

CHAPTER V

SORPTION CAPACITY OF SOIL FOR HEAVY METALS IN KHAM BON LANDFILL LEACHATE

5.1 Characteristics of Selected Samples

5.1.1 Selected Soil Samples

Three subsurface soil samples; namely KBS-1; KBS-2 and KBS-3 collected from the Kham Bon landfill site and adjacent area on the basis of their physical and chemical properties are shown in Figure 5.1. Table 5.1 lists the basic properties of the three soils selected herein. KBS-1 soil is a silty clay loam (SiCL) having a pH value of 7.3. Its cation exchange capacity is $17.8 \text{ cmolc kg}^{-1}$, which is the highest among all samples. KBS-2 is sand (S) with a pH value of 6.3. Its CEC is $1.5 \text{ cmolc kg}^{-1}$, which is the lowest of all samples. KBS-3 is alkaline loamy sand (LS) soil with a pH value of 8.3 in which the CEC is $2.2 \text{ cmolc kg}^{-1}$. The background heavy metal concentrations from the three soils were found to be very low except Mn and Fe as shown in Table 5.2.

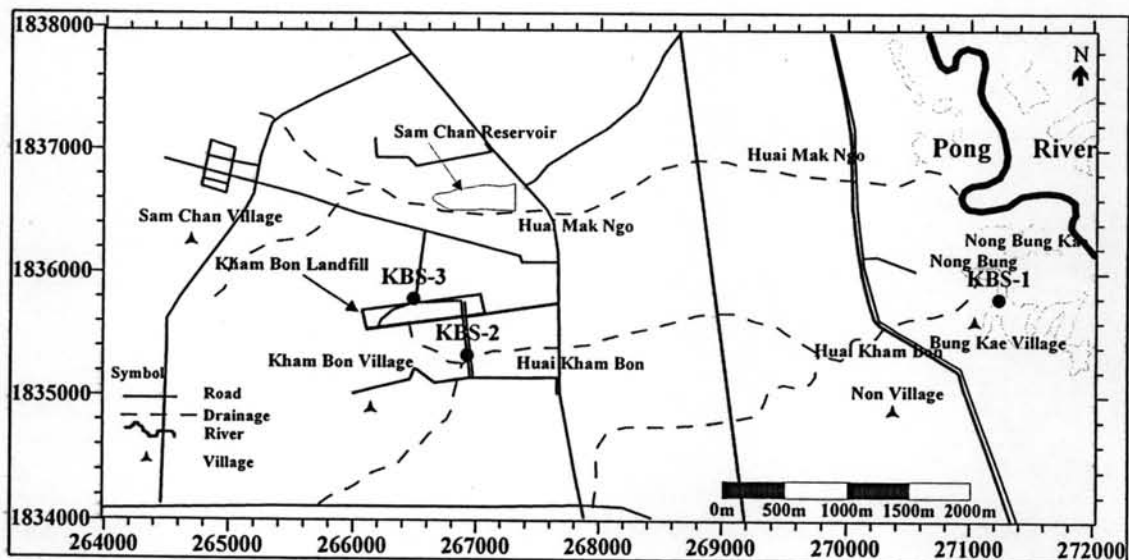


Figure 5.1 Locations of three selected soil samples in the study area for sorption experiment

Table 5.1 Physical and chemical properties of soil collected from landfill site and its vicinity

	Properties	KBS-1	KBS-2	KBS-3
Physical	Texture	siCL	S	LS
	Sand (%)	16.8	93.3	85.3
	Silt (%)	45.7	4.4	10.1
	Clay (%)	37.5	2.3	4.6
	Total Porosity	0.36	0.40	0.39
	Bulk Density (g cm ⁻³)	1.70	1.58	1.62
	Al ₂ O ₃ (%)	26.13	19.43	19.17
	Fe ₂ O ₃ (%)	5.47	2.01	0.97
	MnO (%)	0.31	0.02	0.05
	Clay type	Kaolinite, illite	Kaolinite, illite	Kaolinite, illite
Chemical	pH	7.3	6.3	8.3
	EC (μS/cm)	79	23	743
	OM (%)	1.27	0.19	0.67
	CEC (cmolc kg ⁻¹)	17.78	1.48	2.24

Table 5.2 Background concentration of heavy metals in soil samples

Sample No.	Heavy metals concentration (mg kg ⁻¹ of soil)						
	Mn	Fe	Zn	Cu	Pb	Cd	Cr
KBS-1	302.96	890	24.19	9.39	14.26	0.00	14.71
KBS-2	21.63	370	2.03	1.25	5.64	0.00	2.31
KBS-3	51.50	750	25.40	6.30	5.46	0.00	8.44

5.1.2 Landfill Leachate

The leachate used for batch sorption and column test was collected from the leachate collection pond (called as INF in the previous chapter) of the Kham Bon landfill in operation and inhibited with sodium azide (NaN₃ 0.1% arbitrarily) to suppress the biological activity at site. The leachate samples were stored at 4 °C prior to analysis. Table 5.3 lists the chemical characteristic of landfill leachate.

5.2 Sorption Isotherms: Batch Experiments

The sorption of five heavy metals (Cd, Cr, Pb, Cu and Zn) prepared as the solution of monometal and mixed metals with varied concentrations of the actual leachate and the synthetic leachate were studied to compare the sorption efficiency.

Since the soil used for adsorption was directly taken from the landfill site, it would indicate the adsorption reliability of heavy metal contained in landfill leachate onto soil. It is also simplified to predict the solute transport in the landfill site and its vicinity. This experiment was achieved under an initial pH 8.16 of leachate determined directly at the Kham Bon landfill site. The sorption experiment was fixed at temperature of 25 °C and suppressed micro-biological degradation in landfill leachate by sodium azide preserving for all experiments. As anticipated, the amount of metal adsorption was determined by the sorption capacity of the soil, and the selectivity of different soil for different metals ions (Appendix A).

Table 5.3 Chemical characteristics of influent leachate taken from Kham Bon landfill for batch sorption and column experiments

Parameters	Influent leachate
pH	8.16
Conductivity (mS cm ⁻¹)	12.46
TDS (mg L ⁻¹)	8,910
COD (mg L ⁻¹)	4,116
BOD (mg L ⁻¹)	333
TOC (mg L ⁻¹)	1,290
Na (mg L ⁻¹)	3,320
K (mg L ⁻¹)	2,996
Ca (mg L ⁻¹)	832
Mg (mg L ⁻¹)	354
Cl (mg L ⁻¹)	4,422
CO ₃ (mg L ⁻¹)	480
HCO ₃ (mg L ⁻¹)	4,800
SO ₄ (mg L ⁻¹)	47.12
NO ₃ (mg L ⁻¹)	21.21
Fe (mg L ⁻¹)	9.8
Mn (mg L ⁻¹)	0.63
Total Cr (mg L ⁻¹)	3.42
Cd (mg L ⁻¹)	not detected
Pb (mg L ⁻¹)	0.03
Cu (mg L ⁻¹)	0.19
Zn (mg L ⁻¹)	0.51

The sorption isotherms are determined to accomplish for two purposes. The first purpose is to determine the partitioning coefficient or distribution coefficient, K_d , which is used to compare the behavior of contaminants in different soils under the

same experimental conditions. The distribution coefficient is obtained from the Linear isotherm. The second purpose is to evaluate the sorption capacity of heavy metals by different soils. This sorption capacity is obtained by the application of Freundlich and Langmuir equations. The equilibrium adsorption data obtained are fitted to linearly transform equations. Goodness of fit is assessed by the coefficient of determination (R^2).

5.2.1 Determination of Distribution Coefficient

The Linear isotherm is evaluated by plotting q (mg kg^{-1}) versus C_e (mg L^{-1}) and the distribution coefficient (K_d) is obtained. The distribution coefficient K_d , the slope of a simple Linear model, is often used to characterize the mobility of trace metals in aquatic environments. The low K_d value implies that the metal remain in solution, and the high K_d value indicates that the metal has great affinity to soil (Anderson and Christensen, 1988; Christensen, 1989; Echeverría et al., 1998; Sastre et al., 2006). The distribution coefficient of an ion is one of the variables that should be known to solve the mass transport equation (mentioned in Chapter 2) for the estimation of the retardation, R_f , which is derived from the relationship of

$$R_f = 1 + \frac{\rho_b K_d}{n} \quad (5.1)$$

where ρ_b is the dry bulk density (g cm^{-3}) and n is the dimensionless kinematic porosity of the medium.

5.2.1.1 Monometal Isotherm

Adsorption isotherms of five heavy metals of actual and synthetic leachates in three soils are displayed in Figures 5.2 to 5.3. Table 5.4 summarizes the results of Linear isotherm analysis including distribution coefficient and coefficient of determination (R^2). Moreover, isotherm shapes of different heavy metals in different soils were also characterized. These various isotherm shapes provide information on the strength by which the sorbate is held onto the soil (Sposito, 1989).

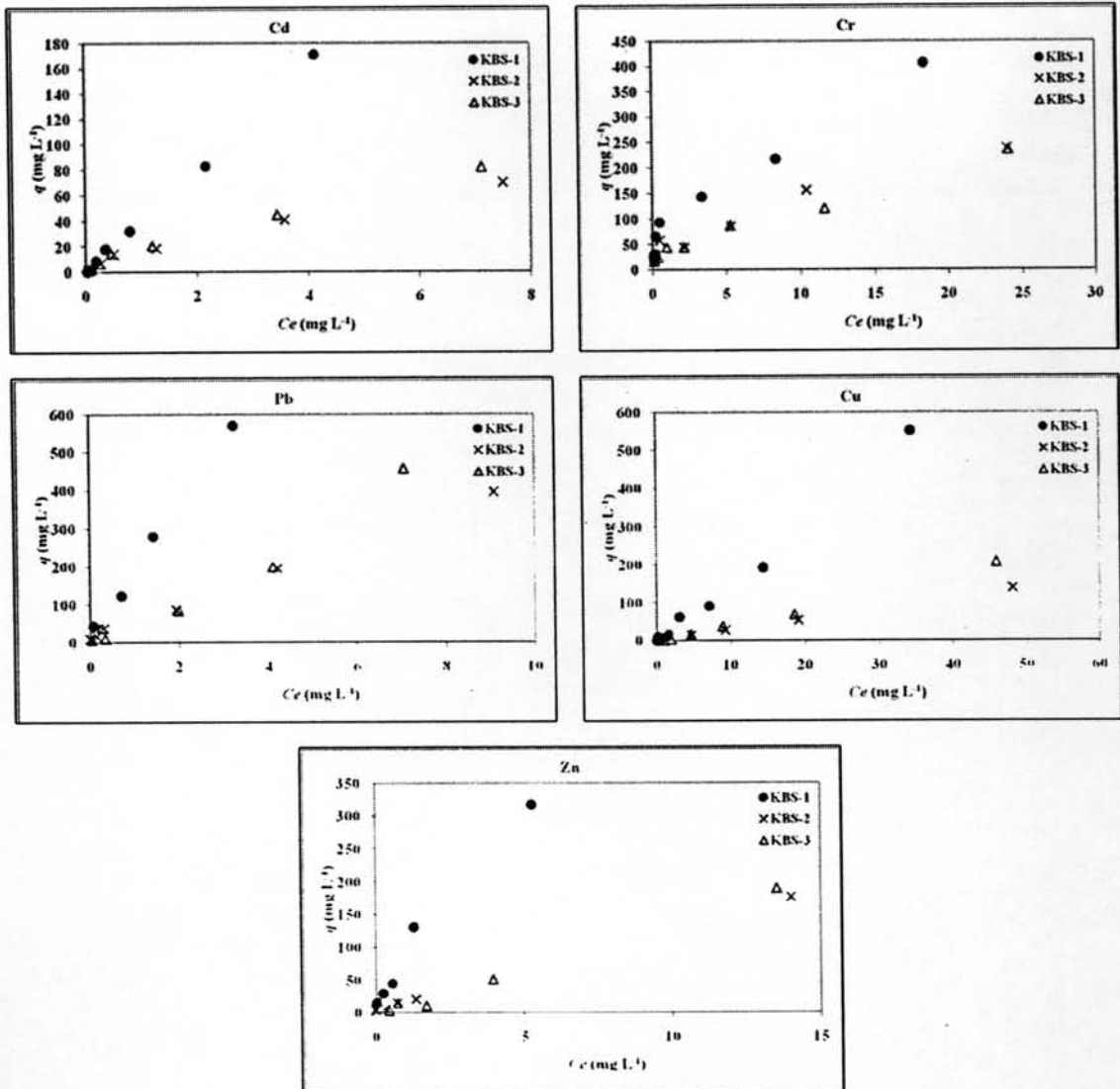


Figure 5.2 Monometal sorption isotherms at 25 °C with initial pH 8.16 for retention of Cd, Cr, Cu, Pb and Zn by three soils treated with actual leachate: KBS-1, KBS-2 and KBS-3

Monometal sorption isotherms for Cd, Cr, Pb, Cu, and Zn by three soils exhibited different in shape and in the amount retained. According to the suggestion of Alloway (1995b) that there are two adsorption sites: (a) high affinity sites belong to the short metal retention time which are responsible for metal sorption at low added metal concentrations, and (b) low affinity sites describe the long retention time which are responsible for the higher added metal concentration.

