

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Heavy metals

2.1.1 Definition

The term “Heavy metals” is somewhat ambiguous but is usually considered those elements in Periodic Table Groups IB to VIIB with atomic number between 21 and 84, excluding the rare earth elements. They have a different electron configuration to the “light metals” which are in Periodic Table Groups IA to IIA. In practice, however, the use of the term “heavy metals” is usually restricted to those metals that may have adverse consequences if they are released to the environment in excess quantities. Common heavy metals are chromium, copper, zinc, silver, cadmium, mercury, and lead (Connel, 1974).

2.1.2 Significant and toxicity of heavy metals to creatures

Heavy metals are unique as a group of “pollutant” in the sense that many of them are considered harmful at relative low concentrations but might still be essential for the growth of biota in trace concentrations. Many biomolecules like enzymes depend on the metal components in their molecular structure to carry out their metabolic functions. For example, trace amounts of Cu, Zn, Mn, Fe, and Mo are found to be essential for microbial life, but it is not sure that these metals are essential for the growth and cell division of every microbial species. The overabundance of these heavy metals can build up to intracellularly toxic levels, which results in chronic and acute problems. Moreover, some heavy metals such as lead, cadmium, and mercury do not have any role in the growth of biota, these metals are considered as non-essential elements.

Heavy metals are probably the oldest toxic substances that human have known. The pollution and toxicological details are very complicated by the diversity of heavy metals and their chemical properties. Table 2.1 lists some common heavy metals and some organic chemicals with their TLVs (Threshold Limiting Values) and effect of poisoning. It can be seen that TLVs for all heavy metals are low even when compared to the TLV of benzene, a well known carcinogen. Especially for lead, cadmium, and mercury, which have extremely low TLV, these heavy metals have long history of poisoning incidents. Thus it is

not surprising that most environmental protection agencies around the world have set priority of these elements and their compounds at the top of their hazard list.

2.1.3 Sources of heavy metal

Natural processes, such as weathering and volcanic activity, continually add heavy metals to the environment (Fostner and Wittman, 1981). These processes result in “background” metal concentrations in various environmental compartments. However, these background concentrations are considered to be low and not likely to adversely affect human. In addition, the contribution from human activities is also the main cause of heavy metal problems. A lot of heavy metals quantities are contributed globally from anthropogenic sources, especially copper, cadmium, and lead (Hart and Lake, 1987). Heavy metals employed in various types of industries are listed in Table 2.2. Up to now, there are increasing usages of heavy metals as raw materials in factories and industrial activities. This enhances adverse affects to creature and environment.

Figure 2.1 summarizes the major routes through which most of the heavy metals may transfer to the environment. Most of the heavy metals emitted to the atmosphere are eventually deposited onto land or water and will tend to be adsorbed to soils and sediments. However, they can become desorbed and return to aquatic environment. It is probably true that some heavy metals such as copper, cadmium, and lead have the most dangerous effect when they are present in water because they can readily transferred to the biosphere.

2.1.4 Legal controls for heavy metals contamination

Legislation around the world rapidly catches up with the fears of environmentalists over heavy metal contaminations. For example, the last few years have seen directives issued by various organizations such as European Commission (EC) and United States Environmental Protection Agency (US-EPA) which are stricter for heavy metal discharges from industry.

In Thailand, the standard of heavy metals concentration in industrial effluent as a legislation have been set by the Ministry of Industry in B.E. 2525 (A.D. 1982) and by the Ministry of Science, Technology and Environment in B.E. 2539 (A.D. 1996). The details are showed in Table 2.3. Surprisingly, the Standard of Thailand has an opposite direction with those around the world as the updated standard of Thailand becomes less strict than the old one especially for Copper and Nickel.

2.1.5 Treatment technologies

There are a lot of treatment technologies for heavy metal including precipitation, electrolytic recovery, membrane separation, ion exchange resin, evaporation, carbon adsorption, and biosorption. These techniques except biosorption have more efficiency with the wastewater containing high concentration of heavy metal. In contrast, if the concentration of heavy metals is low (e.g. less than 100 mg/l), the relatively high cost will render these techniques unattractive. Also, some of the treatment techniques were less effective for wastewater containing low level of heavy metals. Biosorption is the lowest cost treatment method compared with the other techniques (Banerjee, 2000) and suitable with the wastewater containing heavy metal concentration lower than 100 mg/l (Volesky, 1990).

2.2 Basic adsorption theory

Adsorption is fundamentally the attachment of one type of material onto surface of another material type, like dust attaches on the wall. The materials that are adsorbed is called adsorbate whereas the adsorbent is the adsorbing species. Examples of adsorbents include activated carbon (AC), silica gel, alumina, fly ash etc. Good adsorbents must have enormous surface area per unit weight as the number of active site varies directly with its surface area.

2.2.1 Single-component sorption isotherm

Isotherm is the relationship between adsorption capacity and concentration of the remaining adsorbate at constant temperature. Generally the isotherms can be mathematically present in two well-known forms: Langmuir and Freundlich isotherms which are expressed as:

$$\text{Langmuir isotherm:} \quad q = \frac{x}{m} = \frac{q_m b C_e}{1 + b C_e} \quad (2.1)$$

$$\text{Freundlich isotherm:} \quad q = \frac{x}{m} = K_f C_e^{1/n} \quad (2.2)$$

where

x = $V(C_i - C_e)$ = amount of heavy metals's mass adsorbed

V = volume of the heavy metal concentration

C_i = initial concentration of heavy metals

C_e = concentration of heavy metals left in solution at equilibrium

m = mass of adsorbent (in this research we use algae as an adsorbent)

q = x per m ratio , mmol-sorbate/gram-sorbent

q_m = the maximum x per m ratio(adsorption capacities)

b, n = constant

K_f = adsorption capacity of Freundlich isotherm

The assumptions for each of these isotherms are:

For Langmuir isotherm

- 1) There is only a single layer (monolayer) of adsorbate on the adsorbent surface.
- 2) All of adsorbent surface is uniform and has same affinity for all binding sites.
- 3) There is no interaction between adsorbate molecules.
- 4) The sorption reaction can be represented as a coordination reaction with 1:1 stoichiometry.

