CHAPTER 2 LITERATURE REVIEW

2.1 Sources of cadmium

Cadmium is one of heavy metals which are concerned in the environment due to health risk to humans and animals. If cadmium accumulates in plants, it will not toxic to them, unless these plants are consumed. The toxicity of cadmium in humans is higher than animals to the extent that it can accumulate in organs for a very long time especially kidneys and bones by eating cadmium contaminated food (Tudoreanu and Philips, 2004). Moreover, the harmful effects of cadmium consist of Itai-itai disease, renal damage, emphysema, hypertention as well as testicular atrophy. Cadmium passes through the environment by industrial activities of humans such as electroplating, manufacturing of plastics, mining, paint pigments, alloy preparation, and batteries. Furthermore, phosphate fertilisers are major source of heavy metal especially cadmium. The accumulation of cadmium in soil through fertiliser is concerned in many countries such as New Zealand and Australia. Phosphorus (P) compounds contain a range of metals, virtually every known element has been found, at least in trace amounts, in a phosphate mineral. Addition of P compounds to soils not only helps to overcome the deficiency of some of the essential trace elements but also introduces toxic metals, such as Cd. The high cadmium concentration is accumulated in pasture soil that is obtained from phosphorous fertiliser using (Roberts et al. 1994). Phosphate rocks (PRs) can be a source of cadmium pollution in soil and food chain. PRs are mainly used for the manufacturing of phosphate fertilisers. The PRs deposits contains the Cd contents, varying sources by sources. This leads to the variation in Cd contents of manufactured P fertiliser, such as TSP, PAPR, and ammonium phosphates, generally contain lower Cd content relative P.

2.2 Phosphorous

Phosphorous is one of the essential elements for plant growing and livestock agriculture. Phosphorous was used in agricultural fields by inorganic and organic fertililisers. The overusing of phosphate cause a phosphorous accumulation in soil and imbalances of phosphorous in ecology, which can bring the adverse impact to water resources especially eutrophication (Sharpley, 2007). So, the strategies to preserve the excessive phosphorous in soil until cultivation are significantly aspects. The strategy to reduce phosphorous losing can be performed by adding the organic compositions that it similar to increase the amount of microbe due to biological P uptake. The microbes can hold the phosphorous fertilisers for a while. The conditioned soil with organic fertiliser can immobilise phosphorous because the microbes can transform the phosphorous to organic phosphorous that it is the process to accumulate phosphorous and the plants are unable to use inasmuch as the plants are use phosphorous in form of inorganic phosphorous (Ayaga, 2005).

The investigation of the phosphorous retardation in soil depends on many factors. The factors consist of pH of soil, soil mineral, organic matter, amounts of clays, temperature, aeration, moisture and anions. The following factors can affect the phosphorous retardation in soil.

Soil pH: The pH is affected to the availability of phosphate. At lower pH or acidic soil, the phosphate was fixed by metallic ions such as iron (Fe), manganese (Mn) and aluminum (Al). At the pH below 4.0, the iron can be efficiently fixed phosphorous whereas the pH in range 5.0-5.5 the aluminum can be actively fixed phosphorous. The Mn, Fe and Al elements are combined with soluble phosphorous and insoluble compound. In alkaline soil condition (peak at pH is 8.0), the calcium is affected to phosphorous fixing. The maximum available of phosphorous that occurs in form of $H_2PO_4^-$ is performed in range of pH between 6.0 and 7.0. If the pH is happened above 7.0, the phosphorous is mainly in a form of HPO_4^{2-} and this result leads to slow adsorbed (Ludwick, 1997).

Types of soil mineral: the mineral is a major factor in phosphorous sorption rate because phosphorous can react with minerals that came from volcanic soils. Highly weathered soils that include Oxisols and Ultisols had very high sorptive of phosphorous. The aluminum and iron oxides can rapidly react with phosphorous (Ausmin Australia, 2008) that high temperature and rainfall intensity can increase the aluminum and iron oxides (Griffith, 2008) but in case of less weathered soils and organic soil bring the low soptive phosphorous capacities (Brady, 2002).

Organic matter content: The addition of organic matter to soil leads to increase the phosphorous available in four periods. Firstly, organic matter creates the complexes with organic phosphate that can be uptaken by plants. Secondly, organic anions can replace the sorped phosphate. Thirdly, the aluminum and iron oxides are coated by humus that this result shows the decreasing of phosphorous sorption. Lastly, organic matter is used to as a source of phosphorus via mineralisation reactions (Brady, 2002).