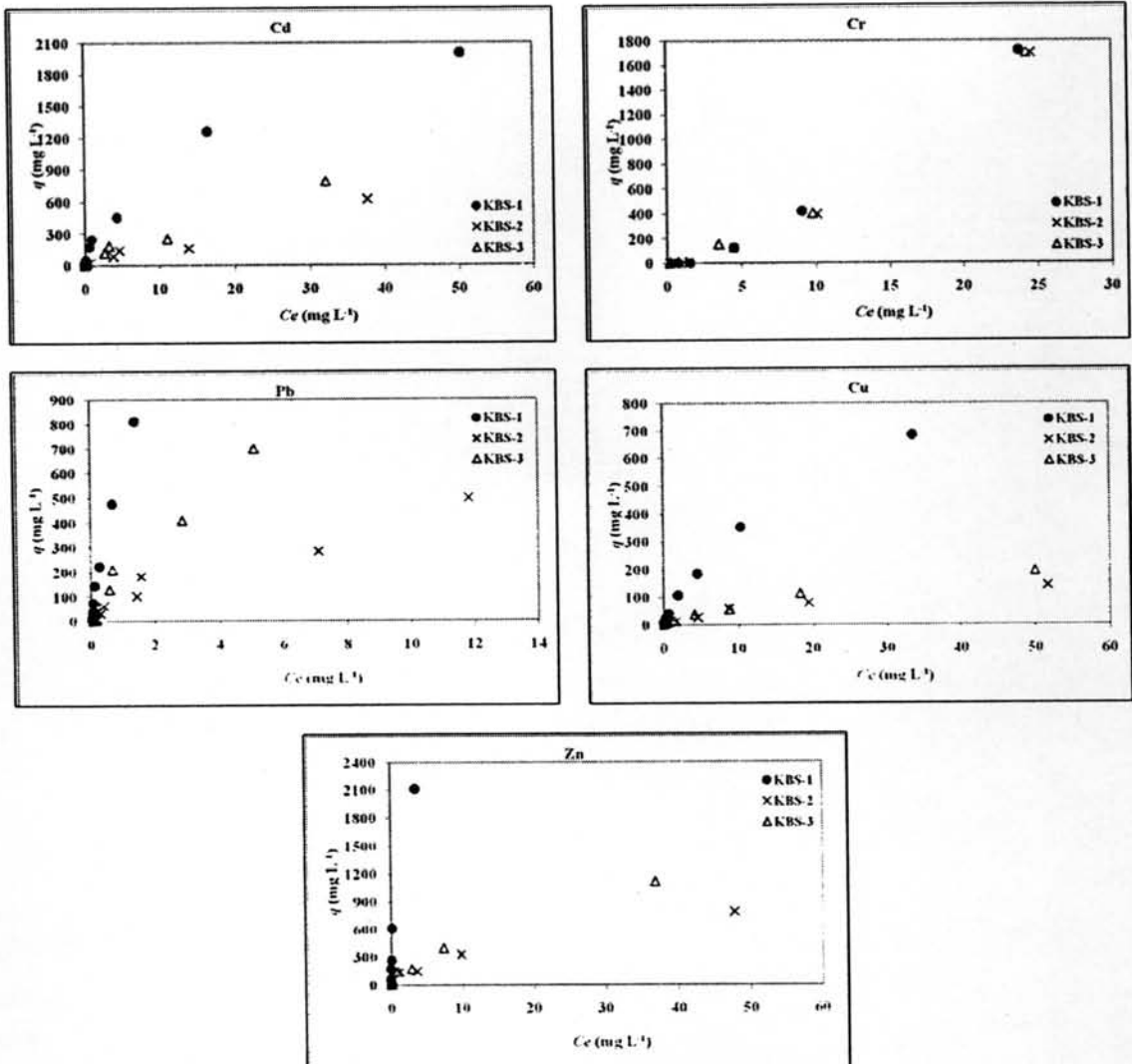


Figure 5.3 Monometal sorption isotherms at 25 °C with initial pH 8.16 for retention of Cd, Cr, Cu, Pb and Zn by three soil treated with synthetic leachate: KBS-1; KBS-2 and KBS-3

From Figures 5.2 and 5.3, these isotherms tended to be rectilinear at equilibrium solution concentration lower than 2 mg L⁻¹ whereas at the higher concentration curvilinear isotherms were obtained. Thus, an *S-type* isotherm was generally observed in this experiment. An *S-type* isotherm is characterized by an initially small slope that increases with adsorbate concentration. This behavior had been already observed in the previous research on lead adsorption onto Kaolinite from a landfill leachate of similar composition (Majone et al., 1993; 1998). They reported

that an *S-shaped* isotherm was found operating in a larger concentration range. The occurrence of an *S-shape* isotherm has been interpreted as being due to the presence of cooperative adsorption or to the presence of competitive effects of other solutes (Sposito, 1989; Hinz, 2001; Limousin et al., 2007). Lead and zinc in KBS-1 soil treated with synthetic leachate exhibited a *L-type* isotherm (Figure 5.3) characterized by an initial slope that did not increase with the concentration of adsorbate in the soil. (Sposito, 1989; Hinz, 2001; Limousin et al., 2007).

The magnitude of K_d value obtained from monometal sorption treated in actual (Table 5.4) ranged from 3.3 L kg⁻¹ for Cu sorption of KBS-2 soil to 97.9 L kg⁻¹ for Pb isotherm of KBS-1 soil. The KBS-1 soil preferentially adsorbed and retained zinc (97.7 L kg⁻¹), followed by lead (79.5 L kg⁻¹) and exhibited least preference of cadmium and copper. The KBS-2 soil preferential adsorbed and retained lead (33.8 L kg⁻¹) and followed by zinc (11.7 L kg⁻¹). Cadmium (9.9 L kg⁻¹) and copper (3.3 L kg⁻¹) were the least preference sorbed and retained. The KBS-3 soil exhibited the same as KBS-2 soil but higher in amount of heavy metals retained. The values of K_d were noticed higher in KBS-1 than KBS-2 and KBS-3 soils. The K_d in soil treated with actual leachate decreased in the order of Zn > Pb > Cr > Cd > Cu of KBS-1 soil; Pb > Zn > Cr > Cd > Cu of KBS-2, and Pb > Zn > Cd > Cr > Cu of KBS-3 respectively. In monometal sorption of heavy metals in soil treated with synthetic leachate, the magnitude of K_d values varied from 4.3 L kg⁻¹ for Cu isotherm of KBS-2 to 600 L kg⁻¹ for Pb isotherm of KBS-1 soil. The highest retention of heavy metals in KBS-1 soil was lead (600 L kg⁻¹), followed by zinc (189 L kg⁻¹). Cadmium (43.8 L kg⁻¹) and copper (35.9 L kg⁻¹) showed the lowest sorbed heavy metals. The KBS-2 and KBS-3 soil were exhibited in the same manner of selectivity of sorbed metals but different in the amount of heavy metal retained. Lead was more retained in these soils, followed by chromium whereas the lowest of sorbed metals were zinc and cadmium. The higher K_d was observed in KBS-1 than KBS-3 and KBS-2 soil. The K_d value of Cr in all soils should be taken into account due to the lowest ($R^2 < 0.9$) of coefficients of determination. The selectivity order of K_d values fell in the order of Pb > Zn > Cr > Cd > Cu of KBS-1; Pb > Cr > Cd > Zn > Cu of KBS-2 and Pb > Cr > Cd > Zn > Cu of KBS-3. The higher K_d was observed in KBS-1 than KBS-3 and KBS-2 soil.

Table 5.4 Linear isotherm parameters of KBS-1, KBS-2 and KBS-3 soil induced from monometal sorption solution at 25 °C with initial pH 8.16

Properties		Linear Isotherm			
Sample No.	Metals	Soil treated with actual leachate		Soil treated with synthetic leachate	
		<i>Kd</i> (L kg ⁻¹)	<i>R</i> ²	<i>Kd</i> (L kg ⁻¹)	<i>R</i> ²
KBS-1	Cd	40.6	0.9977	43.8	0.8869
	Cr	23.0	0.7880	67.0	0.9550
	Pb	79.5	0.9838	600	0.9785
	Cu	18.7	0.9816	35.9	0.9714
	Zn	97.7	0.9708	189.4	0.8313
KBS-2	Cd	9.9	0.9529	16.1	0.9693
	Cr	11.0	0.8070	63.0	0.9490
	Pb	33.8	0.9302	43	0.9153
	Cu	3.3	0.9930	4.6	0.9204
	Zn	11.7	0.9951	10.4	0.8524
KBS-3	Cd	12.0	0.9705	24.9	0.9693
	Cr	10.0	0.8880	65.0	0.9630
	Pb	31.0	0.9749	270	0.9250
	Cu	4.8	0.9907	4.3	0.9214
	Zn	13.8	0.9910	17.0	0.8523

From this experiment, it reveals that most of these sorption sequences (Table 5.5) for soil treated with actual and synthetic leachates indicated the same removal trend but different in amount heavy metals retained in each soil. Most Kham Bon soil treated with synthetic leachate exhibited the higher retention of heavy metals than soil treated with actual leachate. These selectivity sequences are confirmed by a number of studies existed in literatures. Covelo et al (2007) studied the accumulation of metals Cd, Cr, Cu, Ni, Pb and Zn by Kaolinite soil and Fe-oxide soil and reported that the selectivity sequence of kaolinite soil and Fe-oxide soil were Cr > Pb > Zn > Cd > Ni > Cu and Pb > Cu > Zn > Cr > Cd > Ni, respectively. This finding is agreed with the physical and chemical properties of Kham Bon landfill soil which is the red loess soil containing high Fe and Mn oxide and kaolinite clay soil (Table 5.1).

Apart from the physical and chemical properties of soil controlling adsorbed metals, the characterization of ionic interaction of heavy metals as their ionic potential was also discussed. *Ionic potential* (Z/R) is an ion's charge (Z) divided by its radius (R) which is a measure of density of charge (Elliott et al., 1986; Sposito, 1989). Ionic potential uses to characterize how strongly or weakly the ion will be electrostatically attracted to ions of opposite charge and to what the ion will expel other ions of like charge. In case of the ionic potential decreases with increasing ionic

radius, it can imply that the larger spread of electron configuration in space has occurred resulting in the greater tendency of a metal cation to polarize and creating an electric field of a charge surface functional group which leading to inner-sphere complex interaction (Sposito, 1989). In case of the metal retention follows the electrostatic force (outer-sphere complex), this would have led to the sequence of: Cr (0.66 Å) > Cu (0.73 Å) > Zn (0.74 Å) > Cd (0.97 Å) > Pb (1.19 Å). In contrast to the specific sorption (inner-sphere complex), it would predict a different sequence as follows: Pb > Cd > Zn > Cu > Cr. As can be seen in Table 5.5, the metal retention sequences showed that most of the selectivity orders were followed specific sorption. However, they did not follow entirely specific sorption, because in that case metals of lower ionic radii were strongly adsorbed. It was found in case of zinc and chromium sorption for all soil.

Table 5.5 Affinity sequence of Linear isotherm of KBS-1, KBS-2 and KBS-3 soil induced from monometal sorption at 25 °C with initial pH 8.16

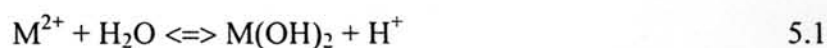
Soil Type	Selectivity sequence	
	Soil treated with actual leachate	Soil treated with synthetic leachate
KBS-1	Zn > Pb > Cr > Cd > Cu	Pb > Zn > Cr > Cd > Cu
KBS-2	Pb > Zn > Cr > Cd > Cu	Pb > Cr > Cd > Zn > Cu
KBS-3	Pb > Zn > Cd > Cr > Cu	Pb > Cr > Cd > Zn > Cu

Considering *atomic weight* of each heavy metal (Erese et al., 2005), the selectivity sequence in the descending order is Pb (207.2) > Cd (112.4) > Zn (65.38) > Cu (63.55) > Cr (55.0). Results in this study showed that the abilities of metal retention in this investigation were not followed entirely this sequence. This is due to the lower atomic weight (Cr), the higher sorbed metals. In contrast to Cd, the higher atomic weight exhibited the lower sorbed metals.

In addition, the electronegativity of ions was also considered (Antoniadis and Tsadilas, 2007). *Electronegativity* is a measure of the tendency of an atom to attract a bonding pair of electrons. The high electronegativity results in the high affinity of

ions itself. Table 5.5 shows that the metal retention sequence obtained from the experiment was not conformed to this high electronegativity sequence (Pb (2.33) > Cu (1.90) > Cd (1.69) > Cr (1.66) > Zn (1.60). However, it seems that this mechanism made a contribution to sorption behavior of all heavy metals except Pb ions.

Apart from ionic potential, atomic weight, and electronegativity, the first hydrolysis product of metals ions are capable of forming inner-sphere complexes with the adsorbent, which result in stronger metal retention than that electrostatics attraction of hydrated ion metals (Pagnamelli et al., 2003; Antoniadis and Tsadilas, 2007). Hydrolysis is a chemical reaction in which a chemical compound is broken down by reaction with water. Many metal ions are strong Lewis acids, and in water they may undergo hydrolysis to form basic salts or they are converted to new ionic species or to precipitates (oxides, hydroxides). These salts contain a hydroxyl group that is directly bounded to the metal ion in place of a water ligand yielding the inner-sphere complex interaction. The hydrolysis constants for cations are tabulated as $-\log K_a$. The term is also used for pK_a , which is equal to the negative decimal logarithm of K_a ($pK_a = -\log K_a$). The pK_a value of the metal hydrolysis reaction is shown in equation 5.1



The pK_a values of metal hydrolysis product determine the adsorption behavior of the studied metals, with specific adsorption decreasing with increasing pK_a . The pK_a values of the first hydrolysis products of the studied metals are Pb (7.7), Zn (9.0), Cd (10.1), Cr (10.0) and Cu (8.0). The selectivity sequences of all soil as lists in Table 5.5 were not followed entirely the specific metal sorption (Pb > Cu > Zn > Cr > Cd).

It would be remarked here that those discrepancies of metal sorption cannot solely be predicted by any given affinity sequence model. Therefore, other factors influencing heavy metals retention in soil such as properties of adsorbate and adsorbent were also conducted (see topic 5.2.3 in more detail). However, it is important to note that the removal rate and sorption affinities of these heavy metals might be carefully referred when comparing with each other. This is due to the different soil type (adsorbent), metal solution, initial concentration added of metal

solution, and condition designed in each experiment (Gray et al, 1999; Arias et al., 2005; Yang et al., 2005; Erses et al., 2007).

5.2.1.2 Competitive Metals Isotherms

Linear isotherm of competitive metals of Kham Bon soil treated with actual and synthetic leachates are shown in Figures 5.4 to 5.5, respectively. Distribution coefficient and coefficient of determination (R^2) of soil treated with actual and synthetic leachate are listed in Table 5.6.

In soil interacted with actual leachate, an *H-type* isotherm was observed in Pb and Zn for KBS-1 soil whereas in KBS-2 and KBS-3 soils the Pb and Zn ions obeyed *L-type* isotherm. In soil treated with synthetic leachate, an *H-type* isotherm played the role in Pb and Zn for KBS-1 soil and in Pb for KBS-2 and KBS-3 soils. Zn in KBS-2 and KBS-3 soils displayed an *L-type* isotherm. The remaining isotherms were characterized by an *S-shape*. An *H-shape* of Pb and Zn ions can be explained by considering that isotherms that have similar equilibrium concentrations for different amounts of metal added reflect a precipitations mechanism (Echeverría et al., 1998). Moreover, precipitation is often associated with neutral to alkaline soil conditions, relatively high concentrations of the heavy metal concerned; low solubility of the metal compound or low specific sorption sites (Sparks, 1995). Isotherms obtained from this experiment belong mainly to the types of *S* and slightly to the type of *H* and *L*. According to Sposito (1989), *L-type* isotherms correspond to great affinity between the metallic cation and the soil surface. Further increase in affinity results in *H-type* isotherms. This condition is usually produced either inner-sphere surface complexation or by significant van der Waals interaction in the adsorption process. *S-type* isotherms can be due to precipitation or competition coefficients are present.

From Tables 5.6, it can be seen that Pb and Zn presented the highest K_d values, showing that they were the most retained cations and also showed that the K_d value of Pb, was more strongly retained than other heavy metals for most soils. The metals with the lowest K_d values were Cd, Cu and Cr, showing that in competition system, they are easily exchanged and substituted by Pb and Zn. However, the degree of reduction in metal sorption was not similar for all metals. Zinc except lead, the most strongly sorbed in this study was much less affected by competitive than Cu, Cd, Cr.

This may be explained by the fact that Zn was strongly retained by the soil constituents and thus competed effectively with the poorly sorbed Cd and others. This was also suggested by Echeverría et al.(1998). There may also be another explanation for the highly competing Zn sorption behavior, Kiekens, 1995, Zn can form insoluble species product ($Zn(OH)_2$) which is the hydrolysis product of Zn. These processes are practically irreversible in the time scale of a laboratory experiment, and can thus cause a significant fraction of the added Zn to be available for the ion exchange reactions. Thus, Zn appears to be much less affected by competition than other metals which are poorly adsorbed. Cu and Cr was the most poorly sorbed and the least specific retained metal compared to Zn and Pb was greatly affected by competition.

