CHAPTER 1

INTRODUCTION

Water pollution by heavy metals and organic substances are serious and complex problem that has been, and still is, a focus of attention all over the world. They occur when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds, and affects plants and organisms living in these bodies of water, and in almost all cases the effect is damaging not only to individual species and populations, but also to the natural biological communities [1]. At present, wastewater pollution increased as a result of the industrial and population growth and the poor control of emissions. The specific contaminants leading to pollution in water include a wide spectrum of chemicals, pathogens, and physical or sensory changes such as elevated temperature and discoloration. While many of the heavy metals and chemicals substances that are regulated may be naturally occurring (calcium, sodium, iron, manganese, etc.) the concentration is often the key in determining what is a natural component of water, and what is a contaminant. High concentrations of naturally-occurring substances can have negative impacts on aquatic flora and fauna [2-3].

The treatment methods for the removal of the contaminated water commonly include precipitation (using lime and caustic soda), alum and iron coagulation, ion exchange [1], membrane filtration, electrolytic reduction, solvent extraction and adsorption process [2]. Adsorption processes have long been used in the water and wastewater industries to remove color, odor and organic pollution. Using the adsorption process for the removal of heavy metals and organic substances has a short history compared to other water purification processes. Adsorption was first observed by Lowitz in 1785 and was soon applies as a process for removal of color from sugar during refining. In the later half of the 19th century, American water treatment plants used inactivated charcoal filters for water purifications. In 1929 the first granular activated carbon (GAC) units for treatment of water supplies were constructed in Hamm, Germany, and in 1930 at Bay City, Michigan. Nowadays adsorption on activated carbon is a recognized method for the wastewater treatment while the high cost of activated carbon limits its use in adsorption. A search for a low-cost and easily available adsorbent has led to the investigation of materials of agricultural and waste materials as potential adsorbent [4]. The adsorption process provides an attractive alternative for the treatment of contaminated waters, especially if the adsorbent is inexpensive and does not require an additional pre-treatment step, such as activation, before its application. Natural materials, biosorbents and waste materials from industry and agriculture represent potentially more economical alternative sorbents [5].

Leonardite or oxihumolite is a frequently used name for a certain kind of oxidatively altered young brown coal that originated on the surface of lignite deposits by post-sedimentary oxidation. Leonardite similarly to the related organic deposits such as humic substances, are exploited for an industrial preparation of humic acids as well as additives to agricultural fertilizers and soil conditioner [6]. It is widely recognized that humic substances have an elevated cation exchange capacity and it is generally accepted that they contain several major functional groups: such as carboxyl (COOH), alcoholic (OH) and carbonyl (C=O). These properties enable leonardite to be used as a wastewater treating medium to remove contaminants [1, 7]. Large deposits of leonardite are in the North-Bohemian Coal Basin in the Czech Republic, Alberta, Saskatchewan, and possibly in British Columbia. And in the United Stated leonardite, humate and weathered coal have been produced commercially from deposits in North Dakota and New Maxico, often as a by-product of lignite or coal mining[5-6, 8].Whereas in Thailand, large deposits of leonardite are located in Lampang province, at Mae Moh lignite mine as shown in Fig. 1.1.

In this study, the leonardite sorption capacity for metal ions and organic substance were studied. Moreover the factors that affect to the sorption will be investigated in batch systems, as novel adsorbing materials for use in wastewater treatment to provide economic benefits.

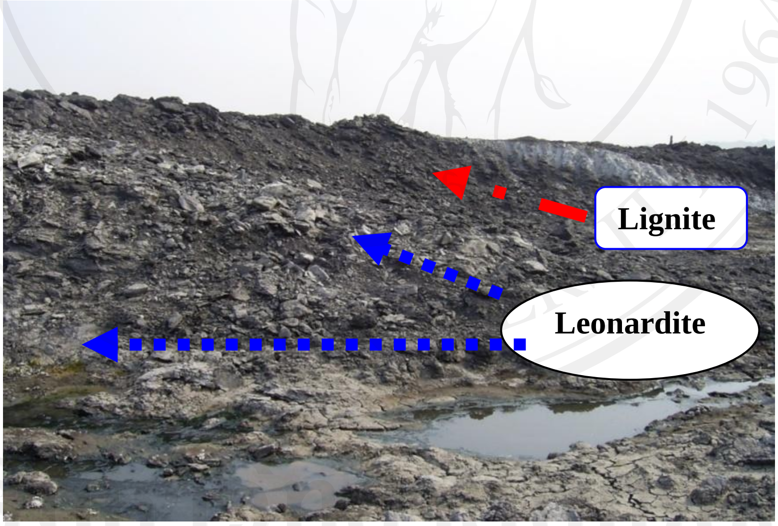

Figure 1.1 Leonardite in Mae Moh mine [9]

1.1 **Heavy metals pollutions**[1, 3-4, 7]

Heavy metals are among the main pollutants of surface and groundwater. Industrial and municipal wastewaters frequently contain metal ions and waste streams containing heavy metals are often encountered in chemical process industries, such as metal, finishing and plating facilities, as well as in mining operations and tanneries. In generally, heavy metals are not biodegradable and they tend to accumulate in living organisms, causing various diseases and disorders.It has been recognized in toxicological studies that heavy metals pose a threat to human health, animal and plants. The toxicity of different types of heavy metal varies. Heavy metal ions have lethal effects on all forms of life and these enter the food chain through the disposal of wastes in water channels. From among various metal ion, lead, mercury, cadmium and chromium (VI) are at the top on the toxicity list. Due to non-biodegradability, metal ions accumulate and their amounts are increased along the food chain. Hence, their toxic effects are more pronounced in the animals at higher trophic levels. Sources and toxicity of certain metal ions are listed in Table 1.1.

Heavy metals are transported into the environment either naturally (such as erosion and natural leaching of surface deposits of metal minerals) or from human activities (such as mining, smelting, fossil fuel combustion, industrial application of metals). Some of them are accumulative poisons capable of being assimilated, stored and concentrated by organisms that are exposed to low concentrations of these substances for long periods. Therefore the removal of heavy metals from wastewaters is required prior to discharge into receiving water.

Table 1.1 Sources and toxic effects of heavy metals on human beings.

Metal	**Source**	**Toxic effect**
Lead	Eletroplating, manufacturing of batteries, pigments, ammunition	Anaemia, brain damage, anorexia, malaise, loss of appetite, diminishing IQ
Cadmium	Electroplating, smelting, alloy manufacturing, pigments, plastic, mining, refining	Carcinogenic, renal disturbances, lung insufficiency, bone lesions, cancer, hypertension, Itai-Itai disease, weight loss
Mercury	Weathering of mercuriferous areas, volcanic eruptions, naturally-caused forest fires, biogenic emission, battery production, fossil fuel burning, mining and metallurgical processes, paint and chloralkali industries	Neurological and renal disturbances, impairment of pulmonary function, corrosive to skin, eyes, muscles, dermatitis, kidney damage
Chromium (VI)	Electroplating, leather tanning, textile, dyeing, metal processing, wood preservatives, paints and pigments, steel fabrication and canning industry	Carcinogenic, mutagenic, teratogenic, epigastric pain nausea, vomiting, severe diarrhea, producing lung tumors
Arsenic	Smelting, mining, energy production from fossil fuels, rock sediments	Gastrointestinal symptoms, disturbances of cardiovascular and nervous system functions, bone marrow depression, haemolysis, hepatomegaly, melanosis
Copper	Printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printing operations	Reproductive and developmental toxicity, neurotoxicity, and acute toxicity, dizziness, diarrhea
Zinc	Mining and manufacturing processes	Causes short team “metal-fume fever”, gastrointestinal distress, nausea and diarrhea
Nickel	Non-ferrous metal, mineral processing, paint formulation, electroplating, porcelain enameling, copper sulphate manufacture and steam-electric power plants	Chronic bronchitis, reduced lung function, lung cancer

