

CHAPTER 1

Introduction

The industrial revolution provides the benefits for human in terms of productive capability, mobility, convenience, cheap consumer goods, and profits. The more the increase in human population, the more the growth of the industries. Rapid growth of manufacturing industries is resulting in the benefits as well as the environmental problems. Lack of effective policies and poor enforcement drive allow many industries to neglect the laws made by the pollution control board which resulted in the mass scale pollution. The inefficiency in disposal of waste is led to the pollution problems. Long term exposure makes the issue of industrial pollution into a severe one. The industrial pollution takes on many faces. It contaminates many sources of drinking water, releases unwanted toxins into the air and reduces the quality of soil.

One of the main reasons behind the problems is the production and the utilization of heavy metals in the industrial activities such as metal smelting and refining, pigments, electroplating, metallurgical alloying, battery manufacturing, fertilizers, and chemical industries. The heavy metals commonly used in the industries including cadmium, zinc, lead, mercury, manganese, chromium, nickel, and copper. Some of them are highly toxic even at low concentration. The introduction of the heavy metals into the environment can be occurred in several pathways, for example, the heavy metals may contaminate in the water during the industrial process. Most industries require large amounts of water for their work. When involved in a series of processes, water comes into contact with heavy metals, later; they are released to the environment along with the wastewater. This can be harmful to aquatic life, animals and human. Most of the heavy metals ions can dissolve in water and accumulate in the environment. Furthermore, they cannot be eliminated by the natural processes. The heavy metals can maintain in the sediments of water sources for many years and introduce to the human via food chain. Heavy metals can enter body and produce the adverse biological effects on survival, activity, growth, metabolism, and

reproduction of organisms [1]. Exposure of heavy metals leads to the acute and/or chronic diseases in human. In order to minimize the risk of the illness and the death, the level of heavy metals in wastewater should be reduced to meet the wastewater quality standards.

1.1 Heavy metals

Heavy metals are defined as metals that have the relatively high density, atomic weight, or atomic number. A density of more than 5 g/cm³ is sometimes quoted as a commonly used criterion. Heavy metals differ widely in their chemical properties. They have been used in many different areas for thousands of years. These metals occur naturally in the earth crust. Although heavy metals are naturally occurring elements that are found throughout the earth's crust, most environmental contamination and human exposure result from the anthropogenic activities such as mining and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal-containing compounds. Many of the heavy metals such as lead, cadmium, mercury, and arsenic, are high toxic at low concentration. Some heavy metals, such as cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, nickel, and zinc, are essential elements for living things. However, the oversupply of these essential elements results in a variety of diseases or syndromes.

In this research, heavy metals of interest are cadmium and zinc. Cadmium and zinc are among the metals that generally used in the industries. Cadmium also occurs naturally in ores together with zinc. Viewed from the standard point of environmental pollution, cadmium and zinc are classified as the very toxic and relatively accessible metals [2].

1.1.1) Cadmium

Cadmium is the element with symbol Cd, atomic number of 48, and atomic weight of 112.414 g/mol. The major sources for cadmium contamination are process of ores, mining, and various industrial activities such as alloy manufacturing, electroplating, pigments, fertilizers, Ni-Cd batteries, and plastics. Cadmium is one of the most toxic metals. Free cadmium ions are highly toxic to plants, animals and human. It is classified as human carcinogen. Cadmium accumulates in humans, causing erythrocyte destruction, nausea, salivation, diarrhea, muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity. It can cause serious damage to the kidneys and bones

which is known as “itai-itai” disease. The Pollution Control Department (PCD) of Thailand recommended the maximum acceptable concentration of cadmium in the industrial discharge as 0.03 mg/L.

1.1.2) Zinc

Zinc is the element with symbol Zn, atomic number of 30, and atomic weight of 65.38 g/mol. Zinc is one of the metals which are usually found in industrial wastewaters. It is widely used in metallurgy, as a constituent of brass and bronze, and in galvanizing, as a coating used to inhibit the corrosion of steel. Other sources of zinc contamination are mining, smelting, battery manufacture and pigment manufacture. Zinc is essential in human, plant, and animal metabolism. Even though zinc is an essential requirement for a healthy body, excess zinc can be harmful, and cause zinc toxicity. Compared to cadmium, zinc has low human toxicity. For human, zinc toxicity can occur in both acute and chronic forms. Acute adverse effects of high zinc intake include nausea, vomiting, abdominal cramps, diarrhea, and headaches. Chronic effects include low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins [3]. The Pollution Control Department (PCD) of Thailand recommended the maximum acceptable concentration of zinc in the industrial discharge as 5.0 mg/L.

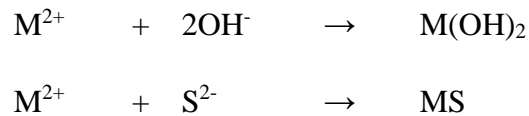
1.2. Wastewater treatment [4-9]

Since the excessive levels of heavy metals in wastewater can be hazardous, the removal of heavy metals from wastewater is essentially required. The removal of heavy metals from the wastewater can be performed by several techniques, for example, precipitation, electrochemical treatment, photocatalysis, ion exchange, membrane filtration, and adsorption. Each technique differs in its concept and has its own advantages and disadvantages.

1.2.1) Precipitation

Precipitation is an effective process and widely used in the wastewater treatment in the industry because it is relatively simple and inexpensive to operate. In the processes, the chemicals are used for the precipitation of metal ions. Generally, the two main methods currently in use are hydroxide precipitation and sulfide precipitation. Both

methods involve a reaction of the metal cation with either OH^- or S^{2-} to form the corresponding insoluble metal hydroxide or sulfide, as shown below.



The most commonly used chemicals for the precipitation are alum, sodium bicarbonates, ferric chloride, ferrous sulfate and lime. The solubility of precipitated metal compounds is the key to the success of this method. If the metal ions can form the insoluble compound, then the compound can be removed via clarification and filtration. The main controlling factors for the precipitation process are pH and temperature.

1.2.2) Electrochemical treatment

Electrochemical treatment has been in use for water production or wastewater treatment. It is the technique in which metal ions are deposited on the surface of the electrodes by electrochemical redox reaction and the metals can be recovered in the elemental metal state. The factors that control the process are pH, temperature, amount of current applied, and contact time. Electrochemical technique has been rarely used at a commercial level for wastewater treatment because of the relatively large capital investment and the expensive electricity supply. However, its applications include the treatment of some industrial effluents especially those enriched with metal ions such as the metal surface finishing industry, and the printed circuit board manufacturing industry. The advantages of this technique comprise the further utilization of the deposited metal ions without any waste management problems.

1.2.3) Photocatalysis

Photocatalysis technique is an alternative method for the treatment of wastewater. Although presently many treatment methods are being used, most of them do not completely destroy the pollutants but only offer phase transfer or partial degradation of the pollutants. In the photocatalytic processes, a semiconductor photocatalyst is activated with ultraviolet (UV) irradiation. The activated photocatalyst promotes the formation of hydroxyl radicals, which in turn completely degrades the pollutants. Photocatalysis can be used to break down a wide variety of organic materials, organic acids, estrogens, pesticides, dyes, crude oil, microbes, inorganic molecules, and

in combination with precipitation or filtration, can also remove metals (such as mercury). There are several potential photocatalysts, but the most promising and widespread substance is titanium dioxide (TiO₂) and zinc oxide (ZnO).

1.2.4) Ion-exchange

Ion-exchange is the process which metal ions presented in the wastewater are exchanged with the ions from a solid material called an ion-exchanger. The ion exchangers are resins of natural or synthetic origin having active sites on their surfaces. There are 2 types of ion-exchanger including cation exchanger and anion exchanger. Cation exchange resins can remove most positively charged ions in wastewater such as metal ions (iron, lead, radium, barium, aluminum, etc.). Anionic exchange resins can remove nitrate, sulfate, and other negatively charged atoms. The most commonly used ion exchangers are sodium silicates, zeolites, polystyrene sulfonic acid, and acrylic and metha-acrylic resins. Ion-exchange method has high treatment capacity, high removal efficiency and fast kinetics. It is a reversible process and requires low energy contents. However, the resins can very sensitive to fouling caused by presence of organic matter in the untreated water. The uptake of heavy metal ions by ion-exchange resins is affected by certain variables such as pH, temperature, initial metal concentration and contact time.