For Freundlich isotherm

- 1) There are many layers (multilayer) of adsorbate on the adsorbent surface.
- 2) Adsorbent surfaces are heterogeneous surface.

There are several other isotherm models for single-component sorption as summarized in Table 2.4.

2.2.2 Binary and multi-component sorption isotherm

The basic concept of binary and multi-component sorption isotherms is similar to single-component sorption isotherm (monolayer or multi-layer) but there will be an increase in the number of metal ions that compete for the binding sites in the adsorbent.

In case of Langmuir single-component sorption isotherm, the assumption of monolayer sorbate and all free binding sites leads to the following adsorption reaction:



where

B = the free binding sites

M = the sorbate in solution (in this case sorbate is metals)

BM = the binding sites with adsorbed metal

Assume that this reaction is already in equilibrium, the sorption equilibrium constant (K) can be expressed as:

$$K = \frac{[BM]}{[B][M]} \quad (2.4)$$

K = equilibrium constant or also represents the affinity of sorbate for the binding site, and [] denotes the concentration.

According to the mass conservation concept, the total binding capacity denoted by B_t is equal to the numbers of free and occupied binding site.

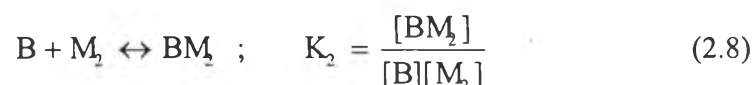
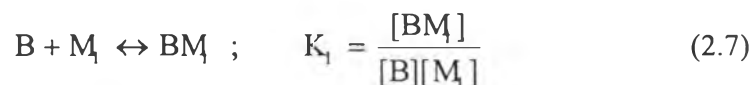
$$[B_t] = [B] + [BM] \quad (2.5)$$

The rearrangement Equations (2.4) - (2.5) leads to a conventional form of Langmuir equation.

$$[BM] = \frac{[B_t] \cdot K[M]}{1 + K[M]} \quad (2.6)$$

where [BM] represents the solid phase concentration (solid phase in this case is the sorbent) or sorbate uptake q , K represents the affinity of sorbate M for the binding site B, and B_t represents the maximum sorption capacity q_{max} .

The binary and multi-component isotherm models based on Langmuir assumption also can be derived using the same principle. In case of binary component sorption, the adsorption reaction can be expressed by two chemical reaction equations with sorption equilibrium constant as shown below



where

M_1 represents the first sorbate (metal) in the solution

M_2 represents the second sorbate (metal) in the solution

The mass balance equation for this case can be written as

$$[B_t] = [B] + [BM_1] + [BM_2] \quad (2.9)$$

Combining Equations (2.7), (2.8), and (2.9) results in

$$[BM] = \frac{[B_t] \cdot K_1 [M_1]}{1 + K_1 [M_1] + K_2 [M_2]} \quad (2.10)$$

$$[BM_2] = \frac{[B_t] \cdot K_2 [M_2]}{1 + K_1 [M_1] + K_2 [M_2]}$$

where $[BM_1]$ and $[BM_2]$ are the sorbent phase concentrations or sorbate uptakes for the first and second metals, respectively.

Equation (2.10) is well known as an extended Langmuir model for binary-component competitive sorption as expressed in Equation (2.11)

$$q_1 = \frac{q_{m,1} b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \quad (2.11)$$

$$q_2 = \frac{q_{m,2} b_2 C_{e,2}}{1 + b_1 C_{e,1} + b_2 C_{e,2}}$$

where

$q_{m,1}$, $q_{m,2}$ = the maximum sorption capacities for components 1 and 2, respectively,

b_1 , b_2 = the affinity constants of Langmuir model for components 1 and 2, respectively,

$C_{e,1}$, $C_{e,2}$ = the equilibrium concentrations for components 1 and 2 respectively in the mixture solution.

q_1 , q_2 = the metal uptakes for components 1 and 2, respectively, in the mixture solution.

A similar derivation for multi-component adsorption isotherm based on Langmuir results in:

$$\begin{aligned}
 q_1 &= \frac{q_{m,1} b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2} + \dots + b_n C_{e,n}} \\
 q_2 &= \frac{q_{m,2} b_2 C_{e,2}}{1 + b_1 C_{e,1} + b_2 C_{e,2} + \dots + b_n C_{e,n}} \\
 &\dots \\
 q_n &= \frac{q_{m,n} b_n C_{e,n}}{1 + b_1 C_{e,1} + b_2 C_{e,2} + \dots + b_n C_{e,n}}
 \end{aligned} \tag{2.12}$$

where

$q_{m,1}, q_{m,2}, \dots, q_{m,n}$ = the maximum sorption capacities for component 1,2,...,n, respectively,

b_1, b_2, \dots, b_n = the affinity constants of Langmuir model for components 1,2,...,n, respectively,

$C_{e,1}, C_{e,2}, \dots, C_{e,n}$ = the equilibrium concentrations for components 1,2,...,n, respectively, in the mixture solution

q_1, q_2, \dots, q_n = the metal uptakes for components 1,2,...,n, respectively, in the mixture solution

2.3 Mechanisms of heavy metals sequestering by biomass

Biomass can sequester heavy metal ions from wastewater by two main types of mechanisms: bioaccumulation and biosorption. Bioaccumulation and biosorption have often been combined into the single heading of metal uptake because the predominant in effect is not known (in case of living biomass). The distinction between bioaccumulation and biosorption is important because these terms often have been poorly understood and described by many researchers.

Bioaccumulation is the active process that living cells accumulate the metal in the environment. This process depends on metabolism activities of the cell. Bioaccumulation has been better studied by microbiologists for its toxicological importance but it is less desirable for eventual metal recovery process design because it requires that the cells be actively metabolizing in what usually is a special culture environment and this is often not found in wastewater.