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The metals chosen for this leonardite sorption study were copper, zinc and lead. The choice of metals had been made with regard to their industrial use and potential pollution impact. Copper is one of the most common of the industrial metals. It is often found in printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printing operations. Zinc is widely used in metallurgy, as a constituent of brass and bronze, in galvanizing, as a coating used to inhibit the corrosion of steel, and used in roller coating operations. For humans, even copper and zinc are an essential element, although large dosed can have harmful, even fatal, effects. Copper causes ‘Wilson’s disease’ in which excess copper is deposited in the brain, skin, liver and pancreas. Symptoms of zinc toxicity include nausea/vomiting, fever, cough, diarrhea, fatigue, neuropathy and dehydration. Whereas, lead is present inwastewaterfrom storage battery manufacture, drainage from leadore mines, paint manufacture, munitions manufacture, andpetroleum refining. Lead has the ability to replace calcium in bones forming a semipermanent reservoir for long-term release well after the initial absorption. The effects of lead on humans include hypertension and brain damage.

1.1.1 Copper [4, 11-12]

Copper, an element of atomic mass 63.546 and atomic number 29, is known that the absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. Humans widely use copper. For instance it is applied in the industries and in agriculture. Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release have already been named. Other examples are mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activity it is very widespread in the environment. Copper is often found near mines, industrial settings, landfills and waste disposals. Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture.

Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death. Whether copper is carcinogenic has not been determined yet. There are scientific articles that indicate a link between long-term exposure to high concentrations of copper and a decline in intelligence with young adolescents. Whether this should be of concern is a topic for further investigation. Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper poisoning results in Wilson's Disease, characterized by a hepatic cirrhosis, brain damage, demyelination, renal disease, and copper deposition in the cornea. The safety level of copper, in water from industrial setting and in drinking water for humans, is not more than 2.0 mg/L.

1.1.2 Zinc [7, 13-14]

Zinc is a very common substance that occurs naturally. Many foodstuffs contain certain concentrations of zinc. Drinking water also contains certain amounts of zinc, which may be higher when it is stored in metal tanks. Industrial sources or toxic waste sites may cause the zinc amounts in drinking water to reach levels that can cause health problems.Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unnaturally, due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing. Some soils are heavily contaminated with zinc, and these are to be found in areas where zinc has to be mined or refined, or were sewage sludge from industrial areas has been used as fertilizer.

Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc-shortages can even cause birth defects. Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to zinc chloride can cause respiratory disorders. Zinc can be a danger to unborn and newborn children. When their mothers have absorbed large concentrations of zinc the children may be exposed to it through blood or milk of their mothers.

Zinc is naturally present in water. The average zinc concentration in seawater is 0.6-5 ppb. Rivers generally contain between 5 and 10 ppb zinc. Algae contain 20-700 ppm, sea fish and shells contain 3-25 ppm, oysters contain 100-900 ppm and lobsters contain 7-50 ppm.

1.1.3 Lead [4, 15-16]

Lead is counted as one of the heavy metals, and can occur naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities. Due to the application of lead in gasoline an unnatural lead-cycle has consisted. In car engines lead is burned, so that lead salts (chlorines, bromines, oxides) will originate. These lead salts enter the environment through the exhausts of cars. The large particles will drop to the ground immediately and pollute soils or surface waters. Moreover, lead is often found in wastewater from printed circuit board factories, electronics assembly plants, battery recycling plants and landfill leachate. In the printed circuit factory, solder plating and etching operations is the lead source. In the electronics assembly operations, the source is solder flux cleaning. In battery breaking, the lead is found in the sulfuric acid from the battery. In landfill leachate, it can be found as an organometallic like tetra ethyl lead.

For the lead poisoning, the human body contains approximately 120 mg of lead. About 10-20% of lead is absorbed by the intestines. Symptoms over overexposure to lead include colics, skin pigmentation and paralysis. Generally, effects of lead poisoning are neurological or teratogenic. Organic lead causes necrosis of neurons. Inorganic lead causes axonal degeneration and demyelination. Both species of lead may cause cerebral oedema and congestion. Organic lead compounds are absorbed quicker, and therefore pose a greater risk. Organic lead derivatives may be carcinogenic. Women are generally more susceptible to lead poisoning than men. Lead causes menstrual disorder, infertility and spontaneous abortion, and it increases the risk of stillbirth. Foetuses are more susceptible to lead poisoning than mothers, and generally foetuses even protect mothers from lead poisoning. A long time ago lead was applied as a measure of birth control, for example as a spermicidal, and to induce abortion. Children may absorb a larger amount of lead per unit body weight than adults (up to 40%). Consequently, children are generally more susceptible for lead poisoning than adults. Symptoms include lower IQs, behavioral changes and concentration disorder. Lead accumulates in leg tissue. The most severe type of lead poisoning causes encephalopathy.Lead toxicity is induced by lead ions reacting with free sulfydryl groups of proteins, such as enzymes. These are deactivated. Furthermore, lead may interact with other metal ions.The safety level of lead, in water from industrial setting and in drinking water for humans, is not more than 0.2 and 0.05 mg/L, respectively.

1.2 **Organic substances** [17-19]

Organic pollution occurs when an excess of organic matter, such as manure or sewage, enters the water. When organic matter increases in a pond, the number of decomposers will increase. These decomposers grow rapidly and use a great deal of oxygen during their growth. This leads to a depletion of oxygen as the decomposition process occurs. A lack of oxygen can kill aquatic organisms. As the aquatic organisms die, they are broken down by decomposer which leads to further depletion of the oxygen levels.

A type of organic pollution can occur when inorganic pollutants such as nitrogen and phosphates accumulate in aquatic ecosystems. High levels of these nutrients cause an overgrowth of plants and algae. As the plants and algae die, they become organic material in the water. The enormous decay of this plant matter, in turn, lowers the oxygen level. The process of rapid plant growth followed by increased activity by decomposers and a depletion of the oxygen level is called eutrophication.The organic pollution chosen for this leonardite sorption study were dyes and pigments.

Dyes and pigments have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Color stuff discharged from these industries poses certain hazards and environmental problems. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. The presence of dyes in water sources is aesthetically unacceptable and may be visible at concentration as low as 1 ppm. Furthermore, many dyes are toxic to some microorganisms and many cause direct destruction or inhibition of their catalytic capabilities. Dyes and pigments are emitted into wastewaters from various industrial branches, such as from the dye manufacturing or textile finishing, and may significantly affect photosynthetic activity in aquatic systems. They represent one of the problematic groups of chemical pollutants, as they are hardly destroyed in conventional wastewater treatment plants and require usually special treatment strategies.

In the present study, aqueous solutions of a basic dye, methylene blue, were used as a model compound in an attempt to use leonardite as an adsorbent.