1.2.5) Membrane filtration

Membrane filtration technologies are the great process for heavy metal removal with high efficiency, and easy operation. There are different types of membrane filtration including ultrafiltration, reverse osmosis, nanofiltration and electrodialysis. The ultrafiltration uses permeable membrane to separate heavy metals, macromolecules and suspended solids from solution on the basis of the pore size and molecular weight of the separating compounds. The reverse osmosis process uses a semi-permeable membrane, allowing the fluid that is being purified to pass through it, while rejecting the contaminants. The nanofiltration is the intermediate process between the ultrafiltration and the reverse osmosis. The electrodialysis is another membrane process for the separation of ions across charged membranes from one solution to another using an electric field as the driving force.

1.2.6) Adsorption

Adsorption is the wastewater treatment process in which the atoms, ions, or molecules of contaminants are removed from the wastewater by their binding to the surface of adsorbent. This process has been applied in the wastewater treatment since long time ago. In the adsorption technique, there are some parameters, such as pH, temperature, concentration of contaminants, contact time, surface area and particle size of the adsorbent, contaminant-adsorbent interaction, and nature of adsorbents and the contaminants that affect the adsorption efficiency. Huang *et al.* [10] studied the cadmium adsorption on the oxidized granular activated carbon. It was found that the cadmium adsorption capacity of oxidized granular activated carbon enlarged with an increase in pH, and reduced with an increase in ionic strength. The adsorption equilibrium capacity decrease with the rise in temperature from 293 to 308 K. Mihajlovic *et al.* [11] investigated the removal of lead, cadmium, and zinc ions from aqueous solutions by natural and Fe(III)-modified zeolite. The adsorption capacities of both zeolites increased with the increasing temperature. Their study revealed that the adsorption capacity of the Fe(III)-modified zeolite is much higher than that of natural zeolite for all investigated ions owing to the higher: specific adsorption caused by the new functional groups formed on the zeolite surface, ion exchange due to the presence of easily exchangeable ions, and hydroxide precipitation caused by higher point of zero charge of the Fe(III)-modified zeolite compared to natural zeolite. According to the results from the literatures, it is evident that the adsorption process is influenced by several parameters. Therefore, the study of these factors is important for the design of the effective adsorption process.

The comparison of wastewater treatment techniques is shown in Table 1.1. Some techniques are expensive and/or complicate for large scale applications. Adsorption is considered as an effective process for metal removal. It has been found to be superior compared to other techniques in terms of initial cost, flexibility and simplicity of design, and ease of operation. Thus, the adsorption process was applied in this research.

Table 1.1 Comparison of techniques for removal of heavy metals

Techniques	Advantages	Disadvantages
Precipitation	<ul style="list-style-type: none"> ▪ Simplicity of process and equipment ▪ Inexpensive ▪ Convenient and safe operations 	<ul style="list-style-type: none"> ▪ Require large amount of chemicals ▪ Sludge generation ▪ Slow metal precipitation and poor settling
Electrochemical methods	<ul style="list-style-type: none"> ▪ Metal selective ▪ No chemicals consumption ▪ Pure metals can be achieved 	<ul style="list-style-type: none"> ▪ Expensive ▪ Frequently replaced the electrodes
Photocatalysis	<ul style="list-style-type: none"> ▪ Less harmful by products ▪ High efficiency 	<ul style="list-style-type: none"> ▪ Long duration time ▪ Limited applications
Ion-exchange	<ul style="list-style-type: none"> ▪ Metal selective ▪ Regeneration of materials 	<ul style="list-style-type: none"> ▪ Expensive ▪ Easily fouled by organic or others solid from wastewater ▪ Highly sensitive to pH of the solutions
Membrane filtration	<ul style="list-style-type: none"> ▪ Metal selective ▪ High efficiency ▪ Less chemical consumption ▪ Less solid waste production 	<ul style="list-style-type: none"> ▪ Expensive ▪ Low flow rates
Adsorption	<ul style="list-style-type: none"> ▪ High efficiency ▪ Simplicity of process and equipment ▪ Inexpensive 	<ul style="list-style-type: none"> ▪ Low selectivity ▪ Production of wastes

Adsorption process occurs on the surfaces because of attractive forces of the atoms and/or molecules that make up the surface. According to the properties of attractive forces, the adsorption can be classified into two types: physical adsorption and chemical adsorption. Particles removed by the physical adsorption are held to the adsorbent by relatively weak van der Waal's forces which do not involve a significant change in the electronic orbital patterns of the species. The energy of interaction between the adsorbate and adsorbent has the same order of magnitude as, but is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed. Physically adsorbed particles are assumed to be free to move on the surface of the adsorbent, and adsorption is assumed to be multilayered with each new layer of molecules forming on top of previously adsorbed layers. Chemical adsorption occurs as a result of a chemical reaction between the adsorbate and adsorbent. The general features which distinguish physical adsorption and chemical adsorption are summarized in Table 1.2. Most of adsorption process in wastewater treatment are neither purely physical nor chemical process but are a combination of the two. It is difficult to distinguish between these two processes.

Table 1.2 The differences between physical adsorption and chemical adsorption

Physical adsorption	Chemical adsorption
<ul style="list-style-type: none"> ▪ The forces operating are weak van der Waal's forces. 	<ul style="list-style-type: none"> ▪ The forces operating are similar to those of a chemical bond.
<ul style="list-style-type: none"> ▪ Low heat of adsorption 	<ul style="list-style-type: none"> ▪ High heat of adsorption
<ul style="list-style-type: none"> ▪ Evidence for the perturbation of the electronic states of adsorbent and adsorbate is minimal. 	<ul style="list-style-type: none"> ▪ Changes in the electronic state may be detectable by suitable physical means.
<ul style="list-style-type: none"> ▪ Non specific 	<ul style="list-style-type: none"> ▪ Highly specific
<ul style="list-style-type: none"> ▪ Monolayer or multilayer 	<ul style="list-style-type: none"> ▪ Monolayer only
<ul style="list-style-type: none"> ▪ The process is reversible. 	<ul style="list-style-type: none"> ▪ The process is irreversible.
<ul style="list-style-type: none"> ▪ It does not involve activation energy. 	<ul style="list-style-type: none"> ▪ It often involves activation energy.

Removal of heavy metals from aqueous solutions by the adsorption procedure has been extensively investigated. The adsorbent plays an important part in the adsorption process. Different kinds of adsorbents are used for wastewater treatment such as activated carbon, zeolite, clay, algae, and peat. The removal efficiency of adsorbents depends on the characteristics of adsorbents. The properties of adsorbent should be high capacity, cheap, easily available, selectivity, and can be regenerated. Recently, attention has been focused on the utilization of natural materials, which are the waste from agricultures and industries as adsorbent. These materials are available in large quantity and the cost is relatively low. The adsorption efficiency of natural materials such as rice husk, peat, tea-industrial waste, fly ash, bottom ash, cellulose, and banana peel had been investigated for the removal of metal from aqueous solutions [12-13].

1.3 Leonardite

Leonardite is a low rank coal which can be naturally found near the surface of lignite coal. It has brown or black color. As compared to lignite, leonardite contains higher oxygen content (leonardite, 28-29 percent; lignite 19-20 percent) and less compact structure [14]. Leonardite possesses low fuel ratios and heating values, which make it unsuitable as fuels. It was first discovered by Leonard, a geologist, in North Dakota. The formation of leonardite can be occurred by 2 pathways [15]:

(1) *Coalification process together with the decomposition and the oxidation:* Coalification is the formation of coal from plant materials via biochemical and geological process. The process starts with the decomposition of dead plant materials under the water (swamps, bogs, marshes, etc.). Over time, the organic materials began to lose oxygen and were transformed into coal under heat and pressure. Different kind of coals were obtained depend on the degree of coalification. Leonardite is the part of these sediments which were not buried deep enough to undergo the complete transformation to coal [16].

(2) *Weathering and oxidation:* leonardite was formed by the weathering and the oxidation of peat, lignite, and sub-bituminous at the sub crop and out crop.

