CHAPTER II

LITERATURE REVIEW

2.1 Heavy Metal Pollution

Heavy metal are metallic elements with high atomic weight and density. These include the transition metals, some metalloids, lanthanides and actinides. Amounting to more than 20 metals generally exist in a positively charged form and can bind on to negatively-charged organic molecules. Being metals ions, heavy metal cannot be degraded or destroyed, therefore their stability make them as the persistent toxic substances in environment. Heavy metal as the environmental contaminants can be found in the air, soil and water, which pose health hazard to the general public.

Presence of heavy metal in water as the contaminants is an indication of global industrialisation attributed to large scale of inappropriate disposal and untreated of wastewater containing heavy metal from anthropogenic sources (United Nations Commission on Sustainable Development, 2010). Water functions as a medium of transport for pollutants and they can be damaging to both living organisms and the environment (Harrison, 2001). Heavy metal can bio-accumulate over a period of time and the concentrations become apparent and measureable. Through food chains and trophic levels, heavy metal bio-accumulation within target organ or tissue of organisms can ultimately threaten human health.

Globally, regulatory organisations have implemented regulations through the maximum permissible limits for the discharge of heavy metal in the aquatic environment and intervention through ISO 14000 in order to control contamination. However, the heavy metal are being released at a higher concentration than the prescribed limits especially through anthropogenic point source, thus leading to the health hazard and water pollution. Table 2.1 summarises the parameter limits and health hazard of heavy metal toxicity. The parameter limits for heavy metal by the international organisations of WHO and USEPA are lower compared to that from the Malaysian Standards of EQA and INWQS, with an exception for copper. This may be due to stringent regulations applied by WHO and USEPA when compared to Malaysia in order to safeguard human health and the environment.

Table 2.1 Parameter limits and health effects of heavy metal

Metal	Parameter limits by Malaysian organisation (mg/L)				Parameter limits by international organisations (mg/L)		Health hazards
	EQA		INWQS				
	Standard A	Standard B	Classes IIA/ IIB	Classes III	WHO	USEPA	
Arsenic	0.05	0.10	0.05	0.4 (0.05)	0.01	0.05	Carcinogenic, producing liver tumors, skin and gastrointestinal effects.
Cadmium	0.01	0.02	0.01	0.01* (0.001)	0.003	0.005	Carcinogenic, cause lung fibrosis, dyspnea and weight loss.
Copper	0.20	1.0	0.02	-	-	1.30	Long term exposure causes irritation of nose, mouth, eyes, headache, stomachache, dizziness, and diarrhea.
Lead	0.10	0.5	0.05	0.02* (0.01)	0.01	0.005	Suspected carcinogen, loss of appetite, anemia, muscle and joint pains, diminishing IQ, cause sterility, kidney problem and high blood pressure.
Mercury	0.005	0.05	0.001	0.004 (0.0001)	0.001	0.002	Corrosive to skin, eyes and muscle membrane, dermatitis, anorexia, kidney damage and muscle pain.
Nickel	0.2	1.0	0.05	0.9*	0.02	0.1	Carsinogenic, dermatitis, allergic sensitization, lung and nervous system damages.

* – at hardness 50 mg/L
\- – not available
EQA – Environmental Quality Act
Standard A – Effluent that is discharge upstream of water supply intake
Standard B – Effluent that is discharge downstream of water supply intake
INWQS – Interim National Water Quality Standard

Classes IIA – Water Supply II – Conventional treatment required
Fishery II – Sensitive aquatic species
Classes IIB – Recreational use with body contact
Classes III – Water Supply III – Extensive treatment required;
Fishery III – Common of economic value and tolerant species; livestock drinking

(Malkoc and Nuhoglu, 2005; Sud *et al.*, 2008; *Environmental Quality Act 1974 (Act 127) and subsidiary legislation*, 2007; Environmental Quality Act 1974 (Act 127) and subsidiary legislation, 2007; Environmental Quality Act 1974 (Act 127) regulations, rules and orders (as at 25th June) 2011, 2011)

Heavy metal naturally enter humans through ingestion, inhalation and absorption in small extent as trace elements. Trace elements are essential to maintain the metabolism of human body. However, trace amount of heavy metal are dangerous because they tend to bio-accumulate and bio-magnify. Bio-accumulation and bio-magnifiction increase the concentration of heavy metal in a biological organism or targeted organ over time until they become hazardous to health (Mata *et al*., 2008). This can lead to deficiencies in certain nutrients and also result in Parkinson's disease, cancer, skin disorders, respiratory abnormalities, abdominal and intestinal problems, central nervous system damage, blood disorders and reproductive failure (United Nations Environmental Programme, 2007). Acute exposure to high concentration of heavy metal can cause nausea, anorexia, vomiting, gastrointestinal abnormalities and dermatitis. From the perspective of human health, each of the heavy metal imparts different effects and symptoms (Lesmana *et al*., 2009).

2.1.1 Water Pollution by Heavy Metal

Rapid acceleration of industrial growth throughout the world exerts negative impacts to the environment. Discharge of contaminated effluents without adequate treatment into the aquatic environment creates such implication. Industrial wastewater which are associated with manufacturing of automobile, purification of metals, electroplating, galvanizing, coating, paint, electronics, pharmaceutical, chemicals and battery manufacturing are the most common source of heavy metal pollution. Arsenic, cadmium, copper, chromium, lead, mercury, nickel and zinc are normally found in heavy metal contaminated wastewater (Duruibe *et al*., 2007).

Heavy metal exhibit toxic and persistent characteristics, can enter into the food chains and the ecosystem where they cause adverse impact on the biotic and abiotic components of ecosystem. Due to the fact that water functions as a medium of transport for pollutants, heavy metal damaging effects on both living organisms and the environment have been observed (Veado *et al.*, 2000; Goodyear and McNeill, 1999). Through aqueous medium, the pollutants can bio-accumulate and bio-magnify over time once they enter the biological system and ultimately they will reach high concentration. When these toxicity by heavy metal become significant in the trophic level, once it reaches human-as the final consumer in the food web, the health will be compromised. Table 2.2 summarizes the heavy metal commonly released by industries.

Table 2.2 Sources of heavy metal from industrial applications

Heavy metal	Sources	Reference
Arsenic (As)	Metal processing plant, burning of fossil fuel, mining and pesticide	Anawar *et al.*, 2002; Alluri *et al.*, 2007
Cadmium (Cd)	Welding, electroplating, pesticides and fertilizer, mineral processing, battery and nuclear fission plant	Lesmana *et al.*, 2009
Copper (Cu)	Copper plating, mining, metal industries and copper-ammonium rayon industries	Han *et al.*, 2006; Salamatinia *et al.*, 2008
Chromium (Cr)	Metal plating, electroplating, leather, mining galvanometry and dye production	Suksabye *et al.*, 2008; Baral *et al.*, 2009
Lead (Pb)	Metal plating, textile, battery manufacturer, automobile and petroleum industries	Jalali *et al.*, 2002; Babarinde *et al.*, 2006
Nickel (Ni)	Electroplating, nonferrous metals mineral processing, dye industries, porcelain enameling and steam-electric power plants	Yu and Kaewsarn, 2000
Mercury (Hg)	Pesticides, batteries, paper industry, metallurgy industries, chemical manufacturing and metal finishing	Igwe and Abia, 2006; Okoronkwo *et al*, 2007
Zinc (Zn)	Refineries, brass manufacture, metal plating and plumbing	Alluri *et al.*, 2007

Various reports on impeccable impact on environmental have been reported to take place because of the contamination by heavy metal to the environment. Cheevaporn and

Menasveta (2003) reported that water pollution at the Gulf of Thailand, which was caused by combination of heavy metal and nutrient together with eutrophication, had resulted in their habitat to be degraded, particularly mangrove forest and coral reef. While for the public health, the threats are posed through seafood contamination. Besides that, several economically important activities such as fishery, tourist and agriculture were also directly affected due to deteriorating conditions. For the classical heavy metal disruptive case of Minamata Bay in Japan, methylmercury poisoning effects are still seen today as the impacts are not only widespread and acute but are also chronic (Powel, 1991; Harada, 1995; Eto, 2000).

