CHAPTER 4

RESULTS AND DISCUSSION

As mentioned in the previous chapter, the experimental studies in this work were divided into three parts. Firstly, the property of leonardite raw material was studied. Secondly, the adsorption behaviors of copper, zinc and lead ions on leonardite were evaluated, and the factors that affect to the adsorption were also studied. Finally, the adsorption behavior of methylene blue on leonardite, and the factors affecting adsorption behavior were studied. The obtained results are reported and discussed as follows.

4.1 Properties of leonardite raw material

4.1.1 Chemical and mineral compositions

The chemical and mineralogical compositions of leonardite were measured using XRF and XRD as shown in Table 4.1 and Fig. 4.1, respectively. As shown in Table 4.1, the major chemical components of leonardite are silica (SiO_2), alumina (Al_2O_3), ferric oxide (Fe_2O_3) and calcium oxide (CaO).These results correspond with the XRD findings. The mineral components of leonardite are silicon dioxide, calcium sulfate dehydrate, kaolinite, muscovite, iron sulfide and calcium carbonate.

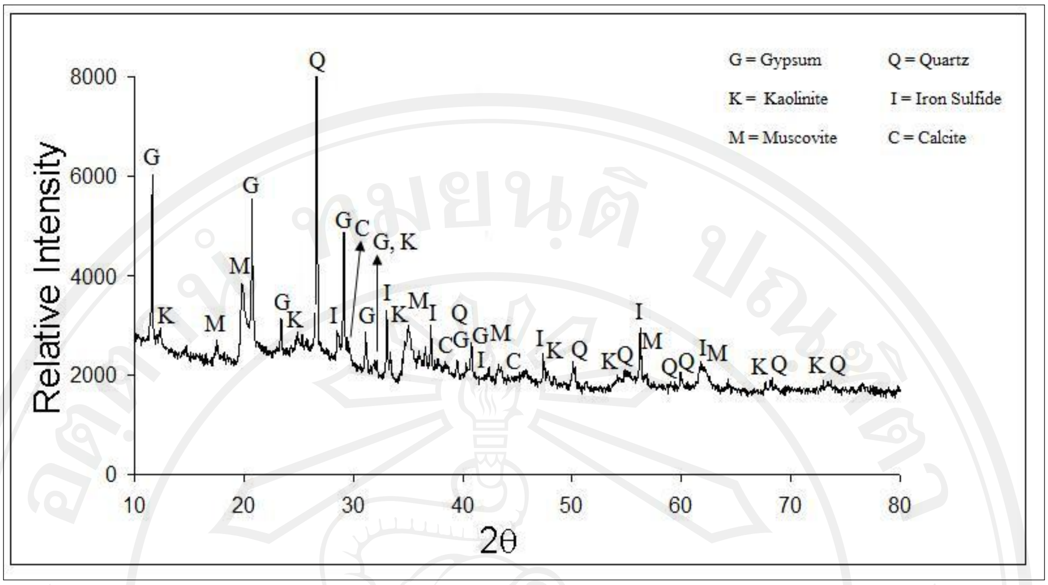

Figure 4.1 X-ray diffraction of leonardite

Table 4.1 Chemical compositions and physical properties of leonardite from Mae Moh mine

Compound	**(wt%)**
SiO_2	29.445
Al_2O_3	15.527
Fe_2O_3	4.528
CaO	2.561
P_2O_5	0.046
K_2O	1.304
TiO_2	0.244
SrO	0.015
Na_2O	1.449
Pb, K, Na, Mg, Ti, and P	<0.01
Loss on Ignition (LOI)+C+SO_3	41.3
BET area (m^2g^{-1})	18.94-26.29
CEC (cmol/kg)	61.95

4.1.2 Chemical compositions determined by AAS (digestion method)

The chemical compositions of leonardite measured using AAS (digestion method) are shown in Table 4.2. The major metal elements in leonardite are calcium, iron, magnesium and potassium.

Table 4.2 Compositions of metal elements in leonardite

Heavy metals	**(mg/kg)**	**(wt%)**
Ca	8741.89	0.88
Fe	6195.65	0.62
K	2544.21	0.25
Na	1917.14	0.19
Mn	273.77	0.02
Zn	93.59	-
Mg	3583.50	0.36
Cu	4.95	-
Pb	< 0.005	-
Cd	< 0.005	-

4.1.3 Surface area, cation exchange capacity and particle size

The measurement was performed in triplicate. The surface area of leonardite was ranging from 18.94-26.29 m^2/g.

CEC of leonardite was high (61.95 cmol/kg), because of the large amount of humic acid in leonardite, that composed of the carboxyl and hydroxyl functional groups. Therefore, it affected to the increase ofion exchange between metal ions and hydrogen ion released from surface groups.

The particle size distribution of leonardite that was sieved through a 80 µm sieve was approximately 22.50 µm.

4.1.4 Characterization of humic acid by FTIR

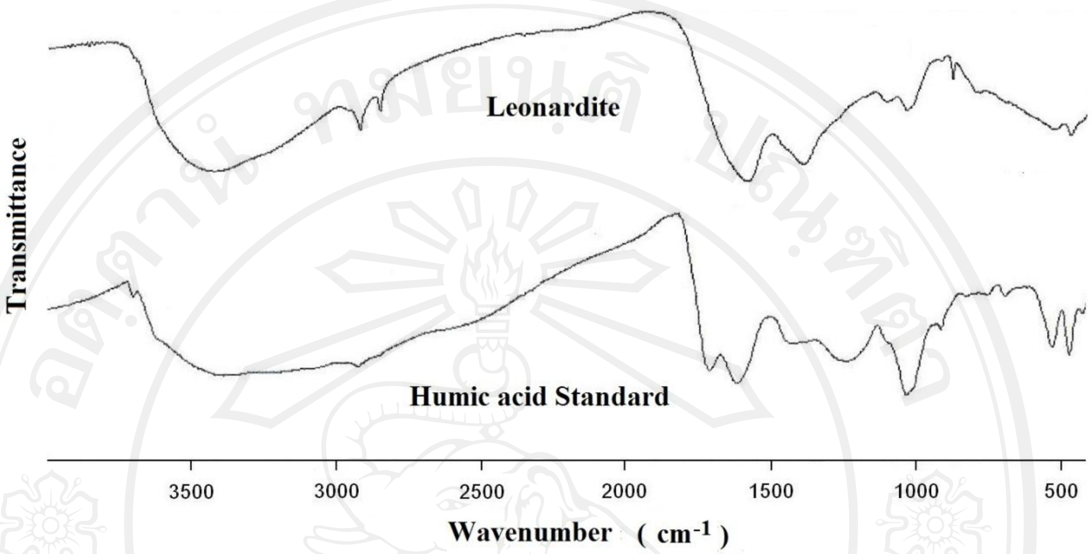

Figure 4.2 FTIR spectra of leonardite compare with humic acids standard

Table 4.3 FTIR spectrum of leonardite compare with humic acid standard

Wavenumber(cm^{-1})		Assignment
Sample	**Reference[77]**	
3400	3400	OH–stretching
2900, 2800	2922, 2860	C-H–stretching
1709	1706	C=O stretching
1606	1615	C=C stretching aromatic
1026	1031	Si–O stretching

4.1.5 Topology of leonardite

According to the SEM images of leonardite in Fig. 4.3, as can be seen that the topology of leonardite showed more layers, the surface is coarse and mainly composed of shaped plate. Leonardite has high plasticity.

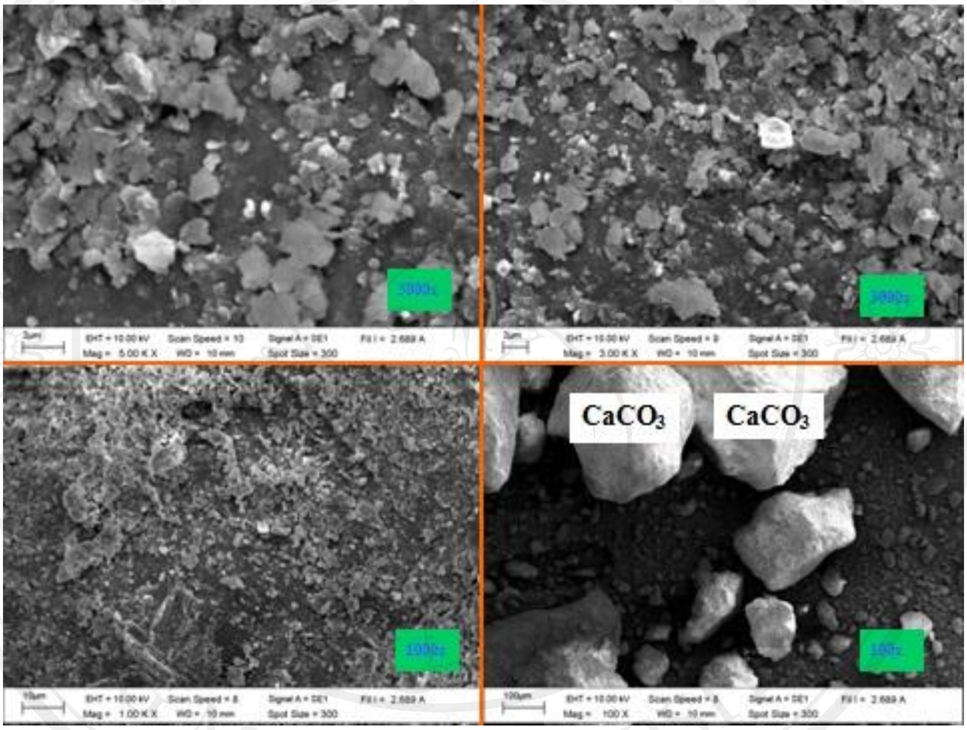

Figure 4.3 Scanning electron microscopy (SEM) images of leonardite

4.2 Adsorption behaviors of copper(II), zinc(II) and lead(II)on leonardite

The adsorption behavior of Cu^{2+}, Zn^{2+} and Pb^{2+}ions on leonardite using the batch-type techniques is expressed in the form of equilibrium concentration, C_e, versus adsorbed concentration, q_e, of the solute. The adsorbed amount, q_e, was calculated using the equation (1.4).

To predict the relationship between the adsorbed and equilibrium concentrations obtained from batch-type tests, the Langmuir and Freundlich isotherm equations were adopted in this study as expressed by equations (1.6)) and (1.8).

4.2.1 Effect of pH

The adsorption of Cu^{2+}, Zn^{2+} and Pb^{2+}ions on leonardite was studied at a pH range of 2-6 for a fixed 0.400 g of leonardite, in order to investigate the optimum pH for the removal of these ions. The amount of metal ions removed for each pH was calculated by comparing the initial concentrations of metal ions with that remaining in the solution after 24 h. Fig. 4.4 shows the removal of metal ions versus initial pH for a fixed adsorbent dose and initial metal concentrations of 5.00mg/L (4.4a) and 20.00 mg/L (4.4b). As can be seen, the removal of Cu^{2+}, Zn^{2+} and Pb^{2+} from aqueous solutions by sorption on leonardite was pH dependent. The analysis of these metal ions in blank solutions showed that there was no leaching of them from the adsorbent. In Fig. 4.4a, at pH 6 the highest removal percentagesof the two metals ions were observed (about 98-99% for Cu^{2+} and 43% for Zn^{2+}). For Pb^{2+} the tests were carried out with 5.00 mg/L concentrations, the almost complete removal of Pb^{2+} was achieved and no pH effect could be observed.Thus, 20.00 mg/L of Pb^{2+} concentration was used. For 20.00 mg/L concentration of metals ions (Fig. 4.3b), it was observed that the removal percentage (about 91% for Cu^{2+} and 40% for Zn^{2+}) was maximum at pH 6. In the case of Pb^{2+}, the highest adsorption was obtained around pH 5-6. Whereas at low pH (in Fig. 4.4a and b) the removal percentage of Zn^{2+} was practically negligible (about 3%), and lower levels of removal for Cu^{2+} and Pb^{2+} were observed. Similar results have been reported by many researches in the studies of the removal of heavy metal ions on various adsorbents [2,6,11,12].