In Thailand, there are several sources of leonardite such as Lamphun, Lampang, Phayao, and Krabi. However, the major source of leonardite is Mae Moh mine in Lampang which is located in the northern region of Thailand. Mae Moh mine has supplied

lignite coal to Mae Moh power plant for generation of electricity. In the mining process, the overburden (i.e., soil, rock, and leonardite) is removed until the lignite coal seam is exposed. The Mae Moh mine supplies 13,536 tons of lignite a day to the power plant [17]. Thus, huge amounts of leonardite are obtained. Large deposits of leonardite were left on the site. Leonardite has a very low economic value. Although leonardite cannot be used as fuels it can be used as soil-conditioner, dispersant and viscosity control in oil-well drilling mud, bio-catalyst, and bio-stimulant for plants, as stabilizer for ion-exchange resin in water treatment, and for remediation of polluted soil. Leonardite is the source of humic substances which are the complex organic molecules that contain various functionalities such as carboxylic acids, phenols and other alcohols, ketones/quinines, aldehydes, amino- and nitro groups, and sulfur containing entities. Humic substances can be subdivided into three major fractions: humic acids, fulvic acids, and humins [18].

- *Humic acids* are the medium-sized molecules with the molecular weight in the range of 10,000 to 100,000. They are soluble in alkali solution but not soluble in acidic solution. Precipitation of humic acids occurs at $\text{pH} < 2$. Their molecules consist of many acids containing the functional groups. The functional groups that contribute most to the surface charge are carboxylic and phenolic groups. On average, 35% of humic acid molecules are aromatic ring, while the remaining components are aliphatic molecules. The functional groups in humic acids play an important role in ion exchange, metal ion binding, and metal ion chelating. The model structure of humic acid is shown in Fig. 1.1.
- *Fulvic acids* are the smallest of these three fractions. Their molecular weights range from 1,000 to 10,000. They are soluble in water at all pH conditions. Fulvic acids have the higher function group density and higher acidity than humic acids. They have many carboxyl and hydroxyl groups but less in aromatic and phenols as compared to humic acids. The model structure of fuvic acid is shown in Fig. 1.2.
- *Humins* are the large molecules with the molecular weight of 100,000 to 10,000,000. They are not soluble in water, alkali solutions, and acidic solutions. The benefits of humins are to increase water-holding capacity, to improve soil structure, and to function as a cation exchange system.

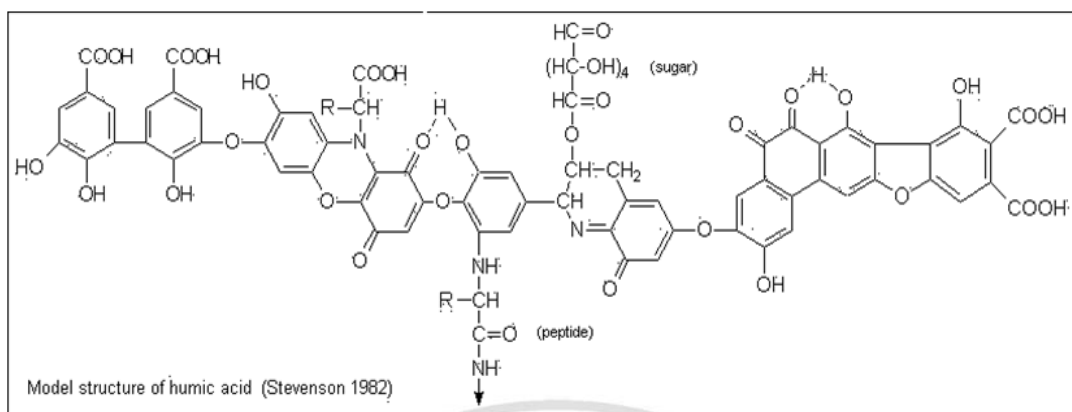


Fig. 1.1 Model structure of humic acid [19]

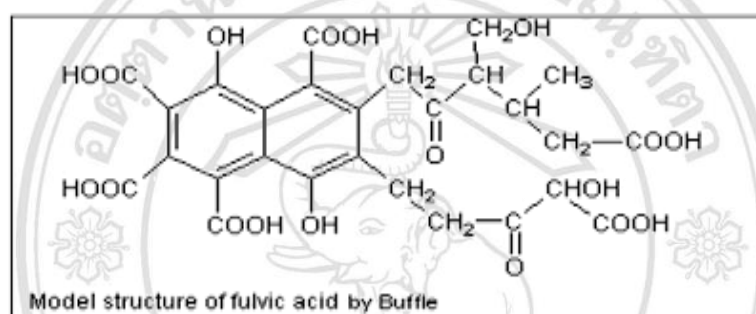


Fig. 1.2 Model structure of fulvic acid [20]

Due to its abundance, properties, and low cost, leonardite was examined for the possibility of removing heavy metals from aqueous solutions. Zeledon *et al.* [21] investigated the removal of copper and nickel from aqueous solutions using leonardite from Spain as adsorbent. The maximum adsorption capacities were 15.26 mg/g and 20.97 mg/g for nickel and copper, respectively. Compare to the other types of adsorbent, the adsorption capacity of leonardite for copper and nickel is the same order of magnitude or greater. The adsorption of Pb(II) ion from aqueous solutions by leonardite was investigated by Lao *et al.* [22]. It was found that the adsorption was pH-dependent and the maximum removal of Pb(II) ion was achieved in the pH range of 5–6. The maximum adsorption capacity obtained was 250.7 mg/g. Solé *et al.* [23] studied the ability of leonardite to remove zinc from aqueous solutions. In their study, leonardite has been shown to be effective for the removal of zinc ions from aqueous solutions with the adsorption capacity of 27.2 mg/g. Chammui *et al.* [24] studied the removal of arsenic from aqueous solution by adsorption on leonardite char. The adsorption capacities were estimated to be 4.46 mg/g for As(III) and 8.40 mg/g for As(V). The leonardite char has

been successfully used for the removal of arsenic ions in real life arsenic contaminated surface water samples without any chemical treatment.

Many research works have focused on adsorption in single-component systems. In fact, wastewater usually contains more than one type of heavy metal. The presence of other metal ions may affect the adsorption system. Hanslik *et al.* [25] investigated the adsorption of silver, cadmium, and copper ions from aqueous solutions by natural carbonaceous materials. Adsorption was tested on a single-component system and on the binary and ternary mixtures. The adsorption of metal ions is significantly affected by the presence of other ions in solution. Total metal ion uptake was considerably higher in a mixture than single ion adsorption. Although the total adsorption increased in the mixture system, the removal of individual species was reduced. Competitive adsorption of Cd and Zn ions onto granular activated carbon was investigated by Gabaldon *et al.* [26]. The removal efficiency of the activated carbon decreased for both metal ions in the competitive system. Srivastava *et al.* [27] reported the competitive adsorptive removal of cadmium (Cd(II)) and zinc (Zn(II)) ions from binary systems using rice husk ash. It was found that the equilibrium metal ion removal decreased with increasing concentrations of the other metal ion. Stietiya *et al.* [28] reported that the adsorption of Zn and Cd ions on nanoparticles of alumina oxides; in the binary-metal ion system was lower than in the respective mono-metal systems. For this reason, adsorption in multi-component systems should be investigated.

1.4 Adsorption kinetic

Adsorption kinetic describes the rate at which adsorbate is transferred from the medium to the surface of adsorbents. The rate of adsorption determines the time required for the treatment. The adsorption kinetic models commonly applied are pseudo first order model, pseudo second order model, and intra-particle diffusion model.