1.2.1 Methylene Blue [20-21]

Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$ (Fig. 1.2). It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. Methylene blue is widely used as a redox indicator in analytical chemistry. Solutions of this substance are blue when in an oxidizing environment, but will turn colorless if exposed to a reducing agent. The redox properties can be seen in a classical demonstration of chemical kinetics in general chemistry, the “blue bottle” experiment. Typically, a solution is made of dextrose, methylene blue, and sodium hydroxide. Upon shaking the bottle, oxygen oxidizes methylene blue, and the solution turns blue. The dextrose will gradually reduce the methylene blue to its colorless, reduced form. Hence, when the dissolved oxygen is entirely consumed, the solution will turn green.

Methylene bluehas lots of applicationareas such as coloring paper, dyeing cottons, wools and coating for paper stocks. Although methylene blue is not considered to be a very toxic dye, it can reveal very harmful effects on living things. After inhalation, symptoms such as difficulties in breathing, vomiting, diarrhea and nausea can occur in humans. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, painful micturition, and methemoglobinemia.

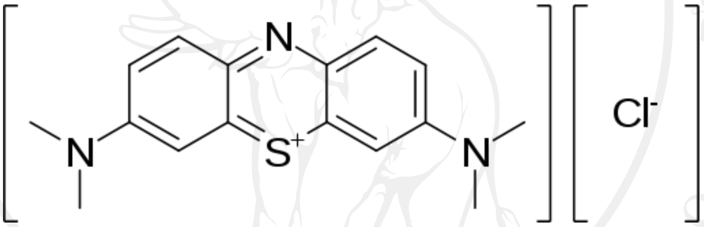

Figure 1.2 The structure of Methylene blue

1.3 **Wastewater treatment** [3]

Owing to the toxic effects of heavy metals and organic contaminants from aqueous waste streams and industrial effluents, the industries are advised that the waste waters be treated systematically to removal/minimize the toxic contaminants content in their wastes. A number of methods are already at operation and Table 1.2 compares selective techniques used for the purpose. From Table 1.2, some of the methods (e.g., precipitation and coagulation) produce concentrated and further toxic wastes, creating yet another disposal problem. Moreover, there are concentration limits to which these methods are economical and become ineffective or too expensive to treat wastes having metal ions in concentrations of 100 mg/L or below. Hence, there is a constant need to search for an optical technology while considering its cost, materials employed and its efficiency.

Table 1.2 Some methods to remove metal ions from wastewaters.

Method	**Advantages**	**Disadvantages**
Chemical Precipitation	• Simple • Inexpensive • Most of metals can be removed	• Large amounts of sludge produced • Disposal problems
Chemical coagulation	• Sludge settling •Dewatering	• High cost •Large consumption of chemicals
Ion-exchange	• High regeneration of materials • Metal selective	• High cost • Less number of metal ions removed
Electrochemical methods	• Metal selective • No consumption of chemicals • Pure metals can be achieved	•High capital cost • High running cost •Initial solution pH and Current density
Adsorption Using activated carbon	•Most of metals can be removed • High efficiency (>99%)	•Cost of activated carbon • No regeneration • Performance depends upon adsorbent
Using natural zeolite	• Most of metals can be removed •Relatively less costly materials	• Low efficiency
Membrane process and ultrafilteration	•Less solid waste produced •Less chemical consumption • High efficiency (>95% for single metal)	•High initial and running cost • Low flow rates • Removal (%) decreases with the presence of other metals

The following is a description of someof the methods that commonly used for wastewater treatments.

1.3.1 Chemical Precipitation [22-23]

Chemical precipitation is a method of wastewater treatment. Wastewater treatment chemicals are added to form particles which settle and remove contaminants (Fig. 1.3). The treated water is then decanted and appropriately disposed of or reused. The resultant sludge can be dewatered to reduce volume and must be appropriately disposed of. Chemical precipitation can be used to remove metals, fats, oils and greases (FOG), suspended solids and some organics. It can also to be used to remove phosphorus, fluoride, ferrocyanide and other inorganics. A variety of recipes can be used perhaps the most common being the addition of lime, NaOH, ferric chloride + lime or NaOH, ferrous sulfate + lime or NaOH, or alum + lime or NaOH, followed by high molecular weight anionic polymer addition to aid the flocculation of the particles. Other recipes involve the use of sodium borohydride, sulfides, sodium carbonate, thiourea, thioacetamide, xanthate, and other agents.

When colloidal matters such as emulsified oil or metal bearing particles are treated with metal salts and lime or NaOH, the metal salts act as primary coagulants. The positively charged metal ions combine with the negative colloid particles and neutralize their charge. The particles then repel each other less strongly and tend to coagulate or collect into larger particles. Lowering the pH to between about 3 to 5 at this stage, before or as a result of adding the metal salts, may result in more effective treatment. When the pH is subsequently adjusted to between 8 and 11 the soluble metal salts and other soluble metals in the solution form insoluble hydroxide particles that are large enough to settle. These hydroxide particles coprecipitate other contaminants in the solution, including oil particles and other colloids.

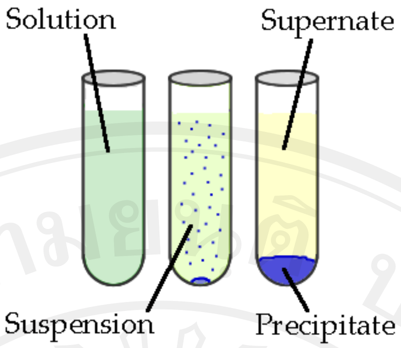

Figure 1.3 Chemical precipitation

1.3.2 Coagulation/Flocculation/Sedimentation [24-26]

In wastewater treatment operations, the processes of coagulation and flocculation are employed to separate suspended solids from water.Finely dispersed solids (colloids) suspended in wastewaters are stabilized by negative electric charges on their surfaces, causing them to repel each other. Since this prevents these charged particles from colliding to form larger masses, called flocs, they do not settle. To assist in the removal of colloidal particles from suspension, chemical coagulation and flocculation are required. These processes, usually done in sequence, are a combination of physical and chemical procedures. Chemicals are mixed with wastewater to promote the aggregation of the suspended solids into particles large enough to settle or be removed.

Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs) in Fig. 1.4. Rapid mixing is required to disperse the coagulant throughout the liquid. Care must be taken not to overdose the coagulants as this can cause a complete charge reversal and restabilize the colloid complex.

Whereas, flocculation is the action of polymers to form bridges between the flocs, and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregateas shown in Fig. 1.5. An anionic flocculant will react against a positively charged suspension, adsorbing on the particles and causing destabilization either by bridging or charge neutralization. In this process it is essential that the flocculating agent be added by slow and gentle mixing to allow for contact between the small flocs and to agglomerate them into larger particles.

Sedimentation is the tendency for particles in suspension to settle out of the fluid in which they are entrained and come to rest against a barrier. This is due to their motion through the fluid in response to the forces acting on them: these forces can be due to gravity, centrifugal acceleration or electromagnetism.

