CHAPTER II

BACKGROUND & LITERATURE REVIEW

2.1 Heavy metal

The term heavy metal generally has been used to describe those metals having atomic Numbers higher than iron (molecular weight > 59) or having density greater than 5 g/mL. From the environmental standpoint, metals may be classified into two groups. The first is essential metals, which are required in trace amount for microorganism as Nutritional components, but are toxic in greater amount. This group consists of As, Cr, Co, Cu, Ni, Se, Va and Zn etc. The second group is highly poisonous and is not known to have any nutritional value. This group consists of Pb, Hg, Cd, Ur, Ag and be etc. (Kojima and Lee, 2001).

2.1.1 Sources of heavy metals

Different types of industries often involve different types of heavy metals. This is because the variety in the properties of heavy metals which might suit for different functions. Examples of main industries with high requirement of heavy metals are listed in Table 2.1.

Table 2.1 Metals employed in various types of industries

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

(Reference: Apiratikul, 2003)

2.1.2 Toxicity of heavy metals

Problems with heavy metals differ greatly from most other forms of pollution. This is primarily because metals do not undergo degradation. Moreover, most heavy metals only require relatively low dosages to cause toxicity. Examples of the threshold limits and the effects caused by heavy metal uptake are given in Table 2.2.

Table 2.2 TLVs and effects of poisoning for heavy metals and some organic chemmicals

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, reduce fertility in woman, altered spermatogenesis for men , impair kidney function
Mercury	0.1 mg/m^j	Damage to nervious system, liver, kidneys
Nickel	No TLV	Lung cancer
Zinc	No TLV	Nuasea, vomiting
Benzene	10 ppm	Nuasea, vomiting, dermatitis, carcinogen
Chlorobiphenyl	No TLV	Nuasea, vomiting, carcinogen, liver damage

(Reference: Apiratikul, 2003)

2.1.3 Legal controls for heavy metals contamination

Because of strict regulations, effluent or water contaminated with heavy metals must be treated to the required level. In Thailand, the standard of heavy metals concentration in industrial effluent as 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 shown in Table 2.3. Surprisingly, this local effluent standard has moved in an opposite direction with those around the world, i.e. the updated for Thai regulation becomes less strict than the old one especially for Copper and Nickel (Apiratikul, 2003).

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^+
			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).

2.1.4 Treatment technologies

Many physico-chemical methods have been developed for the removal of heavy metals from aqueous solution. These include precipitation, electrolytic recovery, membrane separation, ion exchange resin, evaporation, carbon adsorption, and biosorption. However, these techniques are usually ineffective or too expensive when metal concentrations in wastewater are low. Biosorption is often the lowest cost treatment method compared with the other techniques (Apiratikul, 2003) it was reported to be suitable for the wastewater containing heavy metal concentration lower than 100 mg/L (Volesky,1990). The quantitative comparison between various treatment technologies regarding the costs and efficiency are summarized in Table 2.4.

Table 2.4 Removal characteristics of treatment technologies for heavy metals

Propoties	Technology					
	Biosotbtion	Precipitation	Ion Exchange	Activated Carbon	Membrane	Evaporation
Concentration Dependence	Ok	No	Ok	Ok	No	Ok
Effluent quality(mg/l)	<1	>5	<1	No*	1-5	1-5
pH variation	Ok	No	some	some	some	Ok
Selectivity	Ok	No**	Ok	No	No	No
Vesatility	Ok	No	Ok	Ok	Ok	No
Organic tolerance	Ok	Ok	No	Ok	No	Ok
Regeneration	Ok	No	Ok	Ok	No	No
Cost	Ok	Ok	Ok	Ok	No	No

(Reference: Apiratikul, 2003)

Notes: Ok   -good
       No*   -No report on
       No**   -sulphide precipitation can be selective

2.2 Mechanisms of biosorption

The kinetics of metal uptake by green algae is a two step mechanism.

1. The first step is the passive transport mechanism, which is fast (less than 5-10 minutes), reversible and metabolism-independent surface reaction called "biosorption" such as physical sorption or ion exchange of the adsorbate species at the surface of cells.