Biosorption is the passive process that biomass sequesters metals by its external cell components. Biosorption depends on environmental factors and the degree of affinity

resulting in different type of bindings between metal species and active site of a particular molecular structure of the cell wall. An important feature of biosorption is that it can bind and accumulate metal species even the biomass is dead because it is independent of metabolism activities. Biosorption is caused by a number of different physicochemical mechanisms mainly electrostatic attraction, chelation/complexation of metal by functional groups, ion exchange, microprecipitation.

2.4 Mechanism of heavy metal biosorption by non-living biomass

An understanding of the mechanism of biosorption is essential for the development of efficient biosorption processes. Elucidation of metal sequestering mechanism would assist a possible manipulation of the biosorbent material to optimize its performance and control the process parameters employed in biosorption system.

Biosorption is the process of metal binding to the cell wall and external surfaces of biomass, which is independent of metabolic activities of biomass cell. Biosorption mechanisms occur in both living and non-living biomass. However, the non-living biomass seems to be more effective in sequestering metal elements than living biomass (Higgins and Mackey, 1987).

There are many descriptions for sub mechanisms of biosorption including electrostatic attraction, ion exchange, adsorption, inorganic micro-precipitation, and chelation/complexation/coordination of metal by functional groups. It is possible that all these processes are acting individually or in combinations.

The functional groups present on the cell wall surface will bind the metal species by physical-chemical complexation and ion exchange reaction (Shumate and Strandberg, 1985). Also the precipitation of metals can take place near the cell surface, a possible subsequent mechanism to initial biosorption complexation (Tsezos and Volesky, 1982).

The various functional groups were believed to be involved in metal binding include carboxyl, carbonyl, amine, hydroxyl, phosphate, and sulfhydryl groups (Strandberg et al., 1981; Xue et al., 1988). The amount and type of these functional groups were found to differ between biomass species, or even in same species as a result of different environmental conditions in which biomass were grown. For example, the polysaccharide and protein components of certain algal species were significantly greater in spring than in autumn (Madgwick and Ralph, 1972). However, each functional group have different metals affinities, and the present of many functional groups allowed a biosorbent to have a wide range of biosorbing (Hunt, 1986).

2.5 Mechanism of heavy metal biosorption by algae

Many studies on biosorption of heavy metal by non-living algal biomass indicated that algal cell wall is the main site that metal sorption occurs. However, there are varieties in ability of heavy metals sequestering for each algal species, since there are differences in cell wall structure and chemical compositions of each species. A number of different polysaccharides and other chemicals such as cellulose, alginic acid/alginate salt, laminarins, xylan, mannan etc. are commonly found in the algal cell walls which are believed to act as metal binding sites.

Cellulose is also present as a fibrillar material in cell wall of algae. It can be defined as a polymer of β -1,4-linked glucose units and may provide OH^- (hydroxyl) and $\text{C}=\text{O}$ (carbonyl) functional groups. Many or all of these functional groups have ability in complexing with metals. A comparison of electron micrograph of *Sargassum natans* by Kuyucak and Volesky (1989) revealed that cell wall of the biosorbent was the major location for gold deposition. They also showed that the cellulose on the cell wall played an important role in gold sorption. The evidence provided by FT-IR studies indicated that $\text{C}=\text{O}$ (carbonyl) groups of the polysaccharides were probably the main functional group for gold binding, whilst amino groups playing a minor role.

Alginic acid or alginate, the salt of alginic acid, is the common name given to a family of linear polysaccharides containing 1,4-linked β -D-mannuronic (M) and α -L-guluronic (G) acid residues arranged in a non-regular blockwise order along the chain as shown in Figure 2.2. The residues typically occur as $(-M-)_n$, $(-G-)_n$, and $(-MG-)_n$ sequences or blocks and these sequences blocks display significantly different structure and their proportions in the alginate which determines the physical properties and reactivity of polysaccharide. Each algal species have differences in mannuronic acid to guluronic acid ratios (M:G ratios) of alginate in their structure that was believed to be significantly responsible for the variable affinity of alginates for divalent metals binding (Haug, 1961). It was reported in the same work that the affinity of alginates for divalent cations such as Cu^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Ca^{2+} , etc. increased with high guluronic acid content. This phenomenon was explained by the “zigzag” structure of alginates for which high guluronic acid content could accommodate the divalent cations more easily than those alginates with high mannuronic acid content. The alginates were thought to adopt an ordered solution network, through inter-chain dimerization of polyguluronic sequences. The rod-like shape of poly-L-guluronic sections results in an alignment of two chain sections yielding an array of coordination sites (The sites that complexation occurred), with cavities suitable for divalent cations because they are lined with the carboxylate and other oxygen atoms of

guluronic residues. This description is known as the “egg-box” model (Morris et al., 1980 and Rees, 1981).

2.6 Binary, ternary and multi-component biosorption

For the biosorption of binary, ternary and multi-component metal systems, most research demonstrated that sorption capacity and the efficiency of heavy metal removal by biosorption decreased when another metal(s) was simultaneously presented in the mixture solution compared with the single component system. It was possible that there were competitions between cations to the limited binding sites on biosorbent. Some indicated that when two or more metal ions were present together, they might increase or may not significantly change the sorption capacity of the interested metal species (Sag and Kutsal, 1995).

There are a number of factors that affected the competitive biosorption. The factor that affected the single component biosorption such as characteristics of biosorbent surface, pH, contact time, initial concentration of metals, biomass to wastewater ratio, temperature etc. are also important in competitive biosorption. Moreover, there are additional factors for competitive biosorption and these factors included the number of metals competing for binding sites, metals species, affinity of metals to the binding sites etc.

Literature suggested that there were three main factors for competitive biosorption; effect of heavy metal ions contamination, effect of light metal ions, and the effect of cationic or anionic ligands. The detail of each group is summarized in Table 2.5.