The pH effect of adsorption on leonardite can be explained by the surface characteristics of the adsorbent. At low pH functional oxidized groups (hydroxyl, carboxyl, phenol, methoxy, etc.) of humic acids are protonated. This phenomenon would be the competition between H^+ and metal ions for sorption on the leonardite surface sites, leading to poor removal of metal ions. As the pH increases metal ions will replace hydrogen ions from the surface of the leonardite and therefore the extent of the adsorption will increase [13,14]. Metal sorption equilibrium reaction can be considered as follows:

$$-COOH \rightleftharpoons -COO \;+\; H^{+}_{(aq)} \tag{4.1}$$

$$M^{+2}_{(aq)} \;+\; n - COOH^{-} \;\rightleftharpoons\; (-COO)_{n}M \tag{4.2}$$

$$M^{+2}_{(aq)} \;+\; nOH^{-} \;\rightleftharpoons\; M(OH)_{n} \tag{4.3}$$

In the equilibrium reaction, for pH lower than 2, Eq. (4.1) lies to the left which follows the equilibrium law. The ion exchange sites on the leonardite are mainly protonated then the binding sited can be less available. The carboxyl functional group sites on the leonardite can be deprotonated at a solution pH between approximately 2and 5, Eq. (4.2) proceeds continue to the right and the metal ion removal is increased by pH of the solution increased. The ion exchange process is the major mechanism for metal ions removal. The pH studies indicate that at pH below 6 three metals are present in the divalent ion form in the solution. But beyond pH 6, neutral hydrolysis products and precipitated metal hydrolysis are present in a solution, as shown in Eq. (4.3).

Pehlivan and Arslan [13] reported that, the sorption capacity of lignite for Cu^{2+}, Pb^{2+} and Ni^{2+} increased with increasing pH above pH 5, because the coordination bonds between metal ions and phenolic hydroxyl functional groups and other ion exchangeable sites on the surface of lignite are rather weak in the slightly acidic solution. Phenols are weak acidic compounds (pKa= 9) when compared to carboxylic acids. The increase in the pH values would lead to an increase in the metal uptake, since the phenolic groups can release hydrogen ions at pH higher than 9.

In our study, the adsorption of Cu^{2+}, Zn^{2+} and $Pb^{2+}$are negligible at low pH values and increased considerably in the pH range 3-6.

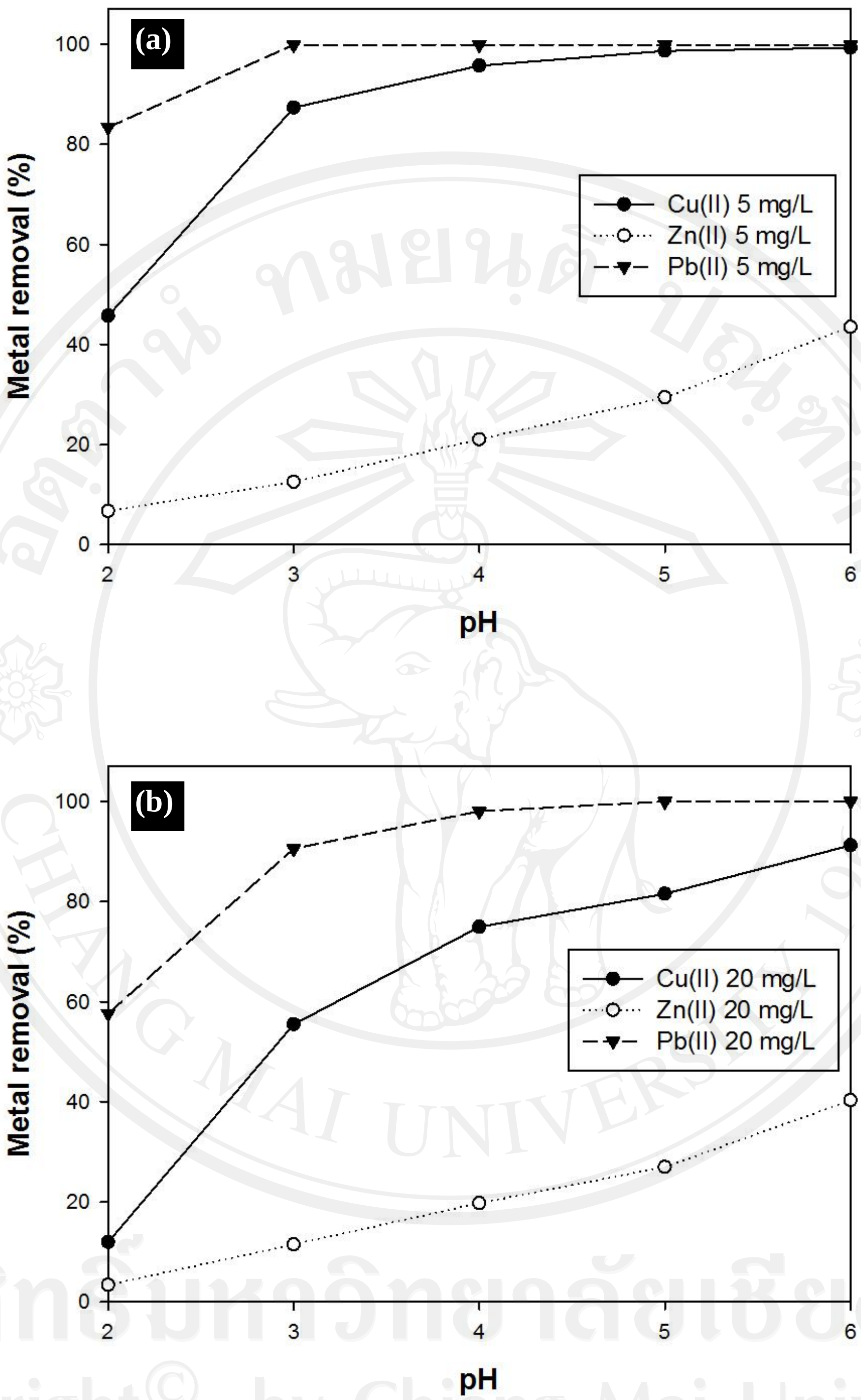

Figure 4.4 Effect of pH on Cu(II), Zn(II) and Pb(II) onto leonardite at initial concentrations of(a) 5.00 mg/L (b) 20.00 mg/L

4.2.2 Effect of contact time

In order to study the time required for equilibrating Cu^{2+}, Zn^{2+} and Pb^{2+}solutions with leonardite, equilibration times were selected at 10, 20, 30, 40, 50, 60, 120, 180, 240, 300 and 360minutes, respectively. The sorption experiments were conducted by shaking 1.600g of leonardite in 200.00 mL of 5.00 and 20.00 mg/L Cu^{2+}, Zn^{2+} and Pb^{2+} solution at 130 rpm at room temperature. At the end of the shaking period, the suspension was filtered and the remaining metal ions concentration was measured by AAS.

The effect of contact time on Cu^{2+}, Zn^{2+} and Pb^{2+}removal at the optimum pH value 6 for Cu^{2+}, Zn^{2+} and pH 5 for $Pb^{2+}$was investigated by using initial concentrations of 5.00 and 20.00 mg/L. It is indicated in Fig. 4.5a that the amount of Cu^{2+} adsorbed reached equilibrium after 60 min, and the removal percentage obtained up to 95 and 85% for the two initial concentrations of Cu^{2+} (5.00 and 20.00 mg/L, respectively). Therefore, the time after 60 min was selected to be equilibrium time for Cu^{2+}.

As can be seen in Fig. 4.5b, the adsorption of Zn^{2+} was found to represent equilibrium in 120 min for initialZn^{2+} concentration 5.00 mg/L, while at higher initial Zn^{2+} concentration (20.00 mg/L), the time necessary to reach equilibrium was after 120 min. However, the experimental data were measured at 180 min to be sure that full equilibrium was achieved.

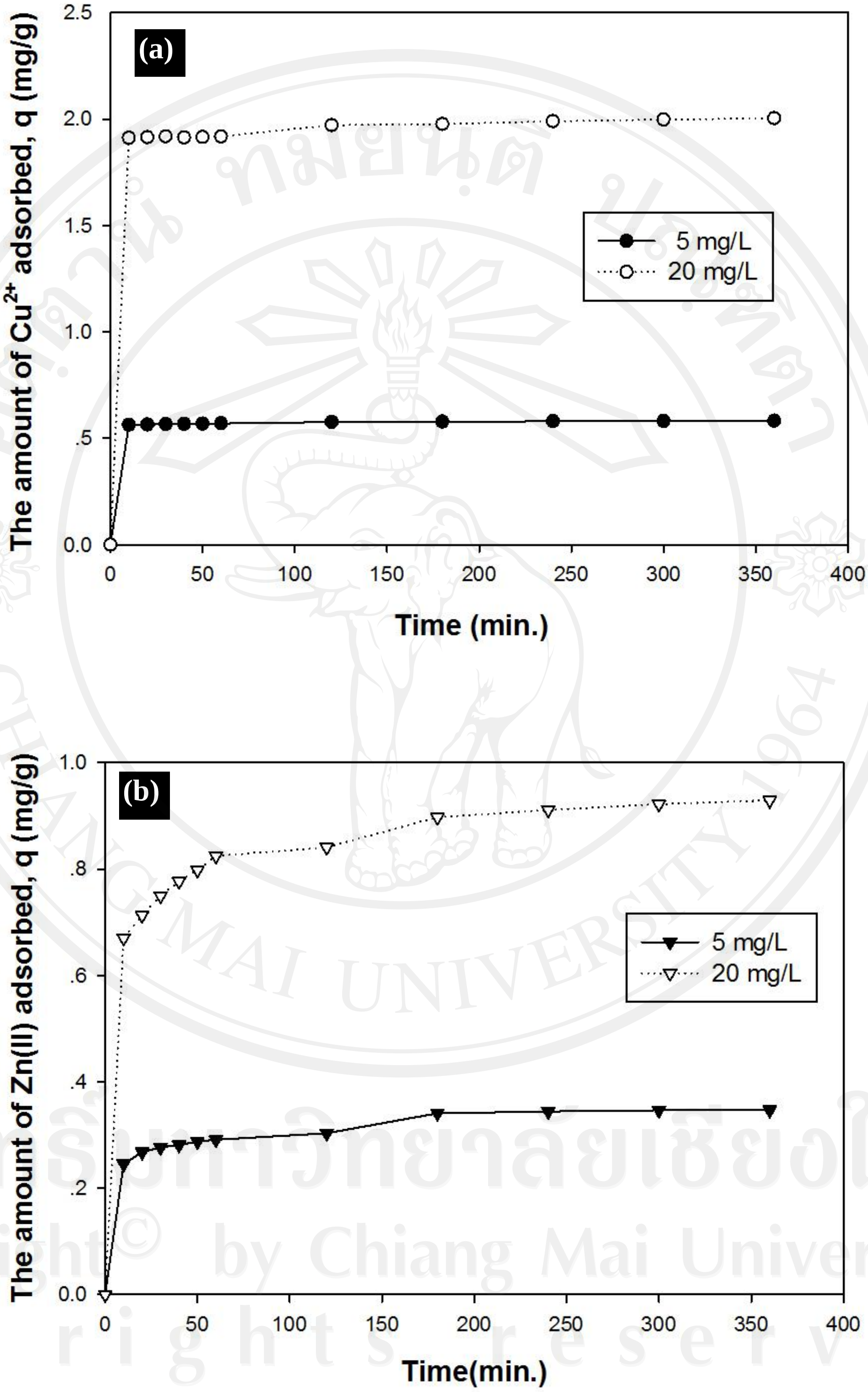

Figure 4.5 Adsorbed amount vs. time for metal ions at the two initial concentrations

(a) Cu^{2+}(b) Zn^{2+}

In the case of Pb^{2+}in Fig. 4.6, it was observed that Pb^{2+} was removed rapidly and the adsorption occurred during the first 60 min. At this time the removal rate of Pb^{2+} exceeded 90% for the two concentration of Pb^{2+}. The results showed that the contact time required to attain equilibrium was about 60 min. According to the kinetic study, the adsorption first followed an initial rapid process, and then a stationary state was observed for the three metal ions. The rate of adsorption depended on the diffusion and transport process in the pore structure of the adsorbent namely, the initial rapid rate of metal ions may be explained by the large, readily uncovered available active sites on the surface of adsorbent. The slow adsorption rate may be attributed to the diffusion of metal ions through the porous structure of the adsorbent [1].Moreover, it can be seen from the results, the amount of Cu^{2+}, Zn^{2+} and Pb^{2+} adsorbed at any time increases from low to high initial metal concentrations. This is associated with the greater driving force at a higher initial concentration, such as gradient concentration between the bulk solution and the surface of adsorbent [1,2].

It is important to observe that the initial slope of the plot obtained for Pb^{2+} (Fig. 4.6) is shaper than the Cu^{2+} or Zn^{2+} plot (Figs. 4.5a and 4.5b, respectively), may be related to a higher affinity of Pb^{2+} than those two metals when they both compete for a binding site. It could be explained by the basis on the ionic properties of the ions (i.e. ionic radius, electronegativity, or ionic potential) [1]. Metal ion, that has the greatest ionic potential, is most strongly attracted to the adsorbent.