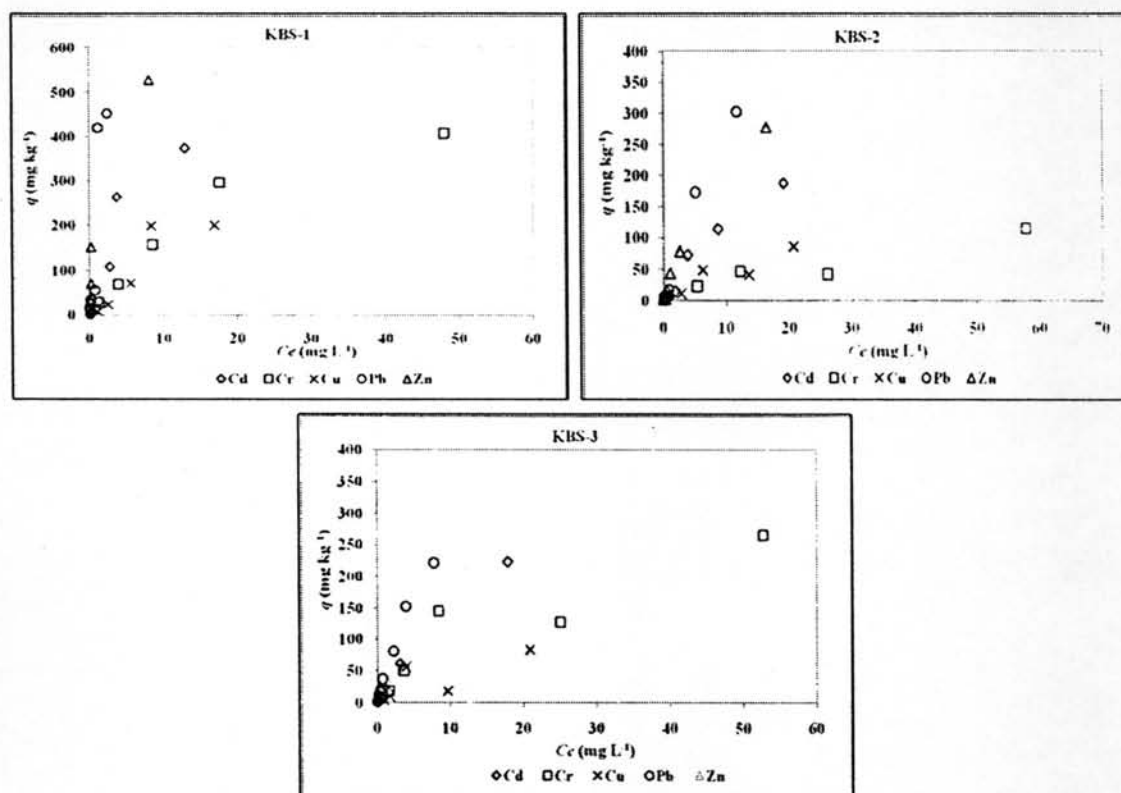


Figure 5.4 Competitive sorption isotherms at 25 °C with initial pH 8.16 for retention of Cd, Cr, Cu, Pb and Zn by three soil treated with actual leachate : KBS-1; KBS-2, and KBS-3

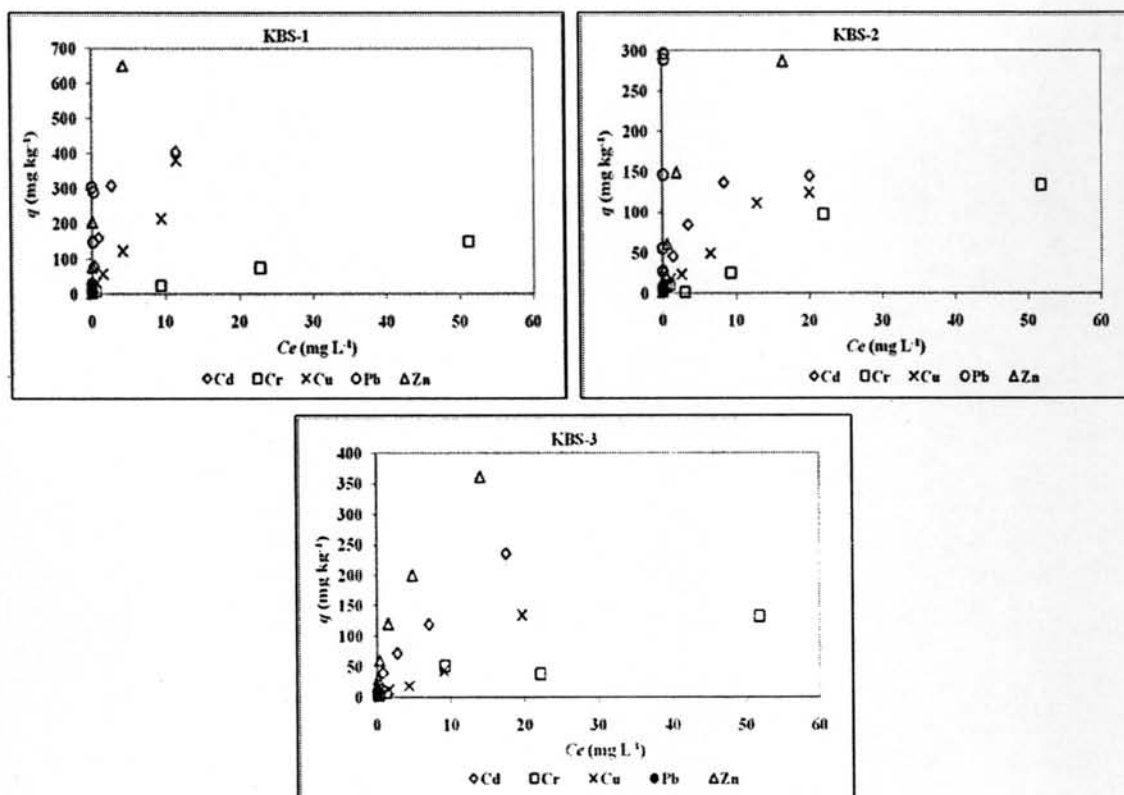


Figure 5.5 Competitive sorption isotherms at 25 °C with initial pH 8.16 for retention of Cd, Cr, Cu, Pb and Zn by three soil treated with synthetic leachate : KBS-1; KBS-2, and KBS-3

The magnitude of K_d value obtained from competitive sorption treated in actual leachate (Table 5.6) varied from 4.1 L kg⁻¹ for Cu sorption of KBS-2 soil to 833 L kg⁻¹ for Pb isotherm of KBS-1 soil. Moreover, values of K_d were remarked higher in KBS-1 than KBS-2 and KBS-3 soils. In the competition of elements in soil treated with synthetic leachate, the K_d values of metals varied from 2.8 L kg⁻¹ for Cr isotherm of KBS-2 to 952 L kg⁻¹ for Pb isotherm of KBS-1 soil. The higher K_d was reported in KBS-1 than KBS-3 and KBS-2 soil. The affinity sequences of K_d values in soil treated with actual leachate (Table 5.7) decreased in the order of Pb > Cd > Cu > Cr of KBS-1 soil; Zn > Cd > Pb > Cr > Cu of KBS-2 and Zn > Pb > Cd > Cr of KBS-3. For zinc value in KBS-1 soil, it could not be ranked in this affinity order. For that reason, it might be mostly removed by soil resulting in lower concentration in the solution. Thus, it was difficult to detect. The K_d value of Cu in all soils should be

taken into account due to the lowest ($R^2 < 0.8$) of coefficients of determination. The selectivity sequences of soil treated with synthetic leachate were observed in descending order of $Pb > Cd > Zn > Cu > Cr$ of KBS-1; $Pb > Zn > Cd > Cu > Cr$ of KBS-2, and $Pb > Zn > Cd > Cu > Cr$ of KBS-3. And the highest sorption capacity of Kham Bon soils was observed descending in the order of $KBS-1 > KBS-3 > KBS-2$. Moreover, it can be noted here that mostly of the K_d value decreased by a factor 1 to 2 in the monometal system compared to the competitive system (from Tables 5.2 and Tables 5.6).

Table 5.6 Linear isotherm parameters of KBS-1, KBS-2 and KBS-3 soil induced from competitive metals sorption at 25 °C with initial pH 8.16

Properties		Linear Isotherm			
		Soil treated with actual leachate		Soil treated with synthetic leachate	
Sample No.	Metals	K_d (L kg ⁻¹)	R^2	K_d (L kg ⁻¹)	R^2
KBS-1	Cd	32.3	0.833	40.5	0.6181
	Cr	9.7	0.7939	3.0	0.9951
	Pb	833.9	0.8339	942.7	0.8931
	Cu	13.9	0.7649	28.9	0.9512
	Zn	515.0	0.3404	20.0	0.8690
KBS-2	Cd	10.7	0.9454	9.0	0.6226
	Cr	4.4	0.7912	2.8	0.9123
	Pb	8.8	0.9780	846.3	0.8739
	Cu	4.1	0.7272	7.0	0.9428
	Zn	34.3	0.9967	80.6	0.9678
KBS-3	Cd	17.2	0.9098	18.6	0.8704
	Cr	16.5	0.9784	2.2	0.3606
	Pb	30.8	0.9583	131.4	0.991
	Cu	629.5	0.6925	4.7	0.9852
	Zn	40.5	0.8538	45.7	0.8148

Table 5.7 Affinity sequence of Linear metals isotherm of KBS-1, KBS-2 and KBS-3 soil induced from competitive metals 25 °C with initial pH 8.16

Soil Type	Selectivity sequence	
	Soil treated with actual leachate	Soil treated with synthetic leachate
KBS-1	$Pb > Cd > Cu > Cr$	$Pb > Cd > Zn > Cu > Cr$
KBS-2	$Zn > Cd > Pb > Cr > Cu$	$Pb > Zn > Cd > Cu > Cr$
KBS-3	$Zn > Pb > Cd > Cr$	$Pb > Zn > Cd > Cu > Cr$

5.2.2 Sorption Capacity of Heavy Metals by Kham Bon Soil

Tables 5.8 through 5.9 show the linear Freundlich and Langmuir sorption isotherms constants and coefficients of determination (R^2) in monometal and competitive metals experiments. When the coefficients of determination (r^2) are used as a criterion for this study, chromium cadmium and lead as well as zinc sorption exhibit a high correlation coefficient. The general trends observed in sorption profiles revealed that the sorption data were better interpreted with the Langmuir equation. Therefore, the sorption capacity of heavy metals in Kham Bon soil was characterized by Langmuir isotherm in terms of maximum adsorption capacity.

Table 5.8 Isotherm parameters of KBS-1, KBS-2 and KBS-3 soil induced from monometal sorption in actual leachate solution at 25 °C with initial pH 8.16

Properties		Isotherm					
Sample No.	Metals	Freundlich			Langmuir		
		K_f (L kg ⁻¹)	n	R^2	K_L (L kg ⁻¹)	M (mg kg ⁻¹)	R^2
KBS-1	Cd	39.5	1.0013	0.9631	475.9	117.2	0.9982
	Cr	51.3	2.1753	0.9635	415.1	182.2	0.9980
	Pb	77.0	1.0560	0.9274	1,211.9	90.3	0.9400
	Cu	33.0	1.4789	0.8430	4,665.3	35.2	0.9214
	Zn	78.5	1.9814	0.8688	13,768	55.2	0.8676
KBS-2	Cd	16.1	1.2910	0.9829	509.3	57.9	0.9985
	Cr	13.8	1.9414	0.9120	2,872	62.4	0.9867
	Pb	29.4	0.6502	0.8312	298.1	364.2	0.9750
	Cu	11.1	1.8709	0.8603	489.5	13.0	0.8158
	Zn	17.9	1.1663	0.9956	132.8	162.6	0.9920
KBS-3	Cd	16.7	1.0964	0.9591	266.3	105.2	0.9649
	Cr	19.5	2.5900	0.9194	1,640.7	81.0	0.8690
	Pb	41.8	1.1986	0.9752	665.4	126.4	0.9870
	Cu	1.4	0.7519	0.9698	a	a	a
	Zn	10.0	0.8992	0.9050	101.0	214.1	0.9911

a: Negative value

5.2.1.1 Monometal Isotherm

The monolayer maximum adsorption (x/m) from the Langmuir equation is usually used for comparing potential adsorption capacity of different soils and soil components (Yang et al., 2005). The processes were linearized by the double-reciprocal Langmuir equation because better fits were obtained with this model. K_L (L kg⁻¹) is a constant related to the energy or net enthalpy of adsorption; M (mg kg⁻¹) (the adsorption maximum) is the amount of solute adsorbed per unit weight of adsorbent

Table 5.9 Freundlich and Langmuir isotherm parameters of KBS-1, KBS-2 and KBS-3 soil induced from monometal sorption in synthetic leachate solution at 25 °C with initial pH 8.16

Properties		Isotherm					
Sample No.	Metals	Freundlich			Langmuir		
		K_f (L kg ⁻¹)	n	R^2	K_L (L kg ⁻¹)	M (mg kg ⁻¹)	R^2
KBS-1	Cd	177.0	1.4399	0.9926	16,661	62.2	0.9571
	Cr	1.8	0.432	0.9211	5,052	327.1	0.8631
	Pb	671.4	1.0102	0.9536	a	a	a
	Cu	65.5	1.5267	0.9866	7.4	150.6	0.9801
	Zn	737.1	1.1732	0.8324	878.3	366.3	0.9476
KBS-2	Cd	36.3	1.6756	0.9407	1,7477	71.2	0.9553
	Cr	10.3	0.6575	0.9286	7.5	366.0	0.9991
	Pb	89.3	1.4445	0.9440	168.6	686.8	0.9190
	Cu	9.4	1.3717	0.9799	905.1	29.7	0.9560
	Zn	71.6	1.5579	0.9615	602.7	414.6	0.9945
KBS-3	Cd	55.7	1.5795	0.9819	2,677.8	75.1	0.9883
	Cr	18.2	0.7348	0.9370	50.5	32.2	0.9997
	Pb	291.3	0.6741	0.980	413.8	863.2	0.9428
	Cu	10.9	1.2817	0.9905	76.9	183.6	0.9963
	Zn	84.7	1.3744	0.9508	834.6	379.6	0.9737

a: Negative value

in forming the complete monolayer on the surface. K_L and M values were also calculated using the least squares method. The linear plot of $1/(x/m)$ versus C_e giving a straight line of slope $1/K_L M$ and intercept $1/M$ can be seen more detail in Appendix B. The values of the Langmuir constants K_L and M are presented in Tables 5.8 to 5.9. Mostly of the correlation coefficient values as list in Tables 5.8 to 5.9 pointed out a good relationship for the data ($R^2 > 0.95$). Results from the experiments revealed that the adsorption capacities of metals were higher for KBS-1 soil than for KBS-2 and KBS-3 soils, also the adsorption capacity for different metals onto the same soil differed from one to another. The preference in adsorption capacity exhibited by KBS-1 over KBS-2 and KBS-3 soils was due mainly to higher pH, CEC, organic matter content and ferrous oxide of the KBS-1 soil. These results are in agreement with previous studies in the literature, suggesting that the most important factors influencing heavy metals accumulation in soils are: clay content and mineralogy; CEC; metal oxides and/or oxyhydroxides (Fe and Al, Mn oxides) and humic substances associated with natural organic matter (Sparks, 1995; Bradl, 2004). The

discrepancies in metal adsorption onto the KBS-1, KBS-2 and KBS-3 soils showed that soil properties had an important influence on adsorption. These results reflected that the affinity of metals for KBS-1 soil was higher than for KBS-2 and KBS-3. In monometal, K_L values were highest for Cu in actual leachate and Cd in synthetic leachate. This can be explained by considering that the sites responsible for copper and cadmium adsorption at low concentration were characterized by much higher energies than those at higher concentrations.