2.6.1 Effect of heavy metal ions contamination

Most of the investigations concluded that the presence of more than one heavy metal caused competitive adsorption, so the adsorption of interested heavy metals decreased when the other metals present in the solution (antagonistic effect) and there would be preferential metals for each algal species.

Sag and Kutsal (1995) studied competitive biosorption of Cr^{6+} and Fe^{3+} by *Rhizopus arrhizus*. They found that instantaneous, equilibrium and maximum uptakes of Cr^{6+} and Fe^{3+} were reduced by increasing concentration of other metals. The combined action of competitive of Cr^{6+} and Fe^{3+} by *Rhizopus arrhizus* was generally found to be antagonistic. The most logical reason for the antagonistic action was claimed to be the competition for sorption site on the cell and/or the screening effect by the second metal.

Sanchez et al. (1999) studied competitive of the Cu^{2+} and Zn^{2+} biosorption by *Cymodocea nodosa* and discovered that Cu^{2+} was preferentially adsorbed by this biomass because the biomass had a higher affinity for Cu than for Zn.

Kaewsarn et al. (2001) also studied the effect of another heavy metal ions on Cu^{2+} uptake by *Durvillaea potatorum*. They reported that Cu uptake was significantly affected by other heavy metals (Ag, Mn, Co, Ni, Zn, Fe, Cd, Pb) and EDTA because the metal binding sites on the biosorbent were limited, so these ions could compete simultaneously for the site. The amount of suppression for Cu^{2+} uptake depended on the affinity of these ions for binding sites and binding strength of the respective heavy metal ions to the biosorbent. Generally, the degree of suppression for Cu^{2+} uptake followed the series : $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Fe}^{3+} > \text{Mn}^{2+} > \text{Ag}^+$.

Singh et al. (2001) studied multi metal combination between Ni^{2+} and Cr^{6+} by *Microcystis*. They found that Ni^{2+} sorption capacity by this biomass was higher than Cr^{6+} as the binding sites in the biomass had a greater affinity for Ni^{2+} .

However, there were also reports that the presence of some heavy metals may increase the adsorption of interested heavy metals (synergistic effect). Muter (2002) studied the effect of another heavy metal ions on Cr^{6+} sorption by dehydrated cell of *Candida utilis*. He reported that Cr^{6+} sorption was inhibited by the presence of Cd^{2+} and Zn^{2+} , while Cu^{2+} and Pb^{2+} gave a synergistic effect. He concluded that affinity of Cd^{2+} and Zn^{2+} was higher than Cr^{6+} while affinity of Cu^{2+} and Pb^{2+} was less than Cr^{6+} for this biomass.

2.6.2 Effect of light metal ions

Competitive sorption was also reported for the case of light metal ions. Figueira et al. (1999) studied biosorption of Cd^{2+} in solution that was presaturated with Ca, Mg, or K by *Durvillaea*, *Laminaria*, *Ecklonia*, and *Homosira*. They reported that by using multicomponent Langmuir model, the biomass affinity toward the metals could be in order from high to low as: $\text{Ca} > \text{Mg} > \text{Cd} > \text{K}$ for *Laminaria*, $\text{Cd} > \text{Ca} > \text{Mg} > \text{K}$ for *Durvillaea*, $\text{Ca} > \text{Cd} > \text{K} > \text{Mg}$ for *Ecklonia* and $\text{Mg} > \text{Cd} > \text{K} > \text{Ca}$ for *Homosira*. The difference in this affinity was reported to be due to the preferential binding of heavier ions to alginates where a larger ion might better fit a binding site with two distinct active groups.

Franca et al. (2002) studied the effect of calcium interference with continuous biosorption of Zinc by *Sargassum* sp. They found that potential Zn biosorptive capacity of the biomass was markedly influenced by the presence of Ca^{2+} , where Zn sorption decreased with increasing Ca^{2+} concentrations. Ca^{2+} uptake rate was also found to be much higher

than Zn uptake rates. They concluded that this phenomenon took place due to the competition of both elements for the same binding site in the biomass.

However, there were also reports that the presence of light metals did not significantly influence the adsorption, Kaewsarn et al. (2001) studied the effect of another light metal ions on Cu^{2+} uptake by *Durvillaea potatorum*. They reported that Cu uptake was not significantly affected by light metal ions (K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) and concluded that light metal ions bound less strongly than the heavy metal on metal binding site of the biosorbent.

2.6.3 Effect of cationic or anionic ligands

The effect of cationic and anionic ligands on heavy metal removal can be categorized in three types including synergistic, antagonistic, and no interaction depending on specification between those ligands to each species of heavy metals.

Kaewsarn et al. (2001) studied the effect of another anionic ligand on Cu^{2+} uptake by *Durvillaea potatorum*. They reported that Cu uptake was not significantly affected by anionic ligands (CO_3^{2-} , SO_4^{2-} and PO_4^{3-}).

Lee et al. (2001) studied the influences of NO_3^- , NH_4^+ , and PO_4^{3-} on the accumulation of metals (Cd, Cr, and Zn) by *Ulva fasciata*. An increase in the ambient NO_3^- concentration resulted in a significant increase in Cd accumulation rate. The rates of accumulation of Cr and Zn were not greatly affected by the ambient NO_3^- level. Zn uptake in nitrate-enriched macroalgae was significantly higher than that in N-starved macroalgae. For the case of NH_4^+ , the accumulation of Cd, Cr, and Zn was not appreciably affected by the concentration of NH_4^+ . For PO_4^{3-} Se accumulation was significantly inversely related to ambient PO_4^{3-} concentration, presumably due to the competitive inhibition by high PO_4^{3-} concentration. Cr accumulation increased significantly with increasing PO_4^{3-} concentration. Finally they concluded that influences of major nutrients on metal accumulation were highly metal-specific.