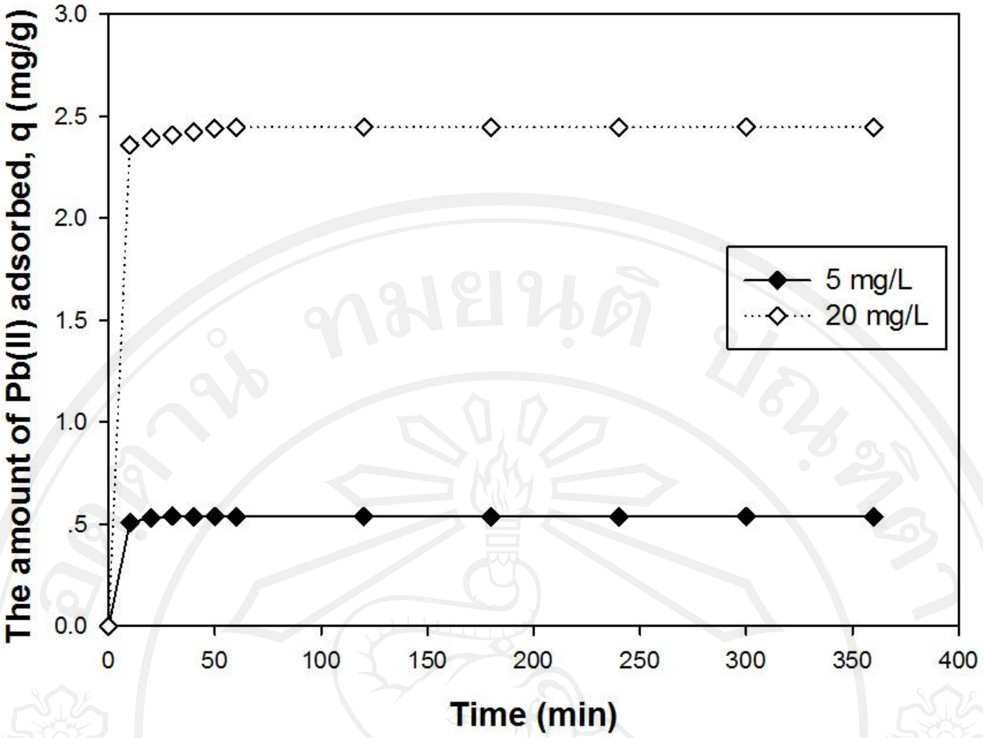

Figure 4.6 Adsorbed amount vs. time for Pb^{2+} at the two initial concentrations

4.2.3 Effect of leonardite quantity

In order to investigate the effect of leonardite quantity on the adsorption of Cu^{2+}, Zn^{2+} and Pb^{2+}a series of adsorption experiment was carried out with different leonardite dosages at the initial metal concentrations of 5.00 and 20.00 mg/L. Fig. 4.7 shows the effect of leonardite quantity on the removal of these metal ions. The results follow the expected pattern, by the removal percentage increased with the increased in leonardite quantity, especially for Zn^{2+}. As can be seen in Fig. 4.7, increasing leonardite quantity affected to the removal of Zn^{2+} more than Cu^{2+} or Pb^{2+} for the two concentrations. The removal percentage of Zn^{2+} increased up to 85% and 65% for the initial concentrations of5.00 and 20.00mg/L, respectively. These might be related to a larger external surface area available for the adsorption of metal ions.

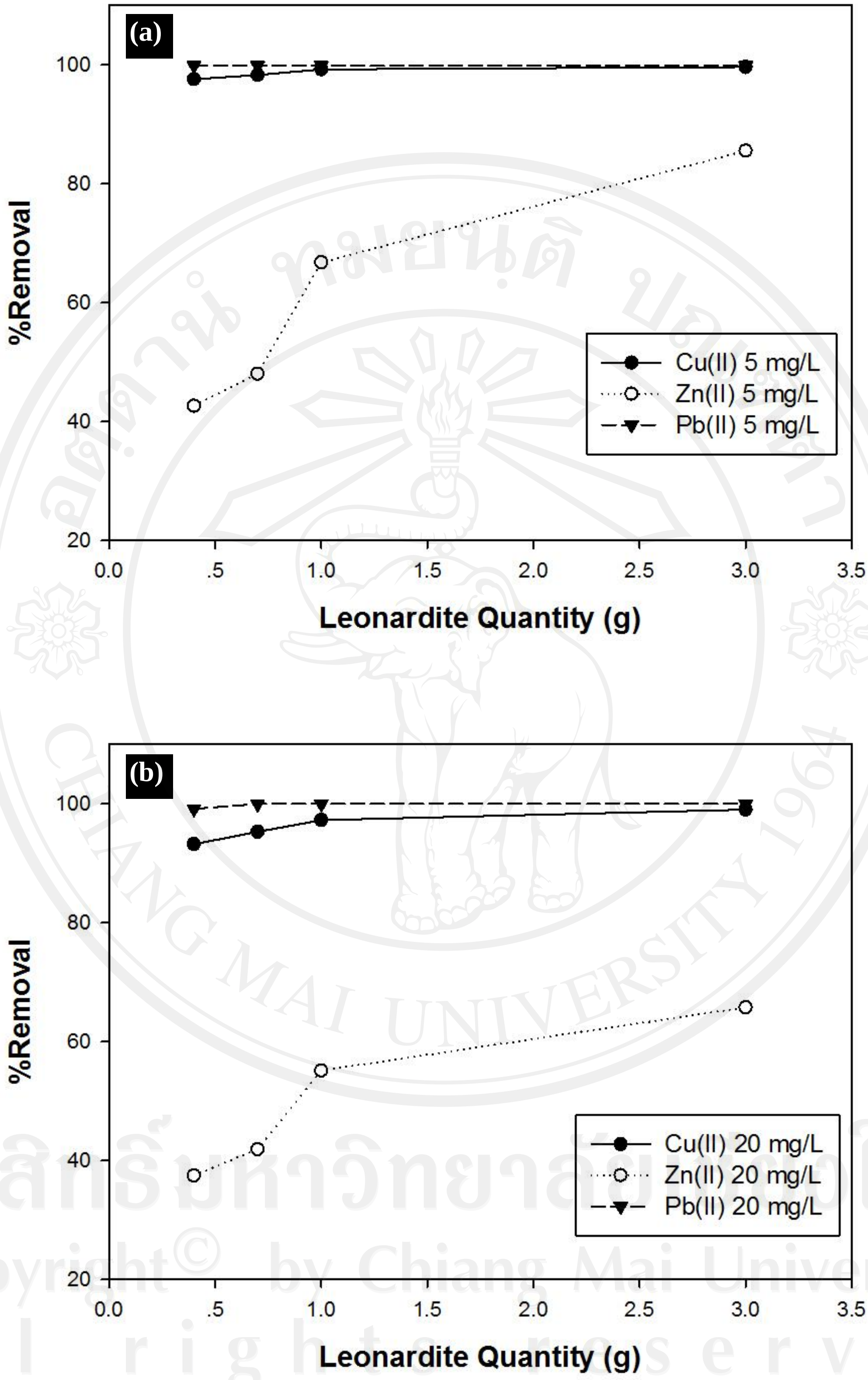

Figure 4.7 Effect of leonardite quantity on Cu^{2+}, Zn^{2+} and Pb^{2+}onto leonardite at initial concentrations of (a) 5.00 mg/L (b) 20.00 mg/L

Whereas, in the case of Cu^{2+} and Pb^{2+}, the increased in leonardite quantity exhibited a minor effect on these two metals removal for initial concentrations 5.00 and 20.00 mg/L. As observed in Fig. 4.8, the removal percentage of Cu^{2+} and Pb^{2+} slightly increased at low dosage of leonardite up to a point, after which the increase in the dosage did not increase the removal percentage significantly. Because of the free surface active site at low dosage of leonardite was sufficient for the metal ions removal, and a higher affinity of Cu^{2+} and Pb^{2+} than Zn^{2+} for the binding site that mentioned above.

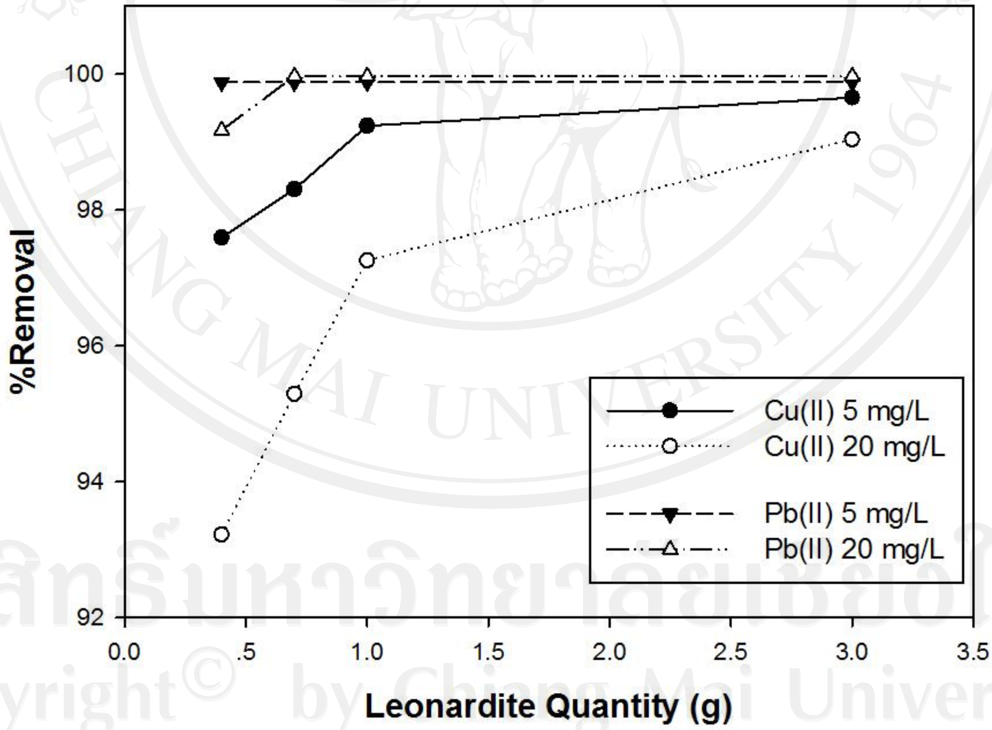

Figure 4.8 Effect of leonardite quantity for adsorption of Cu^{2+} and Pb^{2+} onto leonardite with the two initial concentrations of metals

4.2.4 Sorption equilibrium: adsorption isotherms

The adsorption isotherms were measured for the initial of Cu^{2+}, Zn^{2+} and Pb^{2+} concentrations ranging from 5.00 to 100.0 mg/L. The tests were carried out for a contact time of each metal ions and a 0.4 g L^{-1} of leonardite dose. The amount of metal ion adsorbed per unit mass of leonardite (q, mg g^{-1}) was calculated using the following equation:

$$q = (C_i - C_e)\frac{V}{m}$$

where q is the amount of metal ion adsorbed per unit mass of leonardite, C_i (mg L^{-1}) is the initial metal concentration, C_e (mg L^{-1}) is the final (equilibrium) metal concentration, V (L) is the solution volume and m (g) is the mass of adsorbent. Figs. 4.9- 4.11 show the adsorption isotherms of Cu^{2+} (4.9), Zn^{2+}(4.10) and Pb^{2+}(4.11).