The M values were higher for Pb in actual leachate and for Zn in synthetic leachate, indicating their high adsorptive capacities. The sorption potential (Table 5.10) for metals in actual leachate on soil in terms of the Langmuir constant M was in the order of: Cr > Cd > Pb > Zn > Cu, Pb > Zn > Cr > Cd > Cu and Zn > Pb > Cd > Cr > Cu in KBS-1, KBS-2 and KBS-3 respectively. For the synthetic leachate, the sorption potential for metals was in order of Pb > Zn > Cr > Cu > Cd, Pb > Zn > Cu > Cr > Cd > Cu and Pb > Zn > Cu > Cd > Cr in KBS-1, KBS-2 and KBS-3, respectively.

Table 5.10 Affinity sequence of Langmuir isotherm of KBS-1, KBS-2 and KBS-3 soil induced from monometal sorption at 25 °C with initial pH 8.16

Soil type	Langmuir isotherm	
	Soil treated with actual leachate	Soil treated with Synthetic leachate
KBS-1	Cr > Cd > Pb > Zn > Cu	Pb > Zn > Cr > Cu > Cd
KBS-2	Pb > Zn > Cr > Cd > Cu	Pb > Zn > Cr > Cd > Cu
KBS-3	Zn > Pb > Cd > Cr > Cu	Pb > Zn > Cu > Cd > Cr

Considering the sorption capacity of each soil and each heavy metal from Table 5.8, it can be seen that the maximum adsorption capacity (M) of soil treated with synthetic leachate is slightly higher than soil treated with actual leachate. These results can be explained by considering that the organic compound contained in actual leachate can enhance the mobility of heavy metals (see more detailed in topic 5.2.3).

5.2.2.2 Competitive Metals Isotherms

According to Tables 5.11 to Table 5.12, K_L values were highest for Pb and Cd Cr in all soil treated with actual leachate and synthetic leachate. This can be explained by regarding that the sites responsible for lead and cadmium adsorption at low concentration are characterized by much higher energies than those at higher concentrations. The M values were firstly higher for Cr in all soil treated with actual leachate indicating their high adsorptive capacities. It might be stated that the presence of Cr as one of the most retained cations, in spite of its lower electronegativity and molecular weight values seems to be related to the fact that this metals was applied in its trivalent form which is appeared predominantly in the soil (Smith and McGrath, 1990; Gomes et al., 2001).

Table 5.11 Freundlich and Langmuir isotherm parameters of KBS-1, KBS-2 and KBS-3 soil induced from competitive metals sorption in actual leachate solution at 25 °C with initial pH 8.16

Properties		Isotherm					
Sample No.	Metals	Freundlich			Langmuir		
		K_f (L kg ⁻¹)	n	R^2	K_L (L kg ⁻¹)	M (mg kg ⁻¹)	R^2
KBS-1	Cd	30.0	0.6376	0.9749	11.8	1,474.1	0.9780
	Cr	21.9	1.2034	0.9762	6.8	2,903.6	0.9921
	Pb	179.5	0.9900	0.9267	4,902.0	137.6	0.9950
	Cu	5.7	0.7038	0.9382	258.6	144.2	0.9630
	Zn	94.6	0.8787	0.929	905.5	626.0	0.9225
KBS-2	Cd	5.1	0.6110	0.9832	1,878.5	4.2	0.743
	Cr	3.5	0.9009	0.8270	384.0	106.7	0.888
	Pb	14.5	1.0012	0.8920	965.2	34.2	0.8396
	Cu	5.1	1.0162	0.7367	89,100	105.9	0.9980
	Zn	39.0	1.2201	0.8527	657.0	546.0	0.9940
KBS-3	Cd	10.1	0.9849	0.9459	25,622	17.5	0.8760
	Cr	16.1	1.3414	0.9400	101.1	192.9	0.9355
	Pb	39.3	1.0109	0.8969	233.5	311.9	0.9550
	Cu	6.3	1.2452	0.7721	1850	276.9	0.9910
	Zn	33.9	1.4219	0.9262	1,107.1	67.3	0.8842

a: Negative value

Potential of sorption for metal in actual leachate on soil in terms of Langmuir constant M was in the order of: Cr > Cd > Zn > Cu > Pb, Zn > Cr > Cu > Pb > Cd and Pb > Cu > Cr > Zn > Cd in KBS-1, KBS-2 and KBS-3 respectively. For synthetic leachate,

potential or sorption for metal was in order of Zn > Pb > Cd > Cu > Cr, Cd > Zn > Cr > Cu > Pb and Cr > Zn > Cd in KBS-1, KBS-2 and KBS-3 respectively.

Table 5.12 Freundlich and Langmuir isotherm parameters of KBS-1, KBS-2 and KBS-3 soil induced from competitive metals sorption in synthetic leachate solution at 25 °C with initial pH 8.16

Properties		Isotherm					
Sample No.	Metals	Freundlich			Langmuir		
		K_f (L kg ⁻¹)	n	R^2	K_L (L kg ⁻¹)	M (mg kg ⁻¹)	R^2
KBS-1	Cd	134.4	1.6534	0.9629	11,251	79.2	0.9515
	Cr	19.6	1.5959	0.9975	1,574.0	67.0	0.9768
	Pb	95.9	2.8986	0.9950	60,385	79.6	0.9790
	Cu	45.7	1.3680	0.9859	1,717.5	71.3	0.9377
	Zn	308.0	0.9988	0.6042	1,597.8	221.8	0.8900
KBS-2	Cd	30.4	1.5962	0.9499	138.9	326.1	0.9804
	Cr	10.1	1.5659	0.9485	240.9	61.0	0.9517
	Pb	33.8	1.7637	0.619	16,888	13.6	0.693
	Cu	14.8	1.4251	0.9763	1,148.2	31.2	0.815
	Zn	62.0	1.2806	0.8714	3,954.8	105.2	0.9454
KBS-3	Cd	40.1	1.6532	0.9983	8,348.3	32.1	0.9508
	Cr	4.7	1.2108	0.9502	8.0	585.9	0.9969
	Pb	285.8	1.0917	0.8460	a	a	a
	Cu	4.3	0.8418	0.9506	a	a	a
	Zn	79.7	1.4793	0.9440	1,331.8	213.8	0.9965

a: Negative value

Table 5.13 Affinity sequence of Freundlich and Langmuir isotherm of KBS-1, KBS-2 and KBS-3 soil induced from competitive metals sorption at 25 °C with initial pH 8.16

Soil type	Langmuir isotherm	
	Soil treated with actual leachate	Soil treated with Synthetic leachate
KBS-1	Cr > Cd > Zn > Cu > Pb	Zn > Pb > Cd > Cu > Cr
KBS-2	Zn > Cr > Cu > Pb > Cd	Cd > Zn > Cr > Cu
KBS-3	Pb > Cu > Cr > Zn > Cd	Cr > Zn > Cd

Moreover, the K_L constant was used to predict the favorable or unfavorable shape of isotherm which defined as K_R constant. The values of K_R for all heavy metals are given in Table 5.13. It ranges between 0 and 1 indicate the favorable adsorption of

these heavy metals in all treatment on the Kham Bon landfill soil and reaches to linearity.

Table 5.14 K_R values calculated from Langmuir constant parameters of three soils treated with actual leachate and synthetic leachate

Soil No.	K_R values of different treatments				
	Heavy Metals	Monometal in actual Leachate	Monometal in synthetic Leachate	Mixed metals in actual Leachate	Mixed metals in synthetic Leachate
KBS-1	Cd	0.9546	0.9938	0.8715	0.9921
	Cr	0.9602	0.9683	0.7738	0.9933
	Pb	0.8919	b	0.9864	0.9921
	Cu	0.6819	0.9852	0.9858	0.9929
	Zn	0.4207	0.9647	0.9411	0.9783
KBS-2	Cd	0.9515	0.9929	0.9996	0.9684
	Cr	0.9721	0.9647	0.9728	0.9939
	Pb	0.9711	0.9357	0.9997	0.9986
	Cu	0.9533	0.9970	0.9896	0.9969
	Zn	0.9869	0.9602	0.9482	0.9990
KBS-3	Cd	0.9741	0.9925	0.9998	0.9968
	Cr	0.6024	0.9968	0.9891	0.9447
	Pb	0.9376	0.9205	0.9698	b
	Cu	b	0.9820	0.7887	b
	Zn	0.9899	0.9634	0.9994	0.9791

b : unfavorable shape

Considering the sorption capacity of each soil and each heavy metal from Tables 5.12 to 5.13, it can be seen that the maximum adsorption capacity (M) of soil treated with synthetic leachate is slightly higher than soil treated with actual leachate. These results can be explained by considering that the organic compound contained in actual leachate can enhance the mobility of heavy metals. The CEC of the soil is one of the important factors and is related to the amount of soil colloids that can adsorb the contaminating heavy metals ions. For a high CEC or a high pH value, the cation can easily be attracted by the soil. Experimental results indicated that the adsorption capacity toward heavy metal contaminants should be $KBS-1 > KBS-3 > KBS-2$, thereby corresponding to the above assumption.

It can be stated that the selectivity sequences of competitive ions study of all treatments are not in agreement with the charge-to-radius ratio alone, emphasizing that specific sorption should be considered together with electrostatic interaction within the system.

From the experiments, it can be summarized that the adsorption from the monometal solution was much more effective than adsorption of the same element from the competitive metals solution, agreeing with work elsewhere (Harter, 1992; Echeverría et al, 1998; Gomes et al., 2001; Patkowska et al., 2005;). Comparison of monometal and competitive sorption isotherm parameters, it is revealed that the presence of other cations investigated decreased sorption of almost metals. Metal K_d decrease was even more pronounced in the system, and this indicate that competitive effects among metals increase as available sorption sites decrease (due to the increase in the number of adsorbate).

Precipitation mechanism is often associated with neutral to alkaline soil conditions, relatively high concentrations of the heavy metal concerned, low solubility of the metal compound, or low specific sorption sites. Therefore, the sorption capacity in this study may be overestimated due to the precipitation mechanism in the alkaline soil and alkaline leachate.

5.2.3 Factors Controlling the Mobility of Heavy Metals in Kham Bon Soil

5.2.3.1 Organic and Inorganic Compound Containing in Leachate

Comparing the slope of adsorption isotherm of soil treated with actual leachate and soil treated with synthetic leachate (Figures 5.17 to 5.19), the slope of isotherm of actual leachate solution was lower than the soil interacted with leachate. It indicated the lower of distribution coefficient of the actual leachate. As the actual leachate contain many compounds, e.g. organic matter as TOC or DOC, that have the ability to form complexes with heavy metals, less amount of heavy metals remained for soil adsorption. It is observed that the distribution coefficient of the synthetic leachate (Tables 5.4 and 5.6) was higher than the actual leachate by a factor of 2 to 9 times. This finding is in agreement with Christensen et al.(1996). They compared the metal (Cd, Ni, and Zn) distribution coefficients of leachate polluted groundwater to metal distribution coefficients determined in a synthetic matrix mimicking the leachate polluted groundwater without containing the DOC. They found out that the DOC from landfill leachate polluted groundwater has the ability to form complexes with

Cd, Ni, and Zn and the distribution coefficient was a factor of 2 to 6 lower in the presence of DOC.

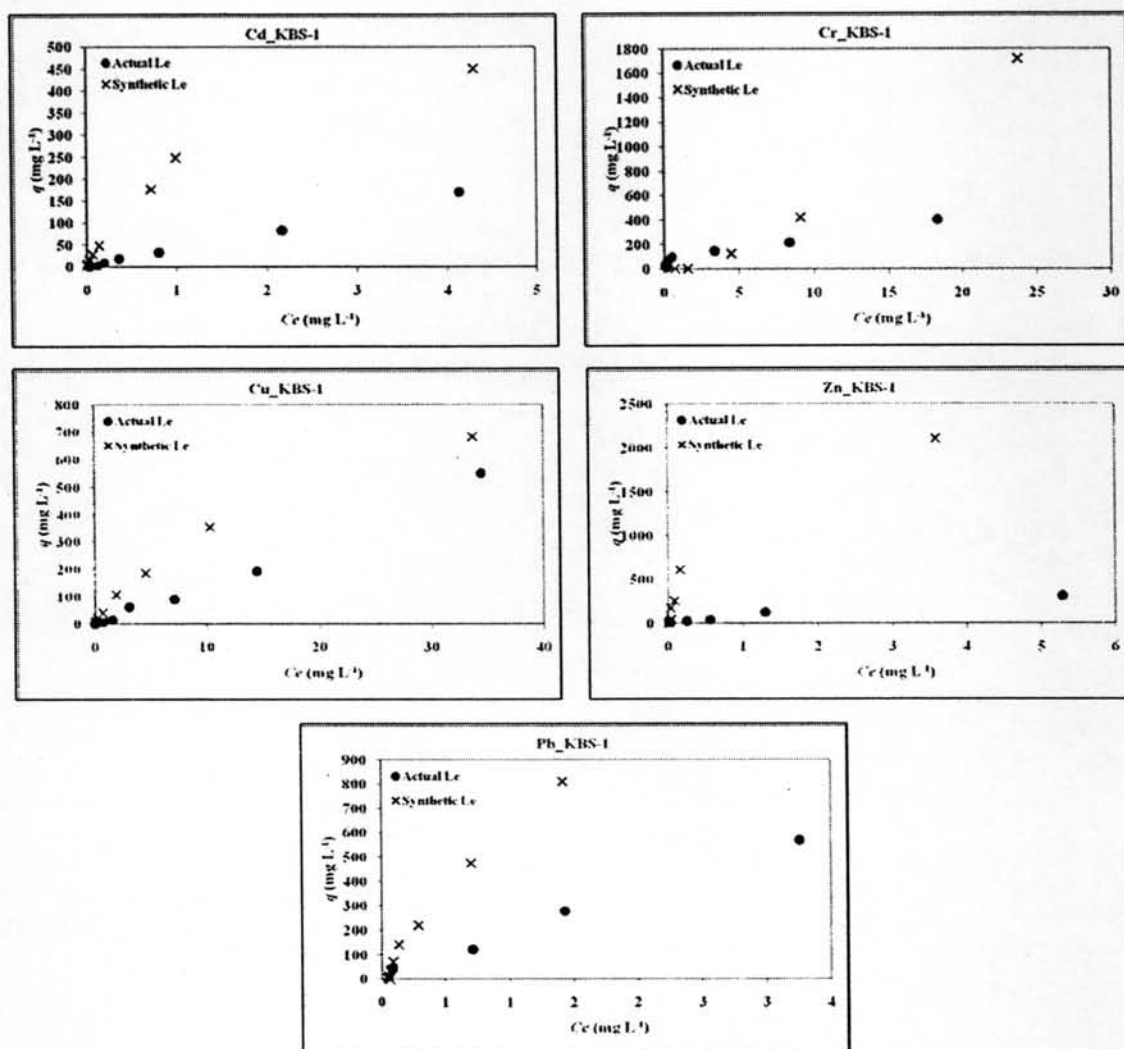


Figure 5.6 Monometal sorption isotherms at 25 °C with initial pH 8.16 for retention of Cd, Cr, Cu, Pb and Zn by KBS-1 soil in actual leachate compared to synthetic leachate

This was also suggested by Antoniadis et al. (2007) that the soils decreased their ability to bind heavy metals over time due to a reduction in the number of sorption site as decomposition of sludge-borne organic matter yielding the DOC take place, especially when metals are in competition for these sites. According to Xu et al. (2006), they reported that the 64 percentage of dissolved organic matter (DOM) was characterized as dissolved organic carbon (DOC). Moreover, Ziyang et al. (2008) also

reported that organic matter in the dissolved fraction ($MW < 1k$ Da) predominated in the leachate, accounting for 65% of TOC. Therefore, the DOC concentration in leachate of Kham Bon landfill could be estimated roughly as the 64 percentage of TOC that measured from the site. Thus, the DOC in Kham Bon landfill would be approximately 800 mg L^{-1} .