2.7 *Caulerpa lentillifera*

Caulerpa lentillifera is a green macroalga classified in

Kingdom: Plantae

Division : Chlorophyta (Green algae)

Class : Chlorophyceae

Order : Caulerpales

Family : Caulerpaceae

Genus : *Caulerpa*

Specie : *Caulerpa lentillifera*

(http://www.itis.usda.gov/servlet/SingleRpt/SingleRpt?search_topic=TSN&search_value=6973)

The characteristics of this algae specie are siphonous form and have septum cover cell to produce gaemetangium in reproducing. Generally *Caulerpa Lentillifera* is found on the rock or sand in shallow water near coral reef. The branch's height are 1-6 cm. and consist of small green bulb with sphere shape that have diameter around 1.5 – 2 mm. and have a small branch under ramulous for each one. They arrange look like a bunch of pepper.

Caulerpa lentillifera is often used to treat wastewater containing nitrogen compounds (Chokwiwattanawanit, 2000). Its rapid growth makes it common for the farmers to discard the excess biomass. Previous work has shown that this algae is an unwanted agricultural material but could well be employed as an effective biosorbent for heavy metal (Sungkhum, 2003).

2.8 MINEQL program

MINEQL program is the analytical computing program for analyzing the chemical constituents that are dissolved in water. Because the chemical constituent in water is very complicate, they may form many chemical complex species or precipitate as solid phase. These may affect the properties of liquid of interest such as solubility in equilibrium conditions. This study employed MINEQL program and compared the solubility of heavy metal solution obtained from simulation with experimental data.

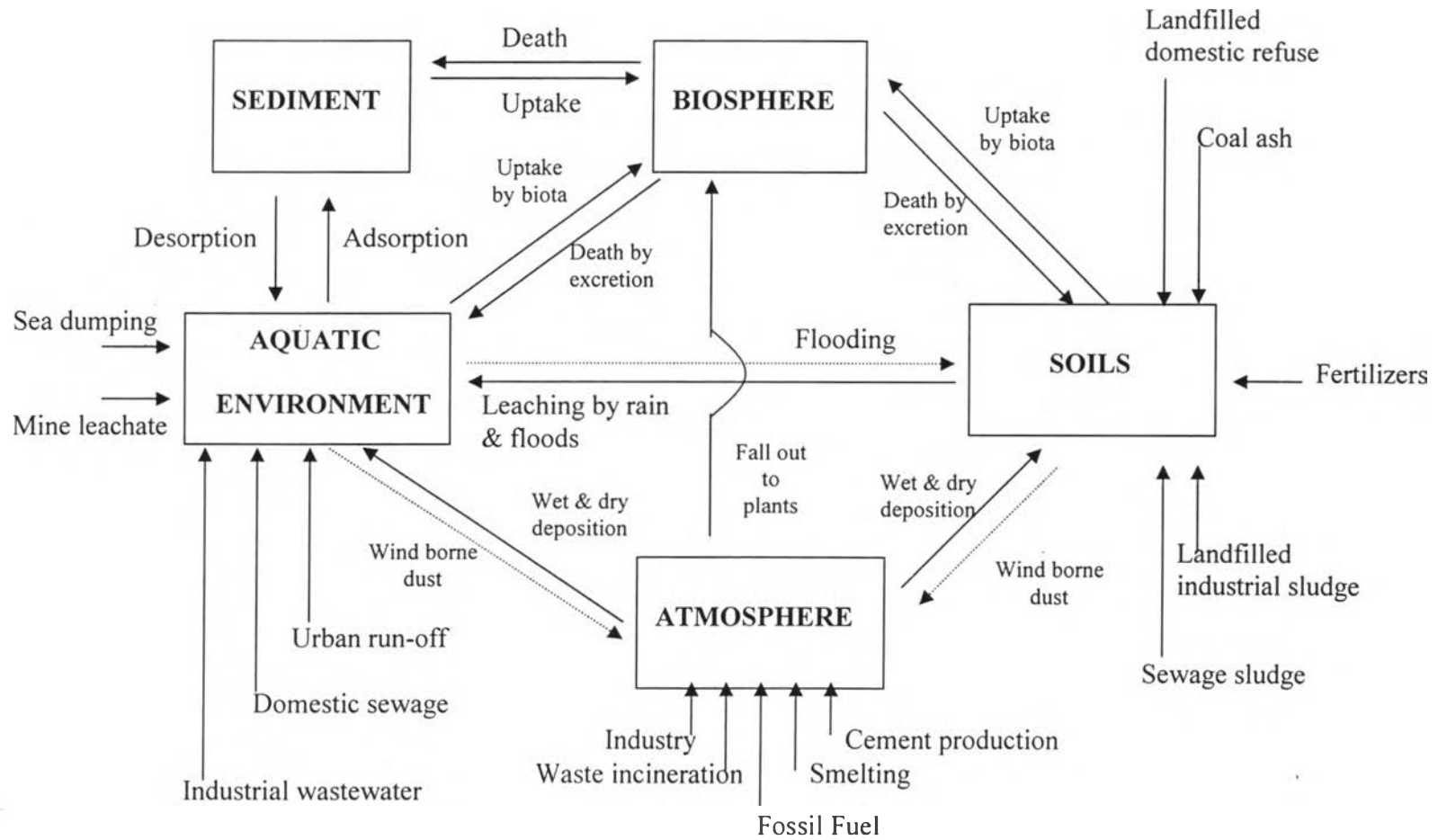
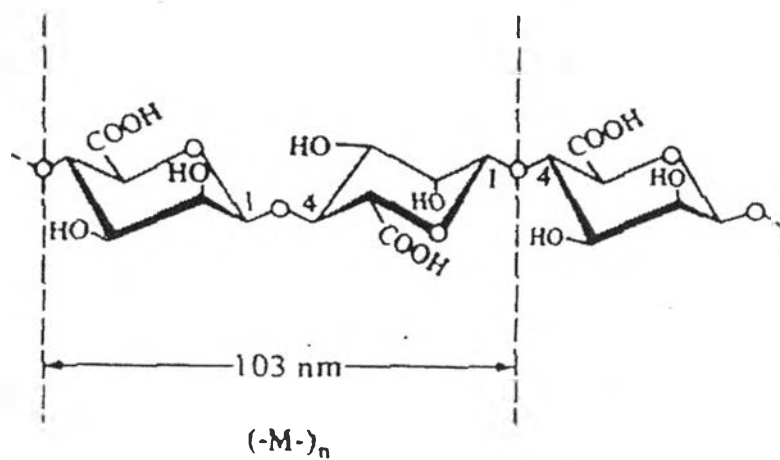
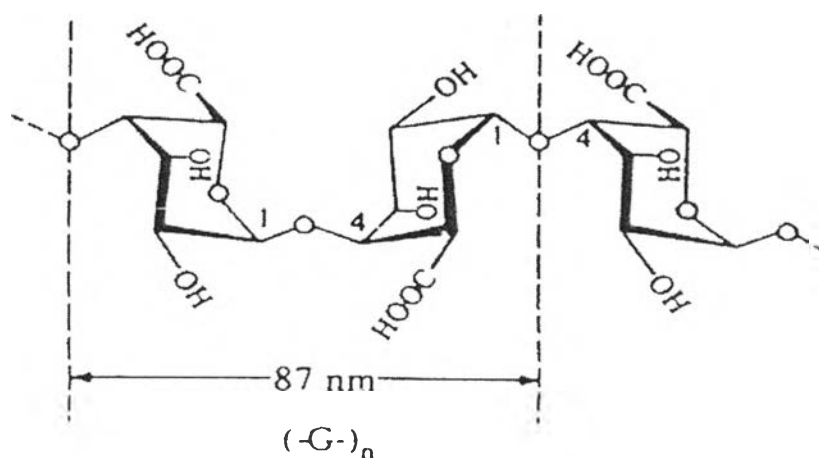
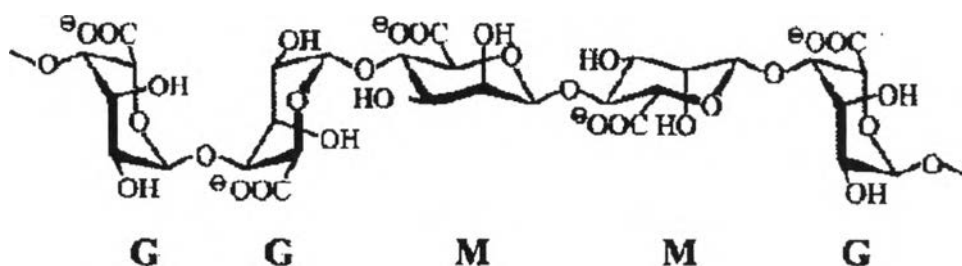