Amounts of clay minerals: Clay particles can fix phosphorous. As soon as the content of clay increases, the adsorptive capacities of phosphorous are also increased. The finer clay particles is observed the highly of phosphorous sorption due to a huge surface area (Griffith, 2008).

Anions: Anions are included silicates, carbonates, sulfates, arsenate and molybdate. They can compete with phosphate for a position on the anion exchange site. As a result, these anions can take place the phosphate at exchangeable site of soil, or desorption. Desorption of phosphate in the soil solution increased (Brady, 2002).

Temperature, aeration and moisture: If these environmental condition such as temperature and aeration are increased, the adsorption of phosphorous is increased (Brady, 2002). Highly of moisture can decrease the oxygen supply and the ability of roots to adsorb phosphorous (Griffith, 2008).

2.3 Sources of soil amendments

2.3.1 Phosphate compounds

Phosphate enters to soils through natural and anthropogenic sources. Although, phosphate accumulates in most soil parent materials, most of phosphate is mainly occurred in fertiliser and manure. Phosphate fertilisers can be separated into two groups: water soluble (fast release) and the water insoluble (slow release) (Bolan et al. 1993). The water soluble phosphorous fertilisers consist of single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). The significant water insoluble phosphorous fertilisers consist of phosphate rock (PRs) and basic slag. The acidulated phosphate rock (PAPR), superphosphate and reactive rock mixtures include not only water soluble but also water insoluble phosphorous components, so these phosphate fertiliser in unspecified group. Monocalcium phosphate (MCP) is the principal phosphorous components in the superphosphates fertiliser, which are presented in single superphosphate and triple superphosphate. Ammonium phosphate (AMP) is the major compositions in ammonium phosphates (MAP as well as DAP). The apatite is another P mineral, which is in phosphate rock (PRs). The addition of water soluble phosphorous compounds, especially MCP, can be bound to calcium as dicalcium phosphate or DCP. The DCP can simultaneously release the phosphoric acid that can cause acidic soil, soil pH is below 2. The equation is given as follows. (Rajan et al. 1996)

$$Ca(H_2PO_4)_2 + H_2O \longrightarrow CaHPO_4.H_2O + H_3PO_4 \qquad (2.1)$$

Phosphoric acid subsequently dissociates into phosphate and hydrogen ions (protons-H^+). The protons reduce the pH of soil, where the fertiliser granules deposit and the soil pH is very low level ($pH < 2$). When ammonium phosphate fertilisers are added to soil, they dissociate into ammonium and phosphate ions. The subsequent oxidation of NH_4^+ to NO_3^- can release the protons as written follows. (Rajan et al. 1996)

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O \qquad (2.2)$$

The iron (Fe) and aluminium (Al) compounds in the soil are dissolved in acidic soil, resulting in the adsorption and precipitation of P. The soil pH where the ammonium phosphate fertiliser are added, it is unlikely to be as low as the one applying with superphosphate fertilisers. The acidic soils always loss P because of less adsorption of phosphate ions. The acidity can also stimulate the mobilisation of metals in soils.

When insoluble P fertilisers, such as PRs, are employed, the phosphate mineral apatite needs to be dissolved in soils to generate available P, which is consumed by plants. Dissolution of PRs is a prerequisite not only for the plant availability of P (Rajan et al. 1996), but also for the immobilisation of metals through precipitation as metal phosphates. In soil, PRs dissolve by the acid produced in the soils. The reaction is presented as follows. (Bolan et al. 1993).

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \longrightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- \qquad (2.3)$$

This is a major reason why PRs are widely used in agriculture. The highly active P can be obtained without disturbing the soil pH ($pH < 6.5$) (Bolan et.al., 1990). This emitting

P can also immobilise metals even in acid environment (e.g. coal refuse and acid mine drainage) (Evangelou and Zhang 1995). Once the PR is dissolved, the P released undergoes similar adsorption and precipitation reactions as in the case of soluble P fertilisers.