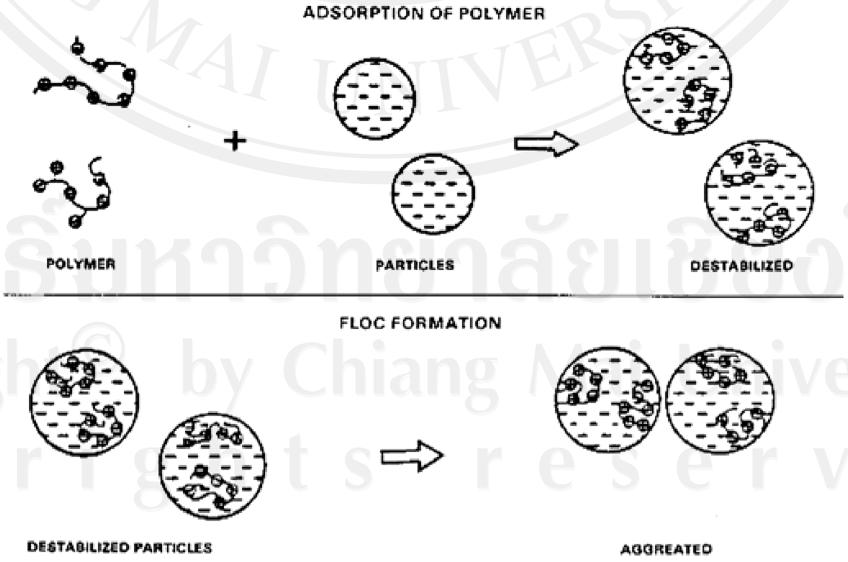

Figure 1.4 Coagulation Process

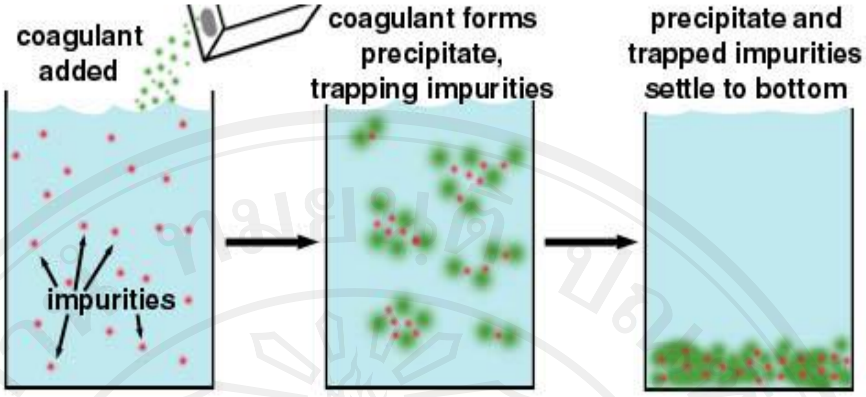

Figure 1.5 Flocculation Process

1.3.3 Filtration [24]

Filtration is commonly the mechanical or physical operation which is used for the separation of solids from fluids (liquids or gases) by interposing a medium through which only the fluid can pass. Oversize solids in the fluid are retained, but the separation is not complete; solids will be contaminated with some fluid and filtrate will contain fine particles (depending on the pore size and filter thickness). Coarse, medium, and fine porous media have been used depending on the requirement. The filter media are artificial membranes, nets, sand filter, and high technological filter systems.

Filtration is also used to describe some biological processes, especially in water treatment and sewage treatment in which undesirable constituents are removed by adsorption into a biological film grown on or in the filter medium.

1.3.4 Membrane Processing [27-28]

Membrane processing is a technique that permits concentration and separation without the use of heat. Particles are separated on the basis of their molecular size and shape with the use of pressure and specially designed semi-permeable membranes (Fig. 1.6). This process commonly used for the removal of dissolved solids, color, and hardness in drinking water.

Figure 1.6 Membrane Processing

1.3.5 Biological methods [27]

Biological treatment method is use microorganisms, mostly bacteria, in the biochemical decomposition of wastewaters to stable end products. More microorganisms, or sludges, are formed and a portion of the waste is converted to carbon dioxide, water and other end products. Generally, biological treatment methods can be divided into aerobic and anaerobic methods, based on availability of dissolved oxygen.

1.3.6 Adsorption Techniques

Adsorption techniques have long been used in the water and wastewater industries to removal toxic metals, color, odor and organic pollution. Liquid-phase adsorption is one of the most efficient methods for the removal of colors, odors and organic and inorganic pollutants from industrial effluents. Granular or powdered activated carbon is the most widely used adsorbent but their use is usually limited due to their high cost. This problem has led many workers to search for the adsorbents that inexpensive and does not require an additional pre-treatment step before its application.

The following is a description of someof the adsorbents that commonly used in adsorption processes for wastewater treatment.

1.3.6.1 Activated carbon [29-31]

Activated carbon, also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. They are widely used as adsorbents in the separation and purification processes both in the gas and liquid phase. They are also used as catalysts and catalyst supports. Branches of industry using activated carbons are the chemical, pharmaceutical, food and others. Activated carbons can be prepared from a variety of raw materials. The most frequently used precursors are hard coal, brown coal, wood, coconut shells and some polymers. In addition agricultural by-products such as fruit stones, various nutshells, and many others can be used as raw materials.

Based on its size and shape, activated carbon is classified into four types: powder (PAC), granular (GAC), fibrous (ACF) and cloth (ACC) as shown in Fig. 1.7. Due to the different sources of raw materials, the extent of chemical activation and the physicochemical characteristics; each type of activated carbon has its specific application as well as inherent advantages and disadvantages in wastewater treatment. Although a significant number of low-cost adsorbents from various materials have been found, commercial activated carbon (CAC) has still been used intensively today.

Figure 1.7 Activated carbon

1.3.6.2 Chitosan [29, 32]

Chitosanis produced by alkaline N-deacetylation of chitin, which is widely found in the exoskeleton of shellfish and crustaceans. Chitosan has a molecular structure similar to cellulose as shown in Fig. 1.8. Presently, chitosan is attracting an increasing amount of research interest, as it is an effective scavenger for heavy metals. Chitosan can also be used in water processing engineering as a part of a filtration process. Chitosan causes the fine sediment particles to bind together, and is subsequently removed with the sediment during sand filtration. Chitosan also removes phosphorus, heavy minerals, and oils from the water.

Chitosan is an important additive in the filtration process. Sand filtration apparently can remove up to 50% of the turbidity alone, while the chitosan with sand filtration removes up to 99% turbidity. It was estimated that chitosan could be produced from fish and crustaceans at a market price of US$ 15.43/kg.

Figure 1.8 Chitosan

1.3.6.3 Zeolite [29, 33]

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents as shown in Fig. 1.9. They are consisted of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms. Zeolites consist of a wide variety of species such as clinoptilolite and chabazite. Clinoptilolite is most abundant in nature and is readily available from more than 40 natural zeolites species. Among the most frequently studied natural zeolites, clinoptilolite was shown to have high selectivity for certain heavy metal ions such as Pb^{2+}, Cd^{2+}, Zn^{2+}, and Cu^{2+}.

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications. In chemistry, zeolites are used to separate molecules (only molecules of certain sizes and shapes can pass through), as traps for molecules so they can be analyzed. Zeolites have the potential of providing precise and specific separation of gases including the removal of H_2O, CO_2 and SO_2 from low-grade natural gas streams. Other separations include noble gases, N_2, O_2, freon and formaldehyde.