Figure 2.1 Pathways of heavy metals in transferring to the environment. (Reference: Matheickal, 2000)

(a) 1,4-linked β -D-mannuronic acid(b) 1,4-linked α -L-guluronic acid

(c) The alginate polymer



(d) Chain sequences of alginate polymer

Figure 2.2 Structural data of alginate, the component in algal cell wall
 (Reference: Matheickal, 1998; Davis et al., 2003)

Table 2.1 TLVs and effects of poisoning for heavy metals and some organic chemicals

Compound	TLV	Effects of poisoning
Cadmium	0.05 mg/m ³	Destructive to membranes, carcinogen, damage to lung, kidneys
Copper	1 mg/m ³	Destructive to membranes, nausea vomiting
Chromium	0.5 mg/m ³	Irritant, vomiting, nausea, carcinogen
Iron	1 mg/m ³	Possible irritant, nausea, vomiting
Lead	0.05 mg/m ³	Toxicity to fetus, reduces fertility in woman, altered spermatogenesis for men, impair kidney function
Mercury	0.1 mg/m ³	Damage to nervous system, liver, kidneys
Nickel	No TLV	Lung cancer
Zinc	No TLV	Nausea, vomiting
Benzene	10 ppm	Nausea, vomiting, dermatitis, carcinogen
Chlorobiphenyl	No TLV	Nausea, vomiting, carcinogen, liver damage

(Reference: Walton, 1995)

Table 2.2 Metals employed in various types of industries

Name of Industry	Metals									
	Ag	Al	As	Cd	Cr	Cu	Ni	Pb	Zn	
Electroplating	*			*	*	*		*	*	
Smelting and Refining	*	*		*		*		*	*	
Paint, ink and associated products		*			*	*		*		
Petroleum and refining					*			*		
Iron and steel manufacturer				*	*	*	*	*	*	
Photographic industry	*									
Leather, tanning and fishing					*					
Wood preserving			*		*	*		*		
Battery manufactory	*			*			*	*		

(Reference: Kaewsarn, 2000)

Table 2.3 Standards for heavy metal concentration in industrial effluent

Heavy Metals	Unit	B.E. 2525 (A.D. 1982)*	B.E. 2539 (A.D. 1996)**
Arsenic	mg/l	Maximum 0.25	Maximum 0.25
Barium	mg/l	Maximum 1.0	Maximum 1.0
Cadmium	mg/l	Maximum 0.03	Maximum 0.03
Copper	mg/l	Maximum 1.0	Maximum 2.0
Chromium	mg/l	Maximum 0.5	Maximum 0.75 for Cr ³⁺ Maximum 0.25 for Cr ⁶⁺
Lead	mg/l	Maximum 0.2	Maximum 0.2
Manganese	mg/l	Maximum 5.0	Maximum 5.0
Mercury	mg/l	Maximum 0.005	Maximum 0.005
Nickel	mg/l	Maximum 0.2	Maximum 1.0
Selenium	mg/l	Maximum 0.02	Maximum 0.02
Zinc	mg/l	Maximum 5.0	Maximum 5.0

Source : * Notification of the Ministry of Industry, No. 12 B.E. 2525 (1982), issued under the Factory Act B.E. 2521 (1978), published in the Royal Gazette, Vol. 99, Part 33, dated March 5, B.E. 2525 (1982).