In Malaysia, heavy metal water pollution issues have grown in large magnitude with higher complexity compared to 30 years ago. This is attributed to the shift of the Malaysian economy from agriculture to industry-based in the 1980s. From the data compiled by the Department of Environment (Malaysia), showed the overall trend points out to that of a slow but steady deterioration in the water quality of rivers. From 116 monitored rivers, 55 rivers have been found to exceed the INWQS maximum limit of 0.001 mg/l for cadmium, 44 rivers exceeded the iron limit of 1.00 mg/L, 36 rivers exceeded the lead limit of 0.01 mg/L and 24 rivers exceeded the mercury limit of 0.0001 mg/L (Abdullah, 2011).

Wastewater contaminated with heavy metal is largely generated from electroplating, mining and metal treatment or fabrication industries. Most of these industries are located along the West coast of peninsular including Klang Valley, Penang, Ipoh and Johor Bahru (Issabayeva *et al.*, 2008). In the Klang Valley, an estimated 50 - 60 tonnes of wastes end up in the river system daily (Abdullah, 2011). Sivalingam and Sani (1980) reported that Sungai Juru in Penang has been polluted by industrial wastewater containing Cd, Zn and Ni. The impact of industrial wastewater discharge with high concentrations of heavy metal is of great concern which warrants appropriate remediation. Therefore, the current society needs to address and create awareness to this issue earnestly.

2.1.2 Selected Case Studies on Heavy Metal Pollution

Heavy metal are hazardous to human health and degrade environment quality. In this study, lead, copper and nickel were the selected heavy metal. Each of those selected heavy metal has different characteristics. Lead is one of the most potent heavy metal that poses significant threat to human health and the environment even in small quantity. On the other hand, small quantity of copper and nickel are essential elements for living organisms. Through bio-accumulation and bio-magnification processes in the tropic levels, concentrations of heavy metal will become noticeable and latter are known to cause adverse effects on human health and the environment. Additional reviews on the three selected heavy metal are discussed as follow.

Lead has the highest atomic number of 82 among all the stable elements, chemical symbol of Pb and placed in group 14 of the Periodic Table. It is a soft, malleable, ductile, bluish-white, dense metallic and poor electric conductivity element. Lead, together with mercury and cadmium, is also classified as one of “The Big Three” heavy metal that has high toxicity, causes damaging effects although at very low concentrations and long term irreparable impact to human health (Volesky, 2007).

Lead is primarily used in the acid battery industry worldwide. In addition, it is extensively used in manufacturing of ammunition, pipes, cable, alloy and paint. Untreated effluent form industries such as the battery manufacturing, coating, automotive, aeronautical and steel, printing, pigments, fuels, photographic materials and explosive manufacturing becomes a major source of lead contamination (Wong *et al.*, 2003; King *et al.,* 2007). The monitoring study by WHO has identified that Sungai Skudai was contaminated by 0.8 mg/L lead (Department of Environment, 1986).

Lead is not essential as trace elements to nutrition in human or animals. It can poison organisms including human even in low concentration as it bio-accumulates and bio-magnifies in the food chain. Contamination food, water, air, soil and consumer products result in the absorption of lead into human body (Ferner, 2001). The concentrations of lead and exposure time are key factor in lead toxicity measurement. Acute poisoning occurs when one is exposed to high concentration of lead for a short duration and the adverse effect is high and severe. Acute condition develops seizures, coma and death quickly. Meanwhile, long time and low level exposure of chronic poisoning is commonly found in case studies. Lead toxicity leads to diseases such as anaemia, neurotoxicity, hemotoxicity, nephrotoxicity and toxic metabolic encephalopathy. It targets organs and tissues including the heart, bones, intestines, kidneys and the reproductive system, thus capable of disrupting metabolic processes and threaten lives (Seiler *et al.*, 1994; Deng *et al.*, 2006). Furthermore, lead toxicity cause brain damage and mental retardation of children (Moncrieff *et al*., 1964; Gibson *et al*., 1967).

For copper, its atomic number is 29 and carries the chemical symbol of Cu. It is placed in Group 11 of the Periodic Table and classified as a “Transition Metal”. Copper is a reddish-brown, malleable and ductile element that has excellent thermal and electrical conductivity. Copper is mainly used in the manufacturing of electric cables and equipments which contributes about half of the world’s production. It is both directly and indirectly utilised for plumbing, alloys, wood preservative, leather and fabrics, pharmaceutical products and agricultural fungicides. The anthropogenic sources of copper contamination comes from smelting industries, copper wire mills, iron and steel producing industries, coal burning industries, metallurgical processes and mining operations. Department of Environment (1998) reported that a high concentration of copper of 5.96 to 21.20 mg/L had been reported in Malaysian rivers.

Copper is an important essential element when in a low concentration, particularly to higher plants and animals. In human, copper is a component of metalloenzymes which can function as electron donor or acceptor. Copper is also present in normal human serum at concentration of 120 to 140 µg/g via binding to ceruloplasmin, albumin and other molecules. Conversely, high levels of copper can cause adverse health effects such as liver and kidney damage, anaemia and gastrointestine irritation. Furthermore, copper is also associated indirectly with neurological disorders including Alzheimer’s disease, Wilson’s disease and prion disease (Desai and Kaler, 2008; Huster, 2010).

However, bio-accumulation and bio-magnification of copper can bring its concentration up to toxic amounts, thus cause apparent impact to living organisms and the environment. Presence of copper at the range of 3.34 to 37.50 mg/g was observed to be in sediment samples at the Chao Phraya River, but it was not detected in water samples (Polprasert, 1982). Copper in the soil is could be as bad as it presence in the water as it also can enter the food chain. This can be found when Badri (1988) had found that the grass has uptaken the copper that leached from power lines through contaminated the soil and subsequently caused high levels of copper found in milk of livestock. While for aquatic ecosystem, the dissolved copper which was generated from a non-point source, the cation was not only progressively influenced the water chemistry and bio-accumulate in fish, but also resulted in bio-magnification through food chain (Lemus and Chung, 1999; McIntyre *et al*., 2008).

Nickel with the chemical symbol of Ni and atomic number of 28, is placed in group of X for the Periodic Table. It is classified as hard, malleable and ductile transition metal. Nickel is a widely-used metal in various industries and consumer products, including stainless steel, alloys, coins, magnets, rechargeable batteries, armour plate, burglarproof vaults, ceramics, domestic cleaning products, oil refining and fungicides. Mining, smelting, refining, casting of alloys and electroplating industries are major contributors of nickel contaminations. Findings by the Department of Environment of Malaysia indicated Sungai Skudai in Johor has concentration of nickel ranging from be 0 – 10 mg/L whilst in Sungai Langat basin, nickel concentration was reported of range from 16.42 to 31.83 mg/mL, implying that the rivers have excessive heavy metal contamination (Universiti Kebangsaan Malaysia - Department of Environment, 2000).

Nickel has been found to be essential for the growth and present in co-enzyme of some living microorganisms and plants, however it can become mildly toxic when present in excessive amounts. The growth of blue-green algae *Oscillataria* spp and bacterium *Alcalegenes eutrophus* has been shown to require nickel when cultures in the laboratory (Eisler, 1981). Like copper, nickel also can bio-accumulate and bio-magnify along food chains, thus cause serious problem to living organisms. Sreedevi *et al*. (1992), Ptashynski *et al*. (2001) and Lapointe and Couture (2010) documented evidences of nickel bio-accumulation and magnification in fish from embryos and non-feeding larvae phase to targeted organs such as gill, kidney, liver, brain and muscle.

Short-term overexposure to the high relative concentration of nickel has not been known to cause any health problems to human health, but long-term exposure represents a serious health hazard. It predominantly affects the respiratory system, acute inflammatory on the nasal membrane, hypersensitive in nature, including bronchial asthma and contact dermatitis (Sivulka, 2005). Among the known health related effects are decrease in body weight, stimulation of neoplastic transformation, kidney and liver damage, cardiovascular system poisoning and skin irritation (Denkhaus and Salnikow, 2002).

2.2 Heavy Metal Treatment Technologies

Heavy metal are well-known toxic agents and heavy metal contamination has caused global deterioration of human health and environmental quality. The needs to comply with the stringent regulatory standards, various treatment technologies have been invented to resolve these issues. In general, heavy metal treatment technologies can be divided into two groups, namely, in-practice and progressing treatment technologies. Elaboration of heavy metal treatment technologies are discussed in subsequent sections.