1.4.1) Pseudo first order model [29]

Pseudo first order kinetic equation was suggested by Lagergren in 1898. It has been widely applied in the liquid-solid adsorption systems. The pseudo first order kinetic is based on the adsorption capacity. In the adsorption procedure, the adsorption rate (dq_t/dt) is proportional to the difference between the adsorbed amount at time “ t ” and

the equilibrium adsorbed amount of the adsorbent ($q_e - q_t$). Let k_1 be the proportionality constant, it gives:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1.1)$$

where q_t and q_e are the adsorbed amount at time “ t ” and at equilibrium, respectively. k_1 is the rate constant of pseudo first-order adsorption. Equation (1.1) was integrated with the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$. After the integration, the equation becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (1.2)$$

1.4.2) Pseudo second order model

Pseudo second order kinetic has been widely applied in many adsorption systems. The most commonly used form of the pseudo second order equation is the form derived by Ho and Mckay [30]. The adsorbate was assumed to get adsorbed onto two surface sites. So, the pseudo second order kinetic is expressed as follows:

$$\frac{d(P)_t}{dt} = k_2[(P)_0 - (P)_t]^2 \quad (1.3)$$

where $(P)_t$ is the number of active sites occupied on the adsorbent at time “ t ”. $(P)_0$ is the number of equilibrium sites available on the adsorbent. It is assumed that the adsorption capacity is proportional to the number of active sites occupied on the adsorbent, then the kinetic rate law can be rewritten as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (1.4)$$

where k_2 is the rate constant of pseudo-second order adsorption. Rearrange the equation (1.4), it gives

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt \quad (1.5)$$

Integrating equation (1.5) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the equation becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (1.6)$$

Rearrange equation (1.6), gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (1.7)$$

1.4.3) Intra-particle diffusion model

Adsorption kinetic can be alternatively explained from the adsorption mechanisms. The intra-particle diffusion model is one of the kinetic models that have been used for predicting the adsorption mechanisms. Generally, the adsorption of adsorbate by the adsorbent consists of three steps [31-32]:

- (1) The adsorbate must be transferred from the bulk phase of the solution to the surface of the adsorbent particle. In this procedure, it must pass through a film of solvent that surrounds the adsorbent particle. This process is called “film diffusion”.
- (2) Diffusion of the adsorbate from the external surface into the pores of the adsorbent (intra-particle diffusion).
- (3) Adsorption of the adsorbate on the external surface through the binding of the ions to the active sites.

From all these three steps, the slowest step is considered as the rate limiting step. Step (3) cannot be the rate limiting step because the process is fast as compared to the first two steps. Thus, the overall rate of adsorption process may be controlled by either the first or the second step or a combination of two steps. The film diffusion is usually the rate-limiting step for a system having poor mixing, low concentration of adsorbate, small particle size of adsorbent, and high affinity of adsorbate towards adsorbent, whereas the intra-particle diffusion is the rate limiting step for a system having good mixing, high concentration of adsorbate, large particle size of adsorbent, and low affinity of adsorbent towards adsorbent [33]. The most widely applied intra-particle diffusion equation was developed by Webber and Morris [34]. The equation is expressed as:

$$q_t = k_{id}t^{0.5} + C \quad (1.8)$$

where k_{id} is intra-particle diffusion rate constant, and C is the constant related to the thickness of boundary layer.

1.5 Adsorption isotherm [35-36]

The study of adsorption is usually performed by adsorption isotherm, which is the relationship between the amounts of adsorbate on the surface and the amounts of adsorbate in medium at constant temperature. Adsorption isotherm is the basic requirements for the design of adsorption systems because it can provide the information about the adsorption capacity, surface area of adsorbent, and adsorption behavior, affinity of the adsorbate to the adsorbent, and homogeneity/heterogeneity of the adsorbent surface. Upon considering the characteristics of isotherm curve, adsorption isotherm can be classified into 6 types (Fig. 1.3).

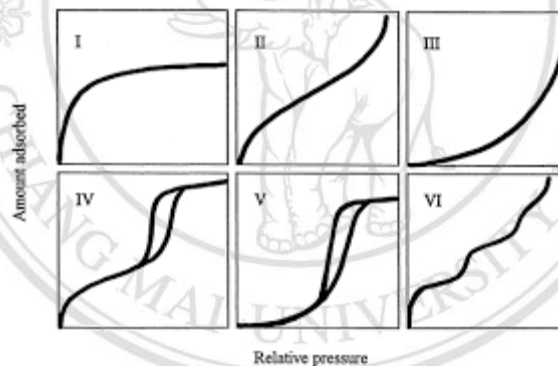


Fig. 1.3 The classification of adsorption isotherms [37]

Type I: The type I isotherm is given by microporous solids having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites, and certain porous oxides), the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area. This graph depicts the monolayer adsorption and can be easily explained using Langmuir adsorption isotherm.

Type II: The type II isotherm represents unrestricted monolayer-multilayer adsorption. This type shows large deviation from Langmuir model of adsorption. The intermediate flat region in the isotherm indicates the state at which monolayer coverage is complete and multilayer adsorption about to begin. It often can be described by the

BET equation. Type II isotherm is the normal form of isotherm obtained with a non-porous or macroporous adsorbent.

Type III: The type III adsorption isotherm also shows large deviation from Langmuir model. The isotherm curve is convex to the x axis over its entire range. There is no flattish portion in the curve which indicates that monolayer formation is missing. It explains the formation of multilayer. It forms because lateral interactions between adsorbed molecules are strong in comparison to interactions between the adsorbent surface and adsorbate.

Type IV: At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer. The saturation level reaches at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure of the gas.

Type V: Explanation of Type V graph is similar to Type IV but the initial part of the type V isotherm is attributed to multilayer adsorption since it follows the same path as the corresponding part of the type III isotherm.

Type VI: The type VI isotherm represents stepwise multilayer adsorption on a uniform non-porous surface. The step-height represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers.

Many isotherm models have been published in the literatures to describe the equilibrium relationship between adsorbent and adsorbate in both single and multi-component systems. For single-component systems, several adsorption isotherms were proposed, for example, Langmuir, Freundlich, Redlich-Peterson, BET, Dubinin-Radushkevich, Sips, and Temkin isotherms. Among these isotherms, Langmuir isotherm and Freundlich isotherm are the most frequently used isotherms. For multi-component systems, many models which are based on Langmuir and Freundlich isotherms have been published, such as Extended Langmuir, Modified Langmuir, Sheindorf-Rebuhn-Sheintuch (SRS), and Extended Freundlich isotherms.

1.5.1) Single adsorption isotherm

1.5.1.1) Langmuir isotherm [38]

The Langmuir isotherm was proposed in 1916. It was originally derived from simple kinetic considerations of the adsorption of gas on solid surfaces; later, it was applied for adsorption in aqueous-solid systems. The basic hypotheses are as follows:

- (1) Molecules are adsorbed on a fixed number of well-localized sites.
- (2) Each site accepts only one molecule, and adsorbed molecules are organized as a monolayer.
- (3) All sites are energetically equivalent.
- (4) There is no interaction between adsorbed molecules.

The adsorption process between molecules A on the vacant surface sites S, and occupied surface sites, SA, can be represented by the equations:



[SA] is proportional to the surface coverage of adsorbed molecules, θ , [S] is proportional to the number of vacant sites, $(1 - \theta)$, and [A] is proportional to the concentration of liquid phase, C. Thus, the adsorption rate and the desorption rate are defined as:

$$\text{adsorption rate} = k_a C(1 - \theta) \quad (1.10)$$

$$\text{desorption rate} = k_d \theta \quad (1.11)$$

At equilibrium, the equality of these two rates leads to

$$k_a C (1 - \theta) = k_d \theta \quad (1.12)$$

$$\frac{\theta}{(1 - \theta)} = \frac{k_a}{k_d} C = bC \quad (1.13)$$

After rearrangement of equation (1.13), it leads to

$$\theta = \frac{bC}{1 + bC} \quad (1.14)$$

$$q = \frac{q_s b C_e}{1 + b C_e} \quad (1.15)$$

where $b = k_a/k_d$ is the adsorption equilibrium constant. k_a and k_d are the adsorption rate constant, and the desorption rate constant, respectively. $\theta = q/q_s$ is the fractional coverage. q is the number of adsorbed molecules per unit mass or volume of adsorbent. q_s is the total number of available sites per unit mass or volume of adsorbent.

1.5.1.2) Freundlich isotherm [39]

The Freundlich isotherm is an empirical model for describing adsorption on heterogeneous surfaces. It assumes an exponential distribution of the adsorption energies. This kind of model is very useful in accounting for heterogeneous surfaces, but it does not reduce to a linear law at low concentrations and does not tend asymptotically to the saturation of the stationary phase. It is therefore restricted to a limited range of concentrations. Since the Freundlich isotherm is obtained when an exponential distribution of adsorption energies is assumed, then

$$N(Q) = \alpha \exp(-nQ/RT) \quad (1.16)$$

where $N(Q)$ is the number of sites having adsorption energy Q , and α, n are constants. It is assumed further that for each energy level, the coverage θ follows the Langmuir isotherm (equation 1.14) and b depends on the adsorption energy in the form:

$$b = b_0 \exp(Q/RT) \quad (1.17)$$

The fraction of adsorption sites having energy of adsorption between Q and $Q + dQ$ occupied by adsorbate is

$$d\theta_T(Q) = \theta(Q)N(Q)dQ \quad (1.18)$$

The total coverage by the adsorbate is obtained by integration of equation (1.18) over the whole range of adsorption energies, i.e., between the limits $-\infty$ and $+\infty$. The integral after substitution of $\theta(Q)$ and $N(Q)$ from equation (1.14), (1.16), and (1.17) is

$$\theta_T = \int_{-\infty}^{\infty} \frac{b_0 \exp(Q/RT)C}{1 + b_0 \exp(Q/RT)C} \times \alpha \exp(-nQ/RT)dQ \quad (1.19)$$

which yields

$$\theta_T = \frac{\alpha RT b_0^n}{n} C^n = AC^n \quad (1.20)$$

where A is constant under isothermal conditions. If the adsorption is expressed in terms of weight of adsorbate per unit weight of adsorbent q , then the Freundlich isotherm is written in the form

$$q = KC^n \quad (1.21)$$

where $K = qA$ and q is the characteristic adsorption capacity.