**Notification of the Ministry of Science, Technology and Environment, No. 3 B.E. 2539 (1996) issued under the Enhancement and Conservation of the National Environmental Quality Act B.E. 2535 (1992), published in the Royal Government Gazette, Vol. 113 Part 13-D, dated February 13, B.E. 2539 (1996).

Table 2.4 Frequently used single-component adsorption isotherm models

Isotherm	Equation	Advantage	Disadvantage	Reference
Langmuir	$q = \frac{q_m b C_e}{1 + b C_e}$	Interpretable parameters	Not structured, Monolayer sorption	Langmuir (1918)
Freundlich	$q = K_f C_e^{1/n}$	Simple expression	Not structured, no leveling off	Freundlich (1915)
Combination of Langmuir and Freundlich	$q = \frac{q_m b C_e^{1/n}}{1 + b C_e^{1/n}}$	Combination of above	Unnecessarily complicated	Sips (1948)
Radke and Prausnitz	$\frac{1}{q} = \frac{1}{a C_e} + \frac{1}{b C_e^\beta}$	Simple expression	Empirical uses 3 parameters	Radke & Preusnitz (1972)
Reddlich – Peterson	$q = \frac{a C_e}{1 + b C_e^n}$	Approaches Freundlich at high conc.	No special advantages	Jossens et al. (1978)
BET	$q = \frac{BCQ^0}{(C_s - C)[1 + (B - 1)C / C_s]}$	Multilayer adsorption; Inflection pt.	No “total capacity” equivalent	Brunauer (1938)
Dubinin – Radushkevich	$\frac{W}{W_0} = \exp\left[-k\left(\frac{\varepsilon}{\beta}\right)^2\right]$ (volume adsorbed) $\ln q = \ln q_m - B[RT \ln(1 + 1/C_e)]^2$ (mass adsorbed)	Temperature independent; Polanyi pot’l. theory	Not limited behavior in the Henry’s law regime	Dubinin (1947)

(Reference: Yu et al., 1990)

Table 2.5 Literature reviews on competitive adsorption of metal in various organisms

Source	Heavy Metal	Biomass	Effect of pH	Effect of temperature	Effect of multi component on biosorption	note.
Sag and Kutsal (1995)	Cr ⁶⁺ and Fe ³⁺	<i>Rhizopus arrhizus</i>	- both Cr ⁶⁺ & Fe ³⁺ were more adsorbed to biomass at very low pH. The optimum initial pH was determined as 2.	- Adsorption capacity for Cr ⁶⁺ & Fe ³⁺ increased with increasing temperature in the range of 25-45°C & 25-35°C, respectively.	The instantaneous, equilibrium and maximum uptake of Cr ⁶⁺ and Fe ³⁺ was reduced by increasing concentration of the other metal.	
Kratochvil and Volesky (1998)	Cu ²⁺ and Fe ³⁺	<i>Sargassum sp.</i>			Effect of Fe on Cu biosorption : - The uptake of a species from a multicomponent mixture was lower than uptake of same species from the single component system.	
Aksu and Acikel (1999)	Cu ²⁺ and Cr ⁶⁺	<i>C. vulgaris</i>	- at pH = 2 , biosorption capacity of Cr ⁶⁺ was higher than Cu ²⁺ but at pH = 4 , biosorption capacity of Cr ⁶⁺ was lower than Cu ²⁺ .		- When the concentration of the second additive metal increased the adsorption capacity of biomass on the first additive metal decreased.	biomass quantity : The higher biomass quantity, the higher purification yields for first metal.

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Source	Heavy Metal	Biomass	Effect of pH	Effect of temperature	Effect of multi component on biosorption	note.
Sanchez et al. (1999)	Cu ²⁺ and Zn ²⁺	<i>Cymodocea nodosa</i>	- pH significantly affected biosorption of this biomass, and the optimal was at pH = 4.5.		- Cu ²⁺ was preferentially adsorbed by this biomass.	At pH 4.5 q _{max} = 52.68 mg-Cu/g and 46.56 mg-Zn/g.
Figueira et al. (1999)	Cd ²⁺	<i>Durvillaea</i> , <i>Laminaria</i> , <i>Ecklonia</i> and <i>Homosira</i>			- By multicomponent Langmuir model Ca > Mg > Cd > K for <i>Laminaria</i> Cd > Ca > Mg > K for <i>Durvillaea</i> Ca > Cd > K > Mg for <i>Ecklonia</i> Mg > Cd > K > Ca for <i>Homosira</i> By ion exchange model All sequence of affinity were the same as multicomponent Langmuir model except for <i>Durvillaea</i> , where there was a change of sequence between Ca and Mg There was a preferential bindings for heavier ions to alginate which could be due to stereochemical effects, larger ion might better fit a binding site with two distinct active groups.	- isotherm model : - using multicomponent Langmuir model and ion exchange model in predicting the behavior of these biosorbents in dynamic flow through biosorption system Both models fitted well with the experimental data.
		presaturated with Ca, Mg or K				

Source	Heavy Metal	Biomass	Effect of pH	Effect of temperature	Effect of multi component on biosorption	note.
Kaewsarn et al. (2001)	Cu ²⁺	<i>Durvilaea potatorum</i>				Cu uptake was significantly affected by other heavy metals (Ag Mn Co Ni Zn Fe Cd Pb) and EDTA in solution but not significantly affected by light metal ions (K ⁺ Na ⁺ Ca ²⁺ Mg ²⁺) and other anionic ligands (CO ₃ ²⁻ , SO ₄ ²⁻ and PO ₄ ³⁻).
Ceribasi and Yetis (2001)	Ni ²⁺ and Pb ²⁺	<i>Phanerochaete chrysosporium</i>	- Some portion of metal ions sorbed by this biomass was released to solution with a reduction in pH. Optimum operating pH was 5 for biosorption of these metals. Under these circumstances Ni(II) and Pb(II) uptake capacities were 55.9 mg Ni/g and 53.6 mg Pb/g, respectively.			initial concentration of heavy metal : Initial metal concentration of both or one of metals increased, then metal sorptions capacity also increased. contact time : - Maximum metal's adsorption capacity were reached in the first 30 min.
Pagnanelli et al. (2001)	Cu ²⁺ and Cd ²⁺	<i>Arthrobacter</i> sp.	- Study at pH 5 and 6 , the biomass tested was still than for Cu ²⁺ than Cd ²⁺ but more of pH , lead to higher effect for selectivity of Cu ²⁺ on Cd ²⁺ ions.			- The tested biomass was more selective for Cu ²⁺ than Cd ²⁺ .