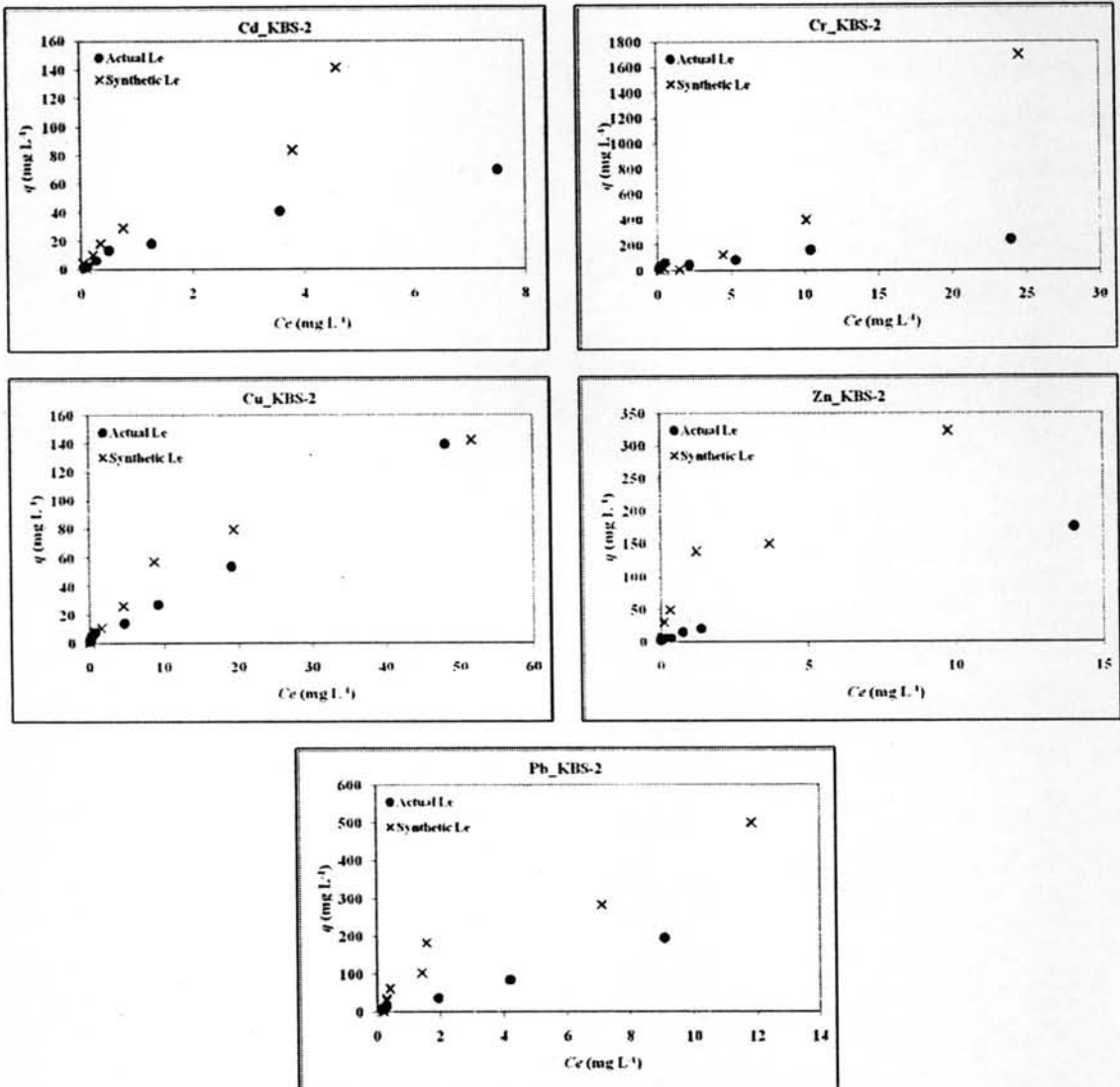


Figure 5.7 Monometal sorption isotherms at 25°C with initial pH 8.16 for retention of Cd, Cr, Cu, Pb and Zn by KBS-2 soil in actual leachate compared to synthetic leachate

5.2.3.2 High pH and Alkaline of Leachate

High pH and alkaline of leachate would result in higher retention in soil. It can be explained that due to the high pH and alkalinity of actual leachate, these heavy metals are induced to form carbonate compounds which will be precipitated in the system (Sparks, 1995). Precipitation mechanism in the system could be reflected by *S*-shape isotherm. This behavior was in agreement with previous literatures (Sparks, 1995; Fetter, 2001; Bradl, 2004) in which the high solution of pH, the Pb, Cd, Cu and Zn being enhanced to precipitate in the system.

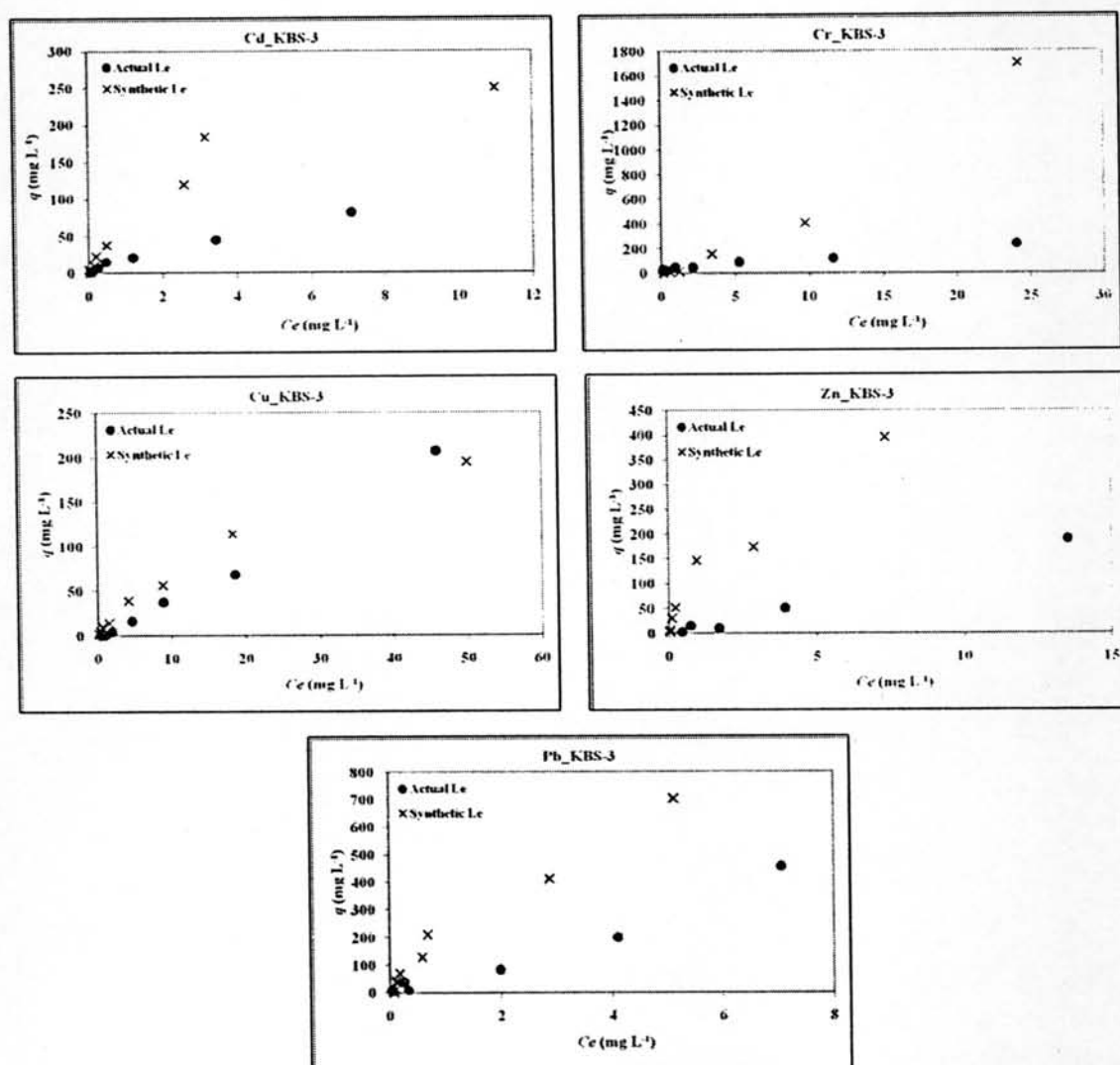


Figure 5.8 Monometal sorption isotherms at 25 °C with initial pH 8.16 for retention of Cd, Cr, Cu, Pb and Zn by KBS-3 soil in actual leachate compared to synthetic leachate

Therefore, it is important to note that at a high pH and alkalinity adsorption mechanism of heavy metal has a chance to occur in parallel with precipitation mechanism. However, it has to be careful for calculation of isotherms dealing with only sorption mechanism.

5.2.3.3 Physical and Chemical Properties of Kham Bon Soil

From the experimental results, the higher metal retention could be observed in KBS-1 (silty clay loam) than that KBS-2 (sand) and KBS-3 (loamy sand) soils both treated with actual and synthetic leachates. As seen in Table 5.1, KBS-1 exhibited the highest of organic matter content, iron and manganese (oxyhydroxide/oxides), clay content, and CEC which are the most significant soil properties influencing sorption reaction. These findings are in agreement with a number of existing literatures (Cavallard and McBride, 1978; Buchter et al., 1989; Christensen, 1989; Harter, 1992; Bejat et al., 2000; Calace et al., 2001; Selim and Sparks, 2001; Appel and Ma, 2002; Arias et al., 2005) reported that the soil type and composition play an important role for heavy metal retention.

The fine-grained soil (KBS-1 soil) has a large surface reactivities and surface areas such as clay minerals, iron and manganese oxyhydroxides. They display adsorption properties enhancement (Sparks, 1986; 1995; 2005; Mclean and Bledsoe, 1992; Hettiarachchi et al., 2003). Surface of precipitated metal (hydro) oxides such as Fe, Mn and Al are known to be highly active site for sorption of most dissolved metal ion species. For soil organic matter, it exhibits a major important parameter influencing metal-solution and soil-surface chemistry (Harter, 1983; Soon, 1981; Msaky and Calvet, 1990). Naturally, heavy metal adsorption is small at low pH value. At high pH value, the metal ions are completely removed (Elzahabi and Yong, 2001). This behavior can be observed in KBS-2 soil presented the lowest metal retention. The CEC is directly related to the soils capacity of adsorbing heavy metals. The greater the CEC values, the more exchange sites on soil minerals will be available for metal retention.

The presence of competitive cations can affect metal adsorption in soils. Results from the study revealed that soil treated with actual leachate exhibited lower metal sorption than soil treated with synthetic leachate. That reason is due to the

presence of high Ca^{2+} value (832 mg L^{-1}) containing in actual leachate. This result is confirmed by the study of Echeverría et al. (1998). They reported that the presence of Ca^{2+} competes effectively with cationic heavy metals for adsorption sites and this competition seemed to be greater for Zn and Cd than for Cu and Pb.

For the highest retention of Pb in Kham Bon soil mostly observed in this experiment, it can be explained by regarding that carbonate content in soils plays an important role in controlling Pb behavior (Sparks, 1995). Furthermore, the presence of Fe oxides in Kham Bon soil known as *loessial soil* may exert a predominant role in Pb adsorption in soils. In addition, the presence of soil organic matter also plays an important role in Pb adsorption. Soil organic matter may immobilize Pb via specific adsorption reactions (Sposito, 1989; Yong, 2001; Sharma and Reddy, 2004). On the other hand, the mobilization of Pb can also be facilitated by its complexation with dissolved organic matter or fulvic acids (Christensen et al. (1996). Same as Pb, Cu adsorption depends on organic matter and the presence of Fe and Mn oxide.

The higher retention of Zn was generally observed in Kham Bon soil. Factors influencing Zn adsorption are: pH; clay mineral; organic matter; CEC and soil type. In calcareous and alkaline soil, zinc is rarely found due to the carbonate precipitation, zinc hydroxide or carbonate and insoluble calcium zincate (Sparks, 1986; Sposito, 1989; McLean and Bledsoe, 1992). Data obtained from the experiment revealed that the retention of Zn in soil treated with actual leachate was found higher than Cd but in the synthetic leachate it presented in the opposite manner. For these reasons, it can be pointed out that the DOC containing in leachate might form complexes with Cd promoting the mobility of Cd in soil and the alkaline actual leachate enhanced the Zn precipitating in the system.

Hexavalent chromium, Cr (VI) was focused on in this experiment. This is because it is widely used in the industrial product, for example: dyeing; staining; tanning leather as bleach and oxidizer; depolarizer for dry cell. In Kham Bon soil, chromium ion expressed the lower sorbed heavy metals. This is because Cr (VI) is highly mobile in soil especially, in alkaline soil (McLean and Bledsoe, 1992). Moreover, the adsorbed Cr (VI) was easily desorbed indicating nonspecific adsorption (McLean and Bledsoe, 1992). However, the presence of chloride and nitrate has little effect on Cr (VI) adsorption whereas sulfate and phosphate inhibited adsorption as

well as dissolved inorganic carbon (Fe and Mn oxide) also suppresses Cr (VI). For that reason, chromium retention was found higher than other metals except Pb in KBS-2 and KBS-3 soils treated with synthetic leachate. The parameters that correlated with Cr (VI) immobilization in the soil are free ion oxides, total manganese, and soil pH whereas the soil properties: CEC; surface area, and clay content have no significant influence on Cr (VI) mobility.

