CHAPTER 4 RESULTS AND DISCUSSIONS

4.1 Sludge sample characteristics

The sewage sludge is sampled from wastewater treatment plant of Sitthinan Co. Ltd., Pathumthani, Thailand. The activated sludge (AS) system is served to treat the wastewater of glass noodle factory. The sludge sample is obtained at the outlet of sedimentation, before adding the polymer. The field observation of sludge was shown in Table 4.1.

Table 4.1 Field observation of sludge characteristics

Parameters	Site observation information
Colour	Dark brown
Texture	Humid, resemble clay
Coarse fragment	Fine
Structure	Dense

The raw sludge samples looked similar to clay with low solids content that was ranged 10-20% of total weight. The sludge sample is relatively dense with a very fine particle of biomass. By the naked eye observations, the sewage sludge samples were relatively moist. Therefore, it is heated in the oven at temperature around 105 °C until the solids content is ranged 15-60% of total weight. It was found that the moisture content of biosoilds was decreased along the heated period. After heat process, the dried sludge is sieved using a standard sieve with a round opening hole at a diameter of 2 mm in order to remove large particles such as rocks, gravels and mung bean peel. The criterions of physical and chemical properties of sludge can be analysed with the ASTM standards method. The physical and chemical properties of sludge were shown in Table 4.2.

Table 4.2 Physical and chemical properties of dried sludge

Parameters	sludge
Physical properties	
Raw and dried sludge water content (%)	84.75 and 3.38
Bulk density (g/cm^3)	0.53
Particle size (mm)	< 2
Chemical properties	
Organic matter (%)	64.22
Soil pH (1:5)	7.38
EC (1:5) (μS/cm)	469.5
CEC (meq/100 g)	12.37
Total Phosphorous (mg-P/kg)	25,427
Soluble Phosphorous (mg-P/kg)	4,174
Olsen-P (mg-P/kg)	2,976
Organic Nitrogen (mg/kg)	62,695
Soluble Cd (mg-Cd/kg)	0

According to the physical properties, the wasted biomass samples can absorb the water very well. The raw sludge contained only biomass that major components of raw sludge are microbial cell. The high moisture content value of initial raw wasted sludge is above 80%. After heated process for 1 day until constant weight, the solid content is met the allowable limit that is higher than 60% of total weight. The densities of dried sludge sample are relatively low as they were grabbed after dewatering. These sludge samples are not contaminated with polymers. Therefore, the bulk densities of the raw sludge are the real density of wasted biomass. The particle sizes of waste sludge are very small and the small pores may be presented in the raw biomass samples. According to the chemical properties, the sludge contains high amounts of organic matter (OM) and phosphorus, which are able to uptake by living organisms in soil and plants because they are wasted biomass cell. The organic matter can highly absorb nutrients and metal ions. The pH (1:5) of sludge is slightly higher than 7, classifying a slightly alkaline biosolids. The EC and values CEC of sludge samples are relatively high, representing the cations are adhered on the cell walls. The total phosphorus (TP) and soluble phosphorous (SP) content of sludge samples are relatively high. For the available phosphorous is high also, which are able to uptake by living organisms in soil and plants. The ratio of C to N is estimated by the content of organic carbon to organic nitrogen, it is 5.94 to 1. The dried sludge cannot be applied as organic feriliser as the

C:N ratio is out of range, which is 20:1 – 25:1 (Toles, et al., 1997). The dried sludge contains less amount of organic carbon but it enriches with organic nitrogen, perhaps it can be used as fertiliser, when mixing with organic carbon. Fortunately, these raw sludge samples are free from soluble Cd (II). The physical appearances of raw sludge are presented in Figure 4.1.

(a) (b)

Figure 4.1 Physical appearances of (a) raw sludge and (b) dried sludge samples

4.2 Properties of chemical fertiliser and organic manure

Fertilisers used in this research are the chemical fertiliser and organic manure. The chemical fertiliser can represent the highly P content and it may be contaminated with Cd. On the other hand, the organic manure can present the effect of organic matter on P adsorption, but it is Cd free. Both fertiliser may present the different forms of P, which can reflect the different mechanisms of primary and secondary P sorption. The chemical fertiliser is potassium dihydrogen phosphate (KH_2PO_4) and the common name is monopotassium phosphate (MKP). This chemical fertiliser is formulated as 0-52-34 (N-P-K). The MKP fertiliser has 52 % of P_2O_5 and 34 % of K_2O. The organic manure used in this study is the dried cattle manure, which is commercially available. The dried manure is sieved using a standard sieve with a round opening hole at a diameter of 2 mm in order to remove the large particles. Both chemical fertiliser and organic manure properties are analysed in accordance with the ASTM standards and Agronomy methods. The summary of chemical fertiliser and organic manure are given in Table 4.3.

Table 4.3 Properties of MKP-fertiliser and Organic manure

Parameters	MKP-fertiliser	Organic manure
Organic matter (%)	0	39.56
pH (1:5)	4.29	7.20
EC (1:5) (µS/cm)	72,530	9,960
Total Phosphorus (mg-P/kg)	280,087	2,610
Soluble Phosphorus (mg-P/kg)	270,115	2,260
Olsen-P (mg-P/kg)	256,050	2,150
Soluble Cd (mg-Cd/kg)	29.88	0

The organic manure and MKP-fertiliser contained different amounts nutrients. The organic manure has low amount of available nutrients and the most of nutrients adhered onto organic matter. On the other hand, the MKP-fertiliser includes only mineral phosphorus compounds that are totally dissolved. The MKP-fertiliser contains the high concentration of available phosphorus because it is totally soluted in the water. Refer to the chemical formula, the aqueous solution of KH_2PO_4 salt is acidic (pH was around 4.29). The pH of organic manure is slightly alkaline (pH was approximately 7.20). A high EC value is observed in MKP fertiliser as it is consisted of amounts of other minerals and soluble ionic constituents such as potassium and phosphoric acid compounds. For the organic manure solution has very high EC values since it has some soluble ionic content and soluble organic contents, typically humin and humic acids. Neither manure nor MKP-fertilisers are over exploitation, the phosphorus could escape and potentially destroy the balance of nutrients in the ecology system. Moreover, the MKP-fertiliser contains amounts of soluble cadmium. In order to solve this problem, soil should be modified to increase the phosphorus and cadmium adsorption capacity without disturbing the cultivation. The alkaline stabilisation is technically applied to neutralise the soil system.

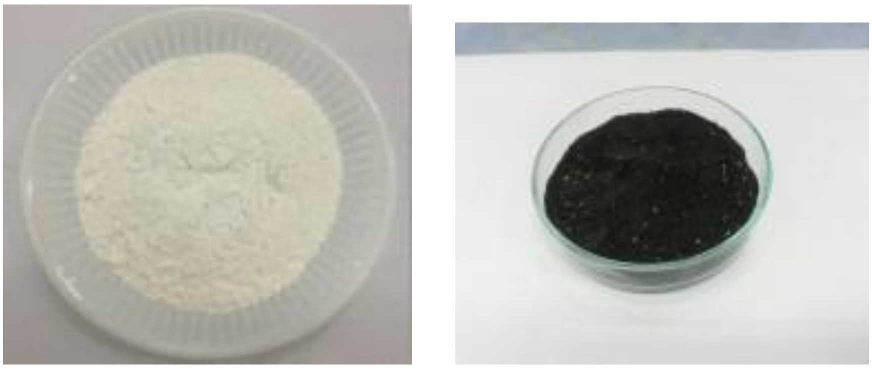
4.3 Properties of alkaline materials

The properties of alkaline additive constituents are summarised in Table 4.4. The quicklime and fly ash are employed to stabilise soil. The chemical formula of quicklime is CaO but fly ash does not have the specific chemical formula. The fly ash is obtained from Sitthinan Co. Ltd, which is residue of biomass burning boiler. However, the quicklime consist significant amounts of alkaline earth elements which are Ca and Mg.

These alkaline earth cations especially Ca^{2+} and Mg^{2+} are added to biosoil to level up the pH of biomass. The increase in pH of biosoils can attribute mainly to the hydrolysis of these alkaline earth minerals. Since the fly ash is accounted as burning industrial furnace (BIF) waste, the more fly ash dosage, the more benefit to waste recycling as it may contain amounts of silica oxide. This silicate mineral can be formed at high temperature and this can strengthen the structure of biosolids. Besides, the silicate mineral can resist the acidic pH solution of Cd(II). Therefore, the mass of alkaline treated biosolids is slightly lost even though the acidic pH Cd(II) influent. Quicklime is highly in EC that correlates with high proportion of the divalent ions. The pH (1:5) of quicklime is 12.36 and it is much higher than fly ash. The lime has the higher portions of calcium and magnesium than fly ash. On the other hand, lime has no available nutrients, but the fly ash has some amounts of minerals and available nutrients for plants, typically phosphorus. The properties of these alkaline elements are analysed according to the ASTM standards and the Agronomy methods. At least triplicate samples are undertaken. The physical appearances of alkaline materials are presented in Figure 4.2.