2.3.2 Liming materials

Although liming is primarily aimed at ameliorating soil acidity, it is increasingly being accepted as an important management tool in reducing the toxicity of heavy metals in soils (Brallier et al. 1996; Brown et al. 1997; Bolan et al. 2003a). A range of liming materials is available, which vary in their ability to neutralise the acidity. These include calcite ($CaCO_3$), quick lime (CaO), slaked lime ($Ca(OH)_2$), dolomite ($CaMg(CO_3)_2$), and slag ($CaSiO_3$). In this study, quick lime is selected to be alkaline material. The general physical characteristics of quicklime are a white, caustic, alkaline crystalline solid at ambient temperature. The quicklime is produced from thermal decomposition. A limestone is supplied to produce quicklime because it contains calcium carbonate ($CaCO_3$; mineral calcite). The materials are crushed and burnt in the furnace. The temperature of lime burning is controlled at 825 °C or above. The quicklime and carbon dioxide (CO_2) are released by heating. The quick lime is unstable, when it is cooled. Moreover, the spontaneously reaction between quicklime and carbon dioxide can be returned to calcium carbonate again. After adding quicklime to sludge, the hydrolysis reaction is occurred. The heat is released and quicklime is turned to calcium hydroxide. The reaction is given as follows (Charles, 2005).

$$CaO_{(s)} + H_2O_{(l)} \longleftrightarrow Ca(OH)_{2(aq)} \; (\Delta H_r = -63.7 \text{ kJ/mol of CaO}) \tag{2.4}$$

Calcium hydroxide is normally called “slaked lime”. Whilst the hydration process is an exothermic reaction, the vapors may puff up. The hydration process is able to eliminate the water in raw sludge through heating. One liter of water comprises of quicklime approximate 3.1 kg to give the significantly quantities of calcium hydroxide and 3.54 MJ of energy (Charles, 2005).

2.3.3 Fly ash

Fly ash is one of byproducts that receive from the solid fuel burning process. The electrostatic or particle filtration equipment is used to trap the fly ash before the flue gases are released to the chimneys. Amount of fly ash depend on the source of solid fuel. The compositions of fly ash vary enormously sources by sources. Basically, fly ash consist of silicon dioxide (SiO_2), which forms of both amorphous and crystalline and the other is calcium oxide (CaO). These are endemic admixtures in many coal-bearing rock strata. The ways of fly ash removing and fly ash applications include dumping or add into landfill materials, soil improvement, road base, land reclamation and using as raw materials for cement production. Moreover, some high value methods consist of fertiliser, filler in plastics and resins and metal matrix composite (ceramic additives), but only a little quantities of fly ash can be consumed in such usages (USEPA).

2.3.4 Sewage sludge

Not only the sewage sludge is low cost or free sources of nutrient, soil buffer and abundant organic matter but also the sewage sludge can be used to agricultural soil amendments (EPA, 1995). The sewage sludge which contains significant amounts of nitrogen, phosphorous, organic matter and other trace elements, represents a good source of nutrients for plant growth which are directly reused. Moreover, the sewage sludge is a good soil conditioner to improve physical and chemical properties of soil (Davis, 1989). Whereas, the problem that disturbs the sewage sludge using is contaminants accumulation in the microbial cells. Inasmuch as the sewage sludge can unintentionally remove the trace metal, the raw sewage sludge is not permitted to loss in land. The risk of toxicity from crop or/and environmental are mentioned because the toxic elements pass through the environmental. The level of risks is estimated from mobility and available contaminated, which are presented. Therefore, the sewage sludge treatments are applied to soil amendment. Many strategies in sewage sludge treatment are used to decrease mass of sludge, volume, odour and/or pathogens. In this context several methods, such as biological digestion, composting, lime stabilisation, heat treatment have been used to eliminate pathogens from sludge. The lime stabilisation has been shown to reduce pathogens in sludge, enabling lime treated sludge to be safely disposed-off in landfills or applied to land (Westphal and Christensen, 1983; Jimenez-Cisneros et al., 2001)

A Part 503 Rule has separated biosolids into two types due to pathogen reduction. These are class A and class B. The requirements of class A are reduce the pathogens in the sewage sludge which consists of *Salmonella sp*, bacteria, enteric virus, and viable helminthes ova. Conversely, the class B biosolids consist of reduced level of pathogens level (USEPA). Both of classes are safe but the applications of Class B biosolids are limited as it still contains pathogens. The class B biosolids cannot be used in the public areas, livestock grazing and crop harvesting, while the class A biosolids are not strict to the applications as well as it can be applied as the organic fertiliser (EPA, 1995). The sewage sludge treatment, which is used to soil amendment generally occur in dairy farm and other land applications. The strategy of class A or class B biosolids producing is combination between alkaline materials and sewage sludge. This process is called alkaline stabilisation. The heat is produced and the pH is increased higher than 12, these condition can get rid of pathogens (Boost and Poon, 1998).