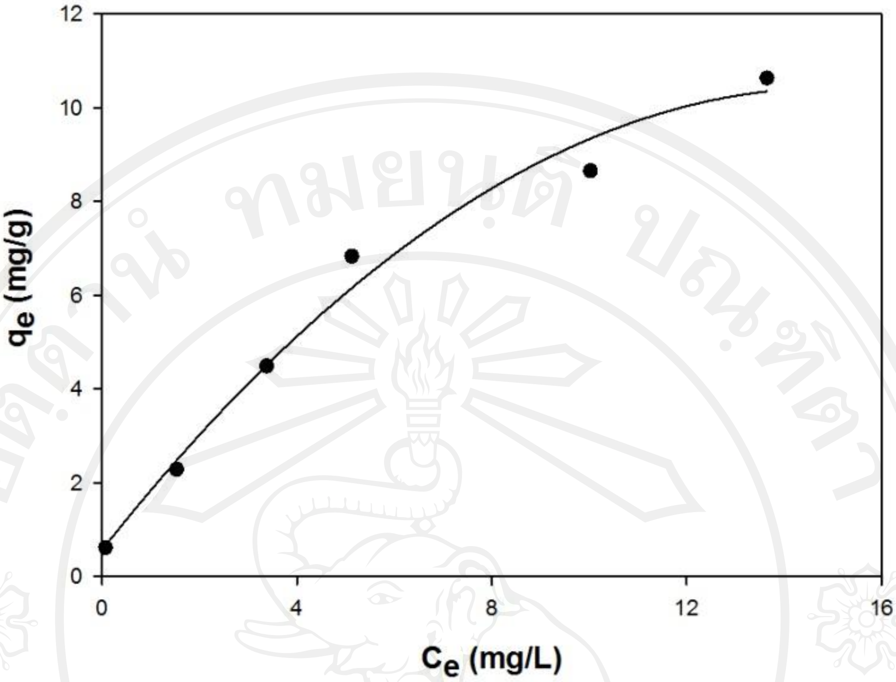

Figure 4.9 Adsorption isotherm of Cu^{2+} on leonardite measured at room temperature

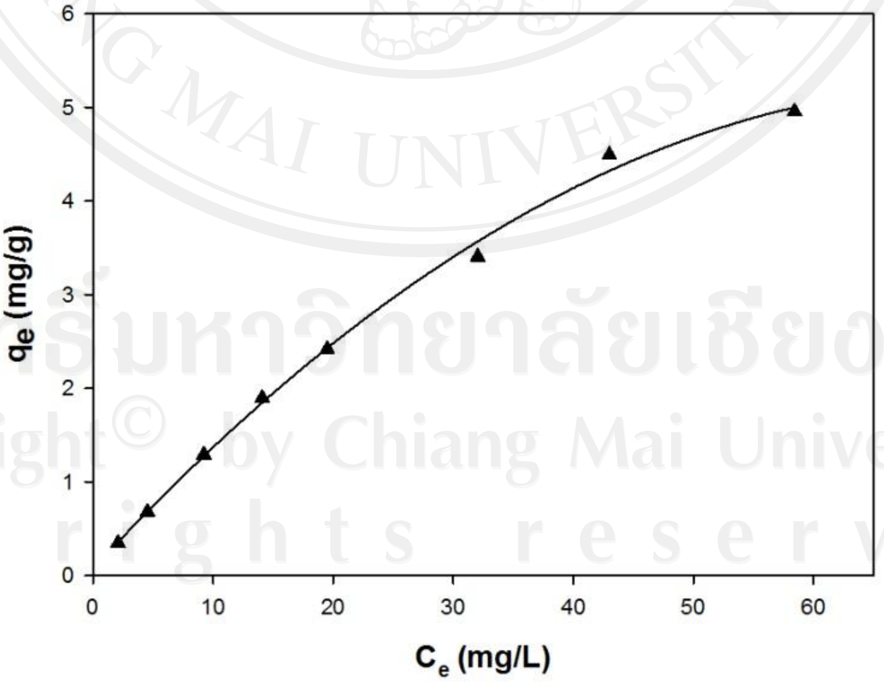

Figure 4.10 Adsorption isotherm of Zn^{2+} on leonardite measured at room temperature

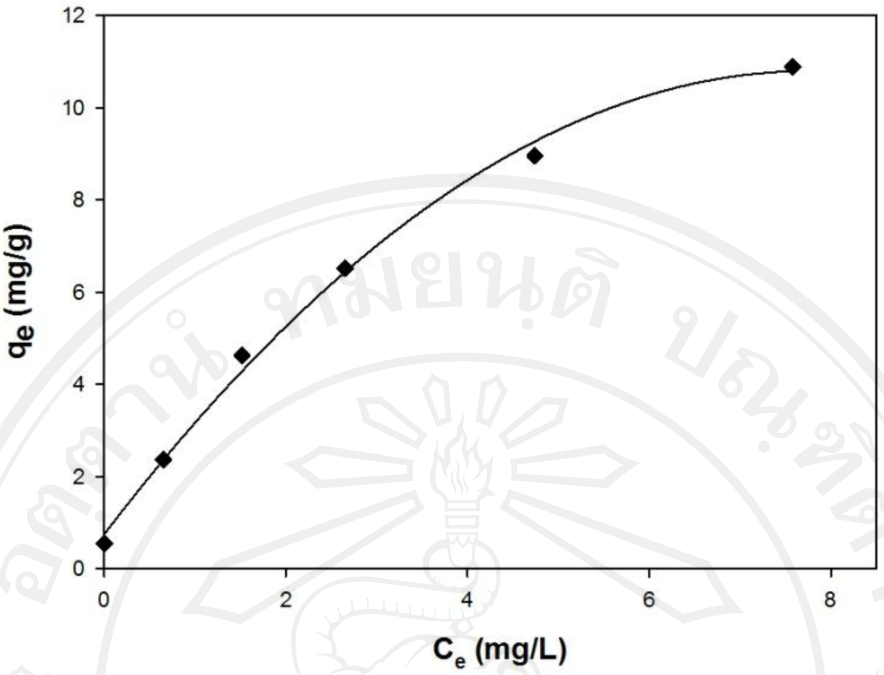

Figure 4.11 Adsorption isotherm ofPb^{2+} on leonardite measured at room temperature

Adsorption isotherm is used to describe the interaction between solutes and adsorbents, and is critical in optimizing the use of adsorbent. Two basically used isotherms, the Langmuir and Freundlich which have been extensively used to describe of the adsorption process in different metal-sorbent systems, were used to fit the equilibrium adsorption data in the present study.

The Langmuir isotherm is based on the assumption of monolayer formation of adsorbate on the homogeneous solid surface of the adsorbent. Furthermore, the adsorption sited are having uniform energies, can accommodate at most one adsorbed atom/molecules, and unimportant interaction between the adsorbed adsorbed atom/molecules. The equation of the Langmuir isotherm is represented as:

$$q = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{4.4}$$

where q is the amount of metal ion adsorbed per unit mass of leonardite, $C_e$is the metal ion concentration at equilibrium, q_{max} indicates the maximum adsorption capacity, and $K_L$is a constant relating to adsorption intensity. The linearized from of Eq. (4.4) for determined the constant $q_{max}$and K_L, presented as:

$$\frac{C_e}{q} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \qquad (4.5)$$

The Freundlich isotherm is an empirical equation that used for non-ideal sorption. Moreover, the curve related to the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. The equation of the Freundlich isotherm is represented as:

$$q = K_F C_e^{1/n} \qquad (4.6)$$

where K_F is the Freundlich sorption constant and n is related to adsorption intensity. The constant K_F and n can be determined from a linearized form of Eq. (4.6). represented by:

$$\log q = \log K + \frac{1}{n}\log C_e \qquad (4.7)$$

The calculated Langmuir and Freundlich constants and the corresponding coefficient of correlation values of the three metals are shown in tables 4.4-4.5. The Langmuir constants q_{max} and K_L values can be calculated from the plot between C_e/q_e

versus C_e as well as the Freundlich constants K_F and n can be calculated from the plot of log C_e and log q_e (Figs. 4.12-4.14). From the correlation coefficient (R^2) values for the three metals in table 4.3, found that the experimental data were fitted to both Langmuir and Freundlich isotherms. This related to the satisfactory correlation coefficient that obtained by using the equations of both isotherms. In the case of Zn^{2+}, the adsorption behavior could not be explained by the Langmuir and Freundlich equations in the total of the concentration range studied. In our study, the experimental data fit the Langmuir equation from an equilibrium concentration of 2 mg/L (Fig. 4.13a), and the Freundlich equation approximately from 30 mg/L of an equilibrium concentration (Fig. 4.13b). However, the adsorption data in the linerized forms also gave satisfactory R^2 values for a part of the covered concentration range. Similar results have been reported by Solé *et al* [6].

According to the Langmuir equation, the maximum adsorption capacities for Cu^{2+}, Zn^{2+} and Pb^{2+} were 18.4 mg g^{-1} (0.289 mmol g^{-1}), 9.19 mg g^{-1} (0.141 mmol g^{-1}) and 16.5 mg g^{-1} (0.079 mmol g^{-1}), respectively.

The Langmuir isotherm take place on the surface of the sorbent and at saturation a monolayer is formed. Although this model gives no detail about the mechanism, but it is still used to obtain the uptake capacities of an adsorbent. Moreover one of the essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant separation factor or equilibrium parameter, K_R define as:

$$K_R = \frac{1}{1 + K_L C_i} \tag{4.8}$$

where K_R is a dimensionless separation factor, C_i is initial concentration (mg L^{-1}) and K_L is Langmuir constant (L mg^{-1}). It can be used to predict whether an adsorption system is 'favorable' or 'unfavorable' both in batch process as well as fixed-bed system. The value of K_R indicates the shape of the isotherm to be unfavorable ($K_R > 1$), linear ($K_R = 1$), irreversible ($K_R = 0$) or favorable ($0 < K_R < 1$) [16-18]. U. Faroog*et al.* suggested that K_R values further indicate the order of preference or selectivity for an adsorbent of certain metal ions. This may be helpful to design the experiments for multi-metal adsorption systems [19]. The values of K_R for Cu^{2+}, Zn^{2+} and Pb^{2+} are given in Fig. 4.15.

Table 4.4 Langmuir constants for Cu(II), Zn(II) and Pb(II) isotherm

Metal ions	**Langmuir Isotherm**					
	C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
Cu^{2+}	1.53	2.28	0.672	18.4	0.098	0.9614
	3.38	4.48	0.753			
	5.13	6.83	0.751			
	10.03	8.65	1.16			
	13.65	10.6	1.28			
Zn^{2+}	2.08	0.348	5.97	9.19	0.018	0.9483
	4.54	0.680	6.67			
	9.23	1.29	7.16			
	14.09	1.90	7.43			
	19.51	2.42	8.07			
Pb^{2+}	0.652	2.37	0.275	16.5	0.254	0.9993
	1.52	4.63	0.328			
	2.65	6.51	0.407			
	4.74	8.96	0.529			
	7.58	10.9	0.696			

Table 4.5 Freundlich constants for Cu(II), Zn(II) and Pb(II) isotherm

Metal ions	**Freundlich Isotherm**				
	log C_e	*log* q_e	K_F (mg L^{-1})	*n*	R^2
Cu^{2+}	0.186	0.358	1.87	1.4	0.9690
	0.529	0.652			
	0.710	0.835			
	1.00	0.937			
	1.14	1.027			
Zn^{2+}	1.15	0.278	0.301	1.4	0.9892
	1.29	0.383			
	1.51	0.532			
	1.63	0.653			
	1.77	0.695			
Pb^{2+}	-0.186	0.374	3.33	1.6	0.9857
	0.181	0.665			
	0.424	0.814			
	0.676	0.952			
	0.880	1.04			