Table 4.4 Properties of alkaline materials

Parameters	**Lime**	**Fly ash**
pH (1:5)	12.36	10.3
EC (1:5) (µS/cm)	7850	841
CEC (meq/100 g soil)	0.55	1.83
Total Phosphorus (mg-P/kg)	0	1641
Soluble Phosphorus (mg-P/kg)	0	1,055
Olsen-P (mg-P/kg)	0	517
Silica (SiO_2) (%)	0.89	93.7
Alumina (Al_2O_3) (%)	0.11	0.137
Ferric oxide (Fe_2O_3) (%)	0.10	0.223
Calcium (CaO) (%)	94.7	0.918
Magnesium (MgO) (%)	2.61	0.419
Potassium (K_2O) (%)	0.01	3.3
Phosphorous (P_2O_5) (%)	0.02	0.86



(a) (b)

Figure 4.2 Physical appearances of alkaline materials (a) quicklime and (b) fly ash

4.4 Biosoil Characteristics

In order to stabilise sewage sludge and retard cadmium and phosphorus in soil, quicklime and fly ash are mixed with sludge to increase pH until it achieved the alkaline level of pH at 12. Many researchers suggested the beneficial effects of pulverised fly ash combine with quicklime are sufficient to produce a final sludge product with improved handling characteristics and reduced leaching potential. Another report indicated that using fly ash as alkaline material in alkaline stabilisation of sludge can prevent the decreasing of pH and regrowth of pathogens during 60 days of storage period (Kocaer et al., 2003). Table 4.5 shows the optimum ratio of CaO: Fly ash is at 2:5 is suitable to adjust the pH of sludge to achieve the criteria of biosolids class A, which the pH of biosolids must be above 12 or higher along 72 hours (USEPA, 1994). At ratio of sludge to alkaline materials are 50:50 is the optimum ratio that can treat the biosolids. The measuring pH has indicated that, the ratio of quicklime to fly ash in alkaline material can directly affect the pH of biosoil. If the higher amount of quicklime is added, the higher pH of biosoil is observed. The amount sludge also influences the pH of biosoil. If the more amount of sludge is applied, the more amount of alkaline materials is required. Furthermore, pH of biosoil seems to be slightly decreased over time. This assumes that the exothermic reaction between CaO and moisture slow down. The byproduct of $Ca(OH)_2$ is slowly generated (Kocaer, et al., 2003). The pH of biosoil may slightly oscillate when the amounts of inert materials such as fly ash and sludge are high. As the fly ash and sludge may present the pH buffering capacity to biosoil.

Table 4.5 pH of treated biosolids

SL:Alk	CaO:Fly ash	pH (1:5) measured at time of						
		0 min	**30 min**	**1 hr**	**5 hr**	**22 hr**	**24 hr**	**72 hr**
70:30	2:5	12.06	11.80	11.58	11.05	10.43	10.34	9.80
	2:6	11.93	11.31	10.92	10.41	10.13	9.93	9.59
	2:7	11.63	10.51	10.36	10.04	9.84	9.60	9.09
	2:8	10.50	10.00	9.88	9.68	9.35	9.27	8.91
60:40	2:5	12.18	12.14	12.11	12.07	11.96	11.93	11.91
	2:6	12.18	12.11	12.10	12.02	11.87	11.80	11.43
	2:7	12.17	12.07	12.04	11.86	11.41	11.34	10.36
	2:8	12.01	11.60	11.22	10.74	10.18	9.77	9.38
50:50	2:5	12.22	12.19	12.19	12.18	12.15	12.13	12.11
	2:6	12.19	12.14	12.14	12.12	12.07	12.01	11.96
	2:7	12.18	12.13	12.13	12.10	12.04	12.00	11.82
	2:8	12.05	12.11	12.10	11.96	11.91	11.68	11.19

The characteristics of synthesis biosoils are presented in Table 4.6. The solid contents of biosoils are above 60% of total mass, which is dehydrated biosolids. The increasing of biosolids content is a result of loss of moisture content due to heat evaporation process. The bulk densities of biosoil samples are slightly increased from the raw sludge. The alkaline materials can be hydrolysed and then reacts with the constituents in the raw sludge, resulting increasing of temperature in the system. The pH of biosoil is above 12, under this highly alkaline level, it can be ensured that the pathogens, vectors and other eggs of worms are destroyed. The biosoil can be safely used in not only to agricultural land but also to public access areas. The fly ash and sludge proportions in alkaline mixtures were evaluated and the expected concentrations were calculated by the addition of parameter concentrations in fly ash and sludge samples according to the following equation (Topac et al., 2008):

$$C_{\text{expected}} = \left[C_S \times \left(\%S/100\right)\right] + \left[C_{FA} \times \left(\%FA/100\right)\right] + [C_{QL} \times (\%QL/100)] \qquad (4.1)$$

where C_S is the TP, SP, OP or OM contents in raw sludge, C_{FA} is the TP, SP, OP or OM contents in fly ash, C_{QL} is the TP, SP, OP or OM contents in quick lime, and %S, %FA and %QL are the percentage of raw sludge, fly ash and quick lime in biosoil, respectively.

Table 4.6 Physical and chemical properties of biosoil

Parameters	Observation	Calculation
Physical properties		
Water content (%)	5.83	-
Bulk density (g/cm^3)	0.55	-
Particle size (mm)	<2	-
Chemical properties		
Organic matter (%)	24.13	32.11
Soil pH (1:5)	12.11	-
EC (1:5) (μS/cm)	5,920	-
CEC (meq/100 g)	3.354	-
Organic nitrogen (mg-N/kg)	31,585	-
Total Phosphorus (mg-P/kg)	13,649	13,299
Soluble Phosphorus (mg-P/kg)	19.51	-
Olsen-P (mg-P/kg)	1,635	-
Soluble Cd (mg-Cd/kg)	0	0

The expected OM content of biosoil is 32.11%. However, the measuring OM content of biosoil is lower than the expectation. Since the OM in sludge can volatile during heat process. Moreover, after the stabilisation process, the organic matters are decreased because the alkaline materials can hydrolyse and then react with the residual water in the air dried sludge and temperature in the system is increased. The expected total phosphorus (TP) content of biosoil is closed to the measured one. However, soluble phosphorus (SP) and available phosphorus (Olsen P) of the biosoil cannot be estimated. Since the soluble phosphorus may decreased owing to dilution process or reactions. The alkaline materials are the source of elements such as calcium (Ca), magnesium (Mg), iron (Fe) and aluminum (Al). These alkaline elements can react with P, resulting in precipitation of P. The solubility of P can be reduced when the system becomes alkaline. The liming capacity of treated biosolids is increased due to the increasing of available P (AP), Mg and Ca (Reference). The ratios of TP: SP: AP in dried sludge and biosoil are 1:0.16:0.117 and 1:0.001:0.119, respectively. This reveals that SP is transformed to be insoluble P in alkaline stabilisation process. On the other hand, the AP is slightly increased when applying the alkaline stabilisation. The ratio of C:N is 4.43: 1, which is slightly lower than the dried sludge. However, the loss of C and N of biosoil can be occurred together. The biosoil is not contained with soluble cadmium because the sludge samples and alkaline materials free from soluble cadmium. The physical appearance of biosoil is presented in Figure 4.3.

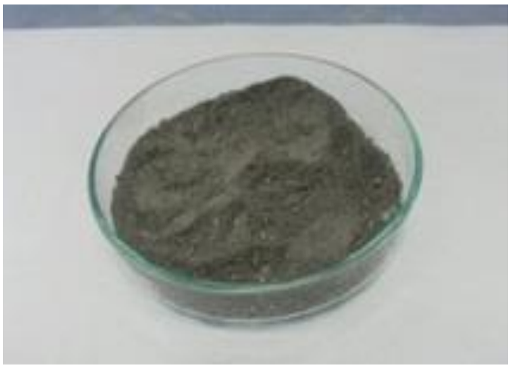


Figure 4.3 Physical appearances of biosoil

4.5 Adsorption of Cadmium

The equilibrium time for the Cd(II) adsorption process was initially evaluated. The stock solution of Cd(II) with pH of 3.42 is prepared to estimate the equilibrium time of Cd(II) adsorption process, as the Cd precipitation is negligible. The equilibrium time of Cd adsorption process is presented in Figure 4.4

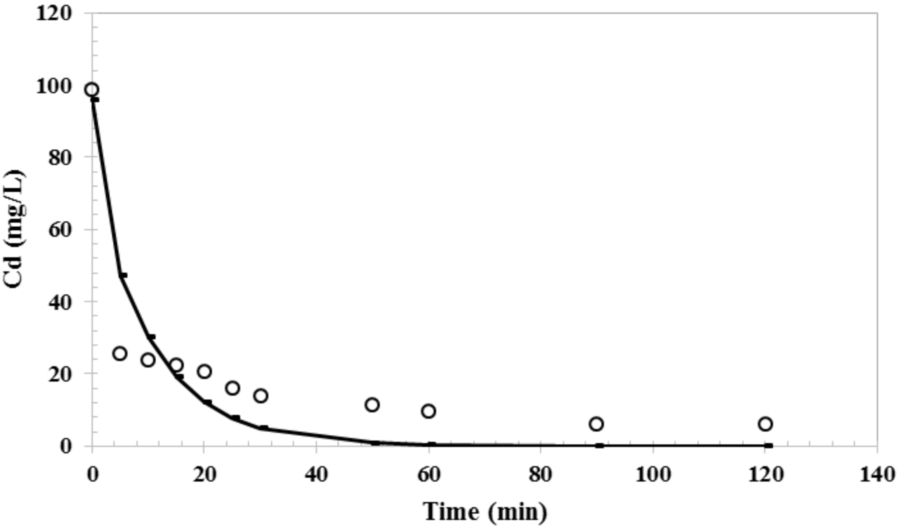


Figure 4.4 Equilibrium times for Cd adsorption process

According to the kinetic rate equation, the adsorption of Cd on biosoil obeys the first order. The equation is $C_t = C_0 e^{-0.0045 \cdot t}$, where C_t and C_0 are the concentration of Cd at time *t* and initial (mg/L), respectively. The rate constant for Cd adsorption is at 0.0045 min^{-1}. The effluent sample has a final constant concentration of Cd(II) at 6.26 mg/L, which is higher than the calculation. Besides, the concentration of Cd observed at 5 and 10 minutes does not well fit to calculation.The Cd(II) can be quickly adsorped by the biosoil within 30 minutes and the adsorption becomes equilibrium within 60 minutes. This phenomenon could be attributed to the instantaneous utilisation of the most readily available adsorbing sites on biosoil surface. The active surfaces of the biosoil is fully covered with the Cd(II), approaching a steady state after 60 minutes. Yang (2002) had suggested that the Cd(II) sorption in the dried activated sludge can reached the equilibrium within 3 hours. The unconditioned sludge can gradually sorb Cd(II). By comparison, the biosoil can quickly sorp the Cd(II). It can be acknowledged as the active biosorbent. After achieving the equilibrium of adsorption, the amount of adsorbed Cd(II) slightly changes over the contact time. The unfit observation data may relate to the change of pH of bioslurry. The change of pH in bioslurry is measured in every intervals. The results are graphically plot as shown in Figure 4.5