The class A requirements can be complied, when the alkaline stabilised biosolids are maintained the temperature at 52 ^{o}C and the pH of mixture is maintained at or above 12 for at least 72 hours. The sewage sludge is air dried to reach over 50% solids after 72 hours incubating time, otherwise the process must be maintained temperature at or above 70 ^{o}C for 30 minutes or longer and pH is maintained at 12. The higher temperature can be reached by overdose of lime, applying an external heat energy or combination (Boost and Poon 1998). For class B biosolids, the sludge is also treated, the alkaline material is mixed with within a shorter time, it is 2 hours . The biosolids may contain small but assent amounts of bacteria. The requirements of class B makes sure that the pathogens in biosolids are reduced to reach the acceptable level. The requirements of class B are met at pH of the mixture between sewage sludge and alkaline material is 12 or above after incubation for 2 hours (USEPA).

2.3.5 Animal manure

With the continuous decline in the availability of land area for crop production, the increase in food demand is likely to be met mainly trough intensive animals production. Confined animal agriculture (i.e. beef cattle, dairy, poultry, and swine) is the major source of manure by-products in most countries. Approximately 900 million tons of organic and inorganic agricultural recyclable byproducts are generated in US, approximately 45.4 million tons are dairy and beef cattle manure and 27 million tons are poultry and swine manure. These manure byproducts have generated annually, 7.5 million tons of N and 2.3 million tons of P are accounted. The reports have claimed that the chemical fertilisers of 9 million tons of N and 1.6 million tons of P are applied to agricultural area (Walker et al. 1997). It can be said that the manure is major source of the natural fertiliser, especially P. In Australia and New Zealand, where open grazing is conducted, a large amount of manure is directly deposited onto pasture land (Haynes and Williams, 1993). The manure byproducts have the potential for being recycled on agricultural land and optimum use of these byproducts requires knowledge of their composition not only in relation to beneficial use but also to environmental implications. Maintaining the quality of the environment is the major consideration when developing management practices to effectively use manure byproducts as a nutrient resource and soil conditioner in agricultural production system

Most manure products contain low levels of heavy metals (except Cu and Zn in swine manure and As in poultry manure). Recently, the advance techniques in the treatment of manure byproducts can reduce the numbers of bioavailability of metals. Westerman and Bicudo (2000) observed that wastewater from swine farm can be treated by adding lime slurry, ferric chloride or polymer. At least 87% of Cu and Zn in swine wastewater can be removed. Moore et al. (1998) applied the alum ($[Al_2(SO_4)_3]$) coagulation process to treat the wastewater from poultry industry. The concentrations of soluble Zn, Cu, and Cd were significantly declined and they meets the allowable limits of trace element loadings. The effluent had a better quality comparing to the one from sewage sludge application. The size of coagulation tank was compacted, it was suited for areas where land application is limited. USEPA (1999) had regulated that the governing livestock and poultry manure byproducts are generally classified based on total N and P loading. Manure byproducts that are low in metal contents can be used to immobilise metals in soils. Since the soil amendments can retard the migration of heavy metals, the immobilisation and bioavailability of Cd in soils are summarised in Table 2.1.

Table 2.1 Immobilisation and bioavailability of cadmium by various soil amendments

Amendments	Observations on immobilisation and bioavailability	References
CM	Cd in soil solution was bound in fast dissociating metal complexes	del Castilho et al. (1993)
KH_2PO_4	Increased immobilisation through phosphate-induced adsorption	Bolan et al. (1999b), Naidu et al. (1994)
LSB, N-Viro; ADB, AADB	Adsorption by inorganic components, metal-organic matter complex formation	Basta et al. (2001), Basta and Sloan (1999), Keefer et al. (1984), Pietz et al. (1983), Soon (1981)
BS	Increased the affinity of inorganic fraction of BS treated soil for Cd adsorption	Brown et al. (1998), Li et al. (2001)
CM, PM, N-Viro	Increased Cd in the organic fraction	Pierzynski and Schwab (1993)
CaO	Decreased phytoavailability	Vasseur et al. (1998)
K_2HPO_4	Increased immobilisation through phosphate-induced adsorption and precipitation	Pierzynski and Schwab (1993), Pearson et al. (2000)
SS	Increased adsorption and complexation	Hyun et al. (1998), John and van Laerhoven (1976), Street et al. (1978)