Cadmium was lower retained in For Cd, factors controlling Cd adsorption in soils: high pH, ionic strength, exchangeable ions. The presence of DOC and chelating agent enhance Cd transport into the environment. Moreover, the presence of Ca results in the high adsorbed of Cd and the low adsorption of Zn as competitive ion. Precipitation of Cd occurs in sandy soil with low CEC, low organic matter as well as alkaline pH, high Cd concentration and Cd solubility.

In this investigation, Cu exhibited the lowest metal retention in all treatments. This indicated the higher tendency of Cu to remain in solution relative to other heavy metals. From this finding, it can be described here that the Cu has ability to form complexes with not only organic matter but also chelating substances as reported by Weber, 2006 (<http://www.ar.wroc.pl/~weber/kombi2.htm>) in which the order of decreasing ability of metal ions to chelating is $Fe^{3+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Mn^{2+}$. That is why the lower metal retention of Cu was observed. Furthermore, the presence of inorganic and organic ligands in the soil solution can affect the adsorption of trace metals. The solubility of Zn, Cu, Cd, and Pb is higher in alkaline pH, as a result of the formation of stable soluble organomineral complexes. On the other hand, if pH ranges between 4 and 6, the solubility of these metals will be lower because of the formation of insoluble sulfides or insoluble organomineral complexes (Ksiezopolska, 2005).

It can be indicated here that, the so called "*red loess or loessial soil*" plays very important role in controlling the mobility of these heavy metals in Kham Bon landfill site and surrounding area. This is due to the prevalent of iron and manganese oxides in *red loess*.

5.2.4 Speciation of Heavy Metals by MINTEQA2

The distribution of aqueous species was calculated using the geochemical speciation program MINTEQA2 version 2.53 (Allison et al., 1991; Jensen et al.,

1998; Jensen and Christensen, 1998; Kishnamurti et al., 1999; Papini et al., 2002). Calculations can be carried out to take into account the pH, ionic strength, temperature and added initial concentration of heavy metals by their corresponding equilibrium constant. The heavy metals speciation was made for actual leachate and synthetic leachate solution.

Precipitation or dissolution of minerals depends upon the activity of its constituents in solution and the energy of formation for the solid, known as *Solubility product* (K_{sp}). The solution parameter representing the total activity of the solid constituents is defined by the *Ion Activity Product* (IAP). Therefore, *Saturation Index* (SI) is used to define whether a solution is oversaturated, undersaturated, or in equilibrium with a specific solid which can be calculated from equation of 5.4.

$$SI = \log (IAP/K_{sp}) \quad 5.4$$

If:

$SI > 0$ --> supersaturation

$SI < 0$ --> undersaturation

$SI = 0$ --> equilibrium

Supersaturation indicates the condition in which the solution IAP for a solid exceeds the K_{sp} for that solid, thus, precipitation of the solid is expected whereas *undersaturation* depicts the condition where the IAP for the solution is less than the K_{sp} for a solid--dissolution of this solid is expected.

The possible precipitates in the leachate samples as suggested by MINTEQA2-calculations model is shown in Table 5.15. The results of study revealed that only zinc carbonate could precipitate and calcium carbonate could be solid precipitated in the natural leachate.

Table 5.15 MINTEQA2 calculated saturation indices for selected metal mineral phase, based on the average equilibrium data during their interaction with actual leachate and synthetic leachate

Metal Speciation	Saturation Index		
	Natural Leachate	Actual Leachate	Synthetic Leachate
CaCrO ₄	-7.876	-4.293	-4.023
Calcite	0**	2.56*	-0.877
Cd(OH) ₂	-7.281	-2.27	-
Cd ₃ (OH) ₄ SO ₄	-23.735	-8.8	-
Cd ₄ (OH) ₆ SO ₄	-23.212	-3.266	-
CdCl ₂	-11.39	-6.402	-
CdCl ₂ ·1H ₂ O	-10.359	-5.368	-
CdCl ₂ ·2.5H ₂ O	-10.144	-5.148	-
CdOHCl	-6.380	-1.381	-
CdSO ₄	-13.728	-8.816	-
CdSO ₄ ·1H ₂ O	-12.177	-7.262	-
CdSO ₄ ·2.67H ₂ O	-12.036	-7.115	-
Cu(OH) ₂	-6.762	-0.133	1.802*
CuCO ₃	-5.742	0.818*	-
Cu ₂ (OH) ₃ NO ₃	-15.952	-2.706	3.02*
CuOCuSO ₄	-25.507	-12.351	-
CuCrO ₄	-13.463	-5.881	-
CuSO ₄	-20.675	-14.145	-3.865
Otavite	-1.397	3.545*	-
Pb(OH) ₂	-5.268	0.094*	3.627*
Pb ₂ (OH) ₃ Cl	-12.235	-1.522	-
Pb ₂ O(OH) ₂	-20.423	-9.702	-2.636
Pb ₂ O ₃	-25.273	-14.552	-
Pb ₂ OCO ₃	-13.445	-2.793	-
Pb ₃ O ₂ CO ₃	-22.138	-6.126	-
Pb ₃ O ₂ SO ₄	-22.298	-6.315	-
Pb ₄ (OH) ₆ SO ₄	-29.837	-8.485	-
Pb ₄ O ₃ SO ₄	-30.603	-9.262	-
PbCrO ₄	-5.949	0.366*	3.98*
Zincite	-1.563	0.513*	1.675*
Zn(NO ₃) ₂ ·6H ₂ O	-17.185	-15.109	-10.237
Hydrozincite	-	10.336*	-
Zn(OH) ₂ (epsilon)	-1.871	0.209*	1.371*
Zn ₂ (OH) ₂ SO ₄	-8.436	-4.376	-
Zn ₂ (OH) ₃ Cl	-5.07	-0.923	-
Zn ₃ O(SO ₄) ₂	-30.446	-24.409	-

Table 5.15 MINTEQA2 calculated saturation indices for selected metal mineral phase, based on the average equilibrium data during their interaction with actual leachate and synthetic leachate (continued) .

Metal Speciation	Saturation Index		
	Natural Leachate	Actual Leachate	Synthetic Leachate
Zn ₄ (OH) ₆ SO ₄	-10.009	-1.791	-
Zn ₅ (OH) ₈ Cl ₂	-8.594	1.779*	-
ZnCl ₂	-15.798	-13.742	-
ZnCO ₃	0.694	2.704*	-
ZnSO ₄ ·1H ₂ O	-9.965	-7.981	-
CrO ₃	-18.224	-17.267	-17.187
Cr(OH) ₂	-13.701	-	-
CrCl ₂	-35.385	-	-

* Supersaturation

** Solid precipitation

For the actual leachate added with various heavy concentrations, the model speciation indicated the precipitation of carbonate and hydroxide species including calcite; copper carbonate; otative; zinc carbonate; lead hydroxide; zincite, and lead chromate. Moreover, the precipitation of hydroxide was observed prevalent in the synthetic leachate system. For chromium mineral, the calculation was not reported precipitating in all system. The mineral precipitations in the leachate samples in the present work were also suggested as possible precipitates in landfill leachate by Jensen et al. (1998). The model speciation indicated that a large, but very varied, part of the heavy metals in the dissolved fraction were complexes with the dissolved organic carbon (DOC). For Cd, Cu and Pb, 20- 80% were organic complexes, whereas less than 1% of Zn was organic complexes. Cr did not form organic complexes. Christensen and Christensen (1998) found that by using the original MINTEQA2 database with respect to organic complexes, the amount of heavy metals (Cd, Ni and Zn) complexes with organic matter may be underestimated in landfill samples. From this experiment, organic complexes the main species in the dissolved fraction with respect to Cd, Zn, Cu and Pb were carbonate complexes, whereas free metal ions were much less essential species. For Cr the main species were hydroxide complexes accounting for 100% of the Cr in the dissolved fraction. The speciation showed that the fraction of free metal ions in the actual leachate samples was very

low accounting for 0.01 ± 11 % of the total metal content in the leachate samples. This indicates that in solutions like landfill leachates, which contain a broad spectrum of organic and inorganic compounds, it is likely that the behavior of the heavy metals is related to the colloidal matter and to complexes metal ions rather than to free ions (Christensen and Christensen, 1998 ; Jensen et al., 1998). The hydroxide species was dominant related to heavy metals precipitation in synthetic leachate system. The highest free ion metal was found in Cd ions whereas the lowest free ions belonged to Cu ions. The MINTEQA2 calculation pointed out that Cu, Pb and Zn ions could be possible precipitated in the system.

These results confirm the important role of organic matter in controlling the transport of heavy metals in landfill leachate. Whereas the chemical processes affecting the distribution of heavy metals cannot be modeled simply in terms of reactions involving inorganic aqueous complexes and free ions. Moreover, the prevalent of precipitation of metal in the system could produce artificially high adsorption values, which affected a number of experiments here.

5.3 Desorption of Sorbed Metal

To better predict the environmental fate and mobility of contaminants, it is critical to study adsorption behavior as well as desorption behavior of contaminants in soil systems. Deionized water was assumed to be infiltration as natural leaching to extract heavy metals sorbed soil. To make comparisons, the desorption data were converted to present heavy metals desorbed by dividing the total amount of heavy metals desorbed at the end of desorption experiments by the total amount of added heavy metals sorbed by each sample. The results from the desorption experiments for the heavy metals sorbed soil samples are summarized as shown in Figures 5.20 through 5.23.

The results of experiment show that the amount of heavy metals readily desorbed from the soil were small. Under infiltration condition, adsorbed metals remained more stable. As expected, from metal to metal, difference in behavior was observed. Among the studied metals Pb showed the greatest resistance to desorption followed by Cr and Zn. Cu and Cd appeared to be the most mobile of the elements

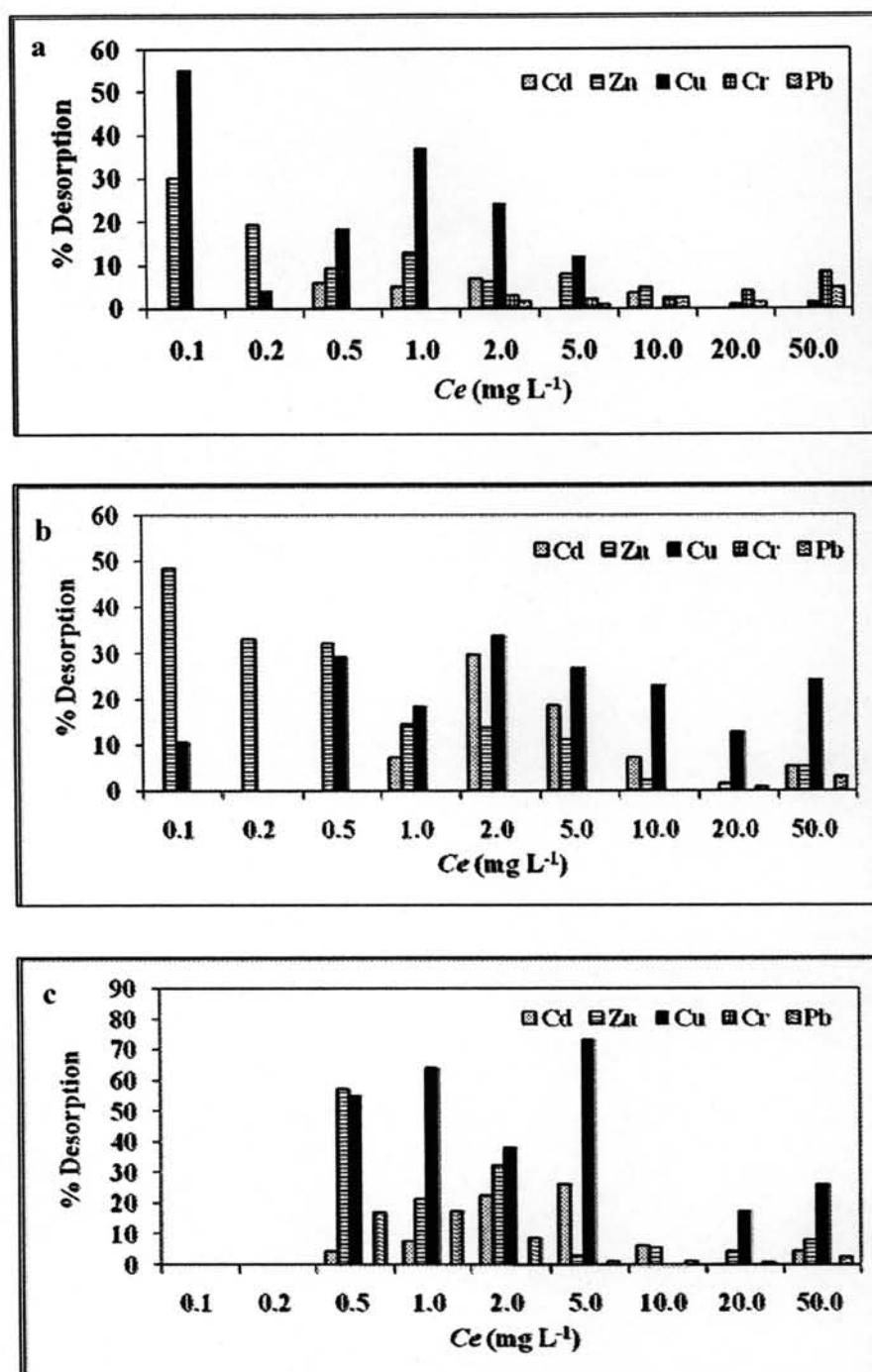


Figure 5.9 Percentage of desorption of sorbed metals in three soil treated with actual leachate in monometal system : KBS-1 (a); KBS-2 (b), and KBS-3 (c)