2. The second step is the active transport mechanism, which involves uptake of the heavy metals into the living or dead cells, slow metal binding process (up to 600 hours in some algae), irreversible and metabolism-dependent called "bioaccumulation" (Kojima and Lee, 2001).

Bacteria, cyanobacteria, algae, fungi and yeasts are able to remove metal ions from their environment by both mechanisms. Metabolism-independent sorption of metal ions to cell wall which is polysaccharides or other materials occurs in living and non-viable cells and is generally rapid. Metabolisms-dependent intracellular uptake or transport occurs in living cells and is usually a slower process than sorption, although greater amounts of metal may be accumulated by this mechanism in some organisms. Although both living and non-viable cells are able to accumulate heavy metals, there may be differences in the mechanisms involved in either case. The choice of living or non-viable biomass for metal ions removal is believed to be due to the advantages and disadvantages of each option. Changes of the cell wall may cause a variation of the number of functional groups or their states which affects the capacity of metal

accumulation. Furthermore, when using non-viable biomass, mechanical or chemical treatments after cell growth may increase the maximum amount of metal ion removed by adsorption (Apiratikul, 2003).

2.3 Sorption kinetics

The kinetics of Cu^{2+}, Cd^{2+} and Pb^{2+} biosorption on the algal biomass were determined with two different kinetics models (Ho and Mckay 1999). The first model is the pseudo-first-order rate Lagergren model, expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.1}$$

where k_1 is the rate constant of first-order biosorption (min^{-1}) and q_e and q_t denote the amounts of the biosorption at equilibrium and at time t (mmol g^{-1}), respectively. Integration by applying the boundary condition $q=0$ at $t=0$ and $q_t=q_t$ at $t=t$, gives:

$$\ln(1 - \frac{q}{q_e}) = -k_1 t \tag{2.2}$$

A plot of ln $(1-(q/q_e))$ against t should give a straight line to confirm the applicability of the first-order kinetic model.

The second model is the pseudo-second-order kinetic model (Ho, 1999) which is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.3}$$

where k_2 (g mmol min^{-1}) is the rate constant of second-order sorption. Eq. (2.3) can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2.4}$$

The plot t/q_t versus t should give a straight line if second-order kinetics are applicable and q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

2.4 Equilibrium behavior and sorption isotherm

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

Langmuir isotherms $\qquad q = \dfrac{x}{m} = \dfrac{q_m b C_e}{1 + b C_e}$ (2.5)

Freundlich isotherms $\qquad q = \dfrac{x}{m} = K_f C_e^{1/n}$ (2.6)

where x = amount of heavy metal'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 sorbent (in this research we use algae as an sorbent)

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

q_{max} = the maximum x per m ratio (maximum sorption capacity)

b, n = constant

K_f = sorption 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 sorbent surface.

2) All of sorbent 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 sorbent surface.

2) Sorbent surfaces are heterogeneous surface.

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

2.5 *Caulerpa lentillifera*

Caulerpa lentillifera is a green macroalga classified in

Kingdom: Plantae

Division : Chlorophyta (Green algae)

Class : Chorophyceae

Order : Caulerpales

Family : Caulerpaceae

Genus : *Caulerpa*

Species : *Caulerpa lentillifera*

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

The characteristics of this algal species 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 remulous 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 alga is an unwanted agricultural material but could well be employed as an effective biosorbent for heavy metals (Apiratikul and Pavasant 2006).

2.6 Controlling factors for the sorption of heavy metals
2.6.1 pH

pH is one of the most important influencing biosorption processes. It has been known that the uptake increases when the pH of the metal solutions increases from 2.5 to 6 (Volesky, 1990). A general trend, observed for different metals and biomass, is that metal uptake is negligible at low pH (pH 1 to 2). The metal uptake increases with an increase in pH (from pH 3 to 5) and there exists an optimum pH for a maximum metal uptake for each individual metal species. The examination given to such a phenomenon include: (1) high competition between metal cations and proton for the binding sites at lower pH values, (2) the unionized functional groups on the cell wall at low pH values, which thus makes the binding sites inaccessible to cations. As pH increases, more ligands with negative

charge would be freed and become available, which enhances the attraction for positively charged metal ions. At high pH, the metal precipitation in solution becomes an important factor as the metal solubility drops dramatically at high pH. Most heavy metals have low solubility and precipitate at pH greater than 5.5, and if the investigation is carried out at higher pH than this, the metal precipitation must also be examined.