2.4 Biosoil

Basically, alkaline stabilisation process is known as a non proprietary process. There is no fee for the patent holder. Although there is no charge on patent, the alkaline stabilised biosolids may produce with several different processes that bring the charge of propriety. BioFIX process, RDP En-Vessel Preurisation system and N-Viro advanced alkaline stabilisation with drying are commercial process of stabilised biosolids. These commercial alkaline stabilised biosolids can be used as a bioorganic and mineral fertiliser to increase soil pH and nutrient values. Moreover, these commercial products are imply called biosoil, and they can be applied to land disposal site as landfill cover materials, a topsoil blending ingredients and land reclamation material. Approximately 20% of the commercial biosoils are utilised at landfills for cover material, and the small amounts are sold for land reclamation. A substantial portion of the biosoil products is sold for agricultural use and a topsoil blending. Although the use of the commercial biosoil is not subject to any federal regulations or restrictions, the facility to treat the raw sewage sludge is typically required to obtain a state and/or local permission. In addition, many states and/or local government require site-specific permits for the use of sludge products, if the bulk amounts are employed (nviro.com).

The N-Viro Process is a patent technology process for the treatment and recycling of bio-organic wastes, which are in forms of digested, waste activated, or raw primary-waste activated sludge with an alkaline material or blend of materials. Solid contents of raw sludge can vary from 15-40% (Barkat et al., 2004). Many types of industrial byproduct can be used as alkaline reagents. They are included cement kiln dust, lime kiln dust, lime, limestone, alkaline fly ash, other coal burning ashes and wood ash. The reagents are used alone or in combination (referred to as alkaline admixture). According to local availability and cost, the pH in the sludge alkaline admixture must be higher than 12. The incubating must be at temperature between 52 and 62 ^{o}C, maintaining for 12 hours. The biosoils must contain the solid content more than 60% of total weight. The pH must remain at 12 for at least 72 hours. At this point, the final product has achieved the USEPA classification for complete pathogen destruction (USEPA). The material must be further dried by windrowing to gain the solid content at least 60% of total weight. A uniform granular product is recommended to beneficially use. The material is usually aerated with a minimum of three times during a period of 3 to 7 days. At this point, the material meets the federal sludge concentration limits for trace elements and the vector attraction requirements (EPA, 1995). The final products can carry the trademark of N-viro soil. This biosoil is used as a substitute for agricultural limestone, as a fertiliser, landscaping, an ingredient with other materials for the manufacture of synthetic topsoil, a substitution for landscaping, an ingredient for the manufacturing of synthetic topsoil and a substitute for soil or landfill cover (nviro.com).

Various processed are available to achieve the treatment of biosoilds to be either Class A or Class B disinfection (EPA, 1995). Based on class of alkaline stabilised biosolid achievement, the Classes A and B can be reused as a landfill cover, commercial fertiliser or modify acid soil. In this research, the biosoil is introduced to adsorb the heavy metals, particularly Cd, which may observe in the leachate.

2.5 Biosorption

Adsorption is a well method to remove the heavy metals from leachate. Although the activated carbon (AC) is the popular adsorbent, which can sorb the heavy metals. The AC is costly and generated difficultly. The efficiency of regenerated AC becomes low, so it cannot be reapplied. At the present, the alternative low cost materials, such as yeast, biomass, clays, siderite, sawdust, fly ash are introduced as heavy metals adsorbent. Besides, these low cost adsorbents are often modified to enhance the heavy metal sorptive capacity, replacing the activated carbon (Vasudevan et al., 2002; Li et al., 2003; Tsai et al., 2004; Jiang et al., 2004; Erdem and Ozverdi, 2005). The biosorbent is another competitive materials, which can be replaced AC in removing of heavy metals from leachate (Holan et al., 1993; Tsezos and Volesky, 1981). The biosorption is method, involving the biologically processes. The ionic metals are bound with organic constituents in dead biomass. This process is known as metabolic independent biosorption. The ionic metals are consumed by the living microbial cell, then the metals are accumulated in the cells. This process is named metabolic dependent biosorption. Some biosorption processes, such as permeable biobarrier, membrane bioreactor and biofiltration are combination processes, living and dead biomass and cellular products sorb the ionic metals.

