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Heavy metals migration through the clayey soil from Telipok, Sabah

Pergerakan logam-logam berat melalui tanah berlempung daripada Telipok, Sabah

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Abstract: The migrations of heavy metals namely Cu, Cr, Ni, Pb and Zn through the soil from weathered rock of the Crocker Formation in Telipok, Sabah were studied by means of leaching test. The leaching test conducted on soil samples shows that most of the heavy metals are retained at the top part of the leaching columns i.e. at the depth of 1.0 cm. All of the heavy metals concentration decreased with the increasing depth within the soil profiles. The leachate analysis indicated that all of the heavy metals except Pb achieved the breakthrough curves at the first 4 pore volume (PV). The breakthrough curve for Pb was achieved after 5 PV of leaching. From this study, based on the breakthrough curves and mass balance calculation, it can be concluded that variation occurs during migration or mobilisation of heavy metals. After leaching 7 PV of solution, the relative concentration (C_i/C_0) of Cu, Cr, Ni, Pb and Zn are maintained at 0.90, 0.82, 0.98, 0.94, and 0.80 respectively. The data obtained indicates that Zn has high mobility followed by Cu, Ni, Cr, and Pb. At the end of the leaching test, the microstructural study showed the occurrence of micro cracks, high pore spaces and the forming of channels at the top part of the columns. Whereas, the bottom part shows tight structure with low pore spaces and low form of channels.

Abstrak: Perpindahan logam-logam berat iaitu Cu, Cr, Ni, Pb, dan Zn melalui tanah terluluhawa yang berasal daripada batuan Formasi Crocker di Telipok, Sabah telah dikaji melalui ujian larut lesap. Ujian larut lesap yang dijalankan ke atas sampel-sampel tanah menunjukkan logam berat kebanyakannya terperangkap di bahagian atas turus larut lesap iaitu pada kedalaman 1.0 cm. Kesemua logam-berat menunjukkan kepekatan yang berkurangan dengan bertambahnya kedalaman profil. Analisis air larut resapan menandakan bahawa kesemua logam-logam berat mencapai lengkung bulus pada empat isipadu pori yang pertama (4 PV), kecuali Pb. Lengkung bulus Pb dicapai selepas larut lesap 5PV larutan. Setelah larut lesapan 7 PV larutan, kepekatan relatif (C_i/C_0) bagi Cu, Cr, Ni, Pb dan Zn masing-masing adalah dikekalkan pada 0.90, 0.82, 0.98, 0.94, dan 0.80. Daripada kajian ini, disimpulkan bahawa berdasarkan lengkung bulus dan kiraan imbangan jisim didapati bahawa perpindahan atau pergerakan logam-logam berat adalah pelbagai. Data yang diperolehi menandakan bahawa Zn mempunyai pergerakan yang lebih pantas diikuti oleh Cu, Ni, Cr dan Pb. Pada akhir ujian larut lesap, kajian struktur mikro menunjukkan pembentukan retakan mikro, ruang-ruang pori yang besar dan pembentukan alur-alur pada bahagian atas turus. Manakala, bahagian bawah menunjukkan struktur yang padat dengan rendahnya ruang-ruang pori dan sedikit permbentukan alur-alur.

INTRODUCTION

Contamination or pollution is any concentration of a potentially harmful substance released into the environment to cause hazards to human health, harm to living resources and ecological system (Holdgate, 1979). Leaching of heavy metals can degrade the land and water systems. The leaching of heavy metals occur in a landfill site or due to the improper handling of hazardous waste. The leachate or the liquid, which contain heavy metal such as copper, chromium, nickel, lead, and zinc is derived from the interaction of rainwater with solid waste or contaminated soil. Leachate upon entering the surface water bodies or groundwater result in water pollution. This could bring damage to human health through drinking water or food from plants and animals, which is assimilated the chemicals from the contaminated land and contaminated water. Soil contaminated with heavy metals can be evaluated by comparing the concentration in the soil with the critical levels of concentration.

