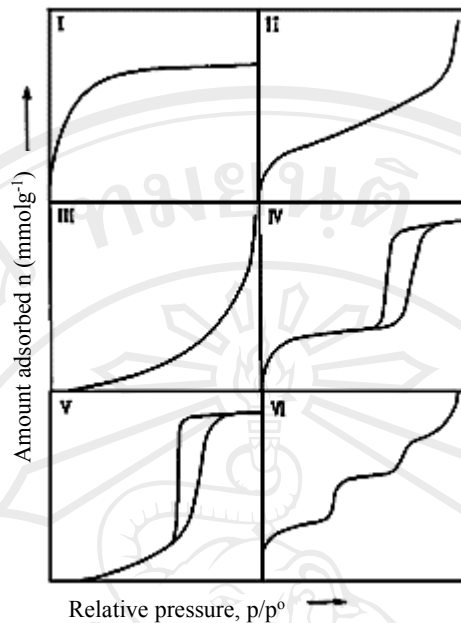


Figure 1.15 Six types of adsorption isotherms.

The Type I isotherm is typical of monolayer adsorption. This type of curve is obtained by low temperature adsorption. The chemisorption phenomena frequently produce this curve. Type II is the most frequently encountered adsorption isotherm and is referred to as the sigmoid or S-shape isotherm. The first portion of the curve up to relative pressure corresponds to monolayer. This is followed by a multilayer region.

Type III and type IV are typical of vapor adsorption (i.e. water vapor on hydrophobic materials). Type VI and V feature a hysteresis loop generated by the capillary condensation of the adsorbate in the mesopores of the solid. Finally, the rare type VI step-like isotherm is shown by gas adsorbed on special adsorbent.

1.6.3 Isotherm equations

1.6.3.1 Langmuir isotherm

The adsorption equation was developed by Langmuir in 1916. Langmuir equation was one of the first and most important equations based on theory. In the assumptions of Langmuir isotherm, the energy of adsorption is constant, and the number of binding sites is finite. The equation for the Langmuir isotherm is shown here:

$$q_e = \frac{q_0 b C_e}{1 + b C_e} \quad \text{Eq. (1.7)}$$

where q_0 = saturation limit and b = a temperature dependent equilibrium constant. The constant q_0 corresponds to the surface concentration at monolayer coverage and represents the maximum value of q_e that can be achieved as the equilibrium concentration C_e is increased. The constant b is related to the energy of adsorption and increases as the strength of the adsorption bond increases. In order to evaluate the Langmuir constants, a linear form of the Langmuir equation is used:

$$\frac{C_e}{q_e} = \frac{1}{b q_0} + \frac{1}{q_0} C_e \quad \text{Eq. (1.8)}$$

A plot of C_e/q_e versus C_e will yield a straight line for data which fits the Langmuir expression. Hence, from the gradient, $1/q_0$, and intercept, $1/bq_0$, the Langmuir constants can be calculated.

1.6.3.2 Freundlich isotherm

This isotherm is an empirical expression and has no physical basis, hence the equilibrium relationship proposed by Freundlich is only valid when the adsorption is a purely physical process without any change in the configuration of the molecules in the adsorbed state. The equilibrium of this model is as follows in equation 1.9.

$$q_e = K_F * C_e^{1/n} \quad \text{Eq. (1.9)}$$

where q_e = equilibrium adsorbed amount on the adsorbent, C_e = equilibrium concentration, K_F and n = empirical constants depending on the nature of adsorbent and adsorbate.

The constant K_F is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption, i.e. the mechanism of adsorption. The constants can be obtained by line arising in equation 1.10.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{Eq. (1.10)}$$

1.6.3.3 BET isotherm [37]

The theory of Brunauer, Emmett and Teller (BET) is a well-known rule for the physical adsorption of gas molecules on a solid surface. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published an article about the BET

theory in a journal for the first time; BET consists of the first initials of their family names.

