# Original Research Adsorption Behavior of Heavy Metals on Various Soils

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## Abstract

This article studies the adsorption behaviours of Cu, Ni, and Zn in various natural soils. The effects of contact time, adsorption isotherm, and temperature were investigated using the batch method. The column method was also adopted, to simulate the conditions found in the field. The results indicate that the adsorption isotherm can be satisfactorily described using the Freundlich and Langmuir models. Almost all soils showed adsorption capacities, in the order of Ni>Cu>Zn. The adsorption capacity of the metals increased when temperatures increased. From the column test, we find that heavy metals can be leached from the soil using distilled water. After leaching, the adsorption capacity of the soils slightly increased.

Keywords: heavy metals, adsorption, isotherm, soil, column test

## Introduction

Heavy metals are one kind of toxin that frequently contaminates industrial and municipal wastewaters [1]. They result from a variety of industries, such as mining, plating, dyeing, electrochemical metal processing, and battery storage, plus human activity [2]. Heavy metals are stable elements and cannot be degraded or eliminated [3, 4]. Discharge of wastewater without appropriate treatment leads to residue, and the accumulation of heavy metals in the environment. Heavy metals may be found in soil [3, 5-10], earth's water, groundwater [11], sediments, plants [12], and even in dust [8]. They cause many health problems, including lung damage, renal damage, Wilson's disease (neurological or psychiatric symptoms of liver disease, compounded with heavy metal deposits), insomnia, dermatitis, nausea, chronic asthma, headache, dizziness, rapid respiration, coughing, cancer, etc. [11, 13].

When wastewater is discharged into soil, it seeps through the soil before it progresses downward into groundwater, or it flows past surface soil to lowland. Many studies have found that heavy metals can be removed by soils [14-23]. Accordingly, soils are natural materials that play a role in treating wastewater, before the metals seep into groundwater, or flow into other areas or rivers. The most important process affecting the behaviors of heavy metals in soil is the adsorption of metals from liquid phase into their solid phase [24, 25]. There have been many studies about the behaviors of heavy metals adsorbed by soils, but only a few soils have been investigated in those studies. Furthermore, the simulation of real conditions when wastewater was released into the soil was not comprehensive.

This study investigates the adsorption of the most common heavy metals (Cu, Ni, and Zn) by various soils. Both the batch method and column method were used. The batch method was used to find the effects of contact time, adsorption isotherm and the effects of temperature on adsorption. The adsorption isotherm is explained in the Freundlich and Langmuir models. The column method was also used to

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Soils	Engineering Properties						Chemical Composition (%)			
	$G_s^{a}$	OMC <sup>b</sup>	$(\gamma_d)_{max}^{c}$	k <sup>d</sup>	S <sub>BET</sub> <sup>e</sup>	РН	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Etc.
		(%)	(kg/m <sup>3</sup> )	(cm/s)	m²/g					
CL1	2.78	16.6	1761	4.8E-05	30.2	7.1	61.1	18.8	11.2	8.9
CL2	2.95	15.6	1698	1.8E-04	8.1	6.8	76.4	14.5	4.7	4.4
CL3	2.54	14.9	1802	4.7E-05	21.6	6.5	71.2	16.2	6.3	6.3
СН	2.74	21.0	1612	6.8E-05	38.5	6.2	67.3	18.4	8.1	6.2
CL-ML1	2.56	11.4	1821	6.6E-05	14.6	5.8	78.9	14.8	3.1	3.2
CL-ML2	2.59	14.6	1764	1.5E-04	5.2	6.3	82.5	10.3	2.9	4.3
CL-ML3	2.59	11.3	1866	7.8E-05	3.5	4.3	85.9	8.7	2.0	3.4
SC	2.73	14.0	1845	4.9E-05	26.0	6.4	67.9	17.3	10.6	4.2
SM1	2.62	9.7	1859	3.5E-04	2.2	6.1	91.8	5.5	1.0	1.7
SM2	2.60	10.2	1809	6.4E-04	1.8	6.5	92.8	4.5	1.8	0.9
SM3	2.58	11.7	1823	2.1E-04	2.6	6.4	87.0	7.5	2.0	3.5
SM4	2.62	8.9	1906	6.4E-05	2.6	7.2	89.8	7.3	1.2	1.7
SM5	2.29	9.3	1972	4.7E-05	3.0	6.7	90.0	7.1	1.2	1.7
SM6	2.68	11.0	1882	2.9E-04	4.7	6.7	82.6	10.3	2.8	4.3
SM7	2.62	10.3	1995	3.4E-05	15.1	6.0	75.9	16.7	4.3	3.1