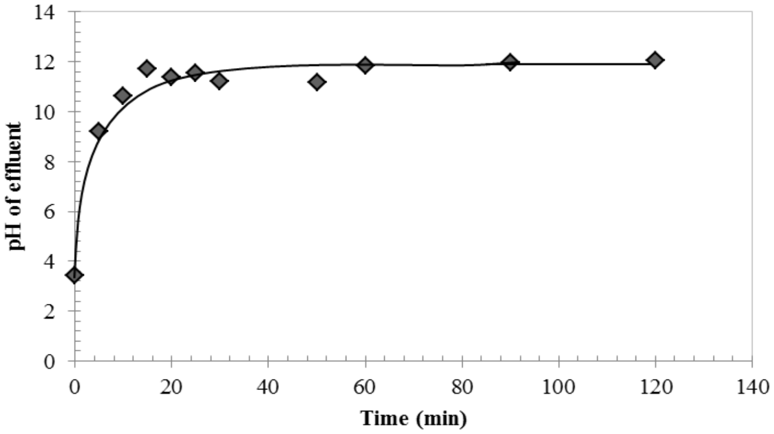


Figure 4.5 pH of bioslurry versus contact time

The pH of bioslurry is rapidly increased from the initial pH of stock Cd(II) solution, the final pH of solution is at 10.7. Hence, the concentration of Cd(II) remaining in effluent samples at contact times between 5 and 15 minutes are declined very quickly since the pH of bioslurry is immediately increased. The pH can indirectly affect Cd(II) adsorption, as the Cd(II) may be precipitated before contacting the surface of treated biosolids. The Cd precipitation in solution may not influence the Cd(II) removal, as the Cd precipitates can be further dissolved, if the bioslurry pH becomes acid. Otherwise, the Cd(II) precipitation can directly affect Cd(II) adsorption by Cd(II) deposition onto biosolids surface (Reference).

To describe the Cd precipitation, the stock Cd(II) solution of 50 mg/L is pH adjusted from 1.0 to 10.0. Then the pH adjusted Cd stock solution is mixed with a 10 g of biosoil. The effluent samples of bioslurry are measured after mixing for 60 minutes. The results are presented in Figure 4.6. When the pH of solution is higher than 8, the concentration of Cd(II) stock solution is dramatically reduced. This can indicate the effect of pH on Cd precipitation.

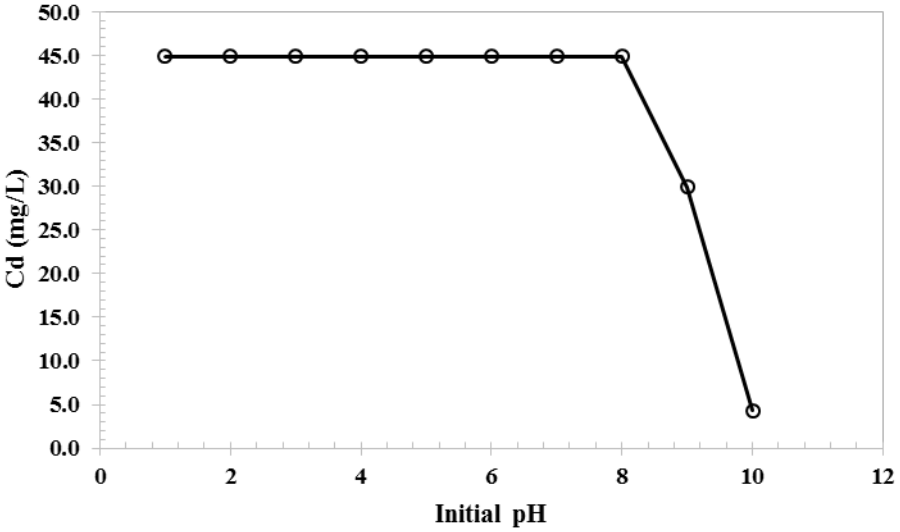


Figure 4.6 Effect of initial pH on Cd(II) precipitation

After mixing the biosoil with the pH adjusted Cd(II) stock solution, the pH of effluent is increased and pH of bioslurry is ranged between 9.8-11.8. All the results are posted in pC versus pH diagram as illustrated in Figure 4.7. The variable pC is Log [Cd(II)]. This diagram can suggest the transformation of Cd(II) in the influent and effluent samples. The uptake of Cd(II) ions depends on pH, where the Cd(II) adsorption capacity is high at pH ranges from 1 to 8, and then decreasing at high pH (above 8). The optimal pH at 3.0 can provide the highest Cd(II) adsorption capacities in biosoil. Reed and Matsumoto (year) constructed a speciation diagram, the Cd(II) ion predominates at pH below 7 and it can be precipitated as $Cd(OH)_2$ at pH above 9. At pH of 8, the species distribution is governed that Cd(II) is 90% and $Cd(OH)^+$ is 10% of the presence Cd. Hence, all of species at pH of 8 and below carry a positive charge either Cd^{2+} or $Cd(OH)^+$ (Leyva-Ramos et al., 1997; Babic et al., 2002). When the pH higher than 9, it can dramatically reduce the solubility of Cd(II). By comparison, it is possible to conclude that the rapidly Cd(II) removing in an equilibrium time test may be the coincident of Cd(II) precipitation, almost Cd precipitant may deposit into an effluent supernatant. The results indicate that the free Cd species (Cd^{2+}) can be observed in influent samples, whenever pH of solution is less than 9. The pH of effluent sample is ranged between 9.8 and 11.8. The Cd^{2+} is turned into immobilise cadmium of $Cd(OH)_2$.

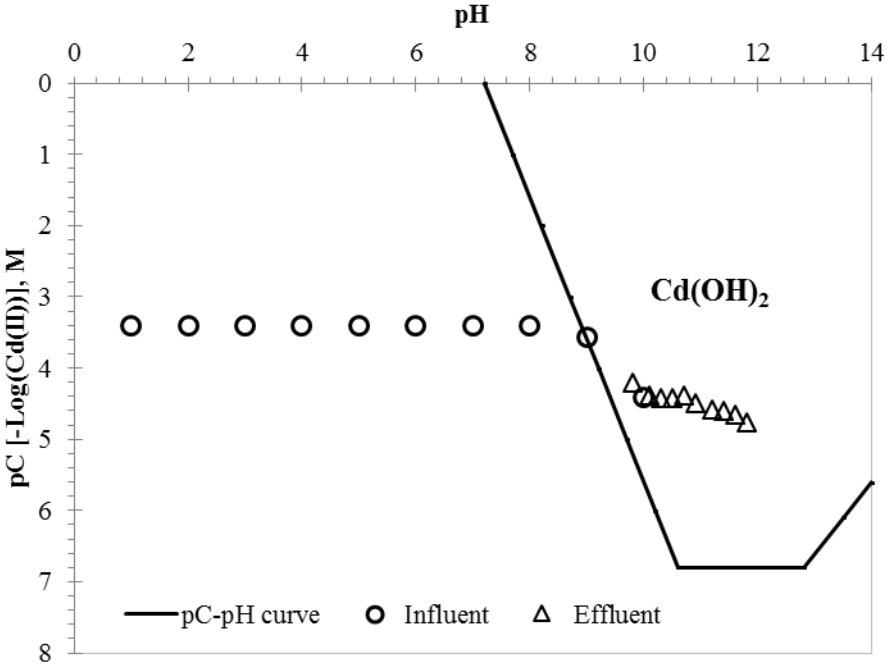


Figure 4.7 pC-pH diagram of Cadmium-H_2O

Figure 4.8 shows the distribution coefficient (K_d), which is functioned as Q_e/C_e. The values of K_d is significantly declined, whenever pH of effluent supernatent is lower than 9.0. The K_d values are increased from 0.05 to 0.15 L/mg, when the final pH is ranged between 9.8 and 11.8, respectively. By estimating, the pH of treated biosolids can conduct the low value of C_e. The final pHs of effluent supernatent of each bioslurry samples are not much different, as a consequence the values of Q_e may less be impacted and it can be assumed as the Q_e is constant. The low value of K_d when the alkaline influent applying, refers that the Cd(II) species may be separated by precipitation or surface deposition. The adsorption isotherm test is conducted by adjusting pH of Cd(II) solution to be 3, ensuring the Cd precipitation is inhibited. Yang (2002) had tested the Cd(II) adsorption onto biomass of activated sludge, the biosorption can be well occurred at pH ranged from 2 to 8. The optimum pH of biosorption can be observed at 6. In case of biosoil, the pH of conditioned sludge is very alkaline. The highly acidic pH of Cd(II) solution is suited, however this assigned pH is still in the possible range, which the biosorption can be occurred.