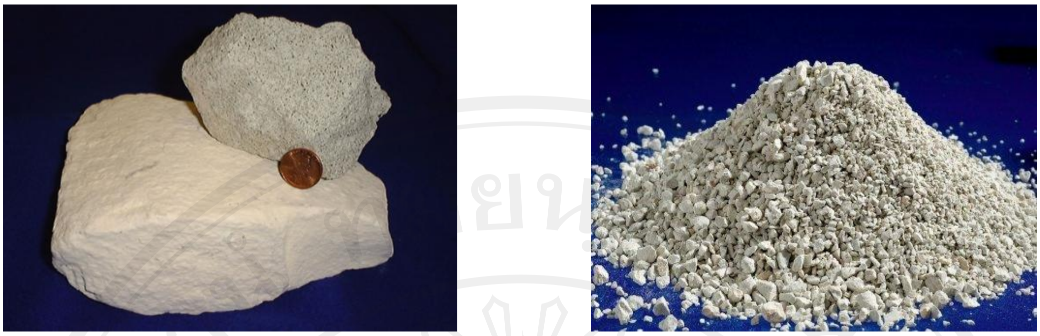

Figure 1.9 Zeolites

1.3.6.4 Clay [29]

It is widely known that there are three basic species of clay: smectites (such as montmorillonite in Fig. 1.10.), kaolinite, and micas; out of which montmorillonitehas the highest cation exchange capacity and that its current market price (about US$ 0.04-0.12/kg) is considered to be 20 times cheaper than that of activated carbon. Montmorillonite is proven to be effective in use as an adsorptive of heavy metals, toxins, and hazardous chemicals. Therefore, a number of studies have been conducted using clays, mainly montmorillonite, to show their effectiveness for removing metal ions such as Zn^{2+}, Pb^{2+}, and Al^{3+} from aqueous solutions.

Figure 1.10 Montmorillonite

1.3.6.5 Peat moss [29, 34]

Peat moss (or Sphagnum as shown in Fig. 1.11), a complex soil material containing lignin and celluloses as major constituents, is a natural substance widely available and abundant, not only in Europe (British and Ireland), but also in the US. They can hold large quantities of water inside their cells, which is why peat moss is commonly sold as a soil conditioner. In addition, the featured characteristics of peat moss were a large of surface area (>200 m^2/g) and highly porous, so that it can be used to bind heavy metals. It is widely known that peat peat moss exhibited a high CEC and complexities towards metals due to the presence of carboxylic, phenolic, and hydroxylic functional groups.

Peat moss is relatively inexpensive material and commercially sold at US$ 0.023/kg in the US.

Figure 1.11 Peat moss

1.3.6.6 Fly ash [29, 35]

Fly ash (Fig. 1.12) is one of the residues generated in combustion, and comprises the fine particles that rise with the flue gases. In an industrial context, fly ash usually refers to ash produced during combustion of coal. Fly ash is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys of coal-fired power plants. Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline) and calcium oxide (CaO), both being endemic ingredients in many coal-bearing rock strata. The most important characteristics of fly ash are the calcium content that provides alkalinity in the system raising pH to strongly alkaline values (~12) and the ($SiO_2 + Al_2O_3 + Fe_2O_3$) content.

Fly ash is one of the cheapest adsorbents having excellent removal capabilities for heavy metals. However, it also contains heavy metals, the possibility of leaching should be considered and evaluated.

Figure 1.12 Fly ash

1.3.6.7 Coal [36]

Basically, coal is a black or brownish-black sedimentary rock composed primarily of carbon, along with other assorted substances, including sulfur. It is extracted by underground mining or open-pit mining. As a readily available, combustible material, it is an extremely significant fuel for the generation of heat and electricity.

Various kinds of coals such as fusinite, bituminous coal and anthracite as shown in Fig. 1.13, can be used as an adsorbent for remove toxic heavy metals.

Fusinite Bituminous Anthracite

Figure 1.13 Various kinds of coals

1.3.6.8 Industrial waste [29, 37]

Natural materials (Fig. 1.14) that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive adsorbents. For example, waste slurry is one of the industrial by-products generated in fertilizer plant showing good sorptive capacities. Lignin extracted from black liquor that is a waste product originated from paper industry. It was investigated that the high adsorption of lignin is due to the presence of polyhydric phenol groups on the surface of lignin.

Moreover, low-cost adsorbents showing capability to adsorb heavy metals are blast-furnace slag and sawdust.

Figure 1.14 Industrial waste

1.3.6.9 Lignite [38-39]

Lignite is a soft brown fuel with characteristics that put it somewhere between coal and peat. It is considered the lowest rank of coal. Macroscopically, lignite is dark brown or black in color when moist and light brown when dry as shown in Fig. 1.15. Its density lies in the range 1.0-1.35 g/cm^3. Lignites are usually amorphous and fibrous or woody in texture. Pore diameters vary; micropores are present, leading to highly porous typical surface areas of 100-200 m^2/g.

Lignite has large amounts of humic and fulvic acids, with the former predominating. It is widely recognized that lignites have an elevated cation exchange capacity and form complexes with metal ions, and it is generally accepted that they contain a high content of oxygen, which is fixed in carboxyl (COOH), alcoholic (OH) and carbonyl groups (C=O). These groups are active centers of the ion exchange materials. These properties enable lignite to be used as a wastewater-treating medium to remove heavy metals.

Figure 1.15 Lignite

1.4 **Leonardite** [40-43]

Leonardite is a naturally occurring hydrocarbon formed in the earth over millions of years by chemical and biological degradation of animal and plant residues as well as synthetic activities of microorganisms. It is an organic material that has a high level of active bacteria in the sediment layer (Fig. 1.16). Leonardite and humified organic matter have been mentioned synonymously for many years. Leonardite and similar materials from oxidized sub-bituminous coals and carbonaceous shales are good sources of humic substances or organic material. Many research works have shown these organic materials can exhibit similar chemical properties as soil humified organic matter. Thousands of years ago, large bodies of water existed where huge quantities of organic matter were deposited which then began to slowly decompose. Over time, the organic material began to lose oxygen and was transformed under heat and pressure. Leonardite is a highly oxidized coal found in superficial strata related to oxidized environments. It has the highest content of humic substances, completely organic in nature and is used as a soil conditioner, as a stabilizer for ion-exchange resins in water treatment, in the remediation of polluted environments. Leonardite was named after Dr. A.G. Leonard in recognition of his work and is associated with lignite coal reserves. Numerous tests have been conducted which substantiate the fact leonardite consistently shows higher levels of carbon content, resulting in a higher humic content.

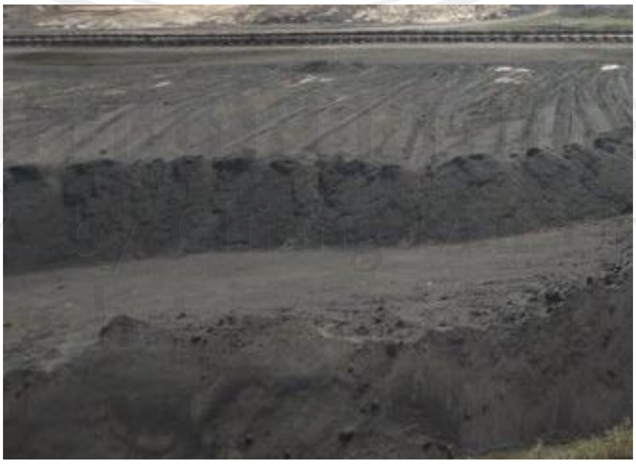

Figure 1.16 Leonardite

Leonardite in Thailand is discovered at the Mae Moh mine. It is situated 25 kilometers east of Lampang province as shown in Fig.1.17. It covers an area of 135 square kilometers, with a maximum width of 8.8 kilometers and a maximum length of 18.3 kilometers. The total geological lignite reserves are estimated to be 1,468 million tones. The plant consists of 13 generating units and has a capacity of 2,625 Megawatts, and is owned and managed by the Electricity Generating Authority of Thailand (EGAT). It provided 12 percent of Thailand's electricity and until 2008, it has been the largest coal-fired power plant in Southeast Asia.