Table 1. Properties of soils.

<sup>a</sup>Gs – specific gravity, <sup>b</sup>OMC – optimum moisture content,  $(\gamma_d)_{max}$  – maximum dry density, <sup>d</sup>k – coefficient of permeability,  ${}^{c}S_{RET}$  – specific surface area

simulate real conditions of heavy metal adsorption. This included the adsorption when wastewater was released into soil, the leaching effects of rain, and the repetitive adsorption rates after rainfall.

## Materials

## Adsorbent

The adsorbents used in this study consisted of 15 soil samples collected from various areas of northeastern Thailand. They were excavated from different depths, ranging from 20 cm to 50 cm below the soil surface. The areas near watercourses and communities or industries were selected as sites from which to excavate the soil samples. Fig. 1 shows the excavation of a soil sample near a canal in a communal area. All soil samples were dried in an oven at 110°C for 48 hours, and then passed through a No. 16 sieve (1.18 mm). From the results of the sieve analysis, and Atterberg limits test, the soil samples can be classified into various types using the unified soil classification system (USCS). The soils included lean clay (CL1, CL2, CL3), fat clay (CH), silty clay (CL-ML1, CL-ML2, and CL-ML3), clayey sand (SC), and silty sand (SM1, SM2, SM3, SM4, SM5, SM6, and SM7). Table 1 shows the engineering properties and chemical compositions of all soil samples.

## Heavy Metal Solutions

Heavy metals chosen as the adsorbed materials in this study were Cu, Ni, and Zn. The lab grades of: copper (II) nitrate hexahydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), and zinc(II) nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) were all used in this experiment. The stock solutions of Cu were completed by dissolving 36.60 g of Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 11itre of distilled water. Similarly, the stock solutions of Ni and Zn were completed



Fig. 1. Excavation of soil sample.

by dissolving 49.61g of Ni(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$  and 45.52 g of Zn(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$  in 1 liter of distilled water, respectively. The stock solutions were then diluted to the desired concentrations, set at a range between 25 mg/l and 1,000 mg/l.

#### **Experimental Work**

#### Batch Test

The procedures of the batch testing began by mixing 2.5 g of soil with 50 cm<sup>3</sup> of heavy metal solutions in bottles. Next, the mixtures were shaken at a velocity rate of 130 cycles per minute using a horizontal shaker. After a defined time, soils were percolated from the heavy metal solutions using a 0.45  $\mu$ m filter. Then the solutions were diluted by mixing them with 1% nitric acid (HNO<sub>3</sub>). These steps were performed at a room temperature of 30°C. Finally, the diluted solution concentrations were determined using an atomic absorption spectrometer (AAS) with the flame method. Batch tests were repeated three times in each experiment in order to establish equilibrium times, adsorption isotherm, and the effects of temperatures on heavy metal adsorption. These are explicated as follows:

## Equilibrium Time Determination

The equilibrium time is the time adsorption takes to reach an equilibrium state. To determine the equilibrium time, the batch method was performed at various lengths of time, i.e. 0.5, 1, 3, 6, 12, 24, 48, and 72 hours, with concentrations of heavy metal solutions at 100 mg/l. By employing this method, the concentrations of solutions at any time were known, and so the adsorption equilibrium time could be established.