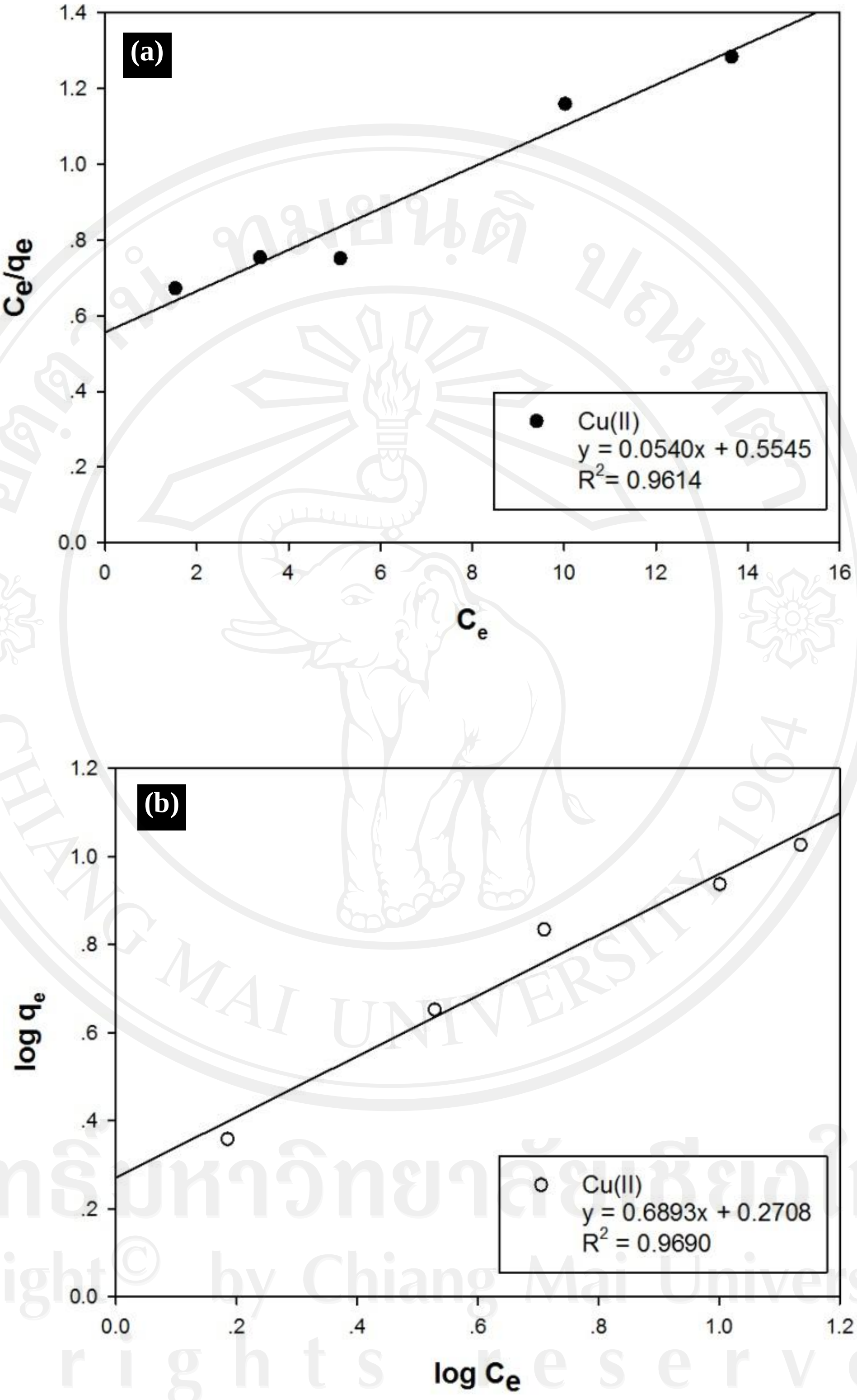

Figure 4.12 Graphical representation

a) Langmuir isotherm of Cu^{2+} b) Freundlich isotherm of Cu^{2+}

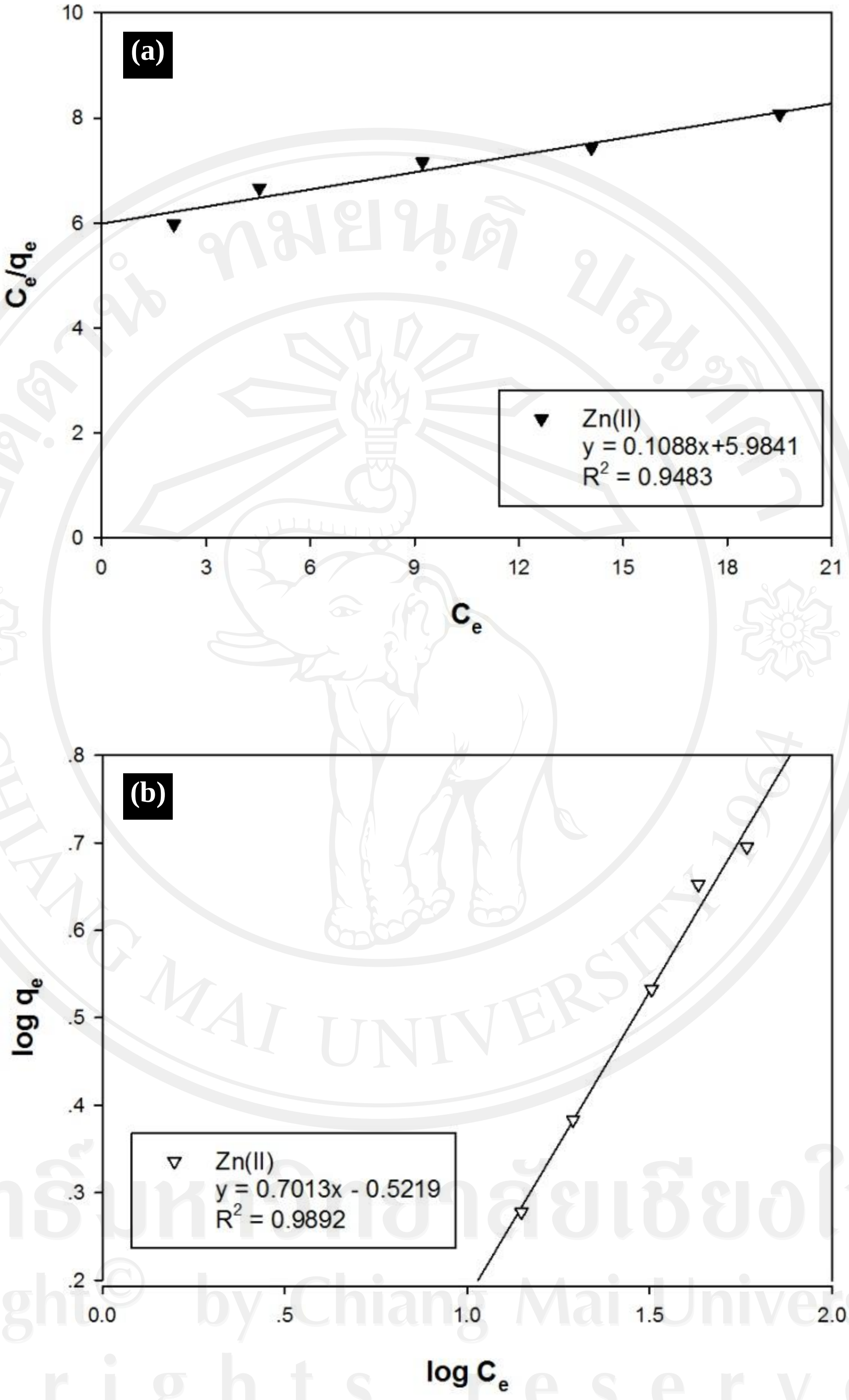

Figure 4.13 Graphical representation

a) Langmuir isotherm of Zn^{2+} b) Freundlich isotherm of Zn^{2+}

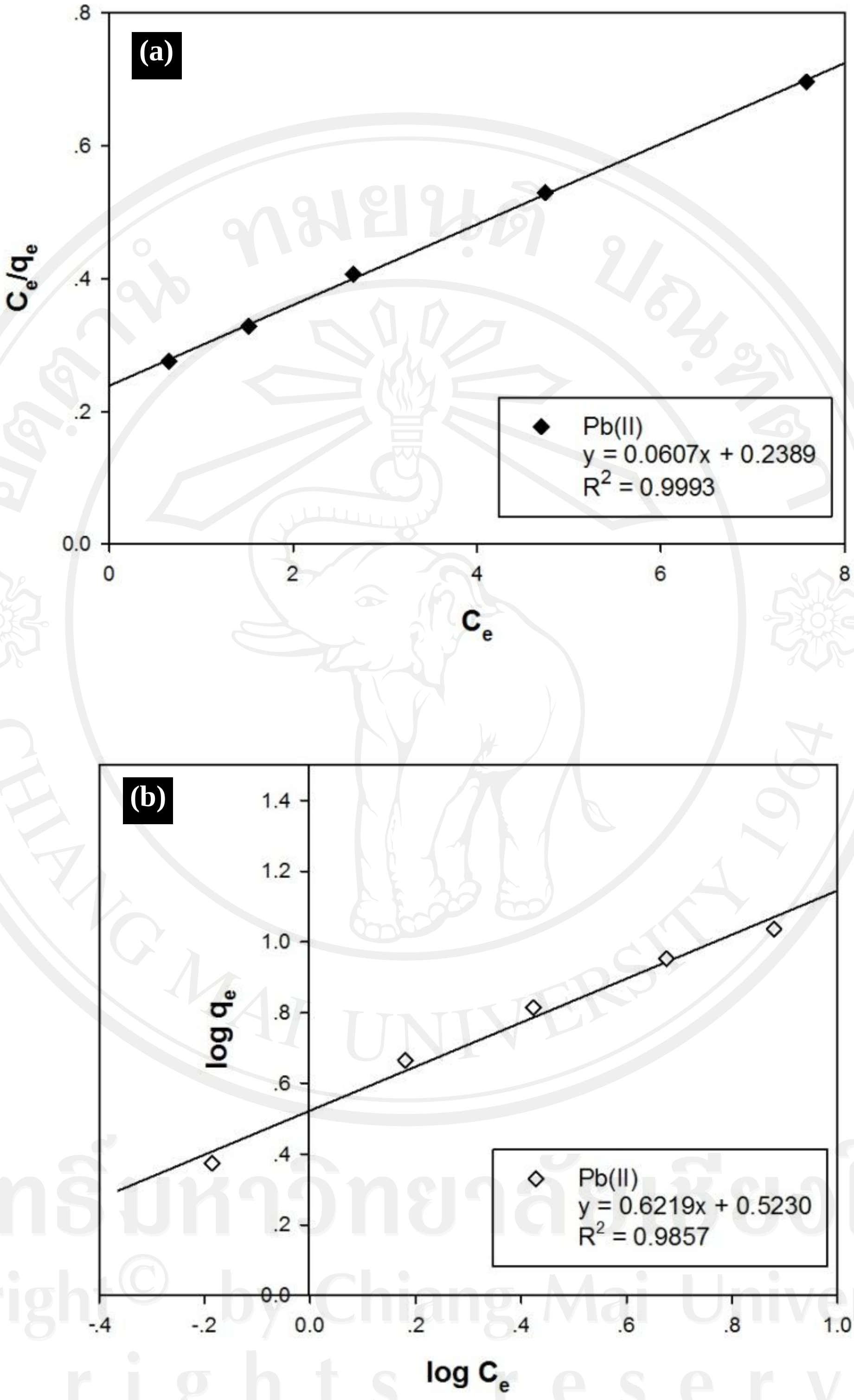

Figure 4.14 Graphical representation

a) Langmuir isotherm of Pb^{2+} b) Freundlich isotherm of Pb^{2+}

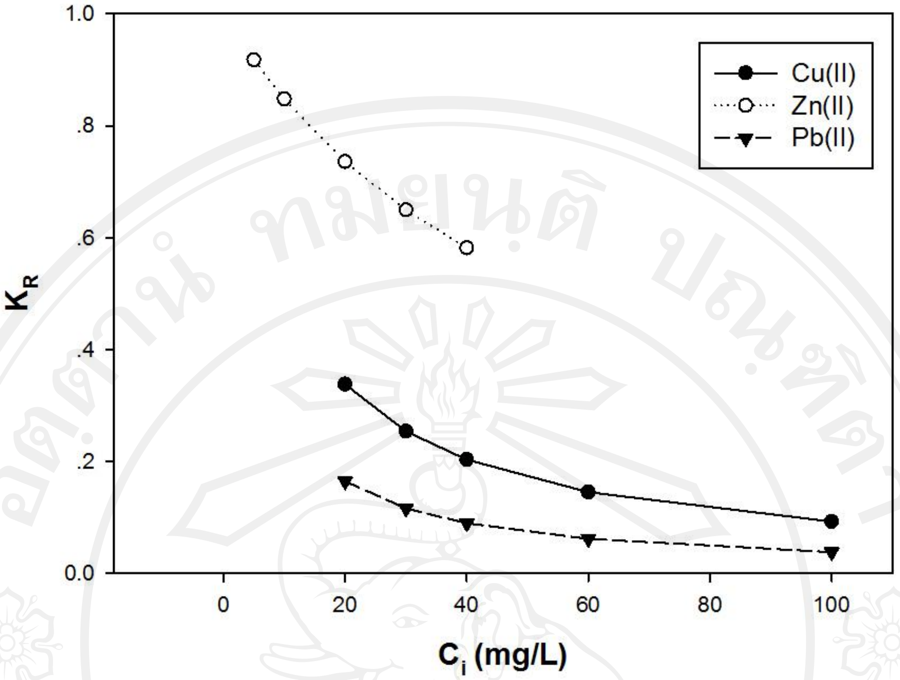

Figure4.15 Plots of K_R versus the initial concentration, C_i, of Cu^{2+}, Zn^{2+} and Pb^{2+}.

The K_R values of the three metals are less than 1 (Fig. 4.15) indicated that the sorption on leonardite is very favorable for $Pb^{2+}$and favorable decreases from $Cu^{2+}$to Zn^{2+}. Hence, the favor ability tends to be in the order of $Pb^{2+}>Cu^{2+}>Zn^{2+}$. The differences adsorption behavior of Cu^{2+}, Zn^{2+} and Pb^{2+} on leonardite could be explained on basis on ionic properties such as electronegativity, ionization potential, ionic potential and ionic radius. Pb^{2+} and Cu^{2+} have the ionic potential and electronegativity higher than Zn^{2+}. It means that the former interact with the active sites on the surface of leonardite strongly than the latter and induces the higher adsorption capacity.

Stevenson and many studied reported that the stability of metal-humic complex (binding strength) order for divalent cation is as follows: Hg >Pb>Cu >Cd ≥ Ni ≥ Zn >Fe(II) >Ca>Mn [20]. The COOH and phenolic OH functional groups represent the active sites of humic substances on the surface of leonardite, and the interaction with metal ions are mostly driven by electrostatic forces. Moreover, the functional groups that containing –N– or –S– donors also display as the active sites for some metal ions binding such as Cd, Zn and Fe [21].