2.2.1 In-Practice Treatment Technology for Heavy Metal Removal

In-practice treatment technology refers to conventional methods applied to treat heavy metal from industrial wastewater. Table 2.3 summarises the process description and performance of the heavy metal treatment technologies. For in-practice technology, the major two subgroups of such treatment consist of high-end technology and low-end technology which are available to treat industrial effluent containing heavy metal. High-end technology includes ultrafiltration, reverse osmosis, electrodialysis and ion exchange. Generally, the use of high-end treatment systems entails high cost in order to achieve desirable removal percentages or to meet the compliance level (Ahalya *et al.*, 2003). For low-end technology heavy metal treatment, the usual chemical precipitation is applied to remove heavy metal from industrial wastewater due to cost effectiveness and simple operation. However, current treatment technology of chemical precipitation which is being applied in industrial wastewater laden of high nickel concentration produces toxic secondary products (Barakat, 2011). This method consumes excessive chemical usage as well as generates large quantity of toxic solid sludge that poses challenges in handling, treating and land filling of such chemical waste substances. Hence, an ideal progressing treatment technology should be in between the cost considerations as well as sustainability of the materials used and amount of waste produced from the treatment technologies.

Table 2.3 Comparison of the process description and performance using different in-practice treatment technologies for heavy metal removal

Method	Process description	Disadvantages	Heavy metal	Removal efficiency	Reference(s)
High-end Technology					
Ultrafiltration	Pressure driven membrane operations that use porous membranes for the removal of heavy metal.	Generation of sludge and expensive	Cr(VI) Ni(II) Cd(II)	95.0 % 98.0 % 99.0 %	Aliane *et al.*, 2001 Yurlova *et al.*, 2002
Reverse osmosis	Heavy metal are separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater.	Expensive	Cu(II) Cd(II)	98.0 % 99.0 %	Qdais and Moussa, 2004
Electrodialysis	Metal ions are separated through the use of semi-permeable ion selective membranes. An electrical potential between the two electrodes causes a separation of cation and anion, thus cells of concentrated and dilute salts are formed.	Metal hydroxides, formed clogged the membrane. Expensive	Pb(II)	n.a	Sadrzadeh *et al.*, 2008
Ion-exchange	Metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin	Expensive and partial removal of certain ions.	Cu(II) Zn(II) Cd(II)	n.a n.a n.a	Lee *et al.*, 2006
Low-end Technology					
Chemical precipitation	Precipitation of metal ions was achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers.	Generation of the sludge poses challenges in handling, treating and land-filling of the solid sludge	Ni(II) Cd(II)	n.a 99.0 %	Dang *et al.*, 2009 Matlock *et al.*, 2001

2.2.2 Progressive Treatment Technology for Heavy Metal Removal

In current years, progressive treatment technology usually serves as alternative methods for heavy metal removal compared to conventional methods. Phytoremediation, activated carbon adsorption and biosorption are progressive treatment technologies for heavy metal removal as shown in Table 2.4. Phytoremediation offers advantages of low cost and sustainability of materials. However, the process takes a long time and depends on environmental abiotic factors. On the other hand, activated carbon adsorption is only applicable for the removal of certain heavy metal and is not environmental friendly due to high energy or chemical require in preparation of activated carbon from plant derived materials. Whilst the on-going research on progressing treatment for heavy metal removal technology by biosorption focussed into areas of adopting biodegradable plant derived materials from industrial and agricultural waste as biosorbent presently. This makes the possibility of exploiting economical, large quantity and locally available biosorbents for heavy metal treatment as well as generates revenue from waste. Therefore, the alternative treatment technology of biosorption that is based on exploration of agricultural waste is highlighted in this study.

Table 2.4 Comparison of progressive treatment technology

Method	Process description	Remarks	Reference
Phytoremediation	Use of certain plants to clean up soil, sediment and water contaminated with heavy metal ions	Long time for metal removal and regeneration of the plant, affect by abiotic factors	Ghosh and Singh, 2005
Activated carbon adsorption	The surface complex formation between the metal ions and the acidic surface functional groups	High energy requirement or chemicals inquiry for preparation of activated carbon.	Monser and Adhoum, 2002
Biosorption	The use of metabolically inactive non-living biomass of microbial or plant origin based material to bind with heavy metal ions (Pb, As)	Widely and in large quantity availability, performance and selectivity	Wang and Chen, 2009

2.3 Biosorption for Heavy Metal Removal

Biosorption has been defined as a passive physical-chemical process that biomolecules of non-living biological material, refer as biosorbent, bind with heavy metal ions from aqueous solutions. It is classified as an alternative sustainable remediation technology in terms of resource and environmental impacts where the biosorbent is biodegradable based material and the heavy metal in dilute acid could be extracted via electrolysis (Poliakoff and Licence, 2007; Hashim *et al*., 2011). Biosorption offers the advantages of low cost, effectiveness for dilute effluents, minimum chemicals usage and reduced toxic sludge generation (Gupta *et al*., 2000). Furthermore, biosorbent has advantages over live and immobilized micro-organism as it does not depends on nutrient availability, toxicity tolerance and metabolic activities (Krishnani and Ayyappan, 2006; Locci *et al*., 2008).

Table 2.5 lists specific studies on biosorption process which have focussed on types of processes that include their functionalities and economic feasibilities. Common independent parameters that have been used for the study of biosorption processes are biosorbent concentration, initial pH, contact time, initial heavy metal concentration, temperature, agitation rate and particle size.

Table 2.5 Specific area of biosorption study and its parameters

Type of study	Parameters	Observation
Process	Biosorbent concentration	Dependent process, maximum dosage or random selection dosage is used in batch study.
	Initial pH	Dependent process, operate under wide range of pH conditions.
	Contact time	Important parameters for kinetic study.
	Initial heavy metal concentration	Important parameters for isotherm study and calculation of q_{max} of biosorbent.
	Temperature	Generally not affected due to biosorbent is inactive. Important for thermodynamic study
	Agitation rate	No consistent profile, depends on type of biosorbent.
	Particle size	No consistent profile, depends on type of biosorbent.
Functionality	Efficiency – percentage	Depands on biosorbent, selected heavy metal and operating condition.
	Effectiveness - uptake	Usually rapid under favourable conditions.
	Versatile	Good. The binding sites on biosorbent can bind with a variety of heavy metal ions.
	Selectivity	Generally poor for raw biosorbent. Modification of biosorbent, types and concentration of heavy metal may improve selectivity.
	Recovery	High recovery using dilute acid, alkaline or others solutions.
Economical feasibility	Reusability	High possibility of reusability.
	Maintenance and cost comparison with conventional methods	Easy handling in operation and storage. Generally low cost. Biosorbent always widely and easily available from industrial or agricultural waste.
Predictive Modelling	Artificial neural network (ANN)	Prediction of output, no equation
	Response surface methodology (RSM)	Prediction of output with equation, depends on selected parameters generate from software

(Vijayaraghan and Yun, 2008; Febrianto *et al*., 2009; Gupta *et al*., 2009; Cerino-Córdova *et al*., 2012; Giri *et al*., 2011)

Biosorption performance can be evaluated through its removal efficiency and uptake effectiveness. While versatile and selectivity of biosorption performance is desired to facilitate the application study. Generally, raw biosorbents are versatile and biosorbent functional groups can bind with variety of heavy metal ions. Selectivity of biosorbent is merely depending on types and concentration of heavy metal. Modifying functional groups in the biosorbent is not only improves selectivity of biosorbent, but also enhances efficiency in selected heavy metal removal. However, this method is not sustainable because excessive chemicals would be used in modification process and may form irreversible bonding between functional groups and heavy metal ions. Currently, laboratory studies related to desorption and regeneration of biosorbent provide a better understanding of reusablility of biosorbent and leaching of heavy metal from biosorbent (Akmar Zakaria *et al*., 2009; Salamatinia *et al*., 2010).

Economical feasibility of biosorption process includes reusability, maintenance and cost comparison with conventional methods (Wang and Chen, 2009; Das *et al*., 2010; Henini *et al*., 2011). From literature review, many researchers are not interested in the economic evaluation. This may be attributed to lack of available economic data, funding, expertise and industry collaborators. However, investigations and evaluations of biosorbent applicability need to be conducted in pilot or large scale in order to provide important information to develop this sustainable technology.