2.6.2 Metal chemistry

A wide range of metals can be adsorbed onto the cell surface at different rates depending on their affinity to the surface. Chemical properties of metals can significantly contribute to the sorption. For instance, metals such as Au and Hg are easily taken up due to the formation of covalent bonds between the metal and the biomass surface, while some other metals such as U can form hydroxides with base that can easily be adsorbed onto cell surfaces. The ability of metals to form complexes with ligands also influences the biosorption process to a large extent. However, the affinity of a metal to be adsorbed on the cell surface of microorganism will depend on the relative affinity of that metal to ligands in the solution. The metal binding also depends on the preferences that they have for certain donor atoms. For example, in the biological environment, Hg and Cd are sulfur seeking elements while Cu shows equal preference to nitrogen and oxygen (Matheickal, 1998).

2.6.3 Size of sorbent

The sorption capacity usually increases with an increase in the surface area of particle or smaller particle size. This occurs along with the decrease in the equilibrium time. For biosorbents, the effect of particle size is some time not clear. Sungkhum (2002) indicated that the effects of size of algae could not be generalized as the sorption depended significantly not only on cell size and shape, but also with cell wall structure which varied widely among the different algal species.

2.6.4 Cations

Biosorption of metals is significantly affected by the presence of other cation species in the system. As the metal binding sites on the biosorbent are limited, these cations can compete for the binding sites. Depending on the affinity of these ions for binding sites, the effect can vary considerably. For the sorption using biosorbent, it has been generally observed that competition from light metal ions is insignificant and cannot reduce the

heavy metal sorption capacity of the biomass (Kuyucak and Volesky, 1989). This is one of the positive aspects of using biosorbents in place of traditional resins. Studies using mixed metal solutions, where two or more heavy metal ions are present, revealed that the two heavy metals systems were often subject to lower sorption rate than that for single species solution, indicating the non-specific nature of cell wall functional groups (Apiratikul, 2003).

2.6.5 Anions

The presence of a number of anionic compounds in the solution matrix was reported to influence the biosorption capacity but an exact trend to which the anion exerts on the sorption capacity cannot be generalized. In general, the anions are capable of forming complexes with dissolved metal ions and the resulting complexes can markedly alter the chemical form of the metal in solution, thereby altering the sorption behavior (Benjamin and Leckie, 1981). Metal sorption sometimes increases and sometimes decreases, depending on the type of metals, anions sorbent and the range of pH being studies. The metal anions complexes may be strongly adsorbed or weakly adsorbed. Another possibility is that anions themselves can interact with the charged cell surface directly so as to enhance or decrease the metal uptake (Matheickal, 1998).

2.6.6 Heavy metal concentration

Sorption is an equilibrium process where there exists an equilibrium concentration between the two phases (adsorbate and sorbent). The effect of heavy metal concentration depends on the type of algae and other factors. Generally, sorption capacity increases with increasing concentration of heavy metal until the binding sites of microorganism are saturated. Past researches on the effect of initial metal concentrations are shown in Table 2.5.

Table 2.5 Effect of initial metal concentration on biosorption

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
Spirogyra sp.	Cu	100-250mg/L	150mg/L	$22 \pm 2\,^{\circ}C$, pH 5 180 min	Maximum biosorption has been observed at 150 mg/L $q_{max} = 133.3$ mg/g	Gupta et al., 2006
Crab shell	Cu, Co	500-2000mg/L	2000 mg/L	$25\,^{\circ}C$, pH 6 150 rpm, 6 h	Cu^{2+}: increased from 75.4 to 197.7 mg/g Co^{2+}: increased from 72.3 to 259.4 mg/g	Vijayaraghavan et al., 2006
Chlamydomonas reinhardtii	Hg, Cd and Pb	20-400mg/L	200 mg/L for Hg^{2+} and Cd^{2+}, 300 mg/L	$25\,^{\circ}C$, pH6 for Hg^{2+} and Cd^{2+} pH 5 for Pb^{2+} 200 rpm, 120 min	Hg^{2+}: $q_{max}= 72.2 \pm 0.67$ mg/g Cd^{2+}: $q_{max}= 42.6 \pm 0.54$ mg/g Pb^{2+}: $q_{max}= 96.3 \pm 0.86$ mg/g	Tüzün et al., 2005