Adsorption reactions can be characterized into outer sphere complexes and inner sphere complexes. Outer sphere complexes occur if at least one solvent (water) molecule is interposed between the surface functional group and the bound ion. They involve electrostatic bonding. Inner sphere complexes are more stable and occur when no molecule of the aqueous solution is interposed and the adsorbing ion forms a direct coordinate covalent bond with surface functional groups on the variable charge surface. The heterogeneous nature of humic substances means that complexation may be regarded as occurring at a large number of reactive sites with binding affinity that ranges from weak forces of attraction (ionic) to formation of stable coordinate inner sphere linkages. As a result, the mechanisms involved in reactions of metal cations with organic matter are complex and probably involve simultaneous chelation, complex formation, adsorption, and coprecipitation. For this reason, they are often described as being "bound" to organic matter. Nevertheless, the high degree of selectivity shown by metals for organic matter reflects the fact that certain metals preferentially coordinate directly with functional groups, forming inner sphere complexes. Generally, those metals that bond most strongly, predominantly as inner sphere complexes (e.g., Pb, Cu), also tend to be most rapidly sorbed and most slowly desorbed. In Fig. 4.16, an example of the complexing of Cu^{2+} to humic material is shown. The Cu was bonded to more than one functional group to form a strongly bound chelated ring structure. Complexing of Pb^{2+} to humic material might be occurred in the same way.

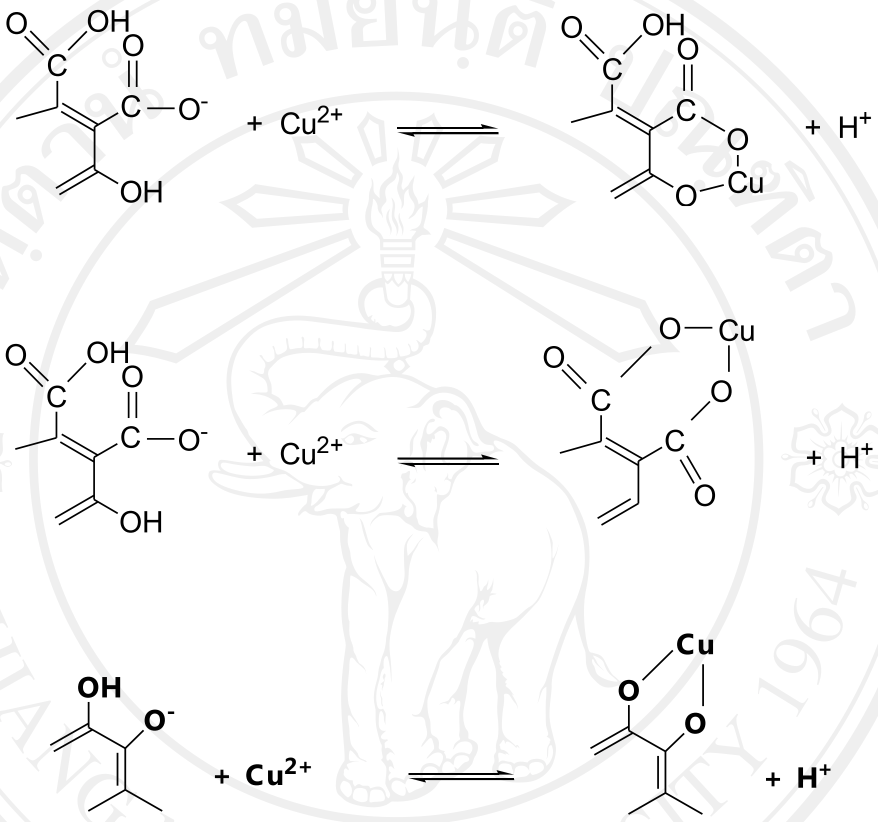

Figure 4.16 Proposed mechanisms for the bonding of Cu^{2+} to humic material

In the case of Zn^{2+}, the complexation of $Zn^{2+}$to humic material can be regarding as occurring at the reactive sites with binding affinities that range from weak forces (i.e., ionic) of attraction to formation of highly stable coordinate linkages. In Fig. 4.17 the structures of types III, IV represent the predominant forms of complexedZn^{2+} when humic material are present in abundance. Binding at the weaker sites (I and II) become increasingly important as the stronger sites become saturated.

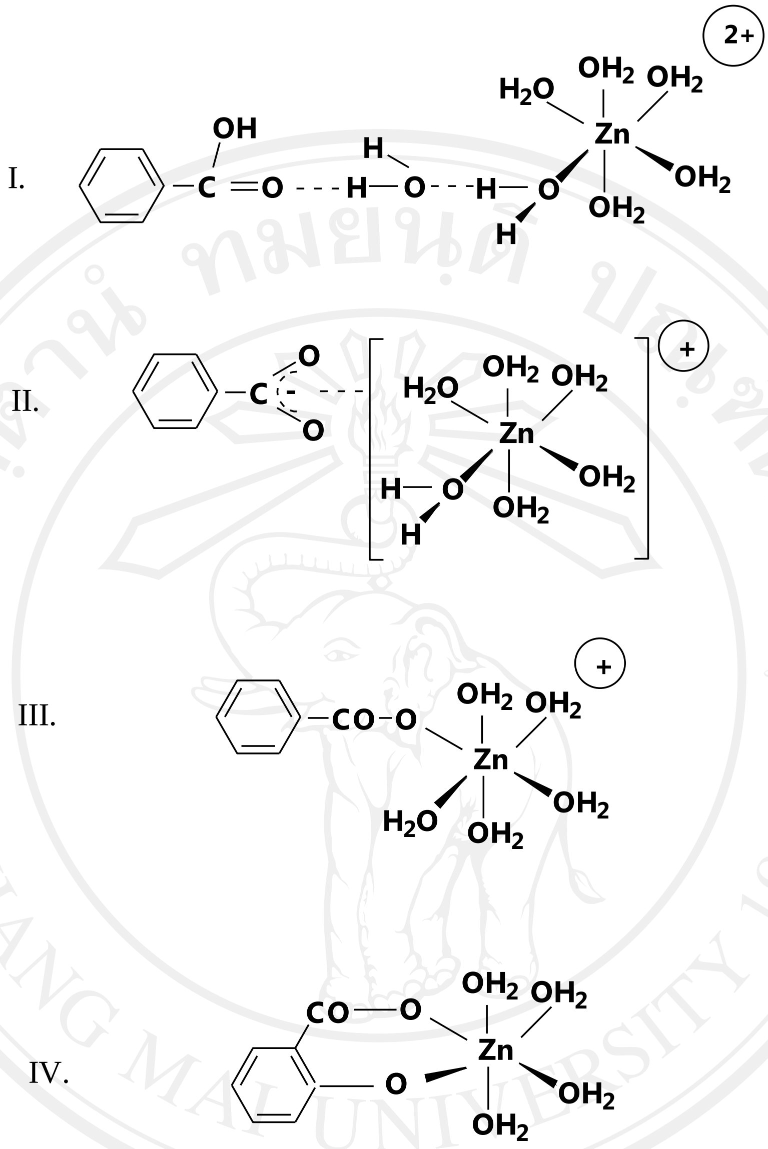

Figure 4.17 The example of Zn^{2+} binding to humic material

In addition, Langmuir equation can be further used to estimate the specific surface area, *S* (m^2 g^{-1}) for the monolayer coverage of the surface by the metal ion on an adsorbent, using the equation as follows:

$$S = \frac{q_{max}NA}{M} \tag{4.9}$$

where S is the specific surface area (m^2 g^{-1} adsorbent), q_{max} is monolayer sorption capacity (mg g^{-1}), N is the Avogrado number (6.02×10^{23}), A is the cross sectional area of metal ion (m^2) and M is the atomic mass of metal [16,19]. For Cu^{2+}, Zn^{2+} and $Pb^{2+}$the specific surface area are calculated and shown in Table 4.6. The maximum specific surface area of leonardite towards Cu^{2+} binding is 2.75 m^2 g^{-1} , Zn^{2+} binding is 1.46 m^2 g^{-1} and Pb^{2+} binding is 2.66 m^2 g^{-1}. The S values of Cu^{2+} and Pb^{2+}shown in Table 4.5 are quite similar. Hydrated radius (0.401, 0.420 and 0.430 nm for Pb^{2+}, Cu^{2+} and Zn^{2+}, respectively), and electronic configuration are main factors affecting sorption capacity. The least sorption for Zn^{2+} can be attributed to its full orbital and largest hydrated radius.

Table 4.6 Specific surface areas for Cu^{2+}, Zn^{2+} and Pb^{2+}

Metal	q_{max} (mg g^{-1}leonardite)	A $(Å)^2$	M	S (m^2 g^{-1})
Cu^{2+}	18.4	1.58	63.55	2.75
Zn^{2+}	9.19	1.72	65.38	1.46
Pb^{2+}	16.5	5.56	207.30	2.66

The Freundlich isotherm is an empirical equation that involved the sorption on a heterogeneous surface. It represented the sorption over a limited concentration range [17]. The result (table 4.5) shows that the n value is greater than unity for the three metals (n = 1.4 for Cu^{2+}, n = 1.4 for Zn^{2+} and n = 1.6 for Pb^{2+}) indicating that these three metals are favorably adsorbed on leonardite. The magnitude of Freundlich constant, *n* indicates easy remove of Cu(II), Zn(II) and Pb(II) from aqueous solution.

The most of heavy metal sorption on heterogeneous sorbents has been interpreted by the aid of both isotherms on various occasions in the environmental literature. However, sometime the data obtained from the metal sorption experimental may be did not always fit these isotherms. Therefore, the application of these isotherms should be careful about the limit of the mathematical representation and the mechanistic inferences [15]. Moreover, it is difficult for the explanation clearly about mechanism of the adsorption reaction of metal ion on heterogeneous sorbent, because of the comprising of various functional groups or active sites on the surface of the sorbent.

4.3 The adsorption behaviors of methylene blue on leonardite

The adsorption behavior of methylene blue on leonardite using the batch system is expressed in the form of equilibrium concentration, C_e, versus adsorbed concentration, q_e, of the solute, and the adsorbed amount, q_e, was calculated same as in 4.2. Whereas, the relationship between the adsorbed and equilibrium concentrations was predicted by using the Langmuir and Freundlich isotherm equation for evaluation the adsorption potential of leonardite for the removal of methylene blue from aqueous solution.

4.3.1 Effect of contact time

In this study, the sorbent leonardite was prepared into 2 types namely, type I is washed leonardite (used water for washing, and dried at 100 °C over night) and type

II is unwashed leonardite, and the results were compared from both types of leonardite, the better one was applied for use in the further studies.

For the study on the equilibrium time of adsorption of methylene on leonardite, the experimental were carried out by shaking 0.400g of leonardite(two types of leonardite) in 50.00 mL of 60.00 and 110.0mg/L methylene blue solution at 130 rpm at room temperature. At the end of the shaking period (10, 20, 30, 40, 50, 60, 120, 180, 240 and 300 minutes, respectively) the suspension was filtered by using a 0.2 μm nylon filtered, and the remaining concentrations were determined by UV-Vis spectrophotometer.

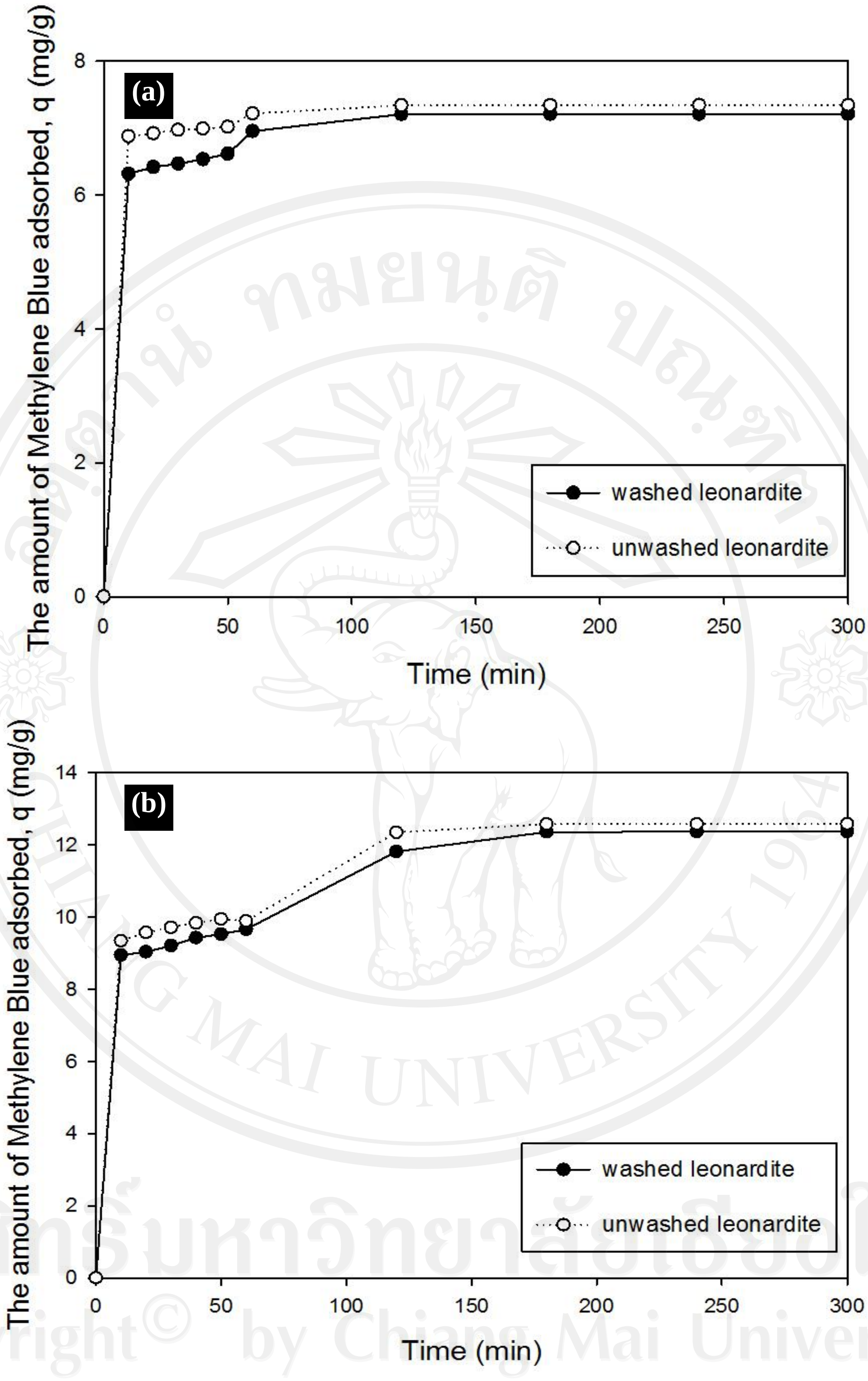

Figure 4.18 Adsorbed amount vs. time for methyleneblue at the two initial concentrations a) 60.00 mg/L b) 110.0 mg/L (using the two types of leonardite)