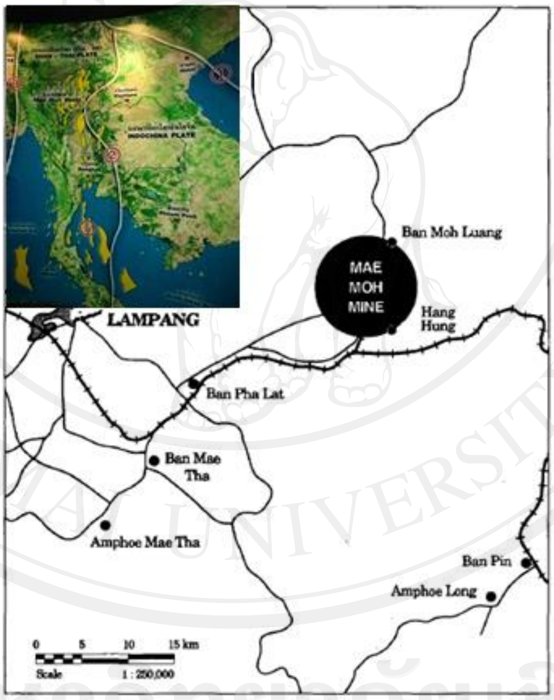

Figure 1.17 Mae Moh lignite mine in Lampang province

1.4.1 Humic substances [44-47]

Humic substances (HS) are major components of the natural organic matter (NOM) in geological organic deposits such as lake sediments, peats, brown coals, shales and leonardite. They are organic materials produced by oxidative decomposition of complex organic molecules including carbohydrates, proteins, lignins, lignans and fats from litter, roots, dead organisms and the excrements of living organisms. These substances affect the pH of natural waters, trace metal aquatic chemistry and bioavailability, and the degradation and transport of hydrophobic organic molecules. Humic substances are colloid and coat soil particles, acting as a cushion and an interface between the non-living mineral of the soil and the living plant root. Native soil humic substances enhance plant growth both directly and indirectly. They make up much of the characteristic brown color of decaying plant debris and contribute to the brown or black color in surface soils. They are major components of NOM in surface waters and at higher concentrations can impart a dark color. Humic substances can be divided into three main fractions. These sub-divisions are based on the solubility of each fraction in water adjusted to different acid/alkaline (pH levels) conditions.

1) Humic acid: The fraction of humic substances is dark brown to black in color that is not soluble in water under acidic conditions ($pH < 2$) but it is soluble at higher pH values. They can be extracted from soil by various reagents and which is insoluble in dilute acid. Humic acids are the major extractable component of soil humic substances.

2) Fulvic acid: The fraction of humic substances is light yellow to yellow-brown in color that is soluble in water under all pH conditions. They remain in solution after removal of humic acid by acidification.

3) Humin: The fraction of humic substances is black in color that is not soluble in water at any pH value and in alkali.

Humic acid is a principal component of humic substances which are the major organic constituents of soil, leonardite, peat, coal, many upland streams, dystrophic lakes and ocean water. It is the end product of the decomposition of organic matter by aerobic organisms. Humic acid is thought to be complex aromatic macromolecules with amino acids, amino sugars, peptides, aliphatic compounds involved in linkages between the aromatic groups. The hypothetical structure for humic acid, shown in Fig. 1.18, contains free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units and COOH groups variously placed on aromatic rings. They are organic acids that are not soluble in water under acidic conditions but are soluble in water under alkaline conditions. On average, 35% of the humic acid molecules are aromatic carbon while the remaining components (65%) are molecules in the form of aliphatic carbon. The molecular weights of humic acid range from approximately 10,000 to 100,000.Humic acid polymers readily bind clay minerals to form stable organic clay complexes.

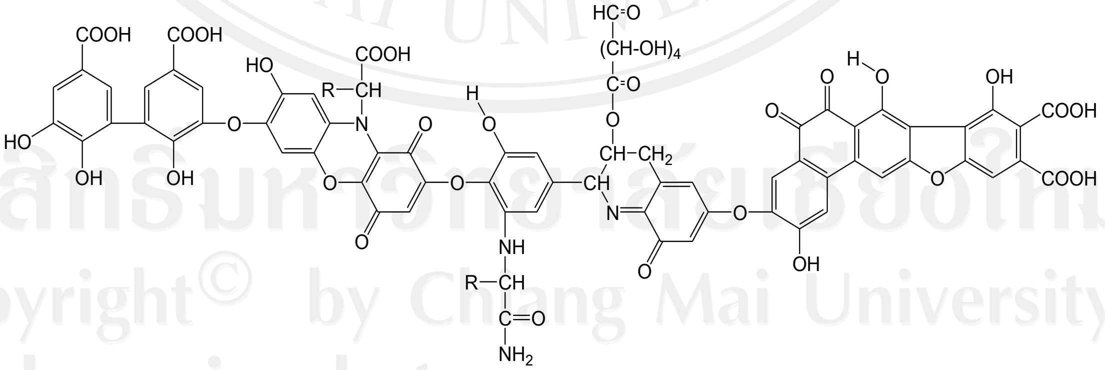

Figure 1.18 Humic acid structure as proposed by Stevenson [44]

Humic acid is importance to life on earth, but they are susceptible to depletion via oxidation and may become deactivated by sodium or aluminum. This creates soil problems which may impact the food chain all the way up. The plant characteristic that the addition of humic substances has consistently enhanced more than any other is root length, especially on sandy soils. Top growth, vigor, and trunk cross-sectional area are also increased in response to stimulation by humates, but the effect is usually more prominent in the roots. A proliferation in root growth results in an increased efficiency of the root system. The trace elements are bound to humic acid molecules in a form that can be readily utilized by various living organisms. As a result humic acid functions as important ion exchange and metal complexing systems.

1.5 Test procedure for physical and chemical analysis

1.5.1 X-ray diffractometry [48-49]

Principles: X-ray diffraction (XRD) analysis is a nondestructive method for the structure analysis of crystals. The sample is irradiated with monochromatic X-raylight 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. 1.19). 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:

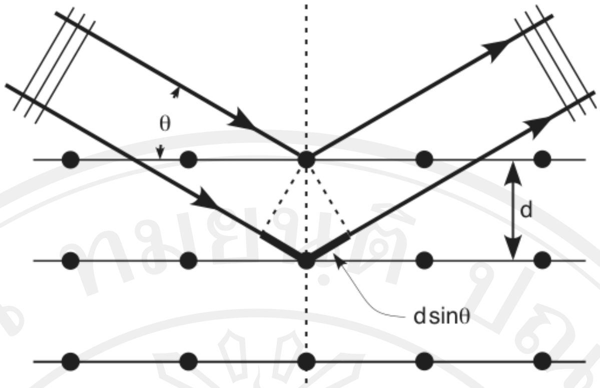

Figure 1.19 Reflection of X-ray from a crystal.