Predictive modelling of the biosorption functionalities also can be either by non-mathematical modelling or mathematical equations. Both ANN and RSM are useful modelling tools for output prediction that have been applied in biosorption study. The input parameters for ANN can be determined by researchers but no equation is generated from modelling when compared to RSM modelling where fixed input and equation are generated from the software. Most of the approach taken by researchers for biosorption studies are time consuming and contribute little to the development of knowledge in this field. Hence, new approaches and methods development are imperative for the development of this sustainable technology.

2.3.1 Biosorption Mechanisms

Biosorption mechanisms play an important role in biosorption performance evaluation. Mechanisms of heavy metal biosorption are influenced by physical and chemical interactions between the biosorbent and biosorbates, thus affecting the biosorption efficiency and effectiveness. Biosorption mechanisms can take place in many forms which are complex and several mechanisms may occur simultaneously. Adsorption, ion exchange, chemisorptions, complexation, chelation and microprecipitation are mechanisms intensely discussed in biosorption process (Sud *et al*., 2008; Park *et al*., 2010). Table 2.6 list the mechanisms with its description.

Table 2.6 Mechanisms in biosorption and its description

Mechanism	Description
Adsorption	Adhesion of molecules to a surface
Ion exchange	Heavy metal ions replacement by heavy metal ions
Chemisorptions	Chemical bonds are formed through sharing electron between functional groups and heavy metal ions.
Complexation	Coordinate bonds are formed through functional groups attached to central metal atom, especially a transition metal atom.
Chelation	Bonds formed between a centre atom with coordinate bonds
Micro-precipitation	A process by which a substance is separated out of a solution as a solid by forming a chemical precipitate fine particles

(adopted from Nurchi and Villaescusa, 2008; Chojnacka, 2010)

Currently, the biosorption mechanism has become focus of research area in most of the published journals. Ion exchange is the most popular mechanism that has been reported amongst other mechanisms. Table 2.7(a-c) shows biosorption mechanism evaluation for ion exchange, chemisorptions and complexation. For ion exchange mechanism, a common trend whereby heavy metal ions replacement by heavy metal are usually observed. These heavy metal ions include alkaline metals of Na^+ and K^+ as well as alkaline earth metals of and Mg^{2+} and Ca^{2+}. The mechanism is usually supported by EDX or biosorption heavy metal analysis using ICP or Atomic Absorption Spectroscopy (AAS) with an exception for Murphy *et al*. (2009). Murphy *et al*. (2009) confirmed the result of FTIR by XPS analysis result. However, the proposed ion exchange mechanism cannot be correlated directly with the biosorbent's biosorption performance.

Table 2.7(a) List of evaluation study for ion exchange mechanism by specific biosorbents

Biosorbent	Heavy metal	Remarks on involved ions	Reference(s)
Sawdust deciduous trees	Cd(II), Cu(II), Fe(II), Mn(II), Ni(II), Zn(II)	Na^+, K^+, Ca^{2+} and Mg^{2+}, biosorption heavy metal analysis	Božić *et al*., 2009
Mango peel waste	Cd(II), Pb(II)	Na^+, K^+, $Ca^{2+}$and Mg^{2+}, EDX analysis	Iqbal *et al*., 2009
Brown seaweed *Fucus vesiculosus*, the green seaweed *Ulva* spp. and the red seaweed *Palmaria palmata*	Cr(VI)	Na^+, K^+, Ca^{2+} and Mg^{2+}, EDX and XPS analysis	Murphy *et al*., 2009
Moringa oleifera bark	Pb(II)	Ca^{2+}, Mg^{2+}, biosorption heavy metal analysis	Reddy *et al*., 2010a
Fungus *Paecilomyces maequandii*	Pb(II), Zn(II)	K^+, EDX analysis	Słaba and Długoński, 2011
Fungus *Pleurotus ostreatus*	Cd(II)	K^+ , EDX analysis	Tay *et al*., 2011a
Olive tree pruning waste	Pb(II)	K^+, Na^+, Ca^{2+} and Mg^{2+}, biosorption heavy metal analysis	Blázquez *et al*., 2011
Fungus *Pleurotus platypus*	Cd(II)	Ca^{2+} and Mg^{2+}, EDX analysis	Vimala and Das, 2011
Cucumis melo seed	Pb(II)	Mg^{2+} and K^+, EDX analysis	Tunali Akar *et al*., 2012

Table 2.7(b) List of evaluation study for chemisorption mechanism by specific biosorbents

Biosorbent	Heavy metal	Remarks on existing model evaluation	Reference(s)
Areca catechu heartwood powder	Cd(II)	The mean free energy of Dubinin-Radushkevich (D-R) isotherm	Chakravarty *et al*., 2010a
Moringa oleifera bark	Pb(II)	Pseudo second-order kinetic	Reddy *et al*., 2010a
Chestnut shell	Cu(II)	Pseudo second-order kinetic	Yao *et al*., 2010
Fungus *Pleurotus ostreatus*	Cd(II)	SEM, The mean free energy of D-R isotherm	Tay *et al*., 2011a
Fungus *Trametes versicolor*	Cu(II)	Pseudo second-order kinetic	Subbaiah *et al*., 2011a
Fungus *Pleurotus platypus*	Cd(II)	Pseudo second-order kinetic	Vimala and Das, 2011
Cucumis melo seed	Pb(II)	The mean free energy of D-R isotherm	Tunali Akar *et al*., 2012

Table 2.7(c) List of evaluation study for complexation mechanism by specific biosorbents

Biosorbent	Heavy metal	Functional groups identified through FTIR	Remarks on function groups involved in complexation	Reference(s)
Fungus *Pleurotus ostreatus*	Cu(II), Ni(II), Zn(II)	-NH, C=O, C=N, -OH, C-O	-	Javaid *et al*., 2011
Fungus *Pleurotus ostreatus*	Cd(II)	-OH, -NH, C=O, C-O, C-N	*N*-acetylglucosamine	Tay *et al*., 2011a
Fungus *Paecilomyces maequandii*	Pb(II), Zn(II)	-OH, -NH, C=O, C-O, C-N	Amide group	Słaba and Długoński, 2011
Olive tree pruning waste	Pb(II)	-OH, -NH, C=O, C-O	-	Blázquez *et al*., 2011
Cucumis melo seed	Pb(II)	-NH, -OH, C-O, C=O, C-O, -SO_3, P=O	-	Tunali Akar *et al*., 2012

As shown in Table 2.7(b), the chemisorptions mechanism can be suggested through the use of existing models, namely, pseudo second order kinetic or the mean free energy of Dubinin-Radushkevich isotherm. Obviously, there is lack of evidence from instrumentation analysis to support this mechanism. Therefore, this mechanism needs be investigated comprehensively and explained by equations.

Complexation mechanism characteristically is tied to double bonds structures of amide, carboxyl or phosphate functional groups as shown in Table 2.7(c). FTIR results are used to support the complexation mechanism. However, the mechanism has not been confirmed by other instrumentation analysis nor evaluated intensively to elucidate the complexes formed. This may due to lack of expertise and instrumentation in advanced characterisation of solid biosorbent. Słaba and Długoński (2011) and Tay *et al*. (2011a) reported that nitrogen derived organic compounds that have double bond in structure are involved in complexation.

It can be concluded that recent studies and publication show that heavy metal biosorption is still needs further study due to little information regarding the mechanism that is responsible for the heavy metal biosorption. Biosorption mechanism is based mainly on functional groups and the affinity between the biosorbent with heavy metal ions, thus mechanisms may differ according to the biosorbent.

2.3.2 Biosorption Modelling of Isotherm, Kinetic and Thermodynamic

Modelling of biosorption process usually used the initial heavy metal concentration, time and temperature as the experimental parameters, which were evaluated with a few existing models. Most of the study carried out the biosorption curve being fitted to existing isotherm, kinetic and thermodynamic models. For isotherm models, include two basic equations of Langmuir and Freundlich. Both contain two parameters equation. Whilst, the derivation from both equations produced three-parameter equations such as Redlich-Peterson, Sips, Khan, koble-Carrigan, Hill, Toth, Radke-Prausnitz, Jossens and Langmuir-Freundlich. Extended derivations have come up with the next four-parameter equations such as Weber-van Vliet, Fritz-Schlunder and Baudu. Five-parameter equation of Fritz-Schlunder also have been derived. Other than the isotherm-based modelling, biosorption parameters also can be derived from Pseudo first-order, pseudo second-order, Elovich and diffusion models are commonly employed existing kinetic models.