### Adsorption Isotherm Determination

After determining the equilibrium time, the adsorption isotherm could be found. The test process was completed using the batch method, with initial concentrations of solutions ranging from 25 mg/l to 1,000 mg/l. This was performed until the adsorptions reached equilibrium. The adsorption isotherm is the relationship between the concentrations of heavy metal solutions, at equilibrium  $C_{eq}$ , and the amounts of heavy metals adsorbed by the soil (q). The value of q can be calculated as follows:

$$q = \frac{(C_o - C_{eq})V_{sol}}{M_s} \tag{1}$$

...where q is the amount of adsorption of heavy metals per unit weight within soil (mg/g),  $C_o$  is the initial concentration of heavy metal solution (mg/l),  $C_{eq}$  is the equilibrium concentration of the solutions (mg/l),  $V_{sol}$  is the volume of solution (cm<sup>3</sup>) and M<sub>s</sub> is the mass of soil (g). The Freundlich isotherm is the most common isotherm model, used to describe physical adsorption in a solid-liquids system [27], and is defined as follows:

$$q_{e} = K(C_{eq})^{1/n}$$
 (2)

...where  $q_e$  is the amount of adsorbed heavy metal per unit weight of soil at equilibrium (mg/g), *K* is Freundlich constant (mg/g), and 1/n is adsorption intensity (dimensionless) [22].

The Langmuir adsorption isotherm has been widely applied to many adsorption processes, specifically those assuming monolayer adsorption on the adsorption surface [28-30]. The Langmuir isotherm is defined as:

$$q_e = \frac{\alpha \beta C_{eq}}{1 + \alpha C_{eq}} \tag{3}$$

...where  $\alpha$  is the Langmuir constant, related to the bonding energy between the adsorbed ion and the adsorbent [27] (l/mg), and  $\beta$  is the maximum adsorption capacity (mg/g).

#### Temperature Effect Determination

Because temperatures of areas around the world fluctuate daily, this research also considered the effects of temperature upon heavy metal adsorption by soil. To establish this, the batch method was performed at specific temperatures (20°C, 30°C, 40°C, and 50°C), with initial concentrations set at 25 mg/l and a contact time of 24 hours. With that set up, the amount of adsorbed metals by soils at each temperature could be identified.

#### Column Test

An important advantage of the batch method is its capability to analyze many samples at the same time. However, a main disadvantage of this method is inconsistency, when compared to real place circumstances. When wastewater is released into soil, adsorption occurs as the wastewater seeps downward through the soil. This is not in accordance with the batch method, but can be simulated using the column method.

The column method is commonly used to determine the dissolve rates of contaminants in contaminated soil. It is also used for the evaluation of groundwater risk, due to the transportation of pollutants from contaminated soils. The apparatus of the column test used in this study are shown in Fig. 2. The method begins with compacting the soil samples in a mould using standard compaction methods with optimum moisture content. Next, a heavy metal solution is



Fig. 2. Column test apparatus.

poured into the top of the container, and the lid then closed. The mould, the top of the container, and the lid are connected using bolts. A pressure pump is applied to create pressure within the container, and in order to push the solution to seep through the soil sample. After seepage, a solution flows out, passing through many small holes at the bottom of the mould, and then falls into a container placed



Fig. 3. Procedures of column method.

under the mould. The flow rates of the heavy metal solutions are controlled by adjusting the pressure from the pressure pump.

To accurately recreate the real conditions of Thailand, where it is continually rainy, three cycles of the column test were completed. In the first cycle, heavy metal solutions were used, in order to simulate the discharge of wastewater, contaminated with heavy metals, into the soil. In the second cycle, distilled water was used. The purpose of this cycle was to simulate the leaching effect of rain. Leached water, which leached the heavy metals surrounding grained soils, was collected, in order to measure the concentrations. The final cycle was performed, again using heavy metal solutions. The purpose of this cycle was to simulate the discharge of wastewater into soils, after rainfall. In each cycle, the solution of distilled water was continuously discharged into the soil samples. The leaked solutions, droplets from the bottom of the mould, were collected in order to find their concentrations, using the AAS technique. This procedure can be summarized as shown in Fig. 3. All steps were performed at room temperature of 30°C.