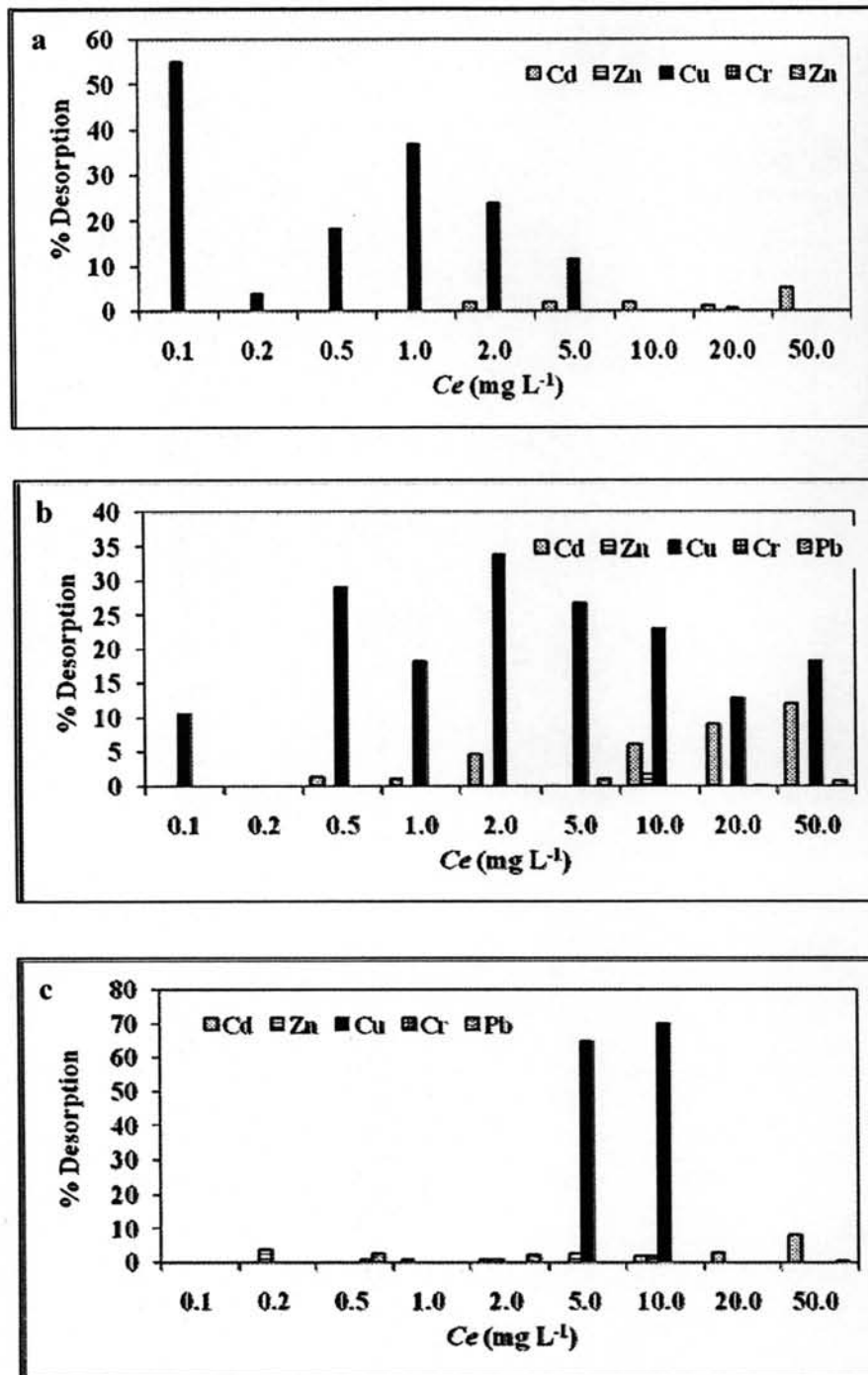


Figure 5.10 Percentage of desorption of sorbed metals in three soil treated with synthetic leachate in monometal system: KBS-1 (a); KBS-2 (b), and KBS-3 (c)

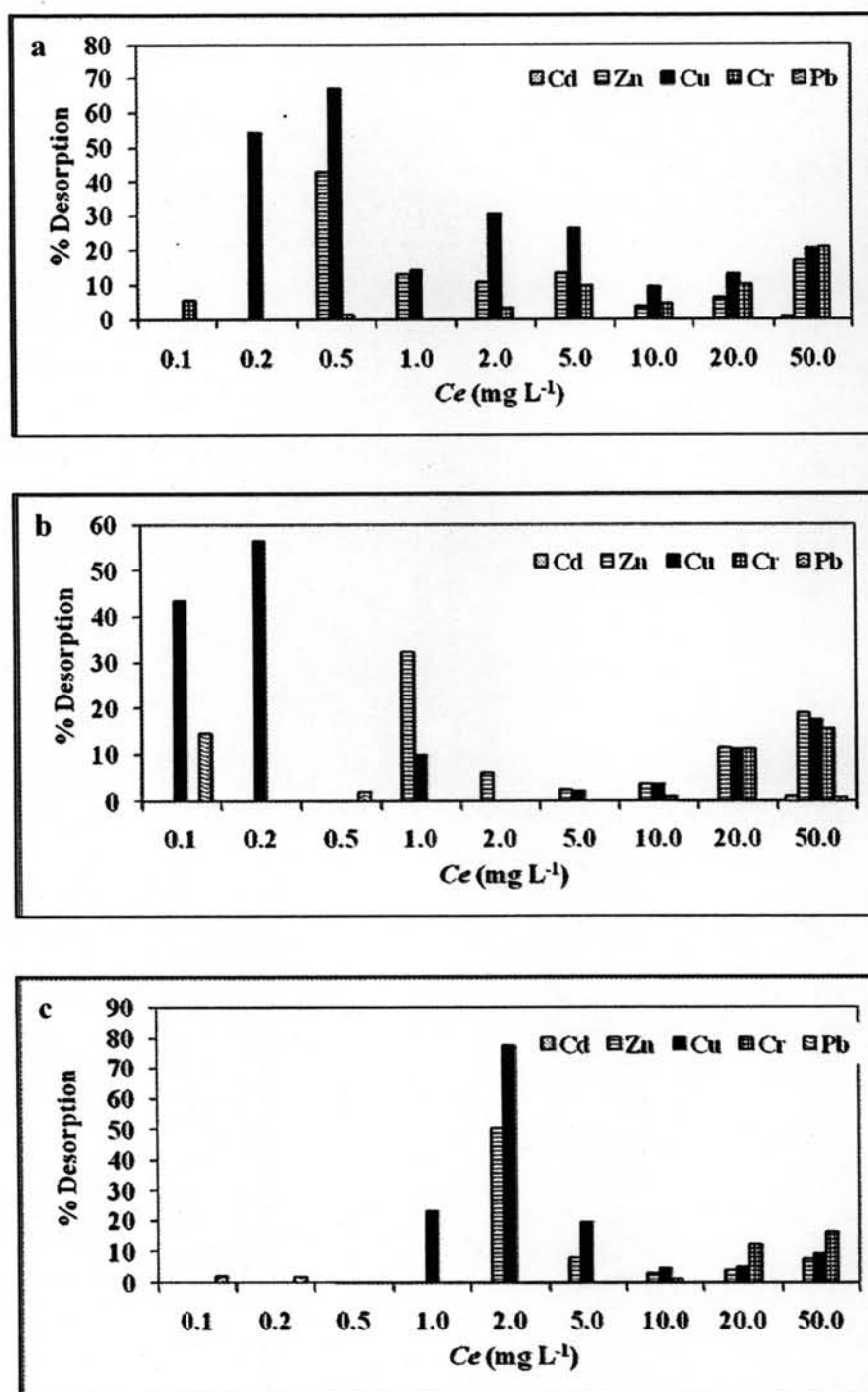


Figure 5.11 Percentage of desorption of sorbed metals in three soil treated with actual leachate in competitive metals system: KBS-1 (a); KBS-2 (b), and KBS-3 (c)

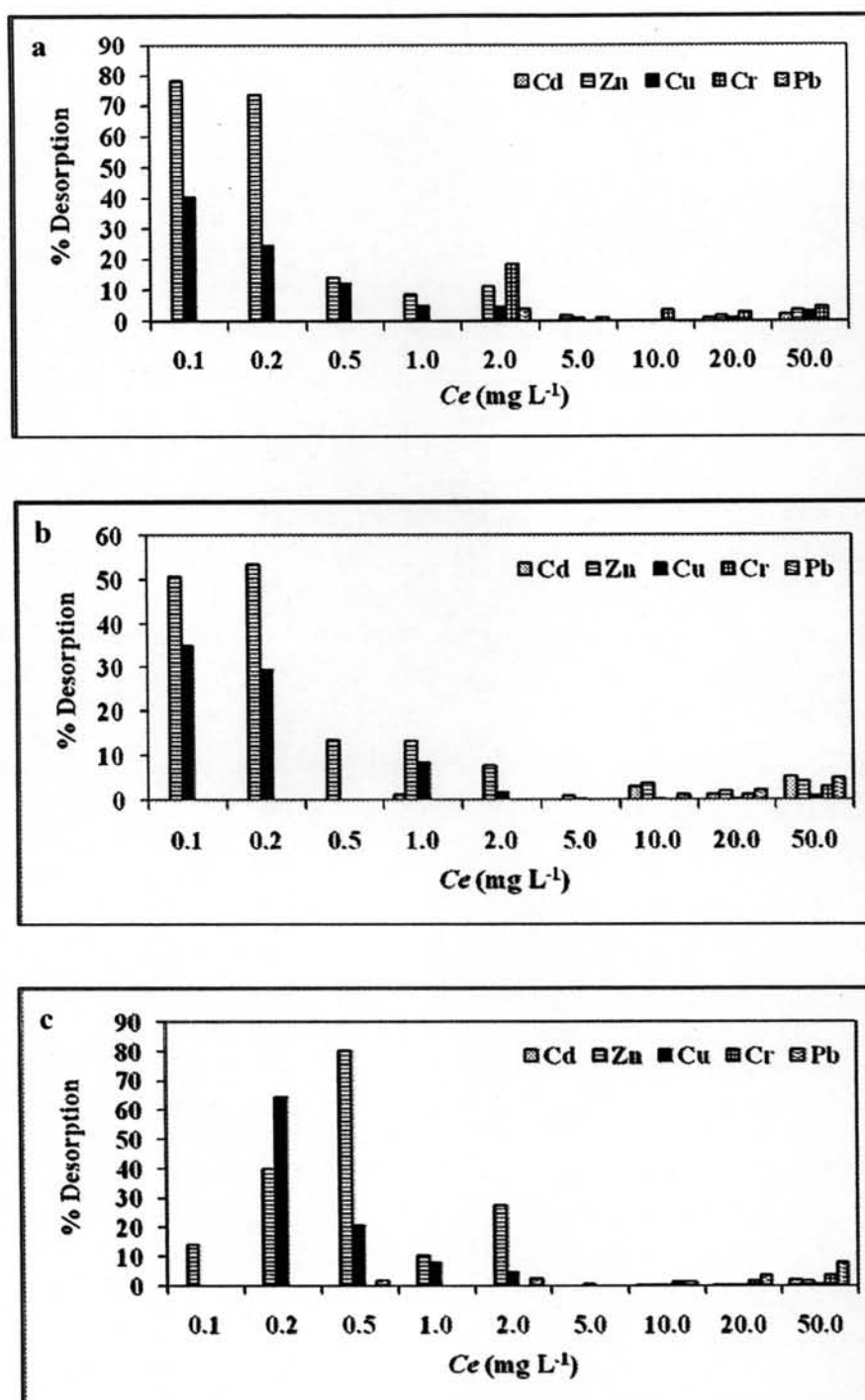


Figure 5.12 Percentage of desorption of sorbed metals in three soil treated with synthetic leachate in competitive metals system : KBS-1 (a); KBS-2 (b), and KBS-3 (c)

studied. This pattern was almost observed for mostly soil. Moreover, this selectivity sequence was also reported in same manner with sorption experiments especially, Cu and Cd (Singh et al., 1968; Alumaa et al., 2001). The different adsorption–desorption behavior of the heavy metals generally suggests that metals strongly adsorbed to soil can stay in the soil for a long time period. The limited desorption of the heavy metals suggested that the sorption reactions taking place were only slowly reversible or a high activation energy is required for desorption. This emphasizes the role of organic matter in the soil heavy metal adsorption, because as previously stated by Sparks, (1995), heavy metals added to soils in the field will be the strongly adsorbed by the first component to which they make contact, i.e. organic matter as the upper part of undisturbed soil horizons. Furthermore, it is almost certain that trace metals adsorbed into oxides and other soil constituents specifically (chemisorption) and sorption reaction generally show poor reversibility (Sposito, 1989) as can be seen in case of Pb from the experiment.

However, it is unclear whether the surface reaction is genuinely irreversible or simply slow in the reverse direction. One explanation for the irreversible nature of metals sorption is that the activation energies (Sposito, 1989).

From the adsorption-desorption study, it is worth mentioning that at least in the first stage after the heavy metals are emitted to the soil environment they remain mainly in the upper horizon of the soil and may not pose environmental problems under normal weather conditions. Heavy metals leach into the water phase also depends on the character of the metal and on the soil type.

5.4 Selective Sequence Extraction

At present, it is widely recognized that the distribution, mobility and bioavailability of heavy metals and radionuclide in the environment depends not only their total concentration but also on the association form in the solid phase to which they are bound (Filgueiras et al., 2002). Some variation of the chemical or physical conditions in the environment can accelerate to some extent the release of toxic metals into it, thus causing contamination.

The distribution of Pb, Zn, Cd, Cr, and Cu within individual fractions of the sequential extraction analysis from natural soil and soil interacted with actual leachate and synthetic leachates are given in Tables 5.24 through 5.26. The geochemical phases at each extraction step are largely operationally defined by the method and reagents used.

5.41 Cadmium

About 25 – 34 % of the total Cd is associated with the exchangeable fraction. The high exchangeability of Cd in some samples agrees with the finding of previous observations (Ramos et al., 1994; Plassard et al., 2000; Thornton, 2001). Hickey and Kittrick, 1984 stated that mobility and bioavailability of the metals decrease approximately in the order of the extraction sequence. The defined extraction sequence follows the order of decreasing solubility of the geochemical forms of the metals; hence the exchangeable fraction may indicate which metals are most available for plant uptake. The carbonate and Fe-Mn oxide fraction are also important phase for Cd in these soils. They fractions accounts for not detected to 73% and 21-50 % (only soil treated with actual leachate), respectively. The organic fraction was not detected in all soils. These results could be explained by the low solubility of cadmium carbonate and the low adsorption constant of the complex formed with the organic matter. The organic matter is being considered labile. This behavior causes Cd becoming more concentrated in the carbonates and the exchangeable fraction. The residual fraction accounts for not detected to 17 % of the total soil Cd concentration. The proportion of Cd fractions follows the order of carbonate > exchangeable > Fe-Mn oxide > residual > organic.

5.4.2 Chromium

The highest contents of Cr were associated with the residual fraction (Lu et al., 2005) and average 59.4 %. Exchangeable, carbonate, Fe-Mn oxide and organic fractions average 9.9 %, 8%, 13.5 %, and 9.2 %, respectively. The amount of Cr in each fraction followed the order of residual > Fe-Mn oxide > exchangeable > organic > carbonate.