Leaching test is one of the common methods used to investigate the migration of heavy metals in the soil. Leaching tests apparatus were design to predict a long-term behaviour of heavy metals contaminant in soil samples. Environmental conditions during the leaching test allow a much greater degree of contact between the soil samples and leachate than that occurring in nature. Hence simulation can be conducted in a relatively short period of time compared to the field conditions. Several studies on soils under leaching conditions has been carried out by researchers interested in determining the long-term effects of hazardous fluids or industrial wastes on clay liner (Yong

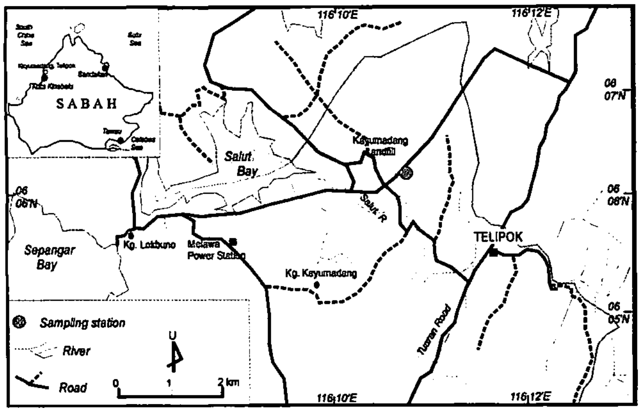

Figure 1. Map of the study area shows the location of sampling station in Kg Kayumadang, Telipok, Sabah.

et al., 1985; Sallfors and Pierce, 1985; Lind *et al.*, 1998; Gelinas *et al.*, 1998; and Albino *et al.*, 1996). However, no such studies have been conducted on the soils from the study area. The objective of this study is to assess the migration of heavy metals namely copper, chromium, nickel, lead, and zinc through the soil columns. Microstructural features before and after the leaching test will also be examined using scanning electron microscope (SEM).

MATERIAL AND METHODOLOGY

Material

A clayey soil at Kg. Kayumadang, Telipok, Sabah was collected from weathered sedimentary rocks of the Crocker Formation (Fig. 1). The study area is controlled by tropical climate, which facilitates the weathering processes resulting in very deep soil profiles. Three representative soil samples were collected near the Kayumadang landfill at Telipok, Sabah area for further analysis. The hand specimen sample was light brown to yellow in colour. Crocker Formation consists of gray sandstone, closely bedded gray sandstone and siltstone, and gray, red, gray and black mudstone and shale (Collennette, 1958). The age of Crocker Formation is Early Miocene to Middle Eocene (Collennette, 1958; Basir *et al.*, 1991). Structural study by Felix Tongkul (1987) found that the thickness of Crocker Formation ranges between 200 m and 600 m.

The X-ray diffraction analysis indicated that soil samples consist of quartz, kaolinite, and montmorillonite. The result gained from the basic physico-chemical properties tests of soil samples are given in Table 1.

Sample Preparation

For the sample preparation, air-dried soil were mixed carefully with distilled water. The percentages of water for each sample were obtained from the compaction standard Proctor test, where the optimum dry density is 1.70 mg/m^3, whereas the optimum moisture content is 15.0%. The soil samples are compacted with 97% of the maximum dry density and water content is 14.6%. The samples were compacted in three layers using static compaction by using ELE Digital Tritesting Instrument in the leaching cell. The leaching cell comprised of 150 mm height and 100 mm diameter cylindrical plexiglass. The samples were saturated for at least 48 hours with distilled water. At the end of the saturation process the distilled water in the leaching cell container was exchanged with the solution of heavy metals spiked with nitrate salts. These salts acted as inorganic complex agents that will be referred to as the multi component contaminants of heavy metals. The spike solution contains 561 ppm copper nitrate [$Cu(NO_3)_2.3H_2$], 563 ppm chromium nitrate [$Cr(NO_3)_3.9H_2O$], 564 ppm nickel nitrate [$Ni(NO_3)_2.6H_2O$], 564 ppm lead nitrate [$Pb(NO_3)_2$], and 571 ppm zinc nitrate [$Zn(NO_3)_3.6H_2O$]. The pH was maintained at pH of 3.2 to keep an acidic environment for the solution of heavy metals.