Table 2.5 (continued)

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
Papaya wood	Cu, Cd and Zn	5-500 mg/L	500 mg/L	25°C, pH 5 100 rpm, 60 min	Cu^{2+}: q_{max}= 19.99 mg/g Cd^{2+}: q_{max}= 17.32 mg/g Zn^{2+}: q_{max}= 13.64 mg/g	Saeed et al., 2005
Wheat shell	Cu	10-250 mg/L	250 mg/L	298 K, pH 5 250 rpm, 2 h	The biosorption capacity increased with increasing Cu^{2+} concentration. Increase from 0.83 to 10.84 mg/g	Basci et al., 2004
Thuja orientalis	Ni	50-400 mg/L	50 mg/L	25°C, pH 4 300 rpm, 30 min	The biosorption capacity decreased with increasing Ni^{2+} concentration. Decrease from 15.00 to 4.24 mg/g	Malkoc 2006

Table 2.5 (continued)

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
Durvillaea potatorum	Cd	44.96-449.6 mg/L	-	$21 \pm 1\,^\circ C$, pH 4.5 200 rpm, 300 min	The biosorption capacity increased with increasing Cd^{2+} concentration . $q_{max} = 123.64$ mg/g	Matheickal et al., 1998
Lentinus Sajor-caju	Cr	20-400 mg/L	100mg/L	$25\,^\circ C$, pH 2 150 rpm, 250 min	The biosorption capacity increased with increasing Cr^{4+} concentration from 20 to 100 mg/L, and 100-400 rather constant. $q_{max} = 35.97$ mg/g	Arica and Bayramoglu 2005
R. basilensis	Cu	5-20 mg/L	20 mg/L	$26\,^\circ C$, pH 5 150 rpm, 30 min	The biosorption capacity increased with increasing	Munoz et al., 2006

Table 2.5 (continued)

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
Entrobacter sp.	Cu, Cd and Pb	0-500 mg/L	-	25°C, pH 5 100 rpm, 100 min	Cu^{2+} concentration. $q_{max} = 8.5 \pm 0.4$ mg/g occurred at 20 mg/L of initial Cu^{2+} concentration. The biosorption capacity increased with increasing Cu^{2+}, Cd^{2+} and Pb^{2+} concentration. Cu^{2+}: $q_{max} = 30.6$ mg/g Cd^{2+}: $q_{max} = 46.2$ mg/g Pb^{2+}: $q_{max} = 50.9$ mg/g	Lu et al., 2005

2.6.7 Temperature

The increase and decrease in temperature can significantly influence the biosorption capacity. For endothermic reaction or chemisorption mechanism, the metal uptake increased with an increase in temperature. However, an extremely high temperature can lead to the destruction of cell surface which can alter the binding site on the alga surface. Exothermic reaction, on the other hand, the sorption capacity can be enhanced by decreasing temperature. Past researches on the effect of temperature are shown in Table 2.6.

2.6.8 Biomass dose

The sorption capacity usually increases with an increase in biomass dose because of an increase in surface area of biosorbent, which in turn increases the binding sites. In certain cases, the metal uptake decreases with increasing the biosorbent dosage, this may be due to complex interactions of several factors. The important factor is that, at high sorbent dosages, the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in low metal uptake. Past researches on the effect of biomass dose are shown in Table 2.7.

2.6.9 Shaking rate

The sorption capacity usually increases with increasing shaking rate. Past researches on the effect of shaking rate are shown in Table 2.8.