Bragg's equation; $n\lambda = 2d \sin \alpha$ (n=1, 2, 3,...) (1.1)

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 calle ddiffractometers.

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 cannot 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 crystallinesubstance, it is also possible to carry out quantitative determinations.

1.5.2 X-ray fluorescence spectrometry [50]

The main principle of X-ray fluorescence spectrometry is that the emission of characteristic "secondary" (or fluorescent) X-rays from a sample that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology. 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 showed in Fig. 1.18. 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. 1.20) includes a source of primary radiation (usually a radioisotope or an X-ray tube) and the equipment for detecting the secondary X-rays.

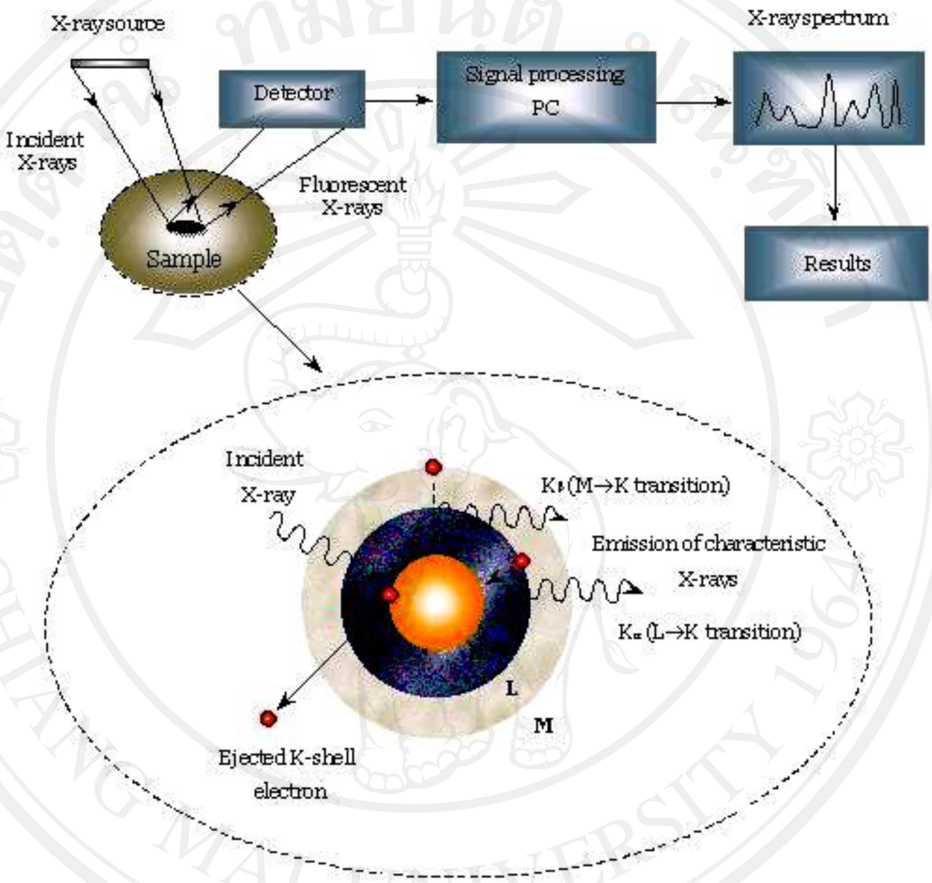

Figure 1.20 Schematic diagrams of XRF and the typical XRF detection arrangement

Instrumentation: It 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 techniques

,but XRF cannot be used to analyze hydrogen, helium, and beryllium and detection limits for other light elements are poor.

1.5.3 Surface area [51-52]

There are different methods used to measure surface area and each method can yield different results. The Brunauer, Emmett and Teller (BET) method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules**.** In general, BET was carried out at very low temperature to ensure only physical adsorption, and to use a relatively inert gas such as nitrogen.

A total surface area S_{total} and a specific surface area S are evaluated by the following equations 1.2 and 1.3, respectively.

$$S_{total} = \frac{(\nu_m N \cdot S)}{M.W} \tag{1.2}$$

$$S = \frac{S_{total}}{W} \tag{1.3}$$

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

1.5.4 Particle size analyzer [53]

A particle size analyzer (Fig.1.21) that measures the intensity of light scattered by moving particles passing through the probe of a crossed beam laser anemometer, verifies that the measured signal was produced by a particle passing through a region near the center of the probe, and stores count values related to the number of particles producing the same scattered light intensity value is disclosed. Since scattered light intensity values are related to particle size, the stored count values equal the number of particles of the same size detected by the analyzer. In the preferred form of the invention, the measured light intensity determines the address of a particular intensity bin of a storage system. After verification to determine if a measured intensity value was produced by a particle passing through a region near the center of the probe, the count value stored in an intensity bin related to the measured value is updated by one. When any bin reaches the maximum value that can be stored therein, the particle light intensity measuring mode of operation ends and the particle size analyzer is placed in a readout mode of operation. In the readout mode of operation, the intensity bin count values are sequentially read out, converted into analog form, and displayed.

Figure 1.21 Particle size analyzer

1.5.5 Cation exchange capacity (CEC) [54-55]

Cation-exchange capacity is defined as the degree to which a soil can adsorb and exchange cations. CEC of a soil is a measurement of its ability to bind or hold exchangeable cations. In other words, it is a measure of the number of negatively charged binding sites in the soil. Moreover, CEC is used as a measure of fertility, nutrient retention capacity, and the capacity to protect groundwater from cation contamination. It is expressed as milliequivalent of hydrogen per 100 g (meq$^+$/100g), or centimol per kg (cmol$^+$/kg). The numeric expression is coincident in both units.

1.5.6 Analysis through spectroscopy at the atomic level

1.5.6.1 Atomic absorption spectroscopy [56-57]

Principle: The sample is vaporized by aspiration of solution into a flame or evaporation from an electrically heated surface. At this condition the electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing in the visible and ultraviolet region. 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.

Instrumentations: There are three basic components of AAS. (Fig. 1.22) namely 1) Sources emitting radiationare hollow cathode lamp, flame or electrically heated furnace. The radiation source could be an element-specific line radiation source or a continuum radiation source. 2) Sample cell and 3) Specific light measurement such as monochromator, detector (photomultiplier) and recorder.

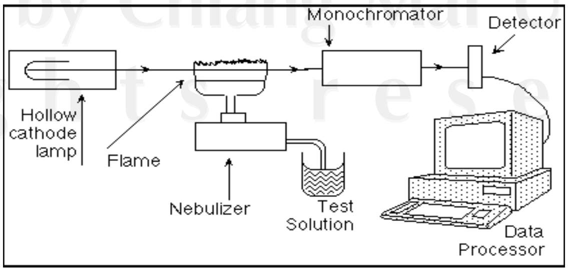

Figure 1.22 The Three basic components of AAS.

Applications: In analytical chemistry the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. 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. The plot will give the useful linear range and the concentrations of the samples can be found out from the plot.

1.5.6.2 Ultraviolet - visible spectroscopy [58]

Principle: 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.