The metal precipitation can take place on the surface of cells. The precipitation is preferred when the microbes produce the compounds in the presence of toxic metals and without cell metabolism dependent. The physico-chemical interaction of the metal and functional groups occur on the surface of microbial cell through non-metabolism dependent biosorption. The surface of microbes capacitate adsorb metal ions from solutions (Beveridge and Koval, 1981; Sağ et al., 1995). This biosorption mechanism depends on physical adsorption, ion exchange and complexation. Although the metabolism of microbial does not relate in the biosorption, cell wall of microbial biomass can react with heavy metals. The cell wall of microbial biomass consists of various biomolecules that include polysaccharides, protein and lipids. These biomolecules on the cell wall are bond with functional groups which are carboxyl, hydroxyl, sulphate, phosphate as well as amino groups (Crist, et al., 1981). These functional groups hold negative charge to the cell surface. The rate of biosorption is usually rapid and the biosorption is reversible process.

In the physical sorption or physiosorption, the electrons exchanging does not observed. The intermolecular attractions come from the attraction between favourable energy sites may take place and the attraction force is non-dependent of molecules electronic properties. The physical adsorption takes place due to weak van der Waals force. The adsorbate holds on surface via multiple layers that can be formed with the same heat of adsorption process. In the chemical sorption or chemiosorption, is explained about electrons exchanging that occurs in between specific surface and solute molecules. The solute molecules are fixed on the surface of sorbent with strength bond and high temperature. The monolayer is typically adsorbed (Rajan, et al., 1996).

The ion exchange can be taken place at specific cell wall sites. Polysaccharides are one of cell wall compositions of microbes and the counter ions such as K^+, Na^+, Ca^{2+} and Mg^{2+} are potion of polysaccharides can be exchanged with bivalent metal ions such as Co^{2+}, Cu^{2+}, Cd^{2+} as well as Zn^{2+} (Cordero, et al., 2004).

The complex formation is another bipsorption type which is occurred on the surface of cell after the interaction between the metals and the active groups. This mechanism is only affected for Ca, Mg, Cd, Zn, Cu and Hg which are accumulated by *Pseudomonas syringae* (VegliÒ and Beolchini 1997). The microorganisms can produce the organic acids that consist of citric, oxalic, gluonic, fumaric, lactic and malic acids. The combination between these acids and the toxic metals are transformed to metallo-organic molecules. These organic acids can enhance the dissolubility of metals and they can leach from the surfactive sites. The carboxylic groups can be found in microbial polysaccahrides and other polymers that it is able to react and form the complex compounds with metals.

The precipitation happens during biosorption. The precipitation is both dependent and non-dependent metabolism. The precipitation of independent on the cellular metabolism may be resulted from the interaction between the surface of cells and metals. In case of dependent metabolism sorption, the metal removal is used as consequences of the reaction between microbes and metals. If the product has high concentration, it can preferably use the precipitation process (Ercole et al. 1994). The design and efficiency of biosorption process to remove the contaminants are very important. So, the understandabilities about the influence factors to biosorption process are also investigated. The following factors can affect the biosorption process.

Temperature: When the temperature of the sorption media is in the range of 20-35 °C the biosorption process is not affected by temperature (Aksu, et al. 1992). Under high temperature, the sorption capacity of biomass is reduced (Aksu, 2001).