1.5.2) Binary adsorption isotherm

1.5.2.1) Extended Langmuir isotherm [40-41]

The Langmuir isotherm was first adjusted for application in multi-component adsorption systems by Butler and Ockrent. The Extended Langmuir isotherm is applicable when each single component obeys Langmuir behavior in a single-component adsorption system. The Extended Langmuir assumes that each component adsorbs onto the surface according to ideal solute behavior under homogeneous conditions with no interaction or competition between molecules taking place. The Extended Langmuir equation is presented as follows:

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{j=1}^N b_j C_{e,j}} \quad (1.22)$$

where $q_{e,i}$ and $C_{e,i}$ are the equilibrium adsorbed amount and the metal concentration, respectively, of each component in a multi-component adsorption system. $q_{m,i}$ and b_i are the Langmuir constants of each component obtained from the single-component adsorption system, therefore, correspond to a monolayer coverage of the adsorbent. N is the number of components. “ j ” takes values from 1 to N . For a binary system, the equation is written as follows:

$$q_{e,1} = \frac{q_{m,1} b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \quad (1.23)$$

$$q_{e,2} = \frac{q_{m,2}b_2C_{e,2}}{1 + b_1C_{e,1} + b_2C_{e,2}} \quad (1.24)$$

1.5.2.2) Modified Langmuir isotherm [38, 42]

For the prediction of adsorption in the multi-component system, application of only isotherm parameters from a single-component system may give unsatisfactory results in some cases. Better accuracy may be achieved by extracting additional coefficients from the multi-component isotherm. An interaction term “ η ” was added to the Extended Langmuir equation. The Modified Langmuir equation is given as follows:

$$q_{e,i} = \frac{q_{m,i}b_i(C_{e,i}/\eta_i)}{1 + \sum_{j=1}^N b_j(C_{e,j}/\eta_j)} \quad (1.25)$$

where $q_{m,i}$ and b_i are derived from the corresponding single-component Langmuir equations. $q_{e,i}$ and $C_{e,i}$ are the adsorption data in the multi-component system. η is the characteristic of each of the components and depends on the concentration of the other components. The parameter η can be determined from the regression of the multi-component adsorption data.

1.5.2.3) Sheindorf-Rebuhn-Sheintuch (SRS) isotherm [39]

The SRS isotherm is a Freundlich-type multi-component adsorption isotherm. It is based on the assumptions that each component individually follows the Freundlich isotherm, and that an exponential distribution of adsorption energies exists for each component. The SRS isotherm is given by the following equation:

$$q_{e,i} = K_{F,i}C_{e,i} \left(\sum_{j=1}^N a_{ij}C_{e,j} \right)^{(1/n_i)-1} \quad (1.26)$$

where a_{ij} is the competition coefficient which describes the inhibition of component i by the adsorption of component j . The parameters $K_{F,i}$ and $1/n_i$ are determined from the single component system, whereas the parameter a_{ij} can be determined from the multi-component system ($a_{ii} = 1$).

1.5.2.4) Extended Freundlich isotherm [27, 43]

The Extended Freundlich isotherm has been proposed by Fritz and Schlunder. The adsorption of the component i in the two-component system can be expressed as follows:

$$q_{e,i} = \frac{K_{F,i} C_{e,i}^{(1/n_i)+x_i}}{C_{e,i}^{x_i} + y_i C_{e,j}^{z_i}} \quad (1.27)$$

where $K_{F,i}$ and $1/n_i$ are obtained from the single-component isotherm. The parameters x_i , y_i , and z_i are determined using the non-linear regression analysis.

1.6 Adsorption Thermodynamic [44-45]

Thermodynamic study plays an important role in thoroughly understanding the adsorption process. It can be used for the consideration of the types and mechanisms of the adsorption process under variations of the solution temperature. The thermodynamic parameters are the Gibb's free energy change (ΔG°), the enthalpy change (ΔH°), and the entropy change (ΔS°). Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibb's free energy change, ΔG° , is an indication of spontaneity of the adsorption process. The adsorptive process will occur favorably and spontaneously at a given temperature if the ΔG° exhibits a negative quantity; in contrast, it will be non-feasible and non-spontaneous adsorption process if the ΔG° exhibits positive quantity.

A negative value of ΔH° implies that the adsorption phenomenon is exothermic while a positive value implies that the adsorption process is endothermic. The adsorption process in the solid–liquid system is a combination of two processes: (a) the desorption of the solvent (water) molecules previously adsorbed, and (b) the adsorption of the adsorbate species. The exothermic phenomenon is because the total energy absorbed in bond breaking is lower than the total energy released in bond making between the adsorbate and adsorbent, causing the release of extra energy in the form of heat. In the endothermic process, the adsorbate species has to displace more than one water molecule for their adsorption and this results in the endothermicity of the adsorption process. Therefore, ΔH° will be positive. The magnitude of ΔH° may also give an idea about the

type of adsorption. The heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e., 2.1–20.9 kJ/mol, while the heats of chemisorption generally falls into a range of 80–200 kJ/mol.

The ΔS° reflects whether the organization of the adsorbate at the solid/solution interface during the adsorption process becomes less random or more random. The positive value of ΔS° reflects the affinity of the adsorbent towards the adsorbate species. In addition, positive value of ΔS° suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. The adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions/molecules, thus allowing for the prevalence of randomness in the system. The positive ΔS° value also corresponds to an increase in the degree of freedom of the adsorbed species. The negative value of ΔS° suggests that the adsorption process is enthalpy driven. A negative value of entropy change also implies a decreased disorder at the solid/liquid interface during the adsorption process causing the adsorbate ions/molecules to escape from the solid phase to the liquid phase. Therefore, the amount of adsorbate that can be adsorbed will decrease.

The thermodynamic parameters can be computed according to the thermodynamic laws through the following equations:

$$\Delta G^\circ = -RT \ln K_d \quad (1.28)$$

The relationship of ΔG° to ΔH° and ΔS° is described as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1.29)$$

The well-known Van't Hoff equation is obtained by substituting Eq. (1.28) into Eq. (1.29)

$$\ln K_d = \left(\frac{-\Delta H^\circ}{R} \right) \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (1.30)$$

where R is an universal gas constant (8.3144 J/mol K), T is the absolute temperature in Kelvin (K), and K_d is the thermodynamic equilibrium constant.

1.7 Data Analysis

1.7.1) Linear regression [46-47]

Linear regression is the most basic type of regression and commonly used predictive analysis. It establishes a mathematical relationship between variables. The linear relationship between two variables is captured by the formula $y = b + mx$, where x represents the independent variable, and y represents the dependent variable, and that predictions of y are made for a given x value. b is the y intercept, and m is the slope. In adsorption isotherm study, the isotherm equation is usually arranged in the linear form to determine the isotherm parameters from slope and intercept.

The goodness of fit of the data to the mathematical relationship is frequently evaluated by the correlation coefficient, R^2 , which is the proportion of the variance in the dependent variable that is predictable from the independent variable. Value of R^2 is in the range of 0 to 1. In general, the higher the R^2 , the better the model fits your data.