2.7 Past work on the biosorption of heavy metals using *Caulerpa lentillifera*

Caulerpa lentillifera has been shown to have sorption capacities for several positive charged contaminants including heavy metals. This started with the work of Sungkhum in 2002 where the dried alga was firstly used to adsorb Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}. This work was continued by Apiratikul (2003) and Suthiparinyanont (2003) where Apiratikul (2003) investigated the competition between the sorption of the binary and tertiary mixture of heavy metals and Suthiparinyanont (2003) examined the effect of pretreatment on the sorption capacity of the metals. Summary of these works are given in Table 2.9.

Table 2.6 Effect of temperature on biosorption

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
Thuja orientalis	Ni	25-60°C	-	300 rpm, pH 4 30 min, C_0 =100 mg/L	The biosorption capacity increased from 16.9 mg/g to 19.24 mg/g when temperature was increased from 25-60°C. Endothermic process.	Malkoc 2006
Sargassum sp.	Cd	298-328 K	-	150 rpm, pH 5.5 120 min, C_0 =390 mg/L	The biosorption capacity decreased from 85.8 mg/g to 70 mg/g when temperature was increased from 298-328 K Exothermic process.	Cruz et al., 2004

Table 2.6 (continued)

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
Gelidiun	Pb	$10\text{-}45\,^\circ$C	-	200rpm, pH 5.3, 20 min, $C_0 = 100$ mg/L	The biosorption capacity decreased from 40.0 ± 0.7 to 39.1 ± 0.5 mg/g when temperature was increased from $10\text{-}45\,^\circ$C. Exothermic process.	Vilar et al., 2005
Chlamydomonas reinhardtii	Hg, Cd and Pb	$5\text{-}35\,^\circ$C	-	pH6 for Hg^{2+} and Cd^{2+} pH 5 for Pb^{2+}, 200 rpm, 120 min, $C_0 = 100$ mg/L	The effect of temperature on biosorption at four different temperature from $5\text{-}35\,^\circ$C, the biosorption capacity did not significant change	Tüzün et al., 2005

Table 2.6 (continued)

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
Lentinus Sajor-caju	Cr	5-40 °C	-	150 rpm, pH 2 250 min, C_0 =100 mg/L	The biosorption capacity increased when temperature was increased from 5-40 °C. Endothermic process.	Arica and Bayramoglu 2005

Table 2.7 Effect of biomass dose on biosorption

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
Crab shell	Cu, Co	1-10 g/L	1 g/L	25°C, pH 6 150 rpm, 6 h	The lowest biosorbent dosage(1 g/L) resulted to highest metal uptake capacity. Cu : q_{max} = 250 mg/g Co : q_{max} = 310 mg/g	Vijayaraghavan et al., 2006
Papaya wood	Cu, Cd and Zn	0.5-20 g/L	-	25°C, pH 5 100 rpm , 60 min	The biosorption capacity decreased when biomass dose was increased from 0.5-20°C. Cu^{2+}: decreased from 12.81 ± 0.39 to 0.49 ± 0.03 mg/g Cd^{2+}: decreased from	Saeed et al., 2005

Table 2.7 (continued)

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
					11.45 ± 0.21 mg/g	
					to 0.48 ± 0.02 mg/g	
					Zn^{2+}: decreased from	
					8.56 ± 0.35 mg/g	
					to 0.64 ± 0.03 mg/g	
Wheat shell	Cu	8-14 g/L	-	298 K, pH 5 250 rpm, 2 h	The biosorption capacity increased with increasing Biomass dose . $q_{max} = 8.255$ mg/g	Basci et al., 2004
R. basilensis	Cu	0-2 mg/L	1.6 ± 0.1 g/L	$26\degree$C, pH 5 150 rpm, 30 min	Cu^{2+} adsorption capacity increased when increasing the biomass concentration from 0.5 to 1.2 ± 0.1g/L,	Munoz et al., 2006

Table 2.7 (continued)