## **Result and Discussion**

## Effect of Contact Time

To find the effects of contact times, the metal adsorptions in 15 soil samples were investigated at different times. Figs. 4 to 6 show the remaining concentrations of Cu, Ni, and Zn solutions at any elapsed time  $C_t$ . It can be seen that the concentrations of solutions decrease rapidly, especially during the first periods of 0-3 hours. After that, they decline slowly, until they reach a constant within 6-12 hours. This happened because there were abundant active sites on the soil surface during the first period [31]. After that, the active sites were saturated, as a result of the accumulation of the



Fig. 4. Effect of contact time on Cu adsorption by soils.



Fig. 5. Effect of contact time on Ni adsorption by soils.



Fig. 6. Effect of contact time on Zn adsorption by soils.

metals on the soil surfaces [32]. It can be concluded that the equilibrium times of Cu, Ni, and Zn adsorption, by all soil samples, occurred within 6-12 hours. The adsorption rate depends on the metal emigrating from its bulk liquid phase to the actual adsorption site [23].

## Adsorption Isotherm

The adsorption isotherm is necessary to be considered in the equilibrium state. Therefore, the contact time used for finding the adsorption isotherm was set at 24 hours. The initial concentrations of Cu, Ni, and Zn solutions were set at 25, 100, 250, 500, and 1,000 mg/l. The amounts of adsorbed heavy metals 'q' and the equilibrium concentrations ' $C_{eq}$ ' are both plotted (Figs. 7 to 9). These are the adsorption isotherm. It can be seen that the amount of adsorption increased with equilibrium concentrations. This most likely occurred when increasing the driving force of the metals toward active sites of the soils, and thus the concentrations increased [23, 33, 34]. The increasing rate of the amount adsorbed tends to gradually decrease, and converge to the maximum value. This could be explained in that at lower initial concentrations, there were sufficient adsorption sites for adsorbed heavy metal, but at higher concentrations, the amount of heavy metal was too much, compared with the adsorption sites [35]. The Freundlich and Langmuir adsorption isotherms were adopted to describe the isotherm. Table 2 shows the parameters of both the



Fig. 7. Adsorption isotherm of Cu.



Fig. 8. Adsorption isotherm of Ni.



Fig. 9. Adsorption isotherm of Zn.

Freundlich and Langmuir isotherms. Higher values of R<sup>2</sup> (almost all being higher than 0.95) indicate that both models can accurately describe the adsorption isotherm.

When comparing the Freundlich isotherm and Langmuir isotherm, it was found that the Freundlich isotherm can describe the adsorption as competently as the Langmuir isotherm. The consistency of the Langmuir isotherm reveals that the surfaces of soils were covered with a monolayer from the metal particles [33]. The  $\beta$ -parameters of the Langmuir isotherm represent the maximum adsorption capacity of soils. These were plotted against the types of soil samples, as shown in Fig. 10, in order to compare the adsorption capacity of each soil. It can clearly be seen that the clayey group (CL1, CL2, CL3, and CH) displayed the highest adsorption capacity, while the sandy group (SM1, SM2, SM3, SM4, SM5, SM6, and SM7) provided the lowest adsorption capacity. This phenomenon occurred similarly with all heavy metals. The adsorption capacities of all soils, except CL1 and SM1, were in the order of Ni>Cu>Zn. This shows both similarity and distinction when compared to other work. The heavy metal ion adsorption by red loess [21] or kaolinite [25] was seen to be Cu>Zn. The natural



Fig. 10. Maximum adsorption capacity  $(\beta)$  of soil samples.



Fig. 11. Normalized values of  $\beta$  and  $S_{BET}$  of soil samples.

Table 2.	Parameters	of Freundlich	and	Langmuir.