1.7.2) Non-linear regression [48-49]

Commonly, the linear regression method based on the magnitude of the correlation coefficient has been applied on the evaluation of the applicability of isotherm model. Although the linear regression method is widely used, it has some drawbacks. The transformation of non-linear isotherm equations to linear forms implicitly alters their error structure and may also violate the error variance and normality assumptions of standard least squares [41]. Non-linear regression is an alternative choice for estimating the adsorption isotherm model. In statistics, non-linear regression is a form of regression analysis in which observational data are modeled by a function which is a non-linear combination of the model parameters and depends on one or more independent variables. The data are fitted by a method of successive approximations. Recently, non-linear regression has been applied for the evaluation of the suitability of adsorption isotherm model to the experimental data, and the determination of isotherm parameters. In the procedure, the isotherm equation is used in the original form, the transformation of isotherm equation to the other forms is not required. Non-linear regression requires the selection of an error function in order to evaluate the fit of the isotherm to the experimental equilibrium data. The error value of each error functions and the isotherm

parameters can be determined by minimizing the respective error function across the concentration range studied. The error functions employed were as follows:

(1) *Root mean square error (RMSE)* [50]

The RMSE is a frequently used measure of the differences between values predicted by a model and the values actually observed. The differences are presented as the sample standard deviation. The RMSE serves to aggregate the magnitudes of the errors in predictions for various times into a single measure of predictive power. The effect of each error on RMSE is proportional to the size of the squared error thus larger errors have a disproportionately large effect on RMSE. Consequently, RMSE is sensitive to outliers. The RMSE equation is expressed as:

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (q_{e,exp} - q_{e,cal})_i^2} \quad (1.31)$$

where $q_{e,exp}$ and $q_{e,cal}$ are the adsorbed amount obtained from the experiment and adsorption isotherm model, respectively. N is the number of data.

(2) *Sum of the square errors (ERRSQ)* [51-52]

The sum of the square errors is a measure of the discrepancy between the observed data and the data obtained from the estimation model. A small value of ERRSQ indicates a tight fit of the model to the data. The ERRSQ error function has one major drawback. The function provides a better fit at the higher end of the liquid phase concentration range. This is because the magnitude of the errors and hence the square of the errors will increase as concentration increases. The ERRSQ equation is expressed as:

$$ERRSQ = \sum_{i=1}^N (q_{e,cal} - q_{e,exp})^2 \quad (1.32)$$

(3) *Mean absolute percentage error (MAPE)* [53]

The mean absolute percentage error (MAPE) is one of the most popular measures of the forecast accuracy. MAPE is scale-independent and easy to interpret, which makes it popular with industry practitioners. However, MAPE has a significant disadvantage: it produces infinite or undefined values when the actual values are zero or close to zero, which is a common occurrence in some fields. If the actual values are very

small (usually less than one), MAPE yields extremely large percentage errors (outliers), while zero actual values result in infinite MAPEs. MAPE equation is defined as:

$$MAPE = \frac{100}{N} \sum_{i=1}^N \left| \frac{q_{e,\text{exp}} - q_{e,\text{cal}}}{q_{e,\text{exp}}} \right|_i \quad (1.33)$$

(4) *Marquardt's percent standard deviation (MPSD)* [54]

This error function is similar to the RMSE which was modified by the dividing by the experimental adsorbed amount, and allow for the number of degrees of freedom of the system. MPSD equation is defined as:

$$MPSD = 100 \sqrt{\left(\frac{1}{N-p} \right) \sum_{i=1}^N \left[\frac{(q_{e,\text{exp}} - q_{e,\text{cal}})^2}{q_{e,\text{exp}}} \right]} \quad (1.34)$$

where p is the number of parameters in the isotherm model.

(5) *Chi-square (χ^2)* [55]

The chi-square test statistic is basically the sum of the squares of the differences between the experimental data and the data obtained by calculating from models with each squared difference divided by the corresponding data obtained by calculating from models. The advantage of using chi-square test is to compare all isotherms on the same abscissa and ordinate. The equivalent mathematical statement was:

$$\chi^2 = \sum_{i=1}^N \left[\frac{(q_{e,\text{exp}} - q_{e,\text{cal}})^2}{q_{e,\text{cal}}} \right] \quad (1.35)$$

1.7.3) Sum of the normalized error [48]

As each of the error criteria is likely to produce a different set of isotherm parameters, an overall optimum parameter set is difficult to identify directly. Hence, in order to try to make a meaningful comparison between the parameter sets, a procedure of normalizing and combining the error results was adopted producing a so-called 'sum of the normalized errors' for each parameter set for each isotherm. The calculation method for the 'sum of the normalized errors' was as follows:

- (1) Select one isotherm and one error function (for example, the *ERRSQ* error function) and get the *solver add-in* output to determine the isotherm parameters in a way that minimizes the applied error function.
- (2) Determine the values of other error functions based on isotherm parameters obtained from step (1).
- (3) Perform the above steps exactly for all other error functions.
- (4) Select the maximum output of each error function from all sets. In order to calculate the normalized error, the value of other sets should be divided into the maximum value. This should be done for all error functions.
- (5) Calculate the summation of all of these normalized errors for each parameter.

1.8 Analytical Techniques

1.8.1) X-ray powder diffraction [56-58]

X-ray diffraction (XRD) by crystalline powder is an instrumental technique that used for the determination of crystal structures and lattice parameters, and identification of crystalline phases and unknown materials (e.g. minerals, inorganic compounds). X-ray powder diffraction does not require samples of a good crystalline quality. Its fields of applications are very wide in mineralogy, petrology, metallurgy, and materials science. X-ray powder diffraction is based on the constructive interference of monochromatic X-rays and sample.

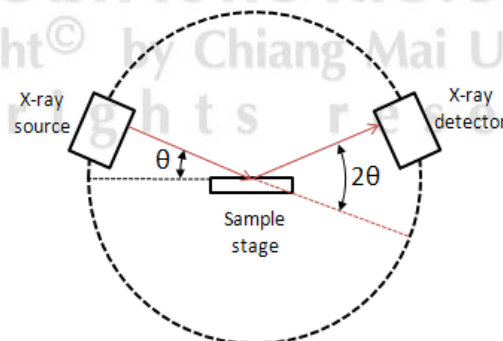


Fig.1.4 Diagram of X-ray diffractometer [59]

X-ray diffractometer consists of three basic parts: an X-ray source, a sample stage, and an X-ray detector (Fig. 1.4). The X-ray is directed on the sample at some angle θ , while the detector opposite the source reads the intensity of the X-ray it receives at 2θ away from the source path. The incident angle is then increased over time while the detector angle always remains 2θ above the source path. To determine the XRD pattern, X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target (anode) by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromators, is required to produce monochromatic X-rays needed for diffraction. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. The detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. The interaction of the incident rays with the sample produces constructive interference when conditions satisfy Bragg's law. The law states that when the X-rays are incident onto the sample at angle θ , it will reflect back with a same angle, and when the path difference, d is equal to an integer multiple of wavelength, a constructive interference will occur (Fig. 1.5).

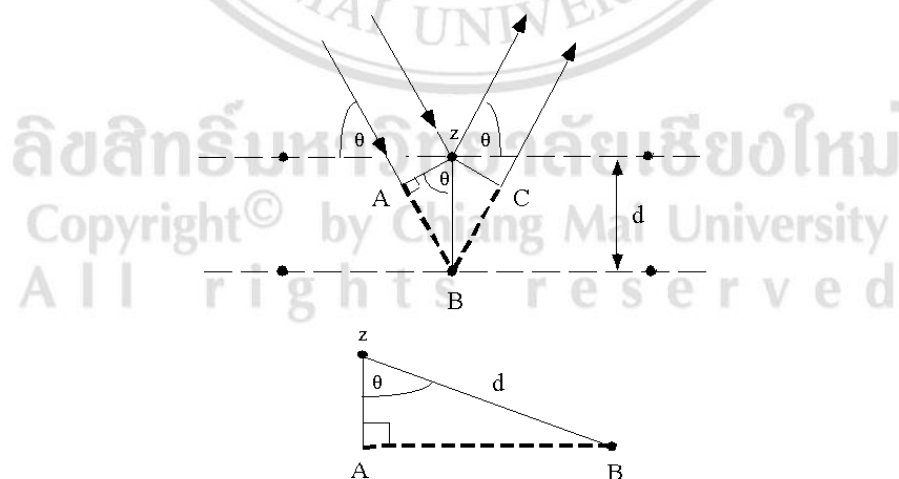


Fig. 1.5 Deriving Bragg's law using reflection geometry and applying trigonometry [60]

The Bragg's law is expressed as:

$$2d \sin \theta = n\lambda \quad (1.36)$$

where d is the distance between adjacent planes of atoms (the d -spacings), θ is the angle of incident X-ray beam, n is the order of the diffracted beam, and λ is the wavelength of the incident X-ray beam. The characteristic set of d -spacings generated in a typical X-ray scan provides a unique "fingerprint" of the crystals or minerals present in the sample. By the comparison with standard reference patterns and measurements, this "fingerprint" allows for identification of the materials.