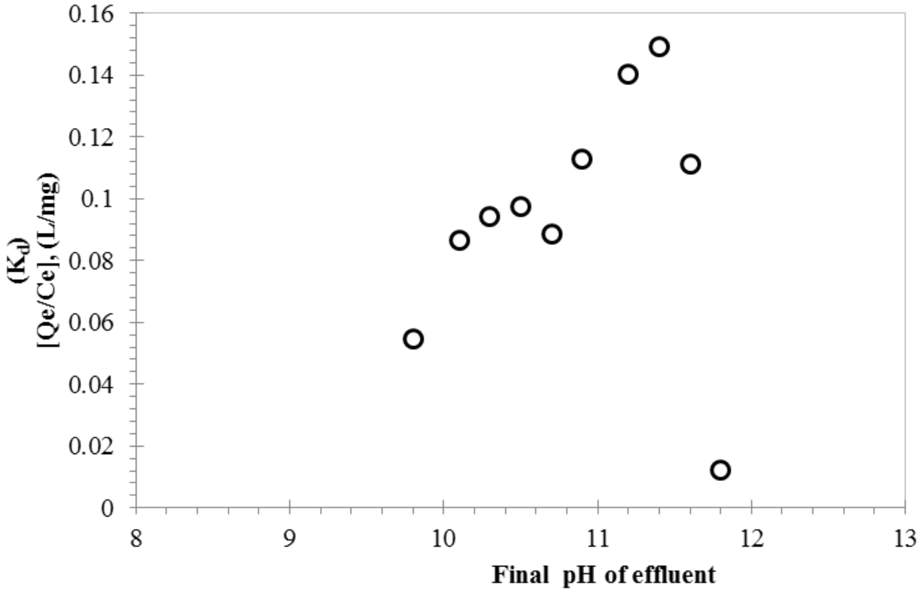


Figure 4.8 K$_d$ versus final pH

The amount of adsorbent can affect the Cd adsorption too. A various amounts of biosoil are mixed with stock Cd(II) solution for 60 minutes, till Cd adsorption reaching the equilibrium. The initial Cd(II) concentration is 50 mg/L with pH of 5.94. The effect of mass of biosorbent onto Cd adsorption is described in Figure 4.9.

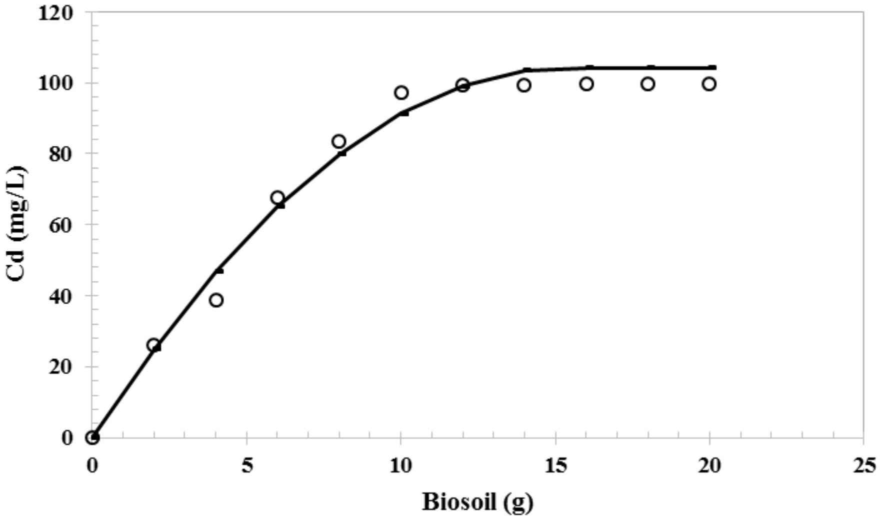


Figure 4.9 Effect of adsorbent dose on Cd(II) Adsorption

The low amount of biosoil, which weight is less than 10 g, can rapidly adsorp Cd(II). If mass of biosoil increases to be higher than 10 g, the Cd(II) adsorbed is insignificantly increased. This result showed that an increase in adsorbent dosage resulted in an increase in Cd(II) removal efficiency owing to increase surface area for adsorption and number of binding sites (Kumar et al., 2006). The adsorption of Cd(II) onto biosoil becomes saturation, after 10 g of biosoil is added. So, a 10 g of biosoil is further employed in the isotherm test.

The adsorption is recognised as a major mechanism between Cd and biosoil. According to previous observation, the biosoil system can reach the equilibrium of Cd adsorption within 60 minutes, the maximum Cd(II) uptake is obtained when the pH of synthesis wastewater is at 3.0 and a 10 g biosoil is suited for the test. The tests of adsorption isotherm indicate that the Cd $^{2+}$ is attached onto the active surface of biosoil. The biosoil has presented the best fit with both Langmuir and Freundlich isotherm equations as shown in Table 4.7.

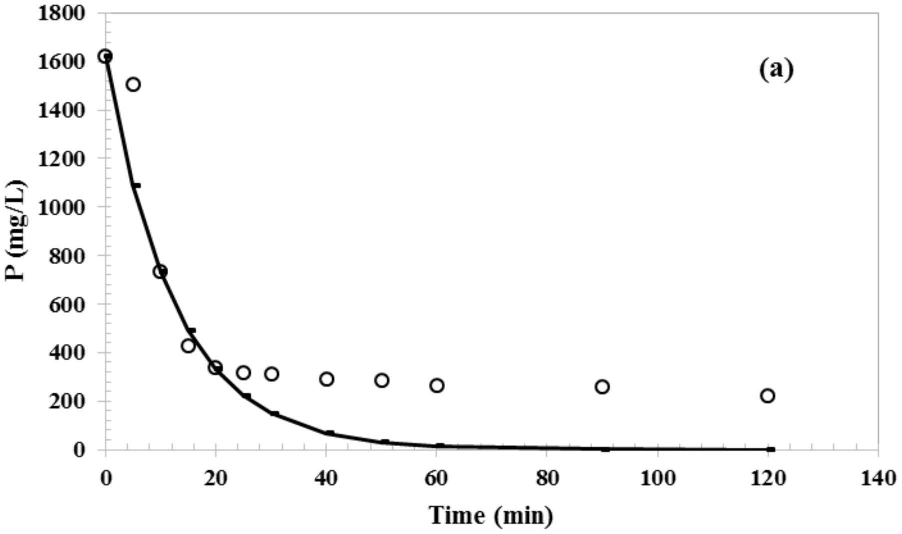
Table 4.7 Cadmium adsorption isotherm constants of biosoil

Langmuir Model				Freundlich Model		
$C_e/Q_e = 0.1632C_e + 0.8697$				$Q_e = 0.9235C_e^{0.7876}$		
Q_{max} (mgCd/gOM)	b (L/mg)	R^2	R_L	K_F (mgCd/gOM)	n (g/L)	R^2
6.127	0.1876	0.98	0.05-0.2	0.924	1.27	0.99

Both models can be fit well the data as indicated by squared of residual error (R^2) value. In particular, "*n*" value, which is related to the distribution of bonded ions on the surface of sorbent. The value of "*n*" between 1 and 10 also shows beneficial adsorption. The adsorption intensity value (*n*) is closed to 1.00 and this can reveal that Cd^{2+} can interact with the active site only and chemiosorption is predominantly (Khankruer et al., 2012). The value of adsorption capacity (K_F) is slightly low, since there are small changes in concentration at equilibrium (C_e). According to Langmuir model, the maximum adsorption capacity (Q_{max}) is declared that Cd can be effectively sorped by organic matter, which can be accounted as primary adsorptive material. The primary adsorption process can be generally occurred due to chemical adsorption. The constant related the adsorption energy (b) is slightly higher than value of K_d, indicating that the Cd precipitation is less influenced the adsorption. The Cd(II) may form the chemical bonds with the organic carbon compounds of the treated biosolids. The sorbed Cd(II) species can slowly release from the treated biosolids, since the irreversible chemical bond is formed. The value R_L is in the range between 0 and 1, referring to the favourable adsorption behavior. Wang et al. (2006) had observed that the dried activated sludge can also sorp Cd(II), and the isotherm data can be fitted well with both Langmuir and Freundlich models. With the initial pH of 6.0, the maximum Cd sorptive capacity of sludge varies from 9.8 to 61.3 mg/g dried sludge. By assuming the OM of activated sludge is 64.22%, the Cd sorptive capacity of sludge varies from 15.26 to 131.6 mgCd/g OM. The biosoil has presented a very low adsorptive capacity as pH of Cd(II) is initially highly acid. The maximum capacity of biosoil may be influenced by pH, as the Cd(II) precipitation is neglible.

4.6 Adsorption of Phosphorus

The equilibrium time for the phosphorus adsorption process is initially evaluated. The MKP-fertiliser and organic manure solutions are added to biosoil samples. The equilibrium times for the adsorption process are presented in Figures 4.10. The experiments were conducted using 5 g of biosoil and 50 mL of MKP-fertiliser solution containing of 1622.41 mg-P/L by conducting batch adsorption experiments. The acidic MKP-fertiliser solution at pH 4.47 was added to the biosoil samples. The experiments were conducted using 3 g of biosoil and 50 mL with initial pH of 6.39 of organic manure solution containing of 54.89 mg-P/L. The P sorptions onto biosoil are well matched to the first order kinetic reaction rate. The kinetic reaction rate equations of P adsorption onto biosoil are $C_t = C_0 e^{-0.0795t}$ and $C_t = C_0 e^{-0.1992t}$, when MKP and manure fertiliser solutions are applied, respectively. The rate constants are 0.0795 and 0.1992 min^{-1} for P originated from MKP and manure fertiliser sorption onto biosoil, respectively. The kinetic rate constants of P originated from MKP and manure fertiliser sorption are totally diffrerent. It seems that biosoil prefer to adsorp P originated from manure fertiliser, rather than P from MKP fertiliser.