Table 2.8 summarises the trend of existing isotherm models evaluation for heavy metal biosorption using raw agricultural, sawdust and fungus based biosorbents. The trend of using existing isotherm models to evaluate biosorption effectiveness was initially simple and only focused on two parameters equations of Langmuir and Freundlich models. For the timeline of 2007 to 2010, a variety of prevalent isotherm models that include multi-parameters equations had been investigated. Most of multiple parameters equations are derivatives of the Langmuir equation. However, the trend has changed back to two parameters equations of Langmuir and Freundlich as well as simple derivatives of the Langmuir equation. The changes of trend throughout the timeline could be due to the small contribution of different existing isotherm models for the evaluation for heavy metal biosorption in order to better understand the biosorption system and mechanism. It can be deduced that the Langmuir isotherm is one of the most important model amongst the existing isotherm models evaluation. This model, as derived from a first-principle stand-by Langmuir, enables effectiveness comparison based on the calculated maximum heavy metal uptake value (q_{max}) of biosorbent and the evaluation on monolayer biosorption system.

Table 2.8 Timeline for prevalent isotherm models used for the evaluation of heavy metal biosorption using various types of biosorbent

Year	Existing isotherm model(s)	Biosorbent	Heavy metal	Reference(s)
2002 -2006	*Two-parameters equations*			
	Langmuir	Sugar beet pulp	Ni(II), Cu(II)	Reddad *et al*., 2002
	Langmuir	Tea waste	Ni(II)	Malkoc and Nuhoglu, 2005
	Langmuir, Freundlich	Sawdust *Dalbergia sissoo*	Ni(II)	Shakirullah *et al*., 2006
2007 - 2010	*Multi-parameters equations*			
	Langmuir, Dubinin-Radushkevich	Sawdust *Deodar cedrus*	Cd(II)	Memon *et al*., 2007
	Langmuir, Freundlich, Dubinin-Radushkevich	Spent grain	Pb(II)	Li *et al*., 2009
	Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Halsey, Redlich-Peterson, Sips, Khan, Koble-Corrigan, Hill, Toth, Radke-Prausnitz, Jossens, Langmuir-Freundlich, Weber-van-Vliet, Fritz-Schlunder, Baudu	Fungus *Pleurotus platypus*	Ag(I)	Das *et al*., 2010
	Langmuir, Freundlich, Dubinin-Radushkevich, Temkin	Fungus Agaricus bisporus	Cu(II)	Ertugay and Bayhan, 2010
	Langmuir, Freundlich,Redlich-Peterson	Egg shell powder	Pb(II)	Kalyani *et al*., 2010
	Langmuir, Freundlich, Temkin	Seed husk *Calophyllum inophyllum*	Pb(II)	Lawal *et al*., 2010
	Langmuir, Freundlich, Scatchard	Fungus *Mucor rouxii*	Pb(II)	Majumdar *et al*., 2010
	Langmuir, Freundlich, Brunner Emmert Teller	Mansonia wood sawdust	Cu(II), Pb(II)	Ofamaja *et al*., 2010

2011 -2012	*Two-parameters equations and simple derivatives of the Langmuir equation*			
	Langmuir, Freundlich	Fungus *Pleurotus mutilus*	Cu(II)	Henini *et al*., 2011
	Langmuir	Sea grape *Caulerpa lentillifera*	Cd(II), Cu(II), Pb(II)	Apiratikul *et al*., 2011
	Langmuir, Freundlich	Fungus *Pleurotus ostreatus*	Cu(II), Ni(II), Zn(II)	Javaid *et al*., 2011
	Langmuir, Freundlich	*Cassia angustifolia* bark	Cd(II), Cu(II), Pb(II)	Mulgund *et al*., 2011
	Langmuir	Fungus *Pleurotus platypus*	Cd(II)	Vimala and Das, 2011
	Langmuir, Freundlich	Fungus *Aspergillus niger*	Cr(VI), Ni(II), Zn(II)	Kumar *et al*., 2012
	Langmuir, Freundlich, Dubinin-Radushkevich	*Cucumis melo* seed	Pb(II)	Tunali Akar *et al*. 2012

Existing kinetic models used are principally applied to suggest the mechanism and rate limiting factors involved in heavy metal biosorption process. Table 2.9 shows the existing kinetic models evaluation for heavy metal biosorption using raw agricultural waste and fungus derived biosorbents in recent years. The pseudo first-order and second-order models suggest the involvement of uni-molecular and bi-molecular system respectively. In addition, good fitting pseudo second-order and Elovich models indicate that chemisorptions are the rate limiting factor in heavy metal biosorption. Diffusion models infer that diffusion process is one of the limiting factors for biosorption rate but assist little in biosorption mechanism explanation. Hence, the pseudo first-order and second-order kinetic models are the two major components used to gain insight into biosorption system, mechanism and rate limiting factor.

Table 2.9 Commonly used kinetic models for the evaluation of heavy metal biosorption using raw agricultural waste and fungus derived biosorbents

Biosorbent	Kinetic models	Heavy metal	Reference(s)
Agricultural waste derived biosorbent			
Areca catechu heartwood powder	Pseudo first-order and second-order, Intra-particle diffusion	Cd(II)	Chakravarty *et al*., 2010b
Mansonia wood sawdust	Pseudo first-order and second-order, intra-particle film and pore diffusion	Pb(II)	Ofomaja, 2010
Moringa oleifera bark	Pseudo first-order and second-order, Intra-particle diffusion	Pb(II)	Reddy *et al*., 2010a
Chestnut shell	Pseudo first-order and second-order, Intra-particles diffusion	Cu(II)	Yao *et al*., 2010
Cork waste	Pseudo first-order and second-order, Chrastil's diffusion model, Rate determining diffusion step	Cd(II), Pb(II)	López-Mesas *et al*., 2011
Olive tree pruning waste	Pseudo first-order and second-order, Intra-particles diffusion	Pb(II)	Blázquez *et al*., 2011
Moringa oleifera bark	Pseudo first-order and second-order, Intra-particles diffusion	Ni(II)	Reddy *et al*., 2011
Peanut shell	Pseudo first-order and second-order, Elovich	Cr(III), Cu(II)	Witek-Krowiak *et al*., 2011
Cucumis melo seed	Pseudo first-order and second-order	Pb(II)	Tunali Akar *et al*., 2012
Sugarcane bagasse	Pseudo first-order and second-order, Elovich	Ni(II)	Alomá *et al*., 2012

Fungus derived biosorbent			
Rhizopus cohnii	Pseudo first-order and second-order	Cd(II)	Luo *et al*., 2010
Pleurotus platypus	Pseudo first-order and second-order	Cd(II)	Vimala and Das, 2011
Pleurotus ostreatus	Pseudo first-order and second-order	Cu(II), Ni(II), Zn(II)	Javaid *et al*., 2011
Mucor indicus	Pseudo second-order	Pb(II)	Javanbakht *et al*., 2011
Mucor hiemalis	Pseudo first-order and second-order, Intra-particles diffusion	Ni(II)	Shroff and Vaidya, 2011
Trametes versicolor	Pseudo first-order and second-order, Intra-particles diffusion	Cu(II)	Subbaiah *et al*., 2011a
Trametes versicolor	Pseudo first-order and second-order, Intra-particles diffusion	Cd(II), Pb(II)	Subbaiah *et al*., 2011b
Pleurotus platypus	Pseudo first-order and second-order	Cd(II)	Vimala and Das, 2011
Aspergillus niger	Pseudo first-order and second-order, Intra-particles diffusion	Cr(VI), Ni(II), Zn(II)	Kumar *et al*., 2012

The nature of biosorption process could be better understood through the thermodynamic model. Table 2.10 shows that most of the research carried out with thermodynamic model, do not include desorption in their studies. For studies conducted both thermodynamic and desorption investigations, these two studies were discussed separately and treated as stand-alone discussion with no consideration or initiative to relate the thermodynamic results with the desorption results. Thermodynamic model not only indicates nature of biosorption process but also type of reversible or irreversible bonding formed after biosorption process. Up to date, there is no attempt to intensively investigate and evaluate the type of bonds involve in the biosorption process. In fact, this piece of information not only can support the deduced formation of proposed complexes formed after biosorption but also imply the mechanisms of biosorption indirectly.