Instrumentations: It consists of a dual light source (tungsten lamp for visual range measurements and deuterium lamp for measurements at ultra-violet regions). Xenon arc lamps, which is continuous from 160-2,000 nm; or more recently, light emitting diodes (LED) for the visible wavelengths, a grating monochromators, detector (photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device(CCD)), mirrors and glass or quartz cells.The type of sample container used must allow radiation to pass over the spectral region of interest. The most widely applicable cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions. Glass and plastic cuvettes are also common, although glass and most plastics absorb in the UV, which limits their usefulness to visible wavelengths. A spectrophotometer can be either single beam or double beam. However, nowadays, double beam spectrophotometers are widely used.

Applications: It is routinely used in analytical chemistry for the quantitative determination of different analyzes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Sometimes it is used in conjunction with other techniques in the identification and structural analysis of organic materials. For qualitative analysis, the “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.

1.5.6.3 Scanning electron microscopy [59]

Principle: In this technique, an electron beam, emitted from an electron gun, is focused onto the sample surface. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. And electronic amplifiers are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronised with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be digitally captured and displayed on a computer monitor.

Instrumentations: The instrumentation is very large. It consists of heated filament as source of electron beam, condenser lenses, aperture, evacuated chamber for placing the sample, electron detector, amplifier, CRT display and computer monitor.

Applications: Scanning electron microscopy (SEM) has been applied to reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

1.6 **Absorption and adsorption** [60-61]

Sorption refers to the action of absorption or adsorption, and generals 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 1.23 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.

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.

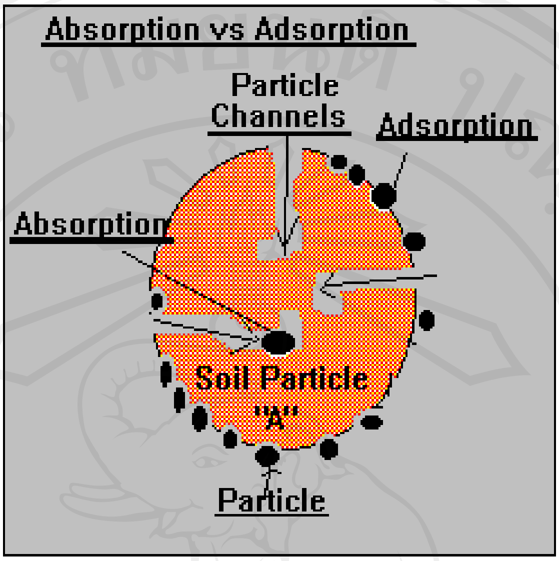

Figure 1.23 Absorption and adsorption.

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 (1.4):

$$q_e \quad = \quad \{(C_i - C_e)V\} / W \qquad (1.4)$$

where C_i = 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 Physisorption and chemisorption [62-63]

Depending on the nature of attractive forces existing between the adsorbate and adsorbent, adsorption can be classified as: physisorption and chemisorption. Physisorption is dependent on van der Waals forces of attraction between molecules and it resembles with the condensation of liquids. Chemisorption, also known as chemical adsorption, requires activation energy as well as chemical forces for the specification of the chemicals involved.

1.6.1.1 Physisorption

Physisorption, also called Physical adsorption, is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption. The weak bonding of physisorption is due to the induced dipole moment of a nonpolar adsorbate interacting with its own image charge in the polarizable solid.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 admolecules 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.

In comparison with chemisorption, in which the electronic structure of bonding atoms or molecules is changed and covalent or ionic bonds form, physisorption, generally speaking, can only be observed in the environment of low temperature (thermal energy at room temperature ~26 meV) and the absence of the relatively strong chemisorptions.

1.6.1.2 Chemisorption

Chemisorption is a sub-class of adsorption, driven by a chemical reaction occurring at the exposed surface. A new chemical species is generated at the adsorbant surface (e.g. corrosion, metallic oxidation). The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds - ionic or covalent, depending on the reactive chemical species involved.

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 orimpossible. 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 1.3.

Table 1.3 Parameters of physical adsorption and chemical adsorption.

Parameter	Physical adsorption	Chemical adsorption
Forces of attraction	Van der Waals	Chemical bonding
Heat of adsorption / kJ mol^{-1}	Low heat of adsorption usually in range of 20-40 kJ/mol	High heat of adsorption in the range of 50-400 kJ/mol
Rate of adsorption (at 273 K)	Fast	Slow
Temperature dependence of uptake (with Increasing T)	Decreases	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	Highly Specific
Monolayer coverage	Mono or multilayer condition dependent	Monolayer
Nature of adsorption	Reversible	Irreversible

1.6.2 Classification of adsorption isotherm [61, 63-65]

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. 1.24 because the systems demonstrate different gas/solid interactions.

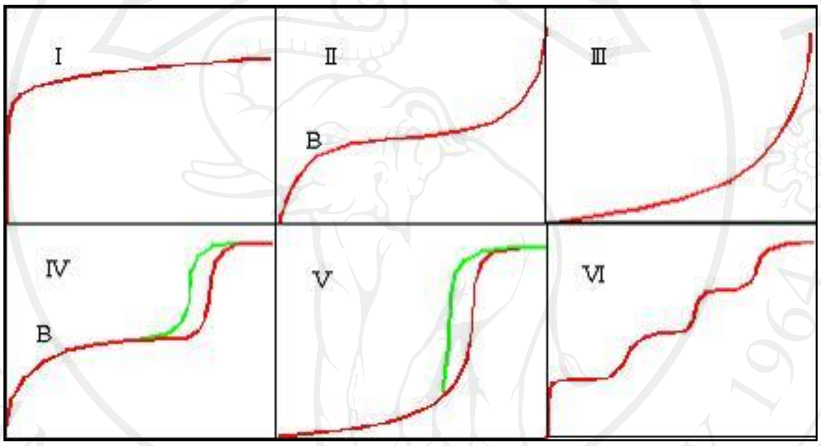

Figure 1.24 Six types of adsorption isotherms.

The Type I isotherm is typical of microporous solids and chemisorption isotherms. Type II is shown by finely divided non-porous solids. Type III and type V 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 nitrogen adsorbed on special carbon.

1.6.3 Isotherm equations [66-67]

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:

$$q_e = \frac{q_o b C_e}{1 + b C_e} \tag{1.5}$$

where q_o = saturation limit and b = a temperature dependent equilibrium constant. The constant q_o 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:

$$\frac{C_e}{q_e} = \frac{1}{bq_o} + \frac{1}{q_o} C_e \tag{1.6}$$

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, $1/q_{o,}$ and intercept, $1/bq_{o,}$ 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 1.7.

$$q_e = K_F * C_e^{1/n} \tag{1.7}$$

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 1.8.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{1.8}$$

1.6.3.3 BET isotherm

The theory of Brunauer, Emmett and Teller (BET) is a well-known rule for the physical adsorption of gasmolecules on a solidsurface. 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 1.9:

$$\frac{1}{\nu[(P_0/P)-1]} = \frac{1}{\nu_m c}\left(\frac{P}{P_0}\right) + \frac{1}{\nu_m} \qquad (1.9)$$

where P and P_o 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 (1.9) is an adsorptionisotherm and can be plotted as a straight line with $1/v[(P_o/P) -1]$ on the y-axis and P/P_o 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

Adsoption behaviors and factors that affect the adsorptionof copper(II), lead(II),zinc(II)and methylene blue on leonardite obtained from Mae Moh, Lampang Province, Thailand have been investigated.