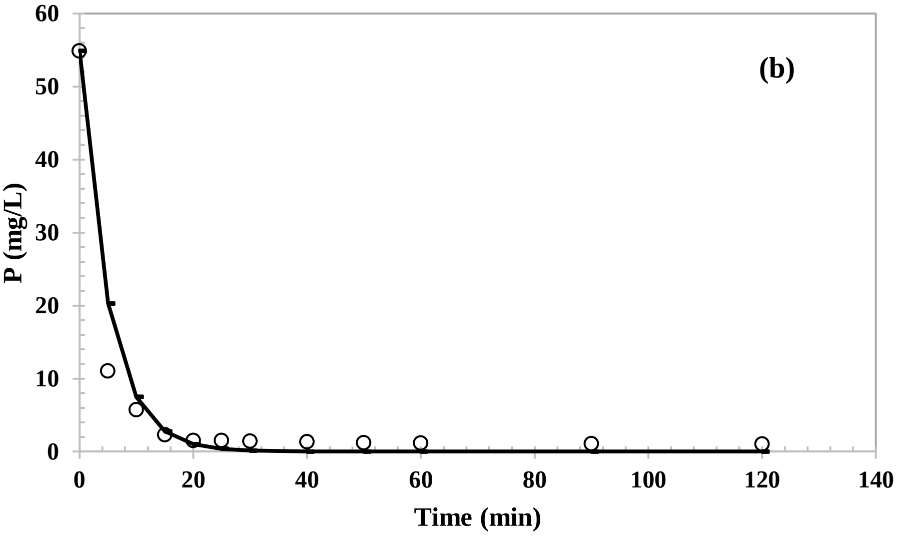


Figure 4.10 Equilibrium times for P adsorption process

(a) MKP-fertiliser (b) Organic manure

Using MKP fertiliser, the equilibrium time of P adsorption is 60 minutes. The first 10 minutes, the adsorption has been rapidly occurred, the effluent contains very low concentration of P. Since the pH of bioslurry is in a range of 6.0-7.0, the precipitation of phosphorus is neglected. Mainly P in bioslurry is in a form of $H_2PO_4^-$ ions that can be readily absorbed by plants. After 10 minutes, the pH of leachate is increased and finally it reaches to 9.2-9.8, which are moderately alkaline. The P is mainly in a form of HPO_4^{2-} ions. Likely, the equilibrium time of P originated from organic manure solution is 20 minutes. This indicates that the adsorption of P onto biosoil is quickly, when applying organic manure solution. After mixing for 5 minutes, the effluent leachate suddenly became to alkaline, even though the initial pH of organic manure solution is neutral. The pH of effluent samples are ranged beteen 8.22-11.02. Under alkaline pH, P is transformed to HPO_4^{2-}, which is highly soluble. This leads to slow P adsorption. Not only MKP-fertiliser but also organic manure solutions, the pH of effluent has been arisen. The calcium ion in biosoil tends to adsorb the soluble phosphorus and then stabilise on soil minerals. Both of quicklime and fly ash contains highly contents of calcium and magnesium, so these alkaline materials are enough to store the soluble phosphorus. The alkaline stabilisation can enhance the phosphorus adsorption capacity.

The adsorption coefficients are determined for both cases. The sorption of P originated from MKP-fertiliser and organic manure into the biosoil samples are fitted with both Langmure and Freundlich isotherm equations as presented in Table 4.8.

Table 4.8 Phosphorous adsorption isotherm of biosoil with MKP-fertiliser and manure

MKP Fertiliser	Langmuir Model				Freundlich Model		
	$C_e/Q_e = 0.0075C_e + 0.1119$				$Q_e = 67.85C_e^{0.1003}$		
	Q_{max} (mgP/gOM)	b (L/mg)	R^2	R_L	K_F (mgP/gOM)	n (g/L)	R^2
	133.33	0.067	0.99	0.01	67.85	9.97	0.97
Organic Manure	Langmuir Model				Freundlich Model		
	$C_e/Q_e = 0.067C_e + 0.157$				$Q_e = 4.48C_e^{0.513}$		
	Q_{max} (mgP/gOM)	b (L/mg)	R^2	R_L	K_F (mgP/gOM)	n (g/L)	R^2
	14.93	0.427	0.99	0.04	4.48	1.9	0.99

The P adsorption onto biosoil, when applying MKP and manure fertiliser solutions is well fitted with both Langmuir and Freundlich isotherm models. The *n* values of biosoil mixed with MKP-fertiliser and organic manure are 9.97 and 1.9, respectively. Both gives the 1/n values are lower than 1.0, it can be explained the biosoil has heterogeneous surface. This expresses that the increased adsorption modifies the sorbent in a manner that increases the sorption capacity, such as forming new sites. Therefore, the Freundlich isotherm is suitable to observation data. The values of K_F refer that the adsorption of soluble P with MKP-fertiliser and organic manure can reach the fully adsorption capability of organic matter, which can be accounted as primary adsorptive material. The primary adsorption process can be generally occurred due to physical adsorption. The maximum adsorption capacity of biosoil with MKP fertiliser and organic manure are 67.85 mg P/g OM and 4.48 mg P/g OM, respectively. The organic manure and MKP-fertiliser could increase the level of nutrients in soil. However, the high concentration of phosphorus in MKP-fertiliser could force the dispersion of phosphorus in biosoil. So, the plume of contaminants might be enlarged resulting in the large size of contaminated area. Although, organic manure contained high organic matter, the phosphorus contained in MKP-fertiliser could be accumulated in biosoil higher than organic manure because the initial pH of manure is slightly neutral, so, when the organic manure solution is added and mixed into biosoil, the pH became alkaline quickly that it brings to rapidly decreasing of soluble P. Since Ca in biosoil can interact with soluble P in manure, it can bring to Ca-P precipitation faster than soluble P adsorbed on organic matter. While characteristic of MKP fertiliser has very high concentration of phosphorus, organic matter free and the initial pH of MKP fertiliser is acidic. When the MKP fertiliser is used together with biosoil, the solution became alkaline, the calcium ion from quick lime tended to precipitate with P slowly because the acidic pH of MKP-fertiliser solution can resist the changing of pH to alkaline. Therefore, the P adsorption with MKP-fertiliser solution is higher than organic manure solution. As quicklime contained high calcium and magnesium contents, it might be enough to store the soluble phosphorus. The possible reaction among calcium ion, proton and phosphate, the ligand of the inorganic $CaHPO_4$ could be formed as (Rajan et al., 1991):

$$Ca^{2+} + H^{+} + PO_4^{3-} \longrightarrow CaHPO_4 \tag{4.2}$$

4.7 Adsorption of Cd on biosoil with P saturation

Then the fully P saturated biosolids is soaked with the Cd solution at pH of 3 to determine the influence of P on secondary Cd adsorption onto biosoil. At pH of 3, the ionic Cd is highly concentrated. The sorption of Cd onto P saturated biosoil samples are fitted with Langmuir and Fruendlich isotherm equations as presented in Table 4.9.

Table 4.9 Cadmium adsorption isotherm on saturated biosoil with P

	Langmuir Model				Freundlich Model		
Cd-P MKP	$C_e/Q_e = 0.008C_e + 0.005$				$Q_e = 82.352C_e^{0.66}$		
	Q_{max} (mgCd/gP)	b (L/mg)	R^2	R_L	K_F (mgCd/gP)	n (g/L)	R^2
	125.00	1.6	0.96	0.007-0.012	82.35	1.5	0.97
	Langmuir Model				Freundlich Model		
Cd-P manure	$C_e/Q_e = 0.00056C_e + 0.005$				$Q_e = 208.3C_e^{0.669}$		
	Q_{max} (mgCd/gP)	b (L/mg)	R^2	R_L	K_F (mgCd/gP)	n (g/L)	R^2
	1,792	0.112	0.99	0.08-0.14	208.3	1.5	0.99

The Cd adsorption isotherm has shown a favorite adsorption condition, referring that Cd can be stored onto biosoil with P saturation. The equilibrium time of Cd to be adsorped onto P saturated biosoil is only an hour. The values of constant *n* for both biosoil samples are higher than 1.00 indicating that the Cd(II) isotherms can be simplified as Freundlich isotherm model. The value maximum adsorptive capacity of Cd(II) onto saturated biosoil with P from MKP fertiliser and organic manure are 82.35 mg Cd/g P and 208.3 mg Cd/g P, respectively. This finding confirms that Cd ions can be bound to sorped P. The organic matter is the primary adsorptive site, which can strain P, and the sorped P can further retard ionic Cd via both primary and secondary adsorption processes. Several mechanisms can be advanced for the positive effect of HPO_4^{2-} on Cd(II) adsorption. These include: (i) precipitation of Cd(II) as $Cd_3(PO_4)_2$; (ii) co-adsorption of HPO_4^{2-} and Cd(II) as an ion pair; (iii) surface complex formation of Cd(II) onto the adsorbed HPO_4^{2-}; and (iv) HPO_4^{2-}induced Cd(II) adsorption (Bolland et al., 1977; Street et al., 1978; Soon, 1981; Kuo and McNeal, 1984). The simplified equation of secondary adsorption process of P on biosoil could be expressed as (Fox and Kamprath, 1971)

$$\begin{aligned} &Ligand + Active\ \ Site \longrightarrow Ligand - site \\ &Ligand - site + PO_4^{3-} \rightarrow Ligand - PO_4^{3} \end{aligned} \tag{4.3}$$

4.8 Interactions of sorbed Cd(II) and P with biopolymers of biosoil

FTIR spectra can reveal the surface functional groups on the surface of the biomass. The fresh raw biomass, the alkaline stabilised biosoil and the exhausted biosoil are given in Figures 4.11.