1.8.2) X-ray fluorescence spectroscopy [61-62]

X-ray fluorescence spectroscopy (XRF) is the analytical method to determine the chemical composition of materials. This method is non-destructive, fast, clean, and safe. In XRF, X-rays generated by the source are sent through the sample and dislodge the electrons from the inner electron shells of atoms in the sample. The vacancies of the inner electron shells make the atom unstable. Thus, electrons from outer electron shells fill the vacancies to correct the instability. The transition of electrons yields a fluorescence radiation that is the characteristic of the different elements in the sample. This fluorescence radiation is detected by the detector. The intensity of the characteristic X-rays is proportional to the number of atoms in the sample. By comparing the intensity of characteristic X-rays for each element to that of a standard with known concentration, the concentration of the element in the sample can be known. The X-ray fluorescence spectrometer can be divided into two groups.

(1) *Energy dispersive XRF (EDXRF)*: In EDXRF, the spectrometer consists of X-ray source, sample holder, and detector. The fluorescence radiation emitted by the sample is directed into the detector. The detector can separate the radiation from the sample into the radiation from the elements in the sample. This separation is called dispersion. The elemental range for EDXRF goes from sodium to uranium. The detection limit, sensitivity, and resolution of EDXRF are good for heavy elements but less optimal for light elements. The cost of this system is relatively inexpensive.

(2) *Wavelength dispersive XRF (WDXRF)*: In WDXRF, the spectrometer consists of X-ray source, sample holder, collimator, diffraction crystal, and detector. The

fluorescent radiation emitted by the sample is sent through a collimator to produce a coherent beam. Then, it diffracts through the diffraction crystal of known d-spacing. Using the Bragg equation, the angle θ that X-rays of known wavelength will be diffracted through the crystal can be known. Thus, the diffraction crystal and detector are set up to diffract only X-rays of the particular wavelength of interest into the detector. The elemental range for WDXRF is wider used than that of EDXRF. It goes from beryllium to uranium. The detection limit and sensitivity of WDXRF are reasonable for light elements and good for heavy elements. For the resolution, it is good for light elements but less optimal for heavy elements. However, the cost of WDXRF is relatively expensive.

1.8.3) Fourier transform infrared spectroscopy [63-64]

Fourier transform infrared spectroscopy (FTIR) is a technique that has been applied in various fields such as chemistry, geology, pharmaceuticals, materials, biology, food, environment, etc. It provides the information about the functional groups, used for confirmation of the identity of the samples, and analysis of composition and structure. It is based on the idea of the interference of radiation between two beams to yield an interferogram. The interferogram is a signal produced as a function of the change of path length between the two beams. The raw data of distance and frequency are converted into the spectrum by the mathematical method of fourier-transformation. FTIR spectrometer consists of a source, interferometer (consists of beam splitter, stationary mirror, and moving mirror), sample compartment, detector, and a computer. The diagram of FTIR spectrometer is shown in Fig. 1.6.

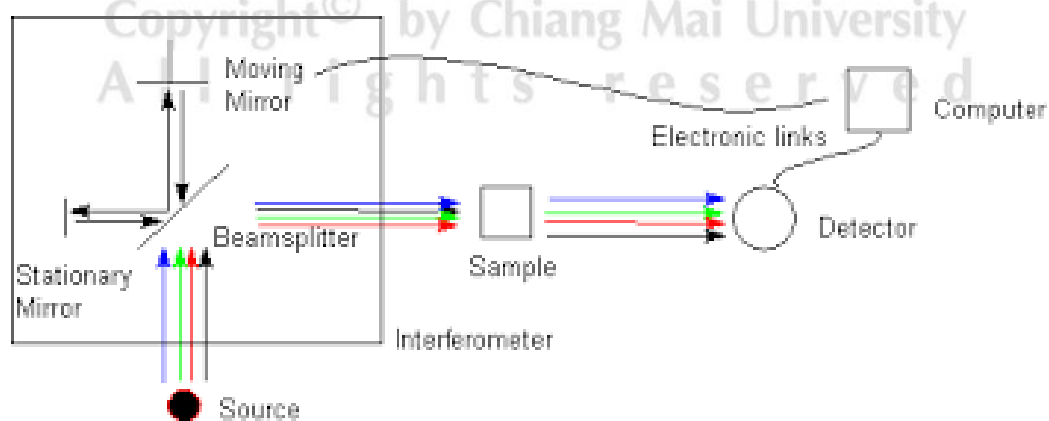


Fig. 1.6 Diagram of FTIR spectrometer [64]

FTIR spectrometer use a Globar source, a thermal light source made from silicon carbide rod, for the mid infrared region. A high-pressure mercury lamp is used as the source of the far-infrared region. The tungsten-halogen lamp is used as the source of near-infrared region. The source generates radiation which sends to the interferometer. The light passes into a beam splitter, which separates the light into two beams. One beam goes to a stationary mirror then back to the beam splitter. The other goes to a moving mirror. The motion of the mirror makes the total path length variable versus that taken by the stationary-mirror beam. When the two meet up again at the beam splitter, they recombine, but the difference in path lengths creates constructive and destructive interference: an interferogram. The recombined beam passes through the sample. The sample absorbs all the different wavelengths characteristic of its spectrum, and this subtracts specific wavelengths from the interferogram. The detector reports the variation in energy versus time for all wavelengths simultaneously. A mathematical function called a Fourier transform converts an “intensity versus time” spectrum into an “intensity versus frequency” spectrum.

1.8.4) Scanning electron microscopy [65-66]

Scanning electron microscopy (SEM) is a method that can generate high-resolution imaging of sample surfaces. This method reveals the information about the sample including external morphology (texture), chemical composition, crystalline structure, and orientation of materials making up the sample. The SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of sample. The obtained signals are the results from the interactions of electron beam with atoms at various depths within the sample. To create SEM image, the incident electron beam is scanned in a raster pattern across the sample surface. The SEM is also capable of performing analyses of selected point locations on the sample. This approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using Energy-Dispersive X-ray spectroscopy, EDS), crystalline structure, and crystal orientations (using Electron Backscatter Diffraction, EBSD). The emitted electrons are detected for each position in the scanned area by an electron detector. The intensity of the emitted electron signal is displayed as brightness on a display monitor and/or in a digital image file. By synchronizing the position in the image scan to that of the scan of the

incident electron beam, the display represents the morphology of the sample surface area. SEM can achieve resolution better than 1 nanometer.

1.8.5) BET surface area analysis [67-69]

In order to study the adsorption, the surface area of adsorbents is one of the properties that should be measured. Generally, the adsorbents have irregular surface and pores within the particles. Therefore, the surface area of adsorbents cannot be directly determined by the calculation from the particle size information. The determination of surface area can be performed using the BET theory, which describes the physical adsorption of gas molecules on solid surface. In the analysis, nitrogen gas is usually used because of its availability in high purity and its strong interaction with most solids. The samples are dried with nitrogen purging or in a vacuum applying elevated temperatures. After that, the sample cell is placed in liquid nitrogen. Nitrogen gas is then released into the sample cell. The amount of gas adsorbed at the relative pressure P/P_0 is measured. P and P_0 are the equilibrium and the saturation pressure of adsorbate gas, respectively. The amount of adsorbed gas is correlated to the total surface area of the particles including pores in the surface. The surface area is calculated using the BET isotherm equation.

The concept of the BET theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses:

- (1) Gas molecules physically adsorb on a solid in layers infinitely
- (2) There is no interaction between each adsorption layer
- (3) The Langmuir theory can be applied to each layer.

The resulting BET equation is

$$\frac{1}{X[(P_0/P)-1]} = \frac{1}{X_m C} + \frac{C-1}{X_m C} \left(\frac{P}{P_0} \right) \quad (1.37)$$

where X is the amount of gas adsorbed at a given relative pressure (P/P_0), X_m is monolayer adsorbed amount of gas, and C is BET constant. X_m and C value can be calculated from the value of slope and intercept of the plot $1/X[(P_0/P)-1]$ against (P/P_0) . The specific surface area, S , in m^2/g , is calculated by the equation:

$$S = \frac{X_m Na}{mV} \quad (1.38)$$

where N is Avogadro's number, a is the effective cross-sectional area of one adsorbate molecule, m is the mass of the solid sample or adsorbent, and V is the volume occupied by 1 mole of the adsorbate gas at STP.