Soil	Heavy metals	Fr	eundlich paramete	ers	Langmuir parameters			
	Treavy metals	K	1/ <i>n</i>	<b>R</b> <sup>2</sup>	β	α	<b>R</b> <sup>2</sup>	
CL1	Cu	1.636	0.329	0.9285	12.66	0.035	0.9782	
	Ni	0.811	0.394	0.9989	11.47	0.014	0.9665	
	Zn	1.422	0.216	0.9851	6.58	0.028	0.9913	
	Cu	0.353	0.343	0.9970	3.93	0.010	0.9731	
CL2	Ni	0.285	0.413	0.9973	5.22	0.008	0.9787	
	Zn	0.297	0.221	0.9991	1.44	0.015	0.9872	
CL3	Cu	0.572	0.367	0.9957	6.69	0.015	0.9827	
	Ni	0.383	0.438	0.9919	7.52	0.010	0.9816	
	Zn	0.467	0.296	0.9801	3.20	0.026	0.9966	
	Cu	0.601	0.342	0.9128	4.90	0.041	0.9993	
СН	Ni	0.722	0.342	0.9976	7.59	0.014	0.9764	
	Zn	0.744	0.223	0.9927	3.34	0.029	0.9960	
	Cu	0.227	0.367	0.9855	2.82	0.011	0.9891	
CL-ML1	Ni	0.148	0.485	0.9904	4.49	0.006	0.9832	
	Zn	0.180	0.253	0.9406	0.94	0.029	0.9994	
	Cu	0.472	0.240	0.9451	2.22	0.038	0.9987	
CL-ML2	Ni	0.220	0.432	0.9968	4.70	0.007	0.9758	
	Zn	0.256	0.260	0.9452	1.44	0.022	0.9965	
	Cu	0.295	0.330	0.9956	3.00	0.011	0.9793	
CL-ML3	Ni	0.140	0.486	0.9944	4.53	0.005	0.9752	
	Zn	0.206	0.235	0.9799	1.09	0.015	0.9943	
	Cu	0.797	0.311	0.9974	7.06	0.014	0.9732	
SC	Ni	0.365	0.442	0.9905	7.33	0.010	0.9862	
	Zn	0.467	0.277	0.9888	2.90	0.025	0.9965	
	Cu	0.199	0.313	0.9892	2.09	0.007	0.9548	
SM1	Ni	0.120	0.418	0.9382	2.09	0.010	0.9934	
	Zn	0.119	0.211	0.9913	0.53	0.017	0.9967	
SM2	Cu	0.101	0.375	0.9783	1.70	0.005	0.9525	
	Ni	0.056	0.572	0.9907	3.64	0.003	0.9726	
	Zn	0.107	0.182	0.9720	0.37	0.022	0.9973	
	Cu	0.580	0.284	0.9615	3.92	0.019	0.9859	
SM3	Ni	0.347	0.357	0.9977	4.68	0.008	0.9650	
	Zn	0.162	0.349	0.7862	1.46	0.027	0.9995	
	Cu	0.436	0.220	0.9989	2.07	0.017	0.9895	
SM4	Ni	0.244	0.391	0.9861	4.59	0.005	0.9416	
	Zn	0.308	0.167	0.9780	0.94	0.035	0.9986	
	Cu	0.405	0.226	0.9936	2.17	0.012	0.9789	
SM5	Ni	0.163	0.437	0.9812	4.17	0.005	0.9546	
	Zn	0.265	0.148	0.9667	0.72	0.036	0.9985	
	Cu	0.093	0.370	0.9597	1.57	0.004	0.9408	
SM6	Ni	0.091	0.434	0.9111	1.65	0.012	0.9960	
	Zn	0.108	0.162	0.9545	0.36	0.015	0.9926	
	Cu	0.164	0.376	0.9968	2.59	0.006	0.9602	
SM7	Ni	0.092	0.516	0.9922	3.91	0.004	0.9692	
	Zn	0.111	0.324	0.9901	1.07	0.010	0.9927	



Fig.12. (a) SEM photograph of soil samples (CL1), (b) SEM photograph of soil samples (CL2), (c) SEM photograph of soil samples (CL3), (d) SEM photograph of soil samples (CH), (e) SEM photograph of soil samples) (CL-ML1), (f) SEM photograph of soil samples (CL-ML2), (g) SEM photograph of soil samples (CL-ML3), (h) SEM photograph of soil samples (SC).