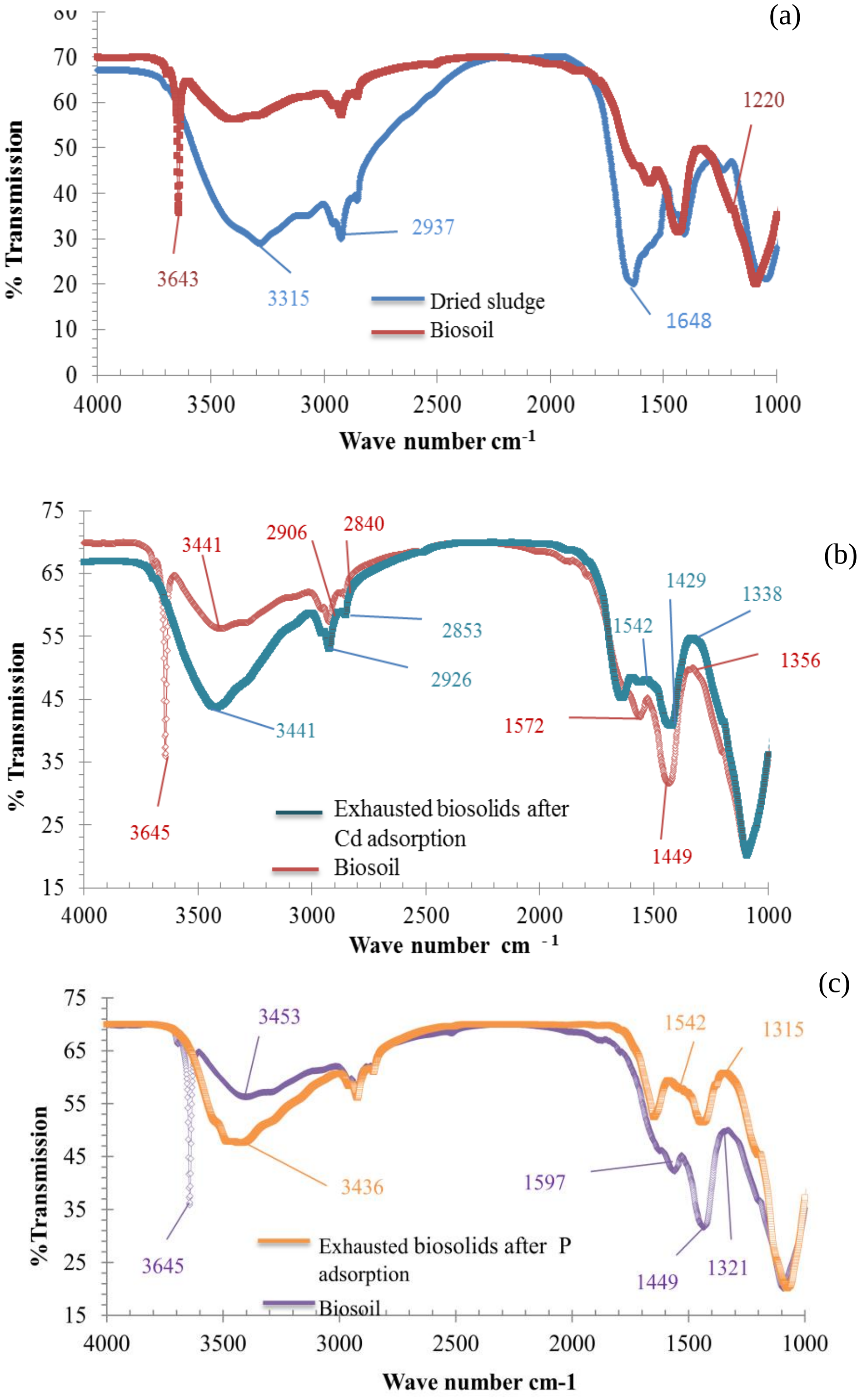


Figure 4.11 FT-IR spectra of biomaterials (a) dried sludge, (b) Cd saturation biosoil, (c) P saturation biosoil applying MKP fertiliser, (d) P saturation biosoil applying manure fertiliser, (e) Cd saturation with biosoil fully P orginated from MKP and (f) Cd saturated with biosoil fully P orginated from manure

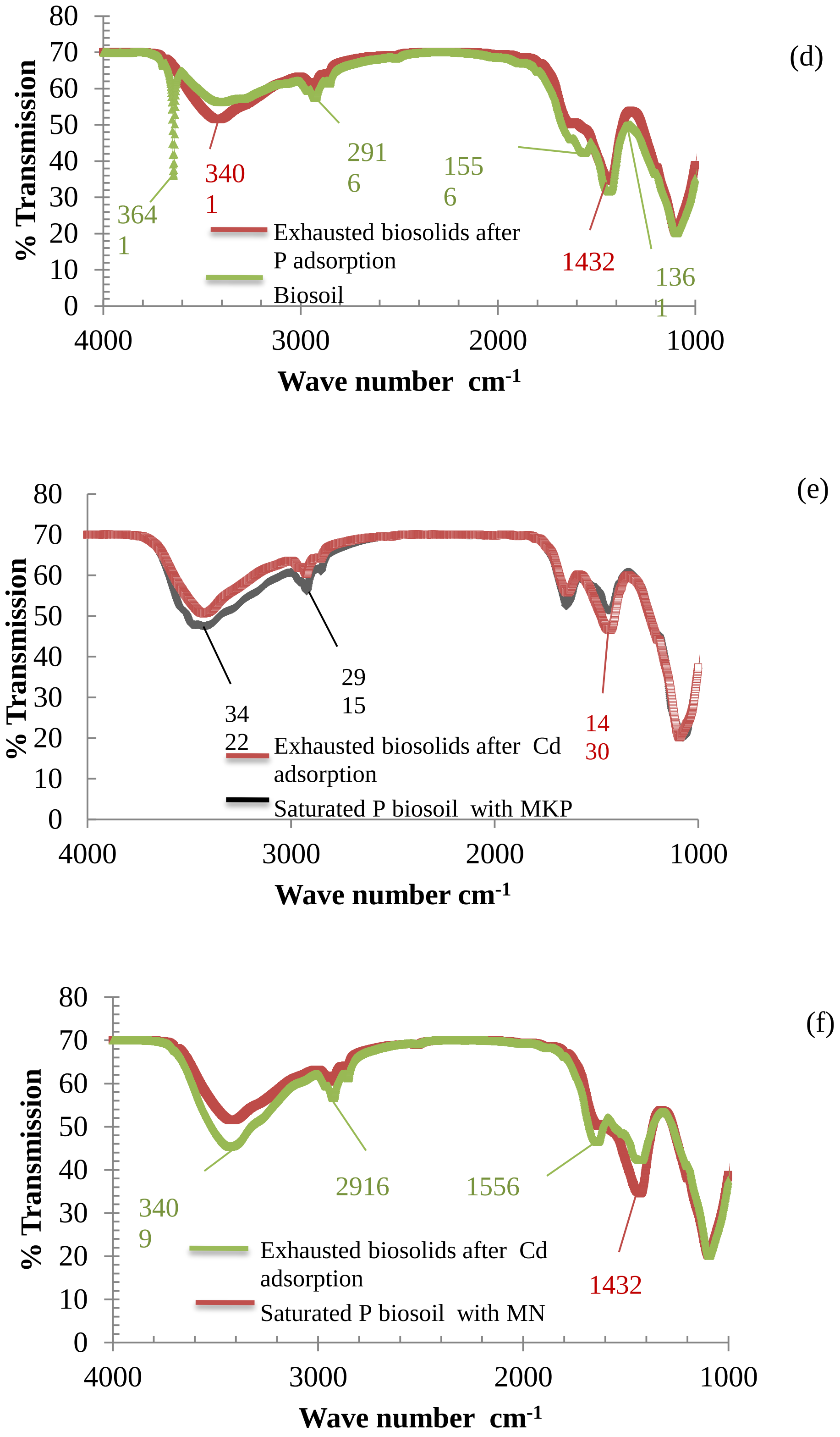


Figure 4.11(cont.) FT-IR spectra of biomaterials (a) dried sludge, (b) Cd saturation biosoil, (c) P saturation biosoil applying MKP fertiliser, (d) P saturation biosoil applying manure fertiliser, (e) Cd saturation with biosoil fully P orginated from MKP and (f) Cd saturated with biosoil fully P orginated from manure

The FT-IR spectra of each specimens are compared to literature in order to identify the functional groups of biopolymers. The possible wave number and functional group is described in Table 4.10.