1.8.6) Particle size analysis [70-71]

There are many different methods employed to measure particle size of materials including laser diffraction, sieving, and dynamic light scattering. Among these methods, laser diffraction has become one of the most commonly used because of the speed, ease of use, and flexibility. It has a wide dynamic range capable of measuring from nanometers to millimeters. Laser diffraction can be applied to many different sample types such as dry powders, suspensions, emulsions and even aerosols. Laser diffraction uses Mie theory of light scattering to calculate the particle size distribution, assuming a volume equivalent sphere model, and ensemble is homogeneous. Mie theory also requires knowledge of the optical properties (refractive index and imaginary component) of both the sample being measured, along with the refractive index of the surrounding medium.

Laser diffraction works on the principle that when a beam of light (a laser) is scattered by a group of particles, the angle of light scattering is inversely proportional to particle size. Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles. The angular scattering intensity data is then analyzed to calculate the size of the particles responsible for creating the scattering pattern. The particle size is reported as a volume equivalent sphere diameter. The particle size analyzer composed of laser light source, focusing lens, sample cell, and detectors.

1.8.7) Atomic absorption spectroscopy [72-74]

Atomic absorption spectroscopy (AAS) is an analytical technique for the determination of the element concentration. This technique is based on the absorption of radiation by the free atoms in the gaseous state. In AAS, the sample is atomized, which converts the sample to the ground state free atoms in the gaseous state. When the light from light source passes through the gaseous sample, some of the light is absorbed by atoms in the sample. Atoms of different elements adsorb characteristic wavelength of

light. After that, the light passes through the monochromator for selection of specific light. Finally, the light is measured by the detector. The greater the number of atoms there is in the sample, the more radiation is adsorbed. The amount of light absorbed is proportional to the number of atoms in sample. A calibration curve is produced by running the standard solutions of known concentration under the same conditions. The absorbance of sample is compared with the calibration curve and this enables the calculation of the element concentration in the sample. The diagram of atomic absorption spectrometer is shown in Fig. 1.7.

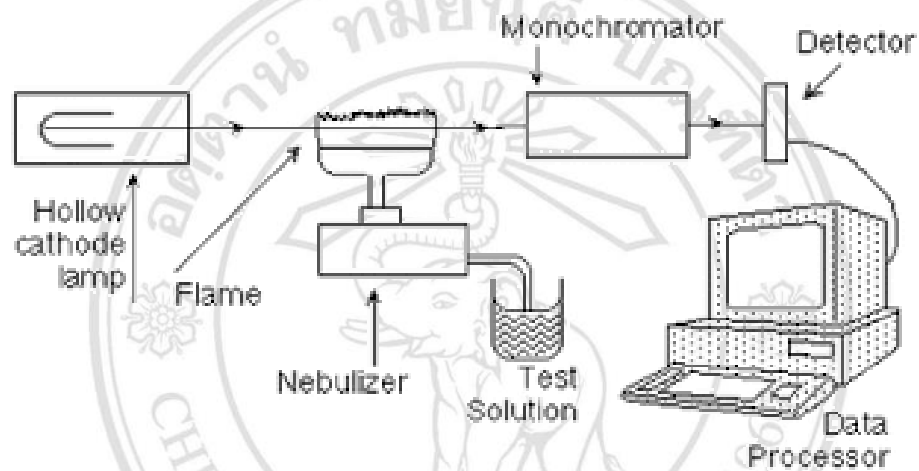


Fig. 1.7 Diagram of atomic absorption spectrometer [74]

Atomic absorption spectrometer consists of

(1) *Light source:* The most common light source for AAS is the hollow cathode lamp. It consists of a tungsten anode and a cylindrical hollow cathode made of the element to be measured. Both anode and cathode are sealed in the glass tube filled with the inert gas (argon or neon) at low pressure. Applying a potential across the anode and cathode, the inert gas is ionized. The gaseous ions bombard the cathode and eject metal atoms from the cathode in a process called “sputtering”. Some sputtered atoms are in excited states and emit radiation characteristic of the metal as they fall back to the ground state. The procedure of the generation of radiation is shown in Fig. 1.8.

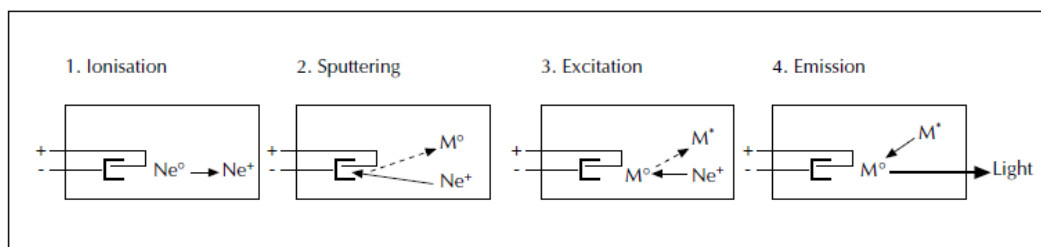


Fig. 1.8 The generation of radiation from hollow cathode lamp [72]

(2) *Atomizer:* Atomization is the process that converts the analyte in the solid or liquid form to the free gaseous atoms. There are two commonly used atomizers including: flame atomizer, and electrothermal atomizer.

- *Flame atomizer:* This type of atomizer is based on the application of flame to convert the sample into atoms. The aqueous sample is drawn into the nebulizer. When the sample exits the nebulizer, it strikes a glass impact bead and converts into small drops within the spray chamber. The larger drops fall out and drain off whereas the smaller drops are swept through the spray chamber by the combustion gases to the burner head. The flame's thermal energy desolvates the small drops of sample to a dry aerosol of small, solid particles. The flame's thermal energy then volatilizes the particles, producing a vapor consisting of molecular species, ionic species, and free atoms.

- *Electrothermal atomizer (graphite furnace):* The electrothermal atomizer consists of cylindrical graphite tube with the platform. The aqueous sample is injected to the graphite tube and heated electrically by passing the current through the graphite tube in three steps. In the first step, the heat is rose up to 150 °C to evaporate the solvent. The next step is an increase of the temperature to 600 °C to char the sample and drive off the volatile organic materials. The last step is the atomization of element by increase the temperature to 2000 – 2500 °C. During these three steps, the graphite tube is flushed with argon gas to protect the graphite tube from the oxidation.

(3) *Monochromator:* The monochromator is used for choosing the specific wavelength of light.

(4) *Detector:* Photomultiplier tubes (PMT) are the most frequently used detectors in AAS. The PMT consists of a photocathode, an anode, and several electrodes called “dynodes” sealed in the evacuated glass tube. The photocathode is made from the metal

coating with an alkali metal or a mixture of elements (e.g., Na/K/Cs/Sb or Ga/As) that emits electrons when struck by photons. When the light passes through the monochromator and enters the PMT, it excites the electrons in the photocathode resulting in the emission of photoelectrons. The photoelectrons are accelerated and strike onto the first dynode surface. This causes several more electrons to be emitted from the surface. These emitted electrons are in turn attracted to a second dynode, where similar electron emission and more multiplication occur. The process is repeated several times until the multiplied secondary emitted from last dynode are collected by the anode. The number of electrons falling on the anode is a measure of the intensity of light falling on the detector [75-76].

(5) *Data processor*: The collected data are processed with the computer.



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1.9 Research objectives

- To study the properties and the characteristics of leonardite from Mae Moh mine, Lampang, Thailand.
- To evaluate the adsorption ability of leonardite for the removal of Cd(II) and Zn(II) ions from aqueous solutions.
- To investigate the influence of various parameters (pH, contact time, initial metal concentration, temperature) on the adsorption of Cd(II) and Zn(II) on leonardite.
- To study adsorption kinetic, and thermodynamic of Cd(II) and Zn(II) on leonardite.
- To study adsorption isotherm models of single and binary adsorption of Cd(II) and Zn(II) on leonardite.
- To study the effect of using linear regression and non-linear regression to determine the adsorption isotherm models and isotherm parameters.
- To evaluate the influence of metal ions on each other in binary component adsorption systems.

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