In Fig. 4.18 a) indicated that the adsorption of methylene blue on leonardite was found to reach equilibrium from 60 min for methylene blue initial concentration 60.00 mg/L. While at higher initial concentration (110.0 mg/L in 4.18 b)), the time necessary to reach equilibrium was after 60 min. The experimental data were measured at 90 min to be sure that full equilibrium was attained, and easy to observe the color of methylene blue.

It can be seenin Fig. 4.18 a) and b) which show the comparison of the results from using the two types of leonardite, namely washed and unwashed leonardite at both initial methylene blue concentrations, respectively. As can be seen, the amount of methylene blue adsorbed when used unwashed leonardite was higher than the results of washed leonardite, may be due to the compositions of leonardite that affect to the adsorption. In general, solutions of methylene blue are blue when in an oxidizing environmental, but will turn colorless if exposed to a reducing agent. Leonardite consists of several components, such as inorganic and organic parts that may be affected to the adsorption behavior on leonardite. It contains a high content of acidic functional groups as a reducing agent that can make the disappearance of methylene blue color.

Therefore, in the next experimental, the washed leonardite was selected to be adsorbent. Prior to the experiment, leonardite was washed by water to remove some reducing agent functional groups, in order to reduce the effect of this group with the colorless of methylene blue.

4.3.2 Effect of pH

In this work, the effect of initial pH on equilibrium uptake of leonardite was studied at 60.00 and 110.0 mg/L initial methylene blue concentration, pH range of 2-7 and shaken until 90 min, to investigate the optimum pH for the removal of methylene blue.

The blank solution showed that no any color leached from leonardite and the color of methylene blue not changed when adjusted to pH 2-7. Fig. 4.19 a) and b) show the results of % methylene blue removal and the amount of methylene blue adsorbed in the range of pH studied, at the two initial concentrations. It can be concluded that, even thoughthe sorption of methylene blue gradually increased with pH in the pH ranges of 2-7,the pH did not have much effect on the adsorption of methylene blue on leonardite.

Generally, the pH of methylene blue solutions is approximately 4.5. Therefore, solutions at non-adjusted pH (4.5-4.8) could be used for the next experimental tests.

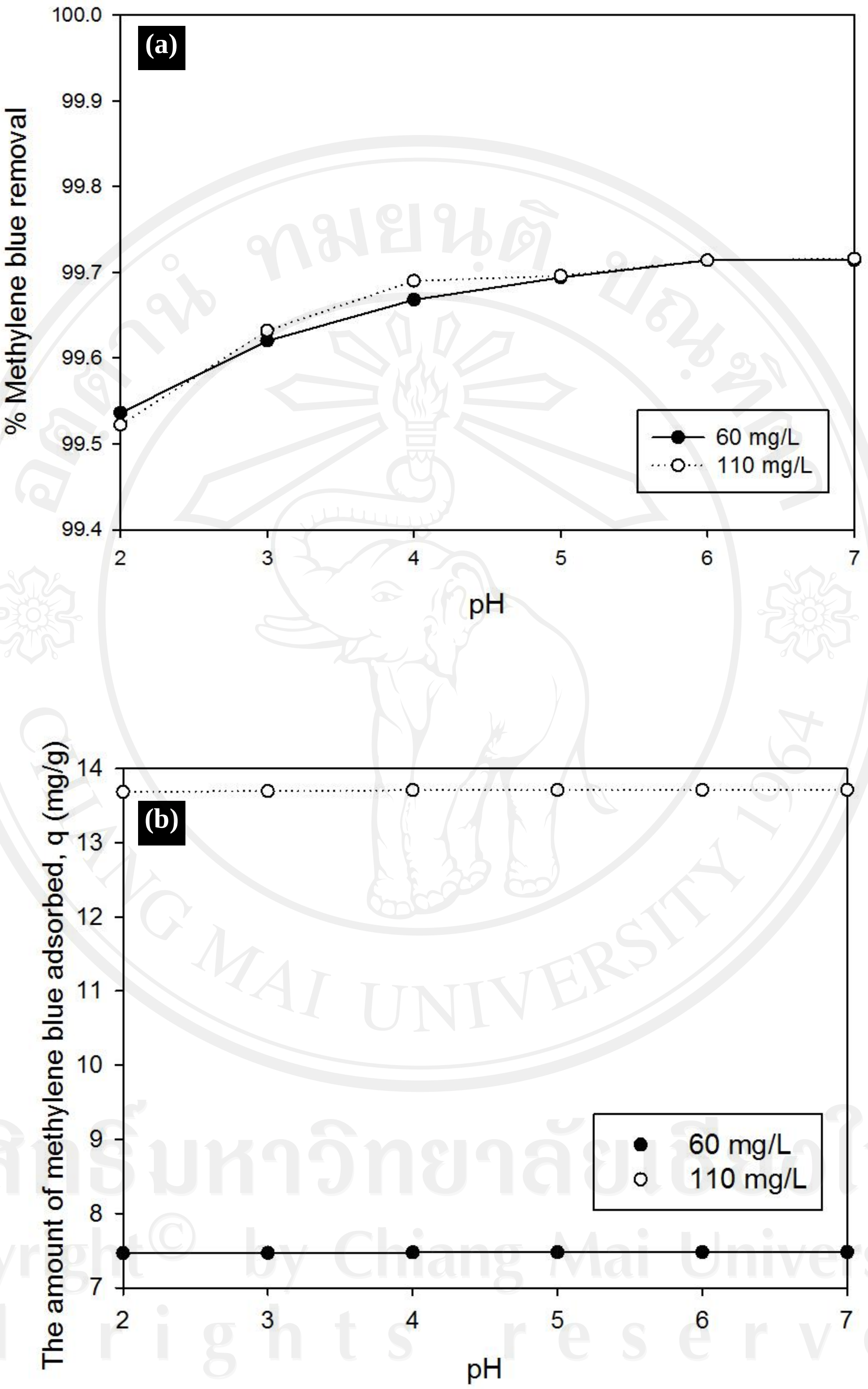

Figure 4.19 Effect of pH on methylene blue onto leonardite

(a) % methylene blue removal(b) the adsorbed amount of methylene blue

4.3.3 Effect of leonardite quantity

For the study on the leonardite quantity for adsorption of methylene blue onto leonardite, the experiment was carried outby using the initial concentrations of 60.00 and 110.0 mg/L of methylene blue with different leonardite dosages (in the range of 0.200 to 3.00 g). Fig. 4.20a) shows the removal of methylene blue as a function of adsorbent dose. Increased in adsorbent dose slightly increased the removal percentage of methylene blue, especially at the initial concentration 110.0 mg/L in which the removal percentage of methylene blue increased from 95 to 99, when adding the amount of leonardite more than 0.200 g.

The increase in %removal was due to the increase of the available sorption surface and availability of more adsorption sites. A similar behavior was reported for the adsorption of methylene blue on papaya seeds [75], jackfruit peels [69] and Tuberose Sticks [76]. Whereas, Fig. 4.20 b) shows the amount of methylene blue adsorbed in the range of leonardite dosage studied. It was found that when the amount of leonardite increased, the amount of methylene blue adsorbed per gram of leonardite decreased.

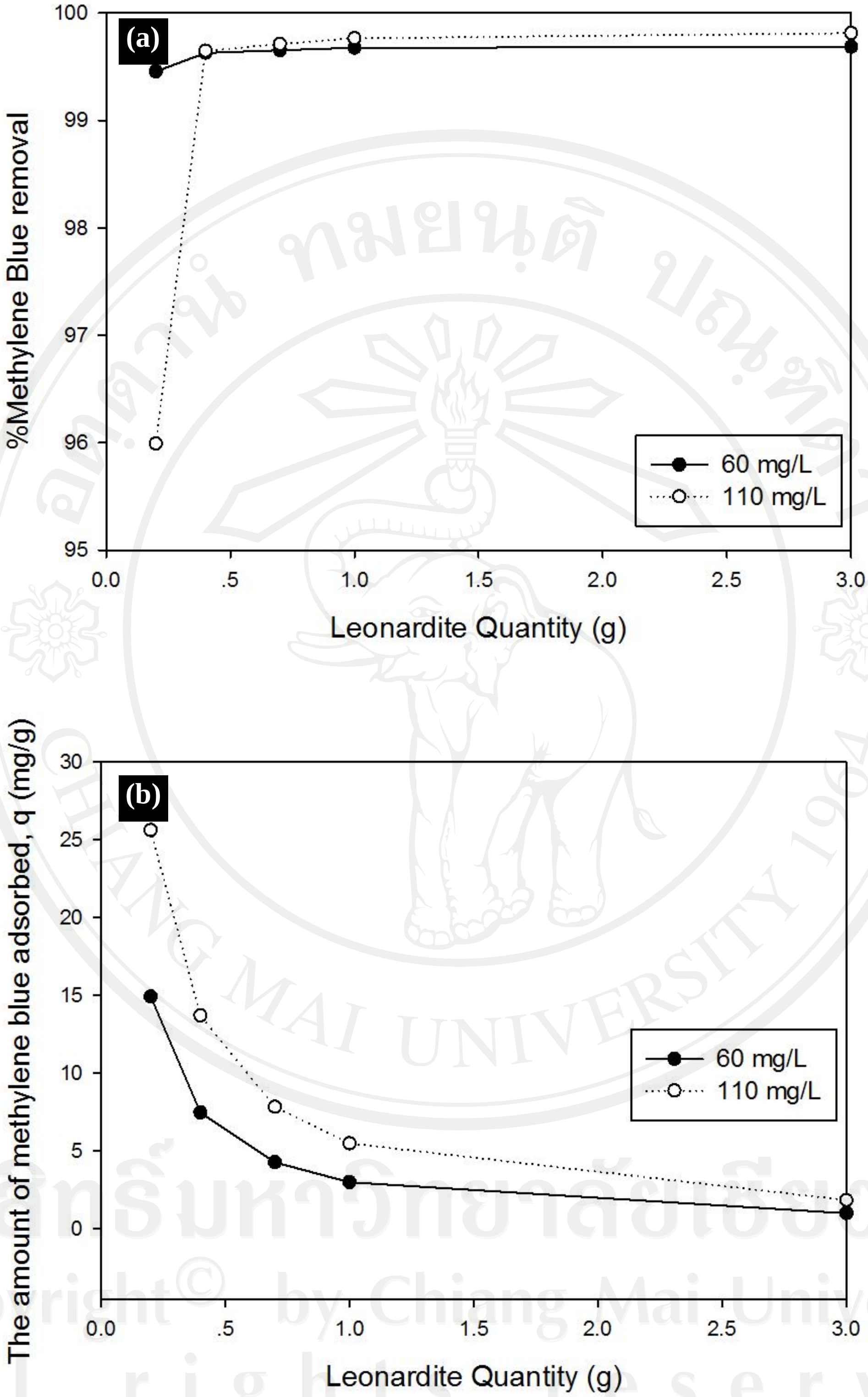

Figure 4.20 Effect of leonardite quantity on methylene blue onto leonardite at the two concentration

a) %methylene blueremoval b) the adsorbed amount of methylene blue

4.3.4 Sorption equilibrium: adsorption isotherms

In order to establish the most appropriate correlations for the equilibrium data in the design of adsorption system, two common isotherm models were tested: the Langmuir and Freundlich models. The applicability of the isotherm equations was compared by judging the correlation coefficients, R^2. For the adsorption isotherms, the experiment was investigated for the initial of methylene blue concentrations ranging from 60.00 to 200.0 mg/L, using the equilibrium time at 90 minutes. Fig. 4.21 shows the adsorption isotherm of methylene blue calculated from equation 1.4.