Table 4.10 FT-IR identification of biomass (Khankruer et al., 2012)

Possible assignments	**Wave number (cm^{-1})**
H-bonded OH groups (polysaccharides) and N-H stretching (proteins)	3650-3200
Aliphatic C-H stretching (fatty acids)	3000–2780
C=O carbonyl streching, -CN stretching (amide I) group of protein peptide bond	1660–1532
C=N stretching (amideII)	1542
Phenolic -OH and C=O carboxylate stretching	1455–1423
C-H bending, CH_3 stretching, COO symmetric stretching (amino acid side chains, fatty acids)	1396–1389
C-O-C and -OH streching of polysaccharides	1027
P-O-C, P-O-H stretching (phospholipids, ribose phosphate chain pyrophosphate)	970-1022

As discussed previously, Cd^{2+} species tend to be sorbed on organic matter. The adsorption capacity depends on amount of anions of organic matter that comes from dissociation process of some compounds, especially carboxylic group and phenolic OH groups. On the other hand, the molecules of organic matter interacting cations such as amide groups that come from protonation or proton adding process. Therefore, the anions can be adsorbed by these cations of organic matter. The differences between dried sludge and alkaline stabilised sludge or biosoil are observed at spectrum bands at 3643, 3315, 2937, 1648 and 1220 cm^{-1}which are the presences of functional groups of O-H (hydroxyl) and N-H stretching (proteins), C-H stretching (alkyl), C=O (carbonyl) and -CN stretching (amide I) and C-O stretching (phenol), respectively. This can refer that the alkaline stabilisation can enhance the adsorptive sites. The peaks of FT-IR spectrum are elevated after the dried biosolids material is treated via alkaline stabilisation. This can confirm that the cytoplasm, which is the liquid in biomass, can escape due to the exothermal reaction between calcium carbonate originated from quicklime. The calcium species may also react with the cytoplasm and form the biopolymers. When the active sites of biosolids are occupied by Cd(II), the spectrum at the bands at 3441, 2926, 1572 and 1429 cm^{-1}are decreased, these present the loss of functional groups of biopolymer, which are O-H (hydroxyl) and N-H stretching (proteins), Aliphatic C-H stretching (fatty acids), C=O (carbonyl) and -CN stretching (amide I), Phenolic –OH and C=O carboxylate stretching, respectively. Results of FT-IR spectra indicate that these ionisable functional groups are able to react with protons or cations in aqueous solution. In case of biosoil mixed with MKP fertiliser, the P saturation biosoil, the FT-IR spectrum is relatively oscillated. The spectrum bands at 3436, 1597, 1542 and 1449 are declined as the reaction may be in regard with a O-H (hydroxyl) and N-H stretching (proteins), C=O (carbonyl) and -CN stretching (amide I), C=N stretching (amide II), phenolic –OH and C=O carboxylate stretching groups bound to phosphorous with MKP fertiliser. If the biosoil is agitated with manure solution, the P fully saturated biosoil has presented the decrease of spectrum bands at 3401, 2916, 1556 and 1432, because the initial pH of manure solution is neutral. When the fertiliser solutions are added into biosoil, the bioslurry becomes alkaline solution quickly. So, Ca-P precipitation plays dominantly than adsorption onto organic matter. The presences of functional groups of O-H (hydroxyl) and N-H stretching (proteins), Aliphatic C-H stretching (fatty acids), C=O (carbonyl) and -CN stretching (amide I), C=N stretching (amide II), phenolic –OH and C=O carboxylate stretching groups are significantly observed and they can be bounded to phosphorous from organic manure. If the P fully saturated biosoil are appied to Cd solution, the primary and secondary Cd adsoroption may be occurred. Whenever the biosoil is exhausted with Cd from saturated P biosoil with MKP fertiliser and organic manure, the FT-IR spectrum shows similarly results that Cd can be slightly trapped by OM because the Cd(II) can also perform the secondary adsorption with these Cd bound phosphate compound. The spectrum bands at 3409, 2916, 1556 and 1432 are slightly declined as the reaction may be in regard with a O-H (hydroxyl) and N-H stretching (proteins), Aliphatic C-H stretching (fatty acids), C=O (carbonyl) and -CN stretching (amide I), C=N stretching (amide II), Phenolic –OH and C=O carboxylate stretching groups bound to Cd.

4.9 Chemical fractions of Cd(II) in biosoil

The alkaline stabilised biosoil and the exhausted biosoil are examined the stability of sorped Cd(II) using the sequential extraction process. The results are summarised as given in Figure 4.12.

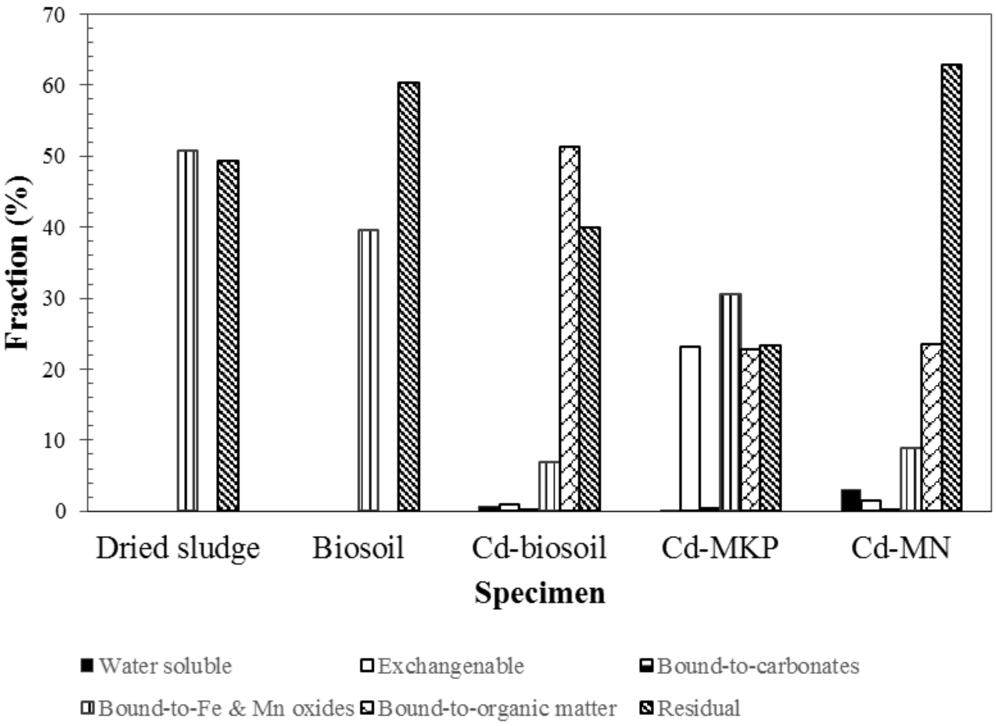


Figure 4.12 Cadmium (II) fractions in biosoil

Note: The symbols Cd-biosoil, Cd-MKP and Cd-MN stand for the exhausted biosoil after Cd adsorption, saturated P biosoil with MKP fertiliser after Cd adsorption and saturated P biosoil with organic manure after Cd adsorption, respectively.

The sequential extraction technique is employed to examine the various forms of Cd(II) adhered onto biosoil due to adsorption. The fresh sludge and biosoil are really free from soluble Cd(II) but the Cd(II) species of sludge and biosoil may observed as Fe, Mn oxide bond and residual originated from sludge and materials components. This result shows the Cd can trap on oxide compounds and formed on residual. These structures are strengthen structure and Cd can be difficulty released when the leachate becomes acid. After leaching with $Cd(NO_3)_2$ $4H_2O$ solution, amounts of Cd species are mostly oxidisable and residual, which is relatively inert Cd(II). The oxidisable Cd(II) refers to the organic bounded Cd(II). The Cd(II) may be consumed and accumulated in biomass cell, which was stable in cell wall of dead biomass. After the active surface of biosoil is full of sorbed Cd(II) species, the other Cd(II) are able to bound on saturated P biosoil with MKP fertiliser, Cd species presented in are mostly fixed on the exchangeable, Fe and Mn oxides, OM and residual. On the other hand, the Cd species on saturated P biosoil with organic manure are mostly in form of residual, OM and Fe and Mn oxides, respectively. This phenomenon was stimulated by the reduction of Cd(II) at acidic pH. The mobile Cd(II) rapidly transformed to be immobile phase owing to the complex formation with biosoil constituents and P onto biosoil. Therefore, the reaction between Cd and P products formed can be examined by XRD technique.

4.10 Reaction between Cd and P and precipitant forming

The Cd-P reaction products forms are identified by X-Ray diffraction (XRD) technique. X-Ray diffractometer (Bruker AXS Model D8 Discover) using Cu Kα radiation. Patterns are recorded from 10° to 65°, the angle of 2θ is observed at scan speed 0.3 sec/step. The XRD pattern for Cd adsorption onto saturated biosoil with P is shown in Figure 4.13. The main characteristic peaks show the presence of Cristobalite alpha (SiO_2), Calcium Carbonate ($CaCO_3$) and Cadmium Phosphate ($Cd_2P_2O_7$). The XRD spectrums can indicate that Cd^{2+} species are deposited onto active surface of treated biosolids. This silica oxide can be formed at high temperature and this can strengthen the structure of biosolids. Besides, the silicate mineral can resist the acidic pH solution of Cd(II). Therefore, the mass of alkaline treated biosolids is slightly lost even though the Cd(II) influent at pH of 3 is employed. The calcium carbonate is sourced from CaO, which is one of alkaline materials to synthesise the biosoil and phosphate can retard the Cd^{2+} species by forming the complex compounds of $Cd_2P_2O_7$ that this form is crystalline structure. The Cd(II) can also perform the secondary adsorption with these Cd bound phosphate compound. According to the sequential extraction, the residue may relate the complex compounds of $Cd_2P_2O_7$, as this precipitate Cd compounds are highly stable as they are in crystal form. The most amount of residual Cd is governed, when the biosoil is fully saturated with P orginated from manure. As same as the intensity of $Cd_2P_2O_7$ is highly observed, in case of Cd sorped on the biosoil with fully sorped P originated from manure. Besides, the silica (SiO_2) and calcium carbonate ($CaCO_3$) are predominantly in both cases. This expresses that the SiO_2 from fly ash is inert material, it cannot react with any constituents in sludge. Only CaO in quicklime can react with sludge, the carbonate is released as pH buffer constituents, in order to resist the change of pH during alkaline stabilisation. The interaction between sludge and quicklime can generate $CaCO_3$. However, the intensity of $CaCO_3$ is not much high, it can be assumed that the CaO prefer to react with water in sludge and form the soluble $Ca(OH)_2$. The active biopolymers and minerals in biosoil can be further formed during alkaline stabilisation. These active biopolymers and mineral compounds play an important role in Cd and P sorption. Furthermore, the sorbed P onto biosoil can further react with Cd and precipitate as non reactive $Cd_2P_2O_7$. The biosoil can be employed as soil amendment and slow P fertiliser.