Fig.12. Continued. (i) SEM photograph of soil samples (SM1), (j) SEM photograph of soil samples (SM2), (k) SEM photograph of soil samples (SM3), (l) SEM photograph of soil samples (SM4), (m) SEM photograph of soil samples (SM5), (n) SEM photograph of soil samples (SM6), (o) SEM photograph of soil samples (SM7).

kaolinite clay adsorbed Ni>Cu [23], while the natural clay adsorbed Zn>Cu [22]. The metal adsorption by three soils in Spain was found to be Cu>Ni>Zn [24]. The important factor affecting the value of  $\beta$  was specific surface area (SBET), which can be evaluated using an 'accelerated surface area and porosimetry analyzer' (ASAP). The values of specific surface area are shown in Table 1. To clearly observe the effects of SBET upon adsorption capacity, the normalized values of  $\beta$  and SBET for each soil were plotted against the types of soil in the same graph, as shown in Fig. 11. It was found that the SBET-value and the  $\beta$ -value generally have similar trends, and this can predicate that the adsorption capacity significantly depended upon the specific surface area. Figs. 12(a) to 12(o) display photographs of 15 soil samples using a 'scanning electron microscope' (SEM) at 1000x magnification. As shown in Figs. 12(a) to 12(o), the surfaces of the clayey group (CL1, CL2, CL3, and CH) are rougher than the other groups, while the sandy group (SM1, SM2, SM3, SM4, SM5, SM6, and SM7) shows only slight roughness. The roughness correlated with the specific surface area. Increasing roughness (including porosity) produced a greater specific surface area, which led to the adsorbent having a higher adsorption capacity.

## Effect of Temperature on Adsorption

To investigate the effect of temperature upon the heavy metal adsorption, four soil samples, i.e. SM1, CL-ML2, CL-ML3, and CL3 were chosen to be tested. The initial concentrations of heavy metal solution were 25mg/l, and the contact time 24 hours. Figs. 13 to 16 show the effects of temperature upon heavy metal adsorption by SM1, CL-ML2, CL-ML3, and CL3, respectively. It was found that temperature had an obvious effect on heavy metal adsorption, displaying the same pattern for all soils. The amount of all metals (Cu, Ni, and Zn) adsorbed (q) increases when the temperature increases from 30°C to 40°C and 50°C. This was consistent with a previous report, which stated that the uptake of Cu and Zn by red loess increases when temperature increases from 25°C to 40°C [21]. The increase of adsorption with temperature could be due to changes in pore size of the adsorbent, causing intra-particle diffusion



Fig. 13. Temperature effect on heavy metal adsorption by SM1.

within the pore [35, 36], or expansion within the active surface site when the temperature increases [13, 36]. It also could be explained that the movement of the metal to the adsorbent increases with an increase in temperature [29]. When the temperature changed from 30°C (the average temperature in Thailand) to 40°C and 50°C, the amount of



Fig. 14. Temperature effect on heavy metal adsorption by CL-ML2.



Fig. 15. Temperature effect on heavy metal adsorption by CL-ML3.



Fig. 16. Temperature effect on heavy metal adsorption by CL3.

Cu, Ni, and Zn adsorbed (q) reached up to 39% (for CL-ML3), 57% (for CL3), and 52% (for CL3), respectively. It was observed that most of the adsorptions dropped slightly when the temperature changed from 40°C to 50°C. This could be due to an increased desorption phenomenon at higher temperatures [35]. At lower temperatures (when the temperature increases from 20°C to 30°C) the amounts adsorbed for all soil samples decreases, especially CL3. The exception here is CL-ML3. The decrease in adsorption with increasing temperature could be a result of an increase in the average kinetic energy of the metal ions. This leads to insufficient attractive forces between the metal ions and the adsorbent, to hold the metal ions at the active site [37].