de Franca et al. (2002)	Zn ²⁺	<i>Sargassum</i> sp.	<ul style="list-style-type: none"> - Potential Zn biosorptive capacity of the biomass was markedly influenced by the presence of Ca²⁺, Zn sorption decreased with increasing Ca²⁺ concentrations.
Singh et al. (2001)	Ni ²⁺ and Cr ⁶⁺	<i>Microcystis</i>	<ul style="list-style-type: none"> - Ca²⁺ uptake rate was also much higher than Zn²⁺ uptake rates. - Ni²⁺ sorption capacity of <i>Microcystis</i> was higher than Cr⁶⁺. - Ni²⁺ sorption was reduced in multi element combination due to changing of chemical nature of the binding sites.
Lee et al. (2001)	Cd, Cr, Zn and Se	<i>Ulva fasciata</i>	<ul style="list-style-type: none"> - Influences of NO₃⁻, NH₄⁺ and PO₄³⁻ on the accumulation of metals. <p><u>For NO₃⁻</u></p> <ul style="list-style-type: none"> - increasing ambient NO₃⁻ concentration resulted in a significant increase in Cd accumulation rate. - the rate of accumulation of Cr and Zn was not greatly affected by ambient NO₃⁻ level. - Zn uptake in nitrate-

enriched macroalgae was significantly higher than its uptake in N-starved macroalgae.

For NH_4^+

- the accumulation of Cd, Cr and Zn was not appreciably affected by the concentration of NH_4^+ .

For PO_4^{3-}

- Se accumulation was significantly inversely related to ambient PO_4^{3-} concentration, presumably due to the competitive inhibition by high P concentration.

- Cr accumulation increased significantly with increasing PO_4^{3-} concentration.

- Influences of major nutrients on metal accumulation were highly metal-specific.

Source	Heavy Metal	Biomass	Effect of pH	Effect of temperature	Effect of multi component on biosorption	note.
Nourbakhsh et al. (2002)	Cr ⁶⁺ and Pb ²⁺ and Cu ²⁺	<i>Bacillus</i> sp.	- study at pH = 4 and 7 , when increasing pH, Pb adsorption did not change significantly, but Cu adsorption increased, and Cr adsorption decreased.		in the metal ions mixture, Pb biosorption increased widely while Cr and Cu biosorptions decreased in compared with only one kind of metal ion.	
Muter et al. (2002)	Cr ⁶⁺ , Cu ²⁺ , Zn ²⁺ , Cd ²⁺ and Pb ²⁺	<i>Candida utilis</i>			- combination of Cu ²⁺ Zn ²⁺ , Cd ²⁺ and Pb ²⁺ . gave a synergistic effect for Cr ⁶⁺ sorption, except Cd and Zn, which inhibited Cr ⁶⁺ sorption by dehydrated biomass cell.	contact time - study in range 20 min to 72 hrs. The higher the contact time, the higher the metal specific uptake.
Aksu and Gulen (2002)	Fe ³⁺ and Fe-CN complex.	<i>Rhizopus arrhizus</i>	- the removal of both the single species of Fe ³⁺ and Fe(III) cyanide complex ions from aqueous solution was more efficient when increasing pH from 1 – 2.5.		- the biosorption rate and equilibrium uptakes of Fe ³⁺ and Fe(III) cyanide complex ions <u>increased</u> by the presence of increasing concentrations of the other ion up to 200 mg/l.	

Source	Heavy Metal	Biomass	Effect of pH	Effect of temperature	Effect of multi component on biosorption	note.
Tien (2002)	Cu ²⁺ , Cd ²⁺ and Pb ²⁺	<i>Oscillatoria limnotica</i> , <i>Anabaena spiroides</i> , <i>Eudorina elegans</i> and <i>Chlorella vulgaris</i>			- The binding activity of Pb by <i>O. limnotica</i> and <i>C. vulgaris</i> increased significantly with initial metal concentrations. - Pb had greater affinity to binding sites presented on the surface of <i>O. limnotica</i> and <i>C. vulgaris</i> in higher metal concentrations compared with Cu and Cd in the same mixture solution.	
Goyal et al. (2002)	Cr ⁶⁺ and Fe ³⁺	<i>Streptococcus equisimiliss</i> , <i>Saccharomyces cerevisiae</i> , <i>Aspergillus niger</i>		- A higher temperature increased the rate of adsorption.	- The amount of adsorbed Cr ⁶⁺ per unit weight of <i>S. cerevisiae</i> at the end of 24 hours was significantly reduced by lower concentrations of Fe ³⁺ , whereas the low concentration of Fe ³⁺ did not appreciably affect the ultimate uptake of Cr ⁶⁺ by <i>A. niger</i> and <i>S. equisimiliss</i> . - The presence of Cr ⁶⁺ was significantly inhibiting the adsorption of Fe ³⁺ by <i>A. niger</i> , <i>S. equisimiliss</i> and <i>S. cerevisiae</i> .	- sorption efficiency of different biomass. <i>A. niger</i> was found to be more efficient than <i>S. equisimiliss</i> and <i>S. cerevisiae</i> in removing the higher concentration of Cr ⁶⁺ .