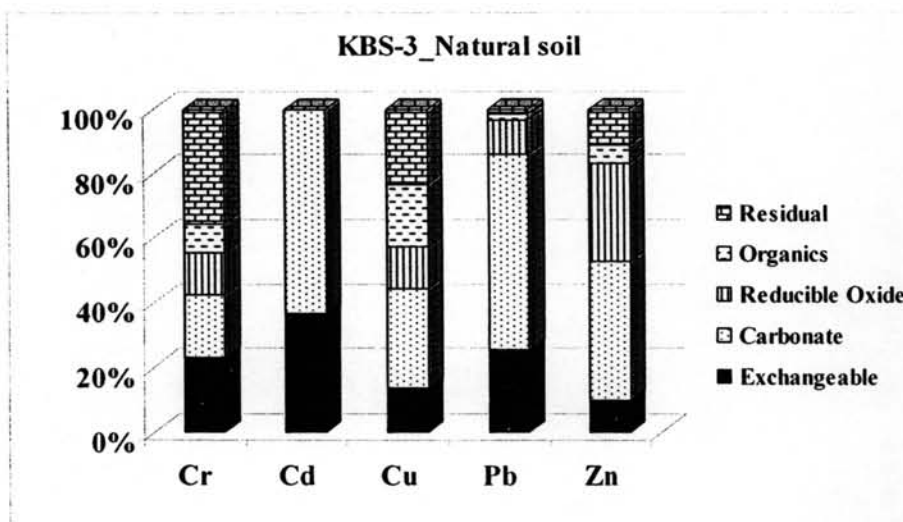
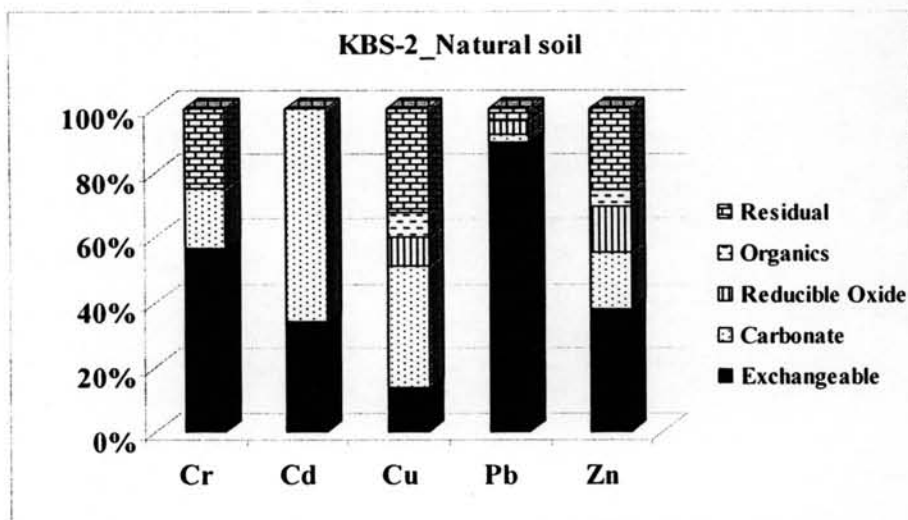
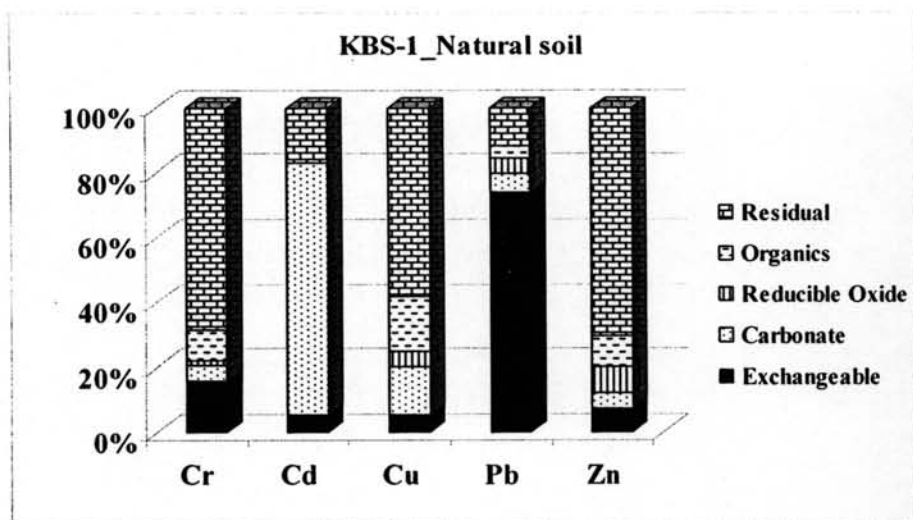


Figure 5.13 Distribution of heavy metals in natural three soils

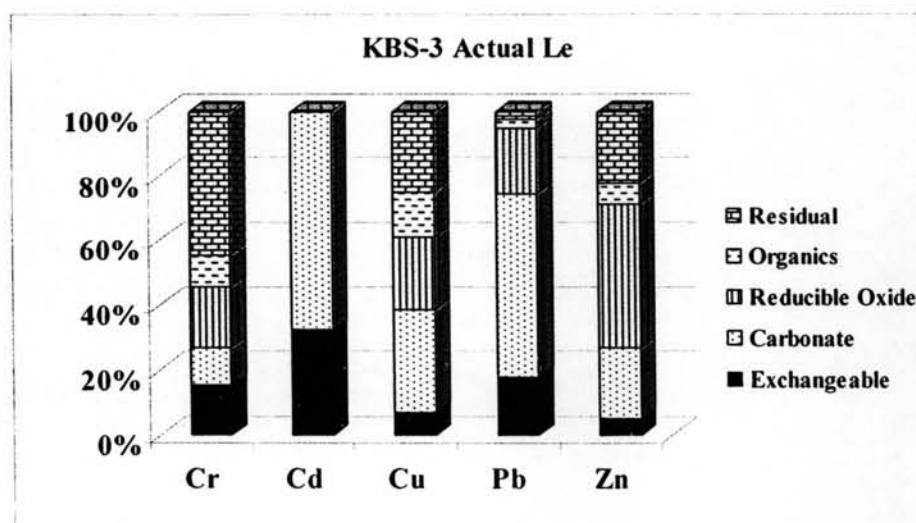
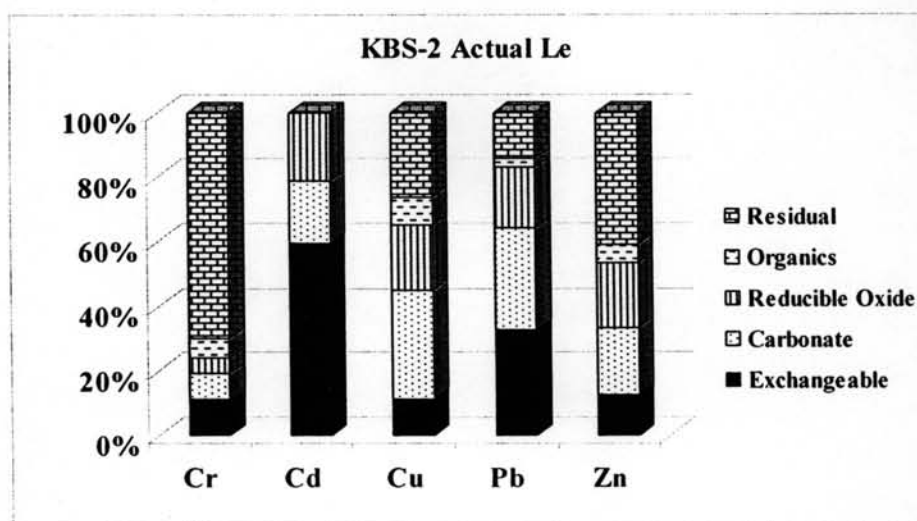
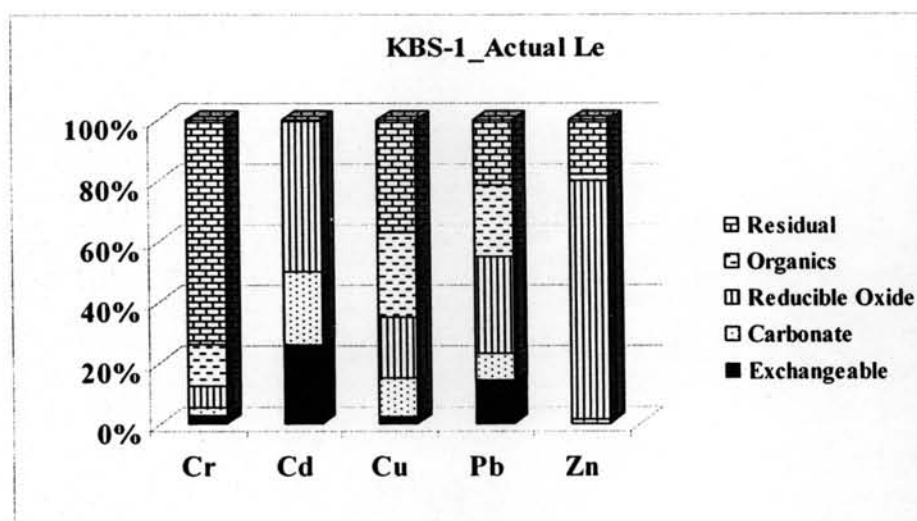


Figure 5.14 Distribution of heavy metals in three soils treated with actual leachate

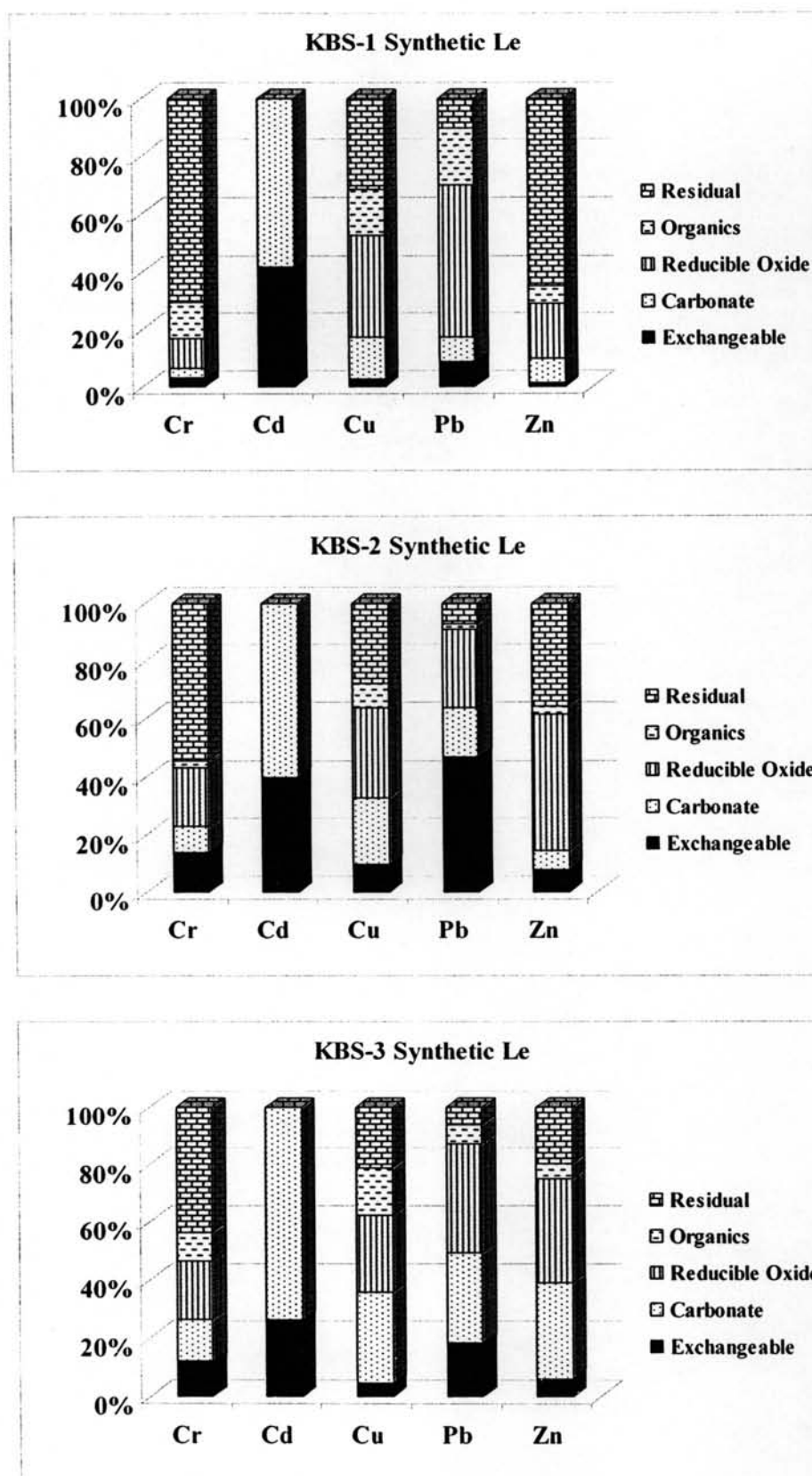


Figure 5.15 Distribution of heavy metals in three soils treated with synthetic leachate

5.4.3 Lead

Lead in soil was shown to be strong associated with Fe-Mn oxide fraction accounts for 31.3 %. The Fe-Mn oxides extracted in this step may indicate that Fe and Mn oxides are of major important in binding Pb in these soils. The next most abundant is carbonate fraction accounts 25.4 %. The exchangeable fraction accounts for 23.3 % of the total Pb in these soils. The percentage of residual is 7.7 %. This fraction may represent the Pb held in the primary mineral. The proportions of Pb fractions follow the order of Fe-Mn oxide > carbonate > exchangeable > organic > residual.

5.4.4 Copper

The highest percentage of Cu associated with carbonate fraction average 31.3 % and the lowest with exchangeable fraction average 7.03 % (Lu et al., 2005). An average 26.9 %, 29.3 % and 16.8 % of Cu is associated with the carbonate, Fe-Mn oxide and organic forms, respectively. The percentage of Cu fraction follows the order as residual > Fe-Mn oxide > carbonate > organic > exchangeable.

5.4.5 Zinc

The majority of Zn is associated with the Fe-Mn oxides (41 %) and residual fractions (33.5 %), which agree with the observation of Hickey and Kittrick (1984) and Li and Thornton (2001) in other contaminated soil. The Zn in carbonate phase accounts for 15.1%. The organic fraction is of minor importance, accounting for less than 5 % of the total Zn in the soils. The exchangeable fraction of Zn is also very low (5.7 %). The percentage of Zn fraction follows the order as Fe-Mn oxide > residual > carbonate > organic > exchangeable.

5.4.6 Mass balance calculations

Mass balance calculation was performed by calculating the deviation of the total heavy metals extracted from SSE and gross heavy metals extracted from acid digestion in KBS-1, KBS-2, and KBS-3 soil. The deviation of SSE ranged from 12% to 50 %. The highest concentration was found in case of Pb in most soil. The percentage of deviation in Pb was very high in comparison with other metals.

From this section, Cd and Cu are focused due to they are easily released from soil. It can be concluded that in Kham Bon soil, cadmium was more observed than other metals in the exchangeable fraction which was the first to be brought into solution and was considered to be easily available for plant uptake. This result is corresponded to the desorption experiment in which cadmium is easily extraction. In contrast to Cd, Cu could be bounded with Fe-Mn oxide and carbonate fractions that play important role in surface complex interaction. It indicates inner sphere complex. However, this behavior of Cu was found the opposite manner in desorption study. Copper was very easily to desorbed in the normal condition in Kham Bon soil. It can be explained by considering that by nature Cu preferentially forms ligand with organic and inorganic compound in the normal condition. When leachate containing chelating agent entered to the soil, Cu also preferentially forms with chelation agent resulting in high detection in the environment. For other metals, oxide and carbonate fractions also played important role in contaminated Kham Bon Soil. These forms indicated the high energy of heavy metals bounded to soil. It is imply that it is hard to expose to the environment in the normal condition. Mostly heavy metals are found lower in the residual fraction. This fraction is not considered to create a bioavailable pool since it is not expected to be solubilized over a reasonable period of time under natural conditions (Tessier et al., 1979).