## Column Test

In the column method, CL-ML2 and SM1, which can generally be found in abundance, were selected to be tested. The initial concentrations of Cu, Ni, and Zn solutions were 500 mg/l. The solutions were applied in the first and the third cycles, with distilled water in the second cycle, and were continuously discharged into the soil samples. When the solutions accumulated to the desired volumes they were then collected in order to determine the concentrations. The flow rates were controlled by adjusting the pressure pump.

Figs. 17 and 18 show the adsorption rates of Cu, Ni, and Zn, by CL-ML2 and SM1, respectively. The horizontal axis represents the volume of a collected solution V, per mass of soil m. The vertical axis represents the concentration of a collected solution C, per the initial concentration of solution  $C_o$ . The results comprise three intervals, which represent the three cycles investigated. We see that in figure 17, the first cycle, the values of  $C/C_o$  for all heavy metals at the beginning were very low. Thereafter, they increased rapidly until they approached a value of 1. This indicates that greater adsorption occurred in the first period and quickly decreased, until the soil approached saturation point. This phenomenon is caused by a reduction of the surface adsorption. In the second cycle, when distilled water was used, the water seeped through the soil and displayed only slight concentrations throughout the intervals. This indicates that the metals can be leached using distilled water, and with frac-



Fig. 17. Heavy metal adsorption of CL-ML2 from the column method.



Fig. 18. Heavy metal adsorption of SM1 from the column method.

tional volume. The leaching of the metals by CL-ML2 ranged in the following order: Ni>Zn>Cu. For the third cycle, a similar shape to the first cycle was observed, although the adsorption capacity was lower than the first cycle. In this cycle, the value of  $C/C_o$  of Cu was greater than 1. This was a result of the fact that the Cu particles, which attached to the soil surface, were leached by the Cu solution. Therefore, both distilled water and Cu solution can leach the particles of Cu from the surface of CL-ML2. The first point of  $C/C_o$  in the last cycle slowly dropped below the last point of  $C/C_o$  in the first cycle, indicating that the adsorption capacity of the soil slightly increased after leaching.

The heavy metal adsorption by SM1 (Fig. 18) was similar to the adsorption by CL-ML2. However, in the first cycle, the value of  $C/C_o$  suddenly increased, and then remained somewhat constant, until the end of the cycle. In the second cycle, leaching occurred with very small volumes which ranged in the following order: Zn>Cu>Ni. In the final cycle, the behavior of the adsorption was similar to the first cycle. It can be seen that the adsorption capacity was better after leaching. For Cu adsorption, the values of C/Co were greater than 1, in both the first and the last cycles. This supports the results which were found in CL-ML2, in that the leaching of Cu was caused by both distilled water and Cu solution.

Generally, there are two mechanisms in heavy metal adsorption, which include specific adsorption and non-specific adsorption. Specific adsorption is a less reversible reaction, and happens slowly. Non-specific adsorption (or ion exchange) is reversible and occurs quite quickly [21]. In this study, it was found that the heavy metal adsorption was reversible (because the metals could be leached) and occurred quickly. Therefore, the principal mechanism of heavy metal adsorption by soil was ion exchange.

#### Conclusion

From this study of the Cu, Ni, and Zn adsorption rates by various soils, the results indicate that the equilibrium condition occurred within 6-12 hours. The adsorption isotherms can satisfactorily be described by both the Freundlich and Langmuir models. Clayey soils displayed the highest adsorption capacity, while sandy soils provided the lowest adsorption capacity. Almost all soils showed adsorption capacity in the order of Ni>Cu >Zn. The adsorption capacity depends significantly upon the specific surface area of the soils. Temperature also affected the adsorption, in that the adsorption capacity increased with increased temperature. Seen from the column test, a large amount of heavy metal adsorbed by soils was observed in the first period. Thereafter, this decreased with time, until almost an inability to adsorb came at the end period. Leaching was possible when the water had seeped through the soil. After leaching, the heavy metal adsorption occurred again in small amounts. The heavy metal solutions can also therefore leach the heavy metals from the soil surface.

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