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
					but decreased at biomass concentrations higher than 1.6 ± 0.1 g/L	
Spirogyra sp.	Cu	5-20 g/L	20 g/L	$22 \pm 2\,^{\circ}C$, pH 5 180 min	q_{max} = 133.3 mg/g at an algal dose of 20 g/L	Gupta et al., 2006
Lentinus sajor-caju	Cr	12.5-100 mg/7.5 mL	-	$25\,^{\circ}C$, pH 2 150 rpm, 250 min	The biosorption capacity increased with increasing biomass dose from 12.5 to 100 mg/7.5 mL. q_{max} = 35.97 mg/g	Arica and Bayramoglu 2005
Chlamydomonas reinhardtii	Hg, Cd and Pb	200-1000 mg/L	800 mg/L	$25\,^{\circ}C$, pH6 for Hg^{2+} and Cd^{2+} pH 5 for Pb^{2+} 200 rpm, 120 min	The biosorption capacity increased with increasing biomass	Tüzün et al., 2005

Table 2.7 (continued)

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
					800 mg/L, and 800 to 1000 mg/L rather constant.	
Thuja orientalis	Ni	1-5 g/L	-	25°C, pH 4 300 rpm, 30 min	The biosorption capacity decreased from 58 mg/g to 18 mg/g when increasingbiomass dose from 1 to 5 g/L. q_{max} =12.42 mg/g	Malkoc 2006

Table 2.8 Effect of shaking rate on biosorption

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
Wheat shell	Cu	50-250 rpm	250 rpm	298 K, pH 5, 2 h	Maximum biosorption Capacity were observed at 250 rpm $q_{max} = 8.255$ mg/g	Basci et al., 2004
Sargassum sp.	Cd	0-200 rpm	150 rpm	298 K, pH 5.5, 120 min	The biosorption capacity increases with the increase in shaking rate. The maximum adsorption capacity of algae at equilibrium being attained for agitation rates than 100rpm. $q_{max} = 5.0$ mg/g	Cruz et al., 2004

Table 2.8 (continued)

Biomass	Heavy metals	Studies range	Optimum	Condition	Results	Ref.
Thuja orientalis	Ni	180-420 rpm	300 rpm	25 °C, pH 4 30 min	An agitating rate on adsorption increased from 180 to 420 rpm., Ni^{2+} adsorption of cone biomass increased from 81 to 86.5%	Malkoc 2006

Table 2.9 Biosorption by *Caulerpa lentillifera*

Source	Heavy metal	Factor	Results
Sungkhum, (2002)	Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}	Desorption test	The heavy metals employed in this work could not be eluted effectively by hot water (60 °C). EDTA, on the other hand, was found to be a much better eluting agent.
		Contact time	The metal uptake was rapid with the system reaching 80-90% of the Equilibrium loading within 20 minutes.
		Biomass dose	The removal efficiency increased with an increase in algal mass.
		Particle size	The removal percentage of heavy metal was independent of particle size.
		pH	The removal efficiency increased steadily with pH. The selected pH sorption should avoid the precipitation and the ineffectiveness range. The pH was always controlled between 4.5-5.5.
		Isotherms	The experimental results fitted well with Langmuir isotherm expression.
Suthiparinyanont (2003)	Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}	Initial metal concentration	The sorption capacity for each metal increased with an increase in initial metal concentration.
		Time period for 0.5 N NaOH treatment	The optimum exposure time for pretreatment by 0.5 N NaOH was found within the range of 0.5 to 1.0 hour.

		Identification of functional groups in algae	The possible functional groups for the sorption of each heavy metals were a covalent bond with C-O, and electrostatic or ionic bond with hydroxide (O-H), and a covalent or ionic bond with amine (N-H), amino, (N-H) and sulfonate (S-O) groups.
		Yield	When pretreatment talgae yield of algae was very low compare before pretreatment.
Apiratikul, (2003)	Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}	pH	An increase in pH meant a lower quantity of protons, resulting in a decrease in the competition between proton and heavy metal ion. Hence, an increase in the sorption capacity was observed.
		Sorption kinetics	External mass transfer coefficients could be ordered from high to low as $Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+}$ while intraparticle diffusion coefficients were: $Cd^{2+} > Zn^{2+} > Cu^{2+} > Pb^{2+}$.
		Sorption Isotherm	A linear regression of experimental results for all four heavy metals fitted better to Langmuir and Freundlich isotherms.