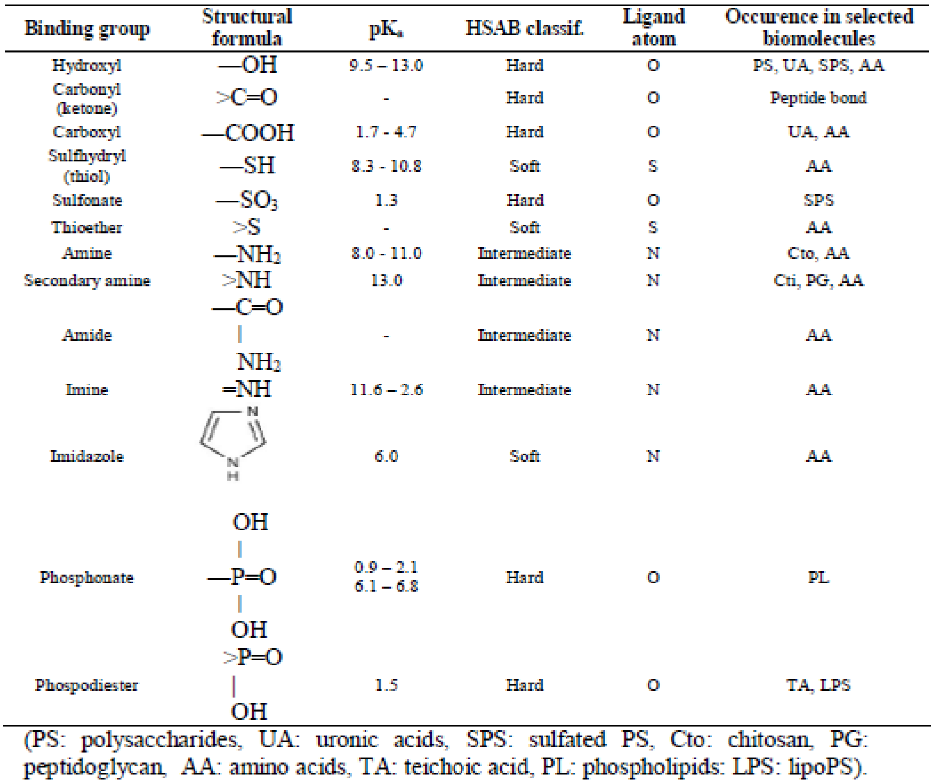
pH: pH is the important factor in biosorptive process because it affects the concentration of soluble metals, the activity of the functional groups in biomass as well as the competition of metallic ions. Table 2.2 shows the functional groups in the biomass that involves the metal binding and acidity constants. The functional groups produce the negative charge on surface at above the isoelectronic point and the biosorption process comes from the attraction between metals and the surface of cell. At a low pH, which is below isoelectronic point, this condition leads to lower uptake metal owing to the functional groups can be blocked the metal uptake (Friis et al. 1986; Galun et al. 1987)

Biomass contents: The biomass concentration in solution can affect the rate of mass transfer, in which metal separates from bulk liquid. Too low biomass content can bring the limited active site to separate metals from aqueous solution. When the amount of biomass is too high, it affects to metals solution, functional groups activity and metallic ions competition (Ahalya et al. 2003).

Cell properties: The structure and cell size can influence the actively sites of biosorbent. The large cell surface area to dry weight ratio conducts the large capacity of metal biosorption by the surface of cell per unit weight.

The biosorption is different from other conventional methods because the biosorption method is more environmental friendly. The biosorption requires no chemical adding and no chemical sludge producing. However, the biosorption is highly metal selective, high efficiency, regenerative and low cost in metal removing (Deans and Dixon, 1992; Sag et al., 1995; Wong et al., 1993).

Table 2.2 Major binding groups for biosorption (Volesky, 2007)



Binding group	Structural formula	pK_a	HSAB classif.	Ligand atom	Occurence in selected biomolecules
Hydroxyl	$—OH$	9.5 – 13.0	Hard	O	PS, UA, SPS, AA
Carbonyl (ketone)	$>C=O$	-	Hard	O	Peptide bond
Carboxyl	$—COOH$	1.7 - 4.7	Hard	O	UA, AA
Sulfhydryl (thiol)	$—SH$	8.3 - 10.8	Soft	S	AA
Sulfonate	$—SO_3$	1.3	Hard	O	SPS
Thioether	$>S$	-	Soft	S	AA
Amine	$—NH_2$	8.0 - 11.0	Intermediate	N	Cto, AA
Secondary amine	$>NH$	13.0	Intermediate	N	Cti, PG, AA
Amide	$—C=O$ | NH_2	-	Intermediate	N	AA
Imine	$=NH$	11.6 – 2.6	Intermediate	N	AA
Imidazole		6.0	Soft	N	AA
Phosphonate	OH | $—P=O$ | OH	0.9 – 2.1 6.1 – 6.8	Hard	O	PL
Phospodiester	$>P=O$ | OH	1.5	Hard	O	TA, LPS

(PS: polysaccharides, UA: uronic acids, SPS: sulfated PS, Cto: chitosan, PG: peptidoglycan, AA: amino acids, TA: teichoic acid, PL: phospholipids: LPS: lipoPS).