Table 2.10 Biosorption of heavy metal by specific biosorbent in association to thermodynamic and desorption models

Biosorbent	Heavy metal	Thermodynamic	Desorption	Reference(s)
Spanish oyster *Scolymus hispanicus*	Cd(II)	+	-	Barka *et al.*, 2010
Fungus *Pleurotus platypus*	Ag(I)	+	-	Das *et al.*, 2010
Fungus *Agaricus bisporus*	Cu(II)	+	-	Ertugay and Bayhan, 2010
Seed husk *Calophyllum inophyllum*	Pb(II)	+	-	Lawal *et al.*, 2010
Fungus *Mucor rouxii*	Pb(II)	+	+	Majumdar *et al.*, 2010
Mansonia wood sawdust	Pb(II)	+	-	Ofomaja, 2010
Mansonia wood sawdust	Cu(II), Pb(II)	+	+	Ofamaja *et al.*, 2010
Chestnut shell	Cu(II)	+	-	Yao *et al.*, 2010
Sugarcane bagasse	Ni(II)	+	-	Alomá *et al.*, 2012
Fungus *Pleurotus mutilus*	Cu(II)	+	-	Henini *et al.*, 2011
Sea grape *Caulerpa lentillifera*	Cd(II), Cu(II), Pb(II)	+	-	Apiratikul *et al.*, 2011
Olive tree pruning waste	Pb(II)	+	-	Blazquez *et al.*, 2011
Moringa oleifera bark	Ni(II)	+	+	Reddy *et al.*, 2011
Fungus *Trametes versicolor*	Cu(II)	+	-	Subbaiah *et al.*, 2011a
Cucumis melo seed	Pb(II)	+	-	Tunali Akar *et al.*, 2012

-	Not applicable
+	Applicable

2.3.3 Predictive Biosorption Modelling by Artificial Neural Network (ANN)

Existing isotherm, kinetic and thermodynamic models are traditionally used in biosorption experimental data evaluation. Recently, predictive modelling in biosorption has received special attention for downstream applications. Approaches to the modelling of biosorption have included the ANN and RSM. Both have been found to be useful tools for output prediction. Advantage of ANN is the output parameters can be the dependent parameters, whilst the fixed input of RSM has become the independent parameter that can be generated by software. ANN is considered as the black-box modelling tool as no equation is generated after the modelling when compared with the RSM modelling where an equation is available. Validity of ANN is usually tested by sensitivity analysis with high coefficient and low m.s.e and s.s.e. Amongst all of the modelling methodologies available, ANN modelling is the most acessible research tool to be used in Malaysia due to the high availability of MATLAB software, coupled with the ease and simplicity in applying such tools to each research scenario.

ANN is a computational model that is inspired by the structure of biological neural network (Basheer and Hajmeer, 2000). Naturally, biological neurons receive signals through synapses located on the dendrites. When the signals pass a certain signal threshold, the neuron is activated and emits a signal through the axon. Figure 2.1 illustrates how the biological neural network is highly abstracted when modelling an artificial neural network system to process the information. In ANN modelling, the input (signals) are multiplied by weights (signals strength) and computed by a mathematical function to process the output. The training algorithms of the ANN can then adjust the weights in order to obtain the desired output from the ANN.

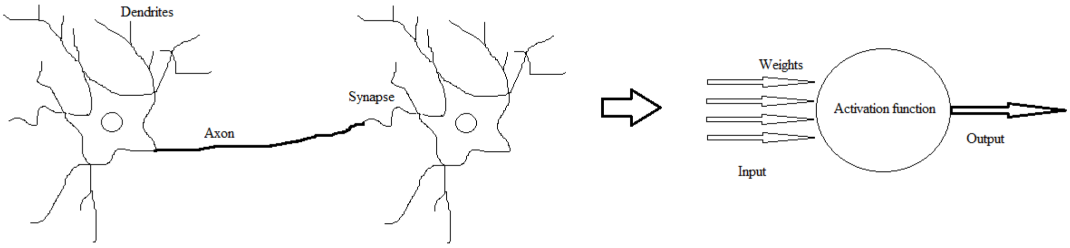

Figure 2.1 The biological neuron network is transformed and extracted to artificial neuron network system
(adopted from Basheer and Hajmeer, 2000; Kumar and Porkodi, 2009)

Table 2.11 summarises the use of ANN as a prediction tool for the heavy metal biosorption. Multiple input data are from heavy metal biosorption optimization parameters such as biosorbent concentration, initial pH, contact time, initial heavy metal concentration, temperature, initial volume of heavy metal and particle size. Meanwhile, the single output is evaluated through the efficiency of heavy metal biosorption together with mean square error (m.s.e). Single output ANN model is thus limited if evaluation of a few outputs simultaneously is desired. Therefore, ANN model is vital for multiple inputs and multiple outputs, in order to predict effectiveness and efficiency of biosorption as well as for the treated effluent water quality. The development and application of a multiple output ANN model is expected to make contribution to the knowledge for the scale-up biosorption of heavy metal technology.

Table 2.11 Input and output of ANN for heavy metal biosorption modelling

Materials	Heavy metal	Input	Output	Reference(s)
Sawdust	Cu(II)	Optimization parameters of initial pH, initial Cu(II) concentration, temperature, particle size	efficiency, mean square error (m.s.e)	Prakesh *et al*., 2008
Antepn pistachio (*Pistacia Vera* L.) shells	Pb(II)	Optimization parameters of biosorbent concentration, initial pH, contact time, initial Pb(II) concentration, temperature	efficiency, m.s.e	Yetilmezsoy and Demirel, 2008
Shelled *Moringa oleifera* seed powder	Cd(II)	Optimization parameters of biosorbent concentration, initial pH, contact time, initial Cd(II) concentration, initial volume of Cd(II)	efficiency, m.s.e	Kardam *et al*., 2010
Shelled *Maringa oleifera* seed powder	Ni(II)	Optimization parameters of biosorbent concentration, initial pH, contect time, initial Ni(II) concentration, initial volume of Ni(II)	efficiency, m.s.e	Raj *et al*., 2010

2.4 Biosorbent

A biosorbent consists of dead and metabolically inactive biological material that participates in biosorption process and is able to extract or concentrate a desired molecule by its selective retention. In recent years, interest has shifted towards the development of biodegradable and sustainable biosorbents for heavy metal treatment, especially for industrial wastewater laden with heavy metal. Table 2.12(a-c) lists the Pb(II), Cu(II) and Ni(II) heavy metal biosorption using available biosorbents and biosorption effectiveness according to their originated country. There is a wide choice of biosorbent in the respective countries, from waste from agriculture to industries that have high potential to be exploited as biosorbent. Major challenges in the selection of a suitable biosorbent are low cost materials and materials that are easily available in large amount in nature (Vieira and Volesky, 2000; Hawari and Mulligan, 2006).

Table 2.12(a) List of Pb(II) biosorption studies by selective biosorbents at various country

Country	Biosorbent(s)	Effectiveness (mg/g)	Reference(s)
Republic of Iran	Rice hull	0.84	Asadi *et al*., 2008
	Papullus sp. sawdust	0.82	
Thailand	Spent fungal corncob based substrate	14.75	Jonglertjunya, 2008
India	Peepul leaves	127.34	Gupta *et al*., 2009
	Banana peels	72.79	
	Peanut hulls	69.75	
	Coir fibres	52.03	
	Rice stems	49.57	
	Teak sawdust	40.70	
	Discard tea leaves	35.89	
	Mango leaves	31.54	
	Rice husk	31.13	
	Grass clippings	29.05	
Pakistan	Mango peel waste	99.05	Iqbal *et al*., 2009
China	Modified Spent grain	35.04	Li *et al*., 2009
Nigeria	Seed husk (*Calophyllum inophyllum*)	11.47	Lawal *et al*., 2010
Taiwan	Algae *Spirogyra*	90.91	Lee and Chang, 2011
	Algae *Cladophora*	46.51	

Table 2.12(b) List of Cu(II) biosorption studies by selective biosorbents at various country