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is expressed by equation 1.11:

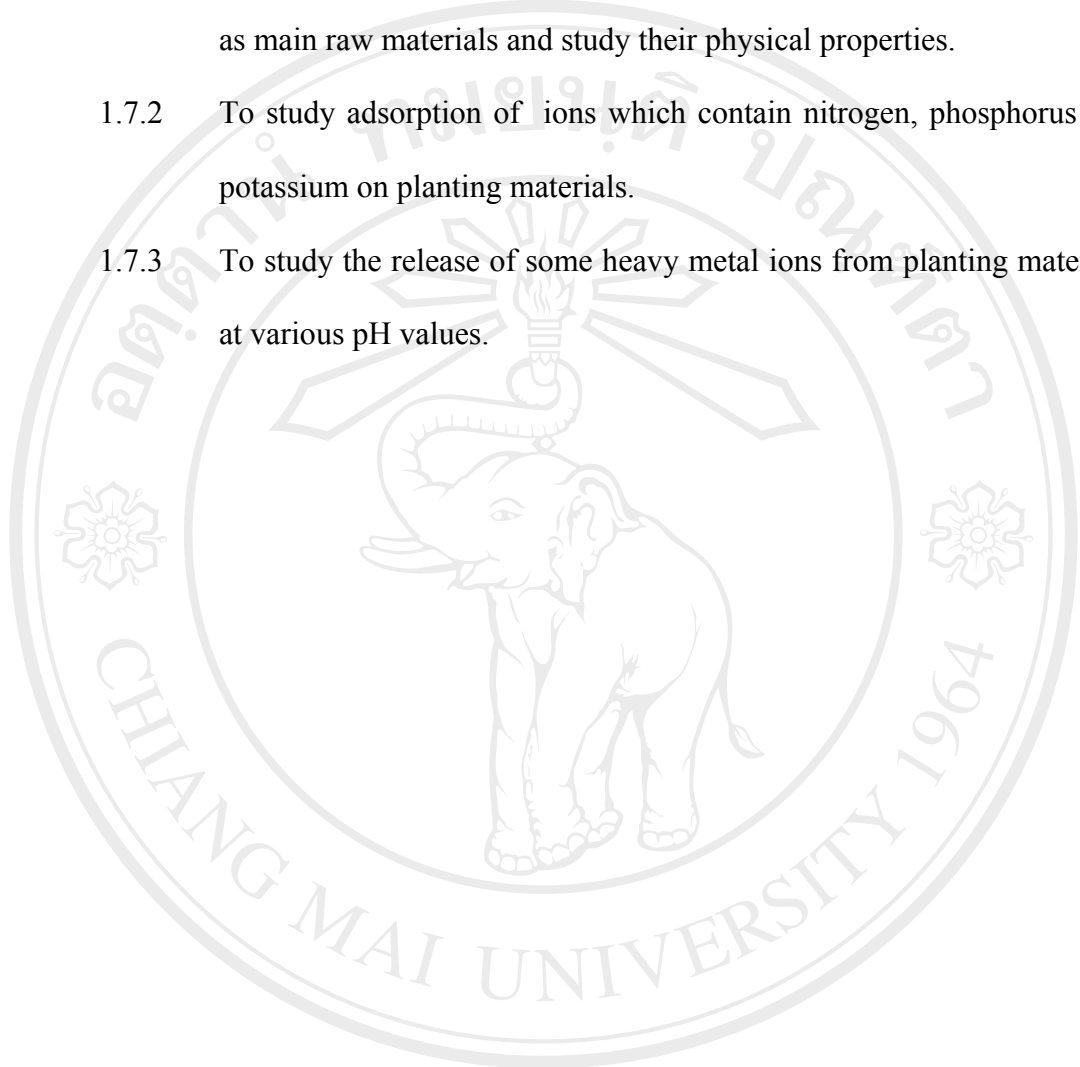
$$\frac{1}{v[(P_0/P) - 1]} = \frac{1}{v_m c} \left(\frac{P}{P_0} \right) + \frac{1}{v_m} \quad \text{Eq. (1.11)}$$

where P and P_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity (for example, in volume units), v_m is the monolayer adsorbed gas quantity and c is the BET constant.

Equation (1.11) is an adsorption isotherm and can be plotted as a straight line with $1/v[(P_0/P) - 1]$ on the y-axis and P/P_0 on the x-axis according to experimental results. The value of the slope and the y-intercept of the line are used to calculate the monolayer adsorbed gas quantity v_m and the BET constant c .

1.7 Research Objectives

- 1.7.1 To produce planting material using bottom ash and FGD gypsum as main raw materials and study their physical properties.
- 1.7.2 To study adsorption of ions which contain nitrogen, phosphorus and potassium on planting materials.
- 1.7.3 To study the release of some heavy metal ions from planting materials at various pH values.



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