2.6 Adsorption isotherm

Adsorption process is a mechanism in which heavy metals restoration onto biosolids. The adsorption isotherm constants are importantly used to explain the mechanism of metals onto biosoil. Two isotherm models are used to describe the equilibrium sorption include Langmuir and Freundlich models

The equilibrium distribution of cadmium ions between the treated biosolids and solution is important in determining the maximum sorption capacity. Two isotherm models are technically applied to describe the equilibrium sorption: Langmuir and Freundlich models. The Langmuir model assumes that the uptake of metal ions on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. The linearised Langmuir isotherm is given as follows (Wang et al., 2006).

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{bQ_{\max}} \tag{2.5}$$

where Q_e (mg/g) is the equilibrium metal adsorption capacity of adsorbent; C_e (mg/L) is the soluble Cd concentration in the solutions at equilibrium; Q_{max} (mg/g) is the maximum adsorption capacity of the adsorbent and b (L/mg) is a constant related to adsorption energy.

The Freundlich model is suitable to describe the adsorption, where the adsorption intensity of the sorbent towards the treated biosolids. This adsorption pattern is served to evaluate the adsorption with the non-uniform distribution of the active adsorbent with heterogeneous surface. The equation is linearised as follows.

$$LnQ_e = LnK_F + \frac{1}{n} LnC_e \tag{2.6}$$

where K_F and n are Freundlich constants. The constant n refers to the level of favourable adsorption and K_F presents the adsorption capacity of adsorbent. If the value of (1/n) is close to 1, it indicates a normal Langmuir isotherm.

In order to evaluate the favourable adsorption, the degree of favourable adsorption is estimated using a dimensionless constant separation factor, R_L. The equation is presented as follows (Nelson, 2001)

$$R_L = \frac{1}{1 + bC_0} \tag{2.7}$$

where C_0 is the initial concentration of Cd (mg/L) in feeding influent. The value of R_L indicates the favourable adsorption when $0< R_L<1$. The unfavourable adsorption is occurred when $R_L>1$, and the linear adsorption is presented when R_L=1. The irreversible adsorption is obtained when R_L =0.

2.7 Sequential Extraction

The sequential extraction are also applied for many purposes, mainly to examine the forms of sorped species (Jing et al., 2004). Sequential extraction is an analytical process that chemically leaches metals out of soil, sediment and sludge samples. The purpose of sequential “selective” extraction is to mimic the release of the selective metals into solution under various environmental conditions. In defining the desired partitioning of trace metals, concern was taken to choose fractions likely to be affected by various environmental conditions; the following five fractions were selected.

Fraction 1. Exchangeable. The sediments or constituents (clays, hydrated oxides of iron and manganese, humic acids) have demonstrated the adsorption of trace metals; changes in water ionic composition (e.g., in estuarine waters) are likely to affect sorption-desorption processes.

Fraction 2. Bound to Carbonates. The significant trace metal concentrations can be associated with sediment carbonates; this fraction would be susceptible to changes of pH.

Fraction 3. Bound to Iron and Manganese Oxides. Iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions.

Fraction 4. Bound to Organic Matters. Trace metals may be bound to various forms of organic matter: living organisms, detritus, coatings on mineral particles, etc. The complexation and peptisation properties of natural organic matter (notably humic and fulvic acids) are well recognised, as is the phenomenon of bioaccumulation in certain living organisms. Under oxidising conditions in natural waters, organic matter can be degraded, leading to a release of soluble trace metals.

Fraction 5. Residual. Once the first four fractions have been removed, the residual solids should contain mainly primary and secondary minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.

2.8 Summary

The alkaline stabilisation process is employed to condition the biosolids, which can enhance the active site of biomass to become the biosorbent. The major mechanism between treated biosolids and cadmium, P is biosorption of dead biomass. The hypothesis of this research is drawn based on the literatures, which can reduce the loss of phosphate and stabilise Cd. However, the suitable ratio between sludge and alkaline is important factor, which can contribute the highly effective surface of stabilised biosolids. The mechanism between treated biosolids and Cd and P is essential to be understood for the purpose of ecology and health safe, if the treated biosolids are applied to adsorb the cadmium and phosphorous emitted from the fertilisers. The experiments are designed to prove the hypothesis of this research. The details of experiments are provided in the following chapter.