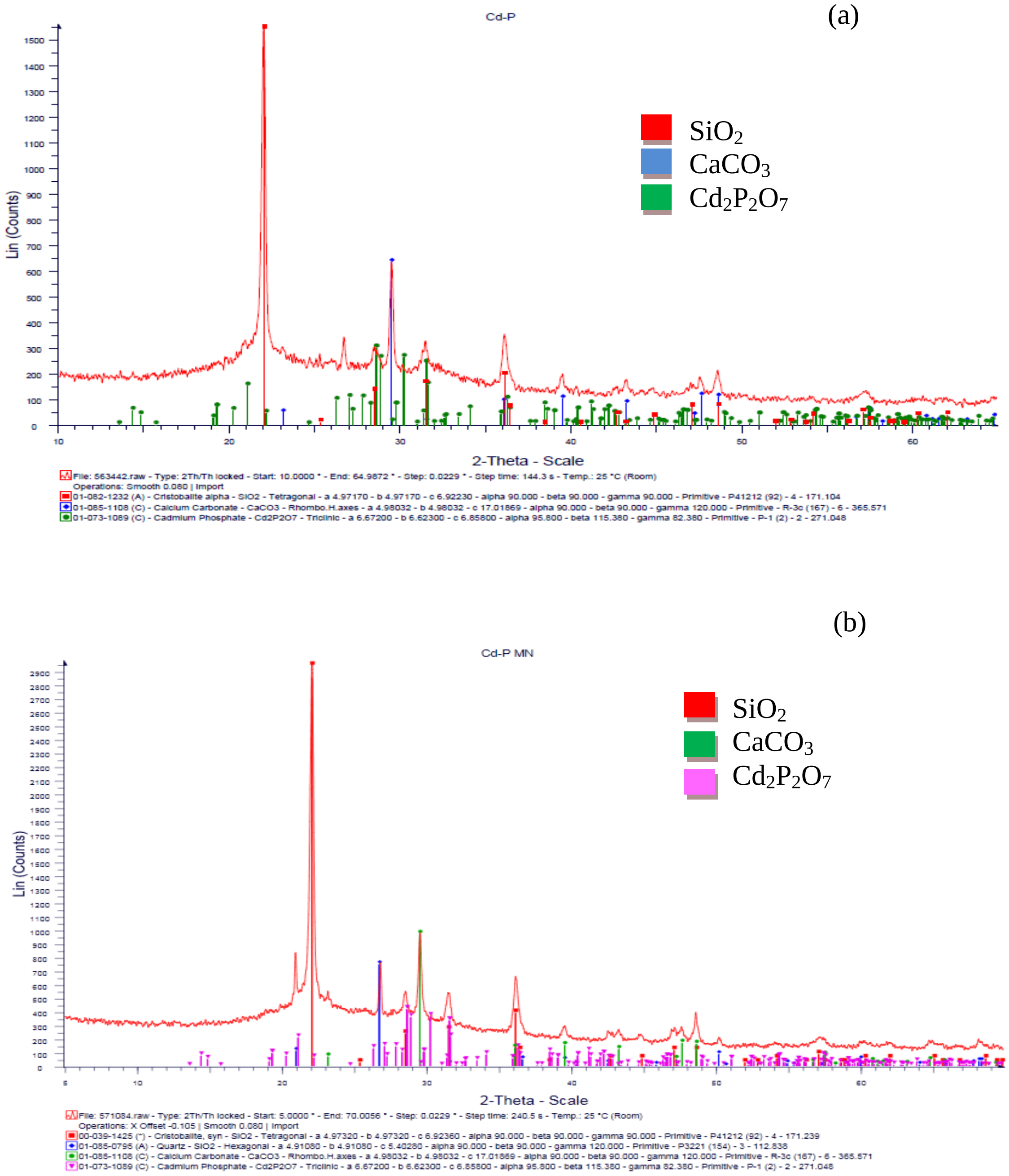


Figure 4.13 XRD pattern of biosoil after Cd adsorption onto biosoil saturated with P (a) biosoil saturated with MKP-P and (b) biosoil saturated with MN-P

The values of the maximum adsorption capacities for the adsorption of Cd(II) on different adsorbents are summarised in Table 4.11. Although direct comparison of the saturated P biosoil with other adsorbent materials is difficult, owing to the differences in experimental conditions, it was found that the maximum adsorption capacity of saturated P biosoil is higher than most adsorbents. The saturated P biosoil with MKP fertiliser and organic manure have a high adsorption capacity as comparable with that of the other adsorbents. Therefore, considering the low cost of this natural adsorbent (waste), it can be used as an alternative material to minimise the concentration of Cd(II).

Table 4.11 Adsorption capacities of various adsorbents

Adsorbents	**Q_{max} (mg/g)**	**References**
Tea-industry waste	11.29	Çay et al. (2004)
Olive cake	10.56	Doyurum and Celik. (2006)
Carboxymethylcellulose	28.70	Yalçinkaya et al. (2002)
Bagasse fly ash	1.24-2.00	Gupta et al. (2003)
Low-grade phosphate	7.54	Kandah. (2004)
Coffee grounds	15.65	Azouaou et al. (2010)
S.anthophorbium	18.90	Benhima et al. (2008)
L.arboresens	11.50	Benhima et al. (2008)
Pantoea sp. TEM18	58.10	Ozdemir et al. (2004)
Ochrobactrum anthropi	37.30	Ozdemir et al. (2003)
Sargassum siliquosum (brown)	82.05	Hashim and Chu. (2004)
Padina tetrastomatica (brown)	59.58	Hashim and Chu. (2004)
Chaetomorpha linum (green)	53.96	Hashim and Chu. (2004)
Gracilaria changii (red)	25.85	Hashim and Chu. (2004)
Gracilaria edulis (red)	26.98	Hashim and Chu. (2004)
Gracilaria salicornia (red)	17.99	Hashim and Chu. (2004)
Activated carbon derived from bagasse	27.47-49.07	Mohan et al. (2002)
Carbon F-400	8.00	Mohan et al. (2007)
Oak bark char	5.40	Mohan et al. (2007)
Calgon F-400	6.35	Toles et al. (1997)
Oak wood char	0.37	Mohan et al. (2007)
Oxidised granular activated carbon	5.73	Huang et al. (2007)
Saturated P bisoil with MKP fertiliser	82.35	Present work
Saturated P bisoil with organic manure	208.30	Present work

4.11 Summary

The wasted activated sludge from wastewater treatment plant of Sitthinan Co. Ltd, which is food industry, is able to be employed as raw material for biosoil fabrication. The alkaline materials are prepared by mixing quicklime and fly ash that is the residue of biomass burning furnace, a massive ratio of quickline to fly ash is 2:5. A sludge to alkaline material ratio at 50:50 anc produce the biosolids class A or biosoil. This biosoil is free from pathogen and odour. The biosoil is introduced to adorp the Cd, and P from MKP and manure fertiliser solution. The organic matter in biosoil can store Cd and P from MKP and manure fertiliser solution at 6.127 mgCd/g OM, 67.85 mg P/g OM and 4.48 mg P/g OM, respectively. The major biopolymers of are O-H (hydroxyl) and N-H stretching (proteins), Aliphatic C-H stretching (fatty acids), C=O (carbonyl) and -CN stretching (amide I), Phenolic –OH and C=O carboxylate stretching, can bond Cd. Most of P from MKP fertiliser solution reacts with O-H (hydroxyl) and N-H stretching (proteins), C=O (carbonyl) and -CN stretching (amide I), C=N stretching (amide II), phenolic –OH and C=O carboxylate stretching groups. Similarly P from manure can be stored in biopolymers of O-H (hydroxyl) and N-H stretching (proteins), Aliphatic C-H stretching (fatty acids), C=O (carbonyl) and -CN stretching (amide I), C=N stretching (amide II), phenolic –OH and C=O carboxylate stretching groups. When the biosoil is fully adsorped P from MKP and manure fertiliser solution, it can further perform secondary Cd adsorption. The Cd adsorption capacities of biosoil wih P orginated from MKP and manure are 82.35 and 208.3 mgCd/ g P, respectively. The biosoil saturated with P from MKP fertiliser solution has presented the slightly alkaline, most of Cd is bounded to Fe and Mn oxides and OM. The biosoil saturated with P from manure fertiliser solution can bond Cd with OM and Fe and Mn oxides. This refers that OM can also react with Cd at the functional group of biopolymers of a O-H (hydroxyl) and N-H stretching (proteins), Aliphatic C-H stretching (fatty acids), C=O (carbonyl) and -CN stretching (amide I), C=N stretching (amide II), Phenolic –OH and C=O carboxylate stretching groups. Besides, the biosoil saturated with P from manure can present the highly content of residue Cd or inert Cd. The residue Cd is acknowledge a $Cd_2P_2O_7$. The biosoil is the competitive biosorbent material, which can adsorp P and Cd, as well as can stabilised Cd from chemical P fertiliser. It can be applied to agriculture.