Country	Biosorbent(s)	Effectiveness (mg/g)	Reference(s)
Republic of Iran	Rice hull *Papullus* sp. sawdust	0.68 0.69	Asadi *et al*., 2008
India	Pretreated sawdust (*Acacia arabica*)	5.64	Meene *et al*., 2008
Sweden	Birch wood *Betula* sp. sawdust	4.9	Grimm *et al*., 2008
Brazil	Pecan nutshell	91.2	Vaghetti *et al*., 2009
Canada	Maple wood sawdust	9.191	Rahman and Islam, 2009
Vietnam	Wheat straw	11.44	Dang *et al*., 2009
Pakistan	Fungus *Pleurotus ostreatus*	8.06	Javaid *et al*., 2011
Turkey	Fungal *Agaricus bisporus*	3.15	Ertugay and Bayhan, 2010
Republic of Bulgaria	Free and immobilised fungus *Aspergillus niger*	0.28 - 0.54	Tsekova *et al*., 2010
Poland	Peanut shell	25.4	Witek-Krowiak *et al*., 2011)

Table 2.12(c) List of Ni(II) biosorption studies by selective biosorbents at various country

Country	Biosorbent(s)	Effectiveness (mg/g)	Reference(s)
United State of America	Maple sawdust	34	Shukla *et al*., 2005
Republic of Iran	Rice hull Sawdust *Papullus* sp	0.57 0.49	Asadi *et al*., 2008
Turkey	Plant *Phaseolus vulgaris* L. from canned food factory immobilized by silica-gel	98.01	Akar *et al*., 2009
Canada	Wheat straw	2.5	Baig *et al*., 2009
India	*Acacis leucocephala* bark	294.1	Subbaiah *et al*., 2009
Canada	Barley straw	35.8	Thevannan *et al*., 2010
Pakistan	Fungus *Pleurotus ostreatus*	18.83	Javaid *et al*., 2011
Thailand	Sea grape *Caulerpa lentillifera*	10.73	Apiratikul *et al*., 2011

In Malaysia, various biosorbents have been tested for heavy metal biosorption. They were derived from agricultural waste as shown in Table 2.13. However, most of the work did not meet the requirements of an ideal biosorbent, which should be cost-effective, easy to obtain locally, available in large quantity, non-toxic and effective. These include fungi, seaweeds, wood sawdust and plant based biosorbents. In addition, Table 2.13 also shows the chemically modified biosorbents that have been extensively explored as to increase performance of heavy metal biosorption. From the perspective of sustainable technology, such biosorbents can be perceived as not environmental friendly and not cost effective, as they are derived from the usage of chemicals to treat heavy metal which poses additional cost through purchase and handling of chemicals waste.

Table 2.13 Agricultural based biosorbent for heavy metal biosorption in Malaysia

Biosorbent	Heavy metal	Reference(s)	Remarks of problem
Fungus *Pycnoporus sanguineus*	Cu(II), Cd(II), Pb(II)	Zulfadhly *et al*., 2001	Availability in abundant, toxic
Seaweeds	Cd(II)	Hashim and Chu, 2004	Availability widely and in abundant
Lalang (*Imperata cylindrica*) leave powder	Cd(II)	Megat Hanafiah *et al*., 2007	Biosorption performance
Oil palm tree biomass (oil palm bark, oil palm frond and empty fruit bunch)	Cu(II), Zn(II)	Salamatinia *et al*., 2007	Biosorption performance
Algae *Spirogyra neglecta* (Hasall) Kutzing	Pb(II)	Hussain *et al*., 2009	Availability widely and in abundant
Fungus *Pleurotus ostreatus*	Cd(II)	Tay *et al*., 2011a	Availability in abundant
Meranti wood	Cd(II)	Rafatullah *et al*., 2012	Biosorption performance
NaOH treated lalang (*Imperata cylindrica*) leave powder	Pb(II)	Hanafiah *et al*., 2006	Chemically Modified
HNO_3 treated rice husk	Cu(II), Cd(II)	Ong *et al*., 2007	Chemically Modified
NaOH treated rubber (*Hevea brasiliensis*) leaves powder	Cu(II)	Ngah and Hanafiah, 2008	Chemically Modified
Chemically treated meranti wood	Cu(II), Pb(II)	Ahmad *et al*., 2009	Chemically Modified
Chemically treated rubber wood sawdust	Cr(VI)	Akmar Zakaria *et al*., 2009	Chemically Modified
Chemically treated rubber (*Hevea brasiliensis*) leaf powder	Pb(II)	Kamal *et al*., 2010	Chemically Modified
NaOH treated oil palm frond	Cu(II), Zn(II)	Salamatinia *et al*., 2010	Chemically Modified
Chemically treated mangrove barks	Cu(II), Ni(II)	Rozaini *et al*., 2010	Chemically Modified
HCl treated mango tree sawdust (*Mangefera indica*)	Cd(II), Zn(II)	Qasimullah *et al*., 2011	Chemically Modified
Chemically treated lignocellulosic waste (rice husk and sugarcane bagasse)	Pb(II)	Yeneneh *et al*., 2011	Chemically Modified

It is interesting to note that in Malaysia, one of the potential candidates for the development of biosorbent can be found in mushroom cultivation farms. It takes the form of *Pleurotus ostreatus* spent mushroom substrate compost (PSMC). In addition, it has not been subjected to any study on it as a biosorbent of heavy metal in aqueous solution.

Currently, researchers have only focused on the exploitation of spent mushroom substrate compost as biofuel and biochar for renewable energy and carbon recycling (Finney *et al*., 2009; Jones *et al*., 2010; Tippayawong *et al*., 2011). However, combustion is limited by lack of oxygen in fluidised bed unit and generates secondary products of acid gas. Whilst, the pyrolysis process that is required to convert biomass to biochar involves both high temperature and pressure.

2.4.1 Preparation of Typical Biosorbents

Generally, all testing of biosorbents for the biosorption process, particularly from agricultural waste, are subjected to the pre-treatment by washing to remove contaminants during the biosorbent preparation. Table 2.14 summarises the pre-treatment methods during the preparation of biosorbents which were collected from agricultural waste and wood based substrates. From the literature review, standardised method for washing as a pre-treatment of biosorbent has to be established. Standard technique of washing as part of the pre-treatment in biosorbent preparation needs to be developed and evaluated in order to provide better understanding of effectiveness of contaminants removal. Most of the washing practices were carried out using water, however the number of washing and other parameters such as biosorbent concentration, immersion time and number of washing cycle during the washing pre-treatment for the preparation of biosorbent were yet to be taken into consideration for its effectiveness.

Table 2.14 Washing pre-treatment methods for agricultural waste and wood based biosorbents

Types of biosorbent(s)	Technique of washing as the pre-treatment method	Reference(s)
Agricultural waste based biosorbent		
Lalang (*Imperata cylindrica*) leave powder	Wash with distilled water	Megat Hanafiah *et al*., 2007
Hazelnut *Corylus avellana* and almond *Prunus dulcis* shells	Wash thoroughly with deionised water	Pehlivan *et al*., 2009a
Banana peels, peanut hulls, coir fibres, rice stems, teak sawdust, discard tea leaves, mango leaves, rice husk, grass clippings	Wash several times firstly with tap water and thereafter with Milli-Q water	Gupta *et al*., 2009
Wheat straw	Wash with distilled water	Muhamad *et al*., 2010
Moringa oleifera bark	Wash twice with deionised water	Reddy *et al*., 2010a
Mangosteen shell	Wash exhaustively with water and finally with deionised water	Zein *et al*., 2010
Pine cone	Wash with water	Ofamaja and Naidoo, 2011
Sugarcane bagasse	Wash with distilled water many times	Alomá *et al*., 2012
Wood based biosorbent		
Walnut Sawdust	Wash with distilled water	Bulut and Tez, 2007
Pine sawdust	Wash with distilled water three times	Uysal and Ar, 2007
Birch wood *Betula* sp. sawdust	Wash several times with deionised water	Grimm *et al*., 2008
Mansion wood sawdust	Wash several times with distilled water	Ofamaja *et al*. 2010
Meranti wood	Wash with distilled water	Rafatullah *et al*., 2012

2.4.2 Characterisation of Recent Tested Biosorbents

The biosorption process is governed by various complex parameters that depend on type of biosorbent, binding sites on surface of biosorbent, chemistry of heavy metal and abiotic effects such as pH, temperature and agitation rate (Mata *et al*., 2008; Vijayaraghavan and Yun, 2008; Baysal *et al*., 2009). Most of the metallic pollutant can be removed by specific functional groups which act as binding sites on biosorbent components of polysaccharides, cellulose, lignin, pectin, protein and chitin (Argun *et al*., 2007; Wuyep *et al*., 2007). Hypothetically, the mentioned biosorbent components may consist of the functional groups like hydroxyl, carboxyl, amide, phenolic, sulfhydryl and phosphate. These functional groups serve as binding sites (hydroxyl, carboxyl, amide, phenolic, sulfhydryl and phosphate) depending on the types of biosorbent components (polysaccharides, cellulose, lignin, pectin, protein and chitin).