In this work, the equilibrium data for methylene blue on leonardite were modeled with both the Langmuir and Freundlich isotherms. The linear plot of C_e/q_e against the equilibrium concentration (C_e) (Fig. 4.22 a)) shows that the adsorption fitted the Langmuir model. The Langmuir constants q_{max} and $K_L$were determined from the slope and intercept of the plot and are presented in Table 4.7. The equilibrium data were further analyzed using the linearized form of Freundlich isotherm, by plotting log q_e and log C_e (Fig. 4.22 b)). The calculated Freundlich isotherm constants and the corresponding coefficient of correlation are shown in Table 4.8.

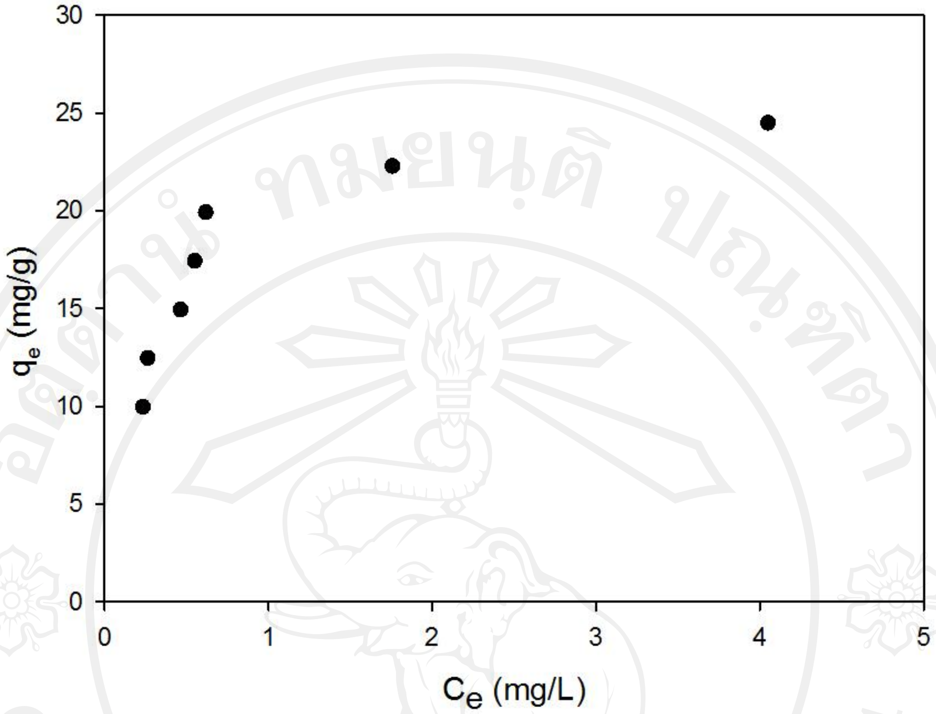

Figure 4.21 Adsorption isotherm of methylene blue on leonardite at room temperature

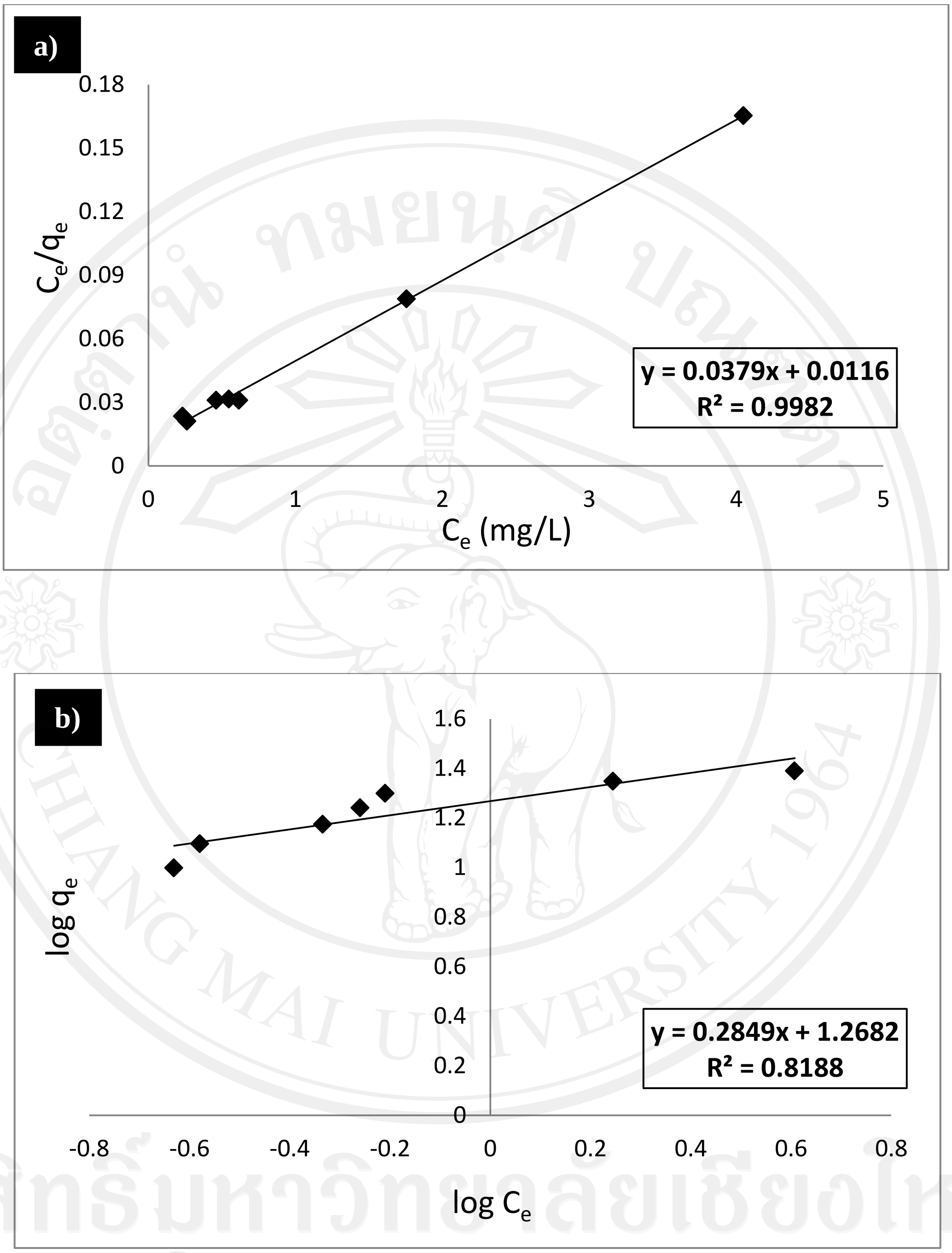

Figure 4.22 Graphical representation of methylene blue on leonardite

a) Langmuir isotherm b) Freundlich isotherm

Table 4.7 Langmuir isotherm for methylene blue adsorption on washed leonardite

Langmuir Isotherm					
C_e (mg L^{-1})	q_e (mg g^{-1})	C_e/q_e (g L^{-1})	q_{max} (mg g^{-1})	K_L (g^{-1}mg)	R^2
0.234	9.97	0.024	26.4	3.3	0.9982
0.264	12.47	0.021			
0.463	14.94	0.031			
0.550	17.43	0.032			
0.617	19.92	0.031			
1.76	22.28	0.079			
4.05	24.49	0.165			

Table 4.8 Freundlichisotherm for methylene blueadsorption on washed leonardite

Freundlich Isotherm				
$\log C_e$	$\log q_e$	K_F (mg L^{-1})	n	R^2
-0.631	0.999			
-0.579	1.10			
-0.334	1.17	18.5	3.5	0.8188
-0.260	1.24			
-0.210	1.30			
0.118	1.32			
0.245	1.35			
0.290	1.37			
0.607	1.39			

From the essential characteristics of the Langmuir isotherm, the dimensionless constant separation factor, K_R that can be calculated from equation 4.8. For methylene blue, the values of K_R are shown in Fig. 4.23.

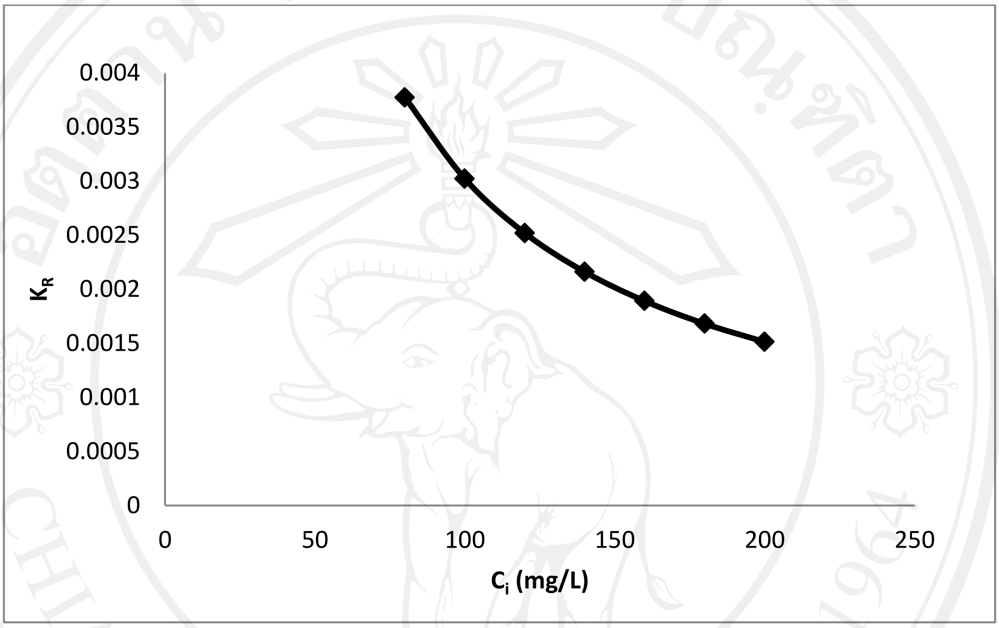

Fig. 4.23 Plot of K_R versus the initial concentration, C_i of methylene blue

The value of the coefficient of correlation (R^2 = 0.9982) obtained from Langmuir expression indicates that Langmuir expression provided a better fit to the experimental data of Methylene blue on leonardite. The maximum adsorption capacity for methylene blue was 26.4 mg g^{-1} (0.082mmol g^{-1}). It can also be concluded that, from Table 4.7, the Freundlich constants, *n*, indicating that methylene blue is favorably adsorbed on leonardite. This is in great agreement with the findings regarding to K_R value. The K_R value for the adsorption of methylene onto leonardite was less than 1 (Fig. 4.23), indicating that the adsorption was a favorable process.

The Langmuir isotherm model was more suitable for the experimental data than the Freundlich isotherm because of the high value of correlation coefficient (R^2 = 0.9982). This indicates that adsorption of methylene blue on leonardite might take place as monolayer adsorption on the surface of leonardite. The interaction between dye molecules and the active site of leonardite possibly might be a weak force of attraction (i.e., ionic or electrostatic attraction) shown in Fig. 4.24.

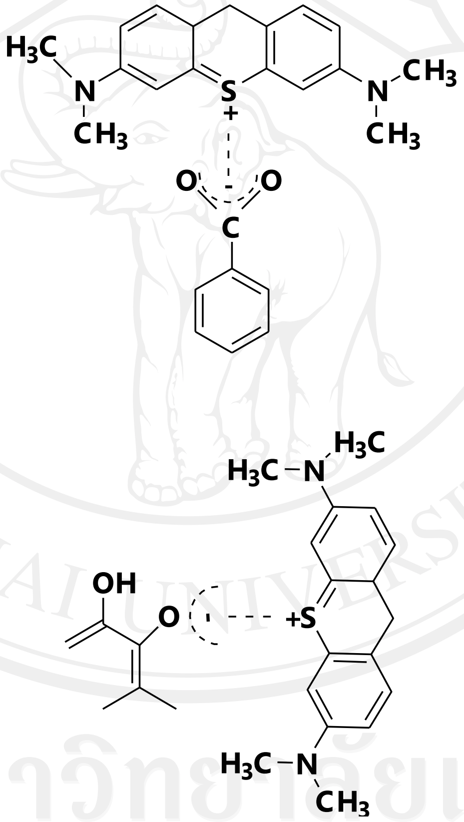

Figure 4.24 Proposed interaction of methylene blue to the surface of leonardite