Table 2.15 lists the types of analysis which were used to characterise the biosorbent before and after heavy metal biosorption. Several specific functional groups have been identified for each biosorbent that was derived from raw agricultural waste, fungal and sawdust. Different types of analysis need to be carried out to determine different categories of characteristics for each biosorbent. For an example, an energy dispersive X-ray (EDX) is used to determine the existence of heavy metal and other elements, fourier transformed infrared spectroscopy system (FTIR) for the identification of functional groups, X-ray Diffraction (XRD) for analysis of compounds, X-ray photoelectron spectrometer (XPS) for analysis species of heavy metal and element. Meanwhile forfunctional groups and mobility of carbon atom, the analysis is carried out using ^{13}C solid state nuclear magnetic resonance (^{13}C ssNMR). For identification of functional groups, FTIR is usually employed either as a stand-alone analysis or with the supportive analysis of ssNMR, XRD or XPS. Generally, many study used FTIR as the sole method for functional groups identification. However, there are some exceptions for the study by Bhanoori and Venkateswerlu (2000), Reddy *et al*. (2010a), Zvinowanda *et al*. (2010) and Słaba and Długoński (2011) where ^{13}C ssNMR, XRD and XPS were used, instead of FTIR alone. There is no attempt has been made to combine the analysis by ^{13}C ssNMR, XPS or XRD results. This is to confirm the assumed identified functional groups which were obtained through FTIR analysis alone. Furthermore, the results for the characterisation were seldom analysed in tandem to elucidate mechanisms of biosorption. It can be deduced that recent studies and publications still show biosorbents with little data on the quantity, types of surface functional groups and mechanisms.

Table 2.15 Identification of functional groups according with the use of specific characterisation analysis for heavy metal biosorbent

Biosorbent	Heavy metal	Characterisation analysis	Identified functional groups	Reference(s)
Assumed identified functional group through FTIR without supportive evidence				
Areca catechu heartwood powder	Cd(II)	SEM, EDX, FTIR	-OH, -HN, C=O, CO, C-O,	Chakravarty *et al.*, 2010a
Seed husk *Calophyllum inophyllum*	Pb(II)	FTIR	C=O, N-H, C-O	Lawal *et al.*, 2010
Fungus *Rhizopus cohnii*	Cd(II)	FTIR	-OH, -NH, C=O, C-O	Luo *et al.*, 2010
Chestnut shell	Cu(II)	Bulk density, moisture and ash content, BET surface area, zero charge, titrations, components, FTIR	C=O, C-O	Yao *et al.*, 2010
Garcinia mangostana L.	Cd(II), Co(II), Pb(II)	FTIR	C=O, C-O, -OH, C-O-C, -NH, $-SO_3$	Zein *et al.*, 2010
Fungus *Pleurotus ostreatus*	Cu(II), Ni(II), Zn(II)	Components, FTIR	-NH, C=O, C=N, -OH, C-O	Javaid *et al.*, 2011
Cassia angustifolia bark	Cd(II), Cu(II), Pb(II)	SEM, FTIR	-OH, O=C-O	Mulgund *et al.*, 2011
Fungus *Pleurotus ostreatus*	Cd(II)	Elemental, SEM, EDX, FTIR	-OH, -NH, C=O, C-O, C-N	Tay *et al.*, 2011a
Olive tree pruning waste	Pb(II)	FTIR, cation exchange capacity	-OH, -NH, C=O, C-O, O-H	Blázquez *et al.*, 2011
Fungus *Trametes*	Cu(II)	BET surface area, FTIR	-OH, -NH, C=O, C-O, C-	Subbaiah *et al.*, 2011a

versicolor			N, $-NH_2$	
Fungus *Trametes versicolor*	Cd(II), Pb(II)	BET surface area, FTIR	-OH, C=O, C-O	Subbaiah *et al*., 2011b
Fungus *Pleurotus platypus*	Cd(II)	TEM, EDX, FTIR	-OH, -NH, C=O, P=O, C-O-C	Vimala and Das, 2011
Cucumis melo seed	Pb(II)	BET surface area, zeta potential, SEM/EDX, FTIR	-NH, -OH, C-O, C=O, C-O, $-SO_3$, P=O	Tunali Akar *et al*., 2012)
Sugarcane bagasse	Ni(II)	Elemental, potentiometric titrations, SEM, FTIR	C=O, C-O, -OH	Alomá *et al*., 2012
Fungus *Aspergillus niger*	Cr(VI), Ni(II), Zn(II)	SEM, FTIR	-OH, -NH, C=O, C-O, C-O, P=O, N-containing bioligands	Kumar *et al*., 2012
Identified functional groups through FTIR with supportive evidence (i.e. ^{13}C ssNMR *XPS, XRD)*				
Fungal cell wall	Cd(II)	FTIR, XRD, ^{13}C ssNMR	-OH, C=O, N-H,	Bhanoori and Venkateswerlu, 2000
Moringa oleifera bark	Pb(II)	Bulk density, moisture and ash content, elemental, XRD, FTIR	C=O, N-H, C-O	Reddy *et al*., 2010a
Zea mays tassel	Pb(II)	Elemental, EDX, FTIR, XPS	-NH, C=O, C-O	Zvinowanda *et al*. 2010
Fungus *Paecilomyces maequandii*	Pb(II), Zn(II)	EDX, XRD, FTIR	-OH, -NH, C=O, C-O, C-N	Słaba and Długoński, 2011

An extended study on advanced characterisation of solid biosorbent could generate a new knowledge area in biosorption mechanism. Findings from such research may eventually lead to the development or even novel knowledge on characterisation of biosorbent and its mechanism for heavy metal biosorption. Advanced technique of characterisation i.e., ^{13}C ssNMR and XPS may ascertain the earlier results obtained from FTIR analysis. This shall enable provision of clearer picture on molecular structural changes of biosorbent, which will allow the evaluation on the mechanisms of biosorption in order to provide better understanding which can lead to proper application. Having integrated knowledge on biosorption and biosorbent will lead to the establishment of alternative for sustainable and effective heavy metal treatment process, which will include the potential biosorbent product to be proposed.

2.4.3 *Pleurotus ostreatus* Spent Mushroom Substrate Compost (PSMC)

Pleurotus ostreatus spent mushroom substrate compost (PSMC) can be considered as a novel material to be used as biosorbent. There is no report has been found on the usability nor material characterisation studies being conducted on PSMC. It is a lignocellulosic based material that is widely available from mushroom farms in Malaysia. The PSMC is mainly made up of rubber tree sawdust and *Pleurotus ostreatus* mycelium. For every 200 g of oyster mushroom produced, 600 g of PSMC would be generated (Singh *et al.*, 2003). The usual disposal of PSMC is by open burning or converted into low commercial value organic fertilizer in order to reduce cost of solid waste handling. Studies on PSMC as a potential biosorbent for heavy metal treatment is yet to be explored. Both the lignocellulosic sawdust as well as the fungal biomass of the oyster mushroom have enable PSMC to be the heavy metal biosorbent. This minimally processed PSMC has the potential to be used as the sustainable materials for biosorption as part of the pollution control technology (Tay *et al*., 2011b). This study is in-line with sustainable remediation technology as well as waste management.

2.5 Concluding Remarks

There are a lot of potential in the development of alternative treatment method for heavy metal treatment technology especially to remediate contaminated water. The application of PSMC biosorbent for sustainable heavy metal biosorption appears to be a good option as the material is widely available at a low cost but poorly studied. It is acknowledged that new approaches in biosorption preparation and biosorption evaluation are essential to develop this biosorption technology. In addition, there is also a need to model the biosorption process as this allows the performance of the biosorbent be predicted and understood under different conditions. The understanding of the biosorption mechanisms in heavy metal biosorption will provide novel insight for the potential industrial application of biosorbents as the alternative and sustainable method to treat wastewater laden with heavy metal. Knowledge from the advanced characteristics of PSMC, together with the mechanism of biosorption is currently lacking, which could hinder the development and use of this material as a viable wastewater treatment method. Hence, it would be useful and interesting to conduct investigation in this area.