The leaching tests were performed under a constant air pressure of 15 psi. This is to reduce the time factor taken by the leachate to permeate through the soil columns. The solution were leached through the leaching cell and the leachates were collected every 1 pore volume (PV). The PV of samples were calculated based on the porosity and the volume of the samples. The PV for the soil sample is 285 ml, which is about 2.5 litre for 7 PV of solution. At the end of the leaching test the samples were extruded and sliced to four layers, which is represented the depth of 1.0 cm, 3.0 cm, 5.0 cm and 7.0 cm respectively. The pH values for each layer were then measured immediately with the ratio of soil and water as 1:2.5. The concentrations of Cu, Cr, Pb Ni, and Zn at the leached samples, as well as leachate collection samples were measured using flamed

Table 1. The physical-chemical properties of soil samples.

Parameter	Values
Moisture content, Wo (%)	19.53 – 22.55
Liquid Limit, LL (%)	46 – 51
Plastic Limit, PL (%)	23 – 25
Plasticity Index, PI (%)	23 – 26
Specific Gravity, SG	2.65 – 2.66
Clay (%)	22.91 – 32.38
Silt (%)	21.59 – 33.25
Sand (%)	22.91 – 46.03
Dry Density, _D (mg/m^3)	1.69 – 1.73
Optimum moisture content, (%)	14.0 – 16.0
Compressive strength, q_u (kPa)	184 – 228
Permeability, k (m/s)	(4.81 x 10^{-7} – 4.73 x 10^{-9})
Organic Matter (%)	0.74 – 1.78
Specific surface area, SSA (cm^2/g)	21.1
Cation exchange capacity, CEC (meq/100gm)	0.14 – 0.29
Cr (ppm)	103
Cu (ppm)	17
Ni (ppm)	8
Pb (ppm)	16
Zn (ppm)	28

atomic absorption spectrometer (FAAS) Model 1400 Perkin Elmer. Microstructural features after the leaching test were evaluated using scanning electron microscope (SEM) model Philips XL40.

RESULT AND DISCUSSIONS

The migration of heavy metals in the soil samples was presented based on the migration profile analysis on the soil column. The migration profile shows the characteristic pollutant sorption curves that indicate sorption of the pollutants results from continuous input of the influent pollutant leachate. The concentration of leachate from the leaching cell is analysed using the breakthrough curve. The breakthrough curve is expressed as relative concentration C_i/C_o i.e. the ratio of the concentration of the target pollutant in the leachate at the instant of time *i* to the concentration of the influent target pollutant. According to Yong (2000) the 50% point on the ordinate marks the point of breakthrough of the target pollutant in the candidate soil being tested. The mass balance was calculated to examine the percentage of heavy metals retained compared to the acid digestion.

The migration profiles and breakthrough curves of pH, and heavy metals namely Cu, Cr, Ni, Pb, and Zn are described as following.

pH

The migration profile of pH in leached samples as illustrated in the Figure 2 shows that after 7 PV of leaching the range of pH was within 3.2 and 3.4. This indicates the soil solution has high H^+, which is contributed from the contaminant solution. Figure 3 shows the leachate has an acidic environment. From the figure, it is noted that the soils tend to resist changes in the pH at 1 PV of leaching. This indicates the high buffering of soil at the early process of leaching. After 1 PV of leaching the pH was seen decreased immediately from 6.8 to 4.1 before maintaining around 4.0 until the end of the leaching period. This allowed high concentration of heavy metals to migrate.

Copper (Cu)

The soil samples show high concentration of Cu at the depth of 1.0 cm that is 580 ppm, which gradually decreased with the depth of the soil column (Fig. 2). The relative concentration (C_i/C_o) for Cu shows the immediate increase of C_i/C_o from 0.08 to 0.53 after 2 PV of leaching (Fig. 3). The C_i/C_o value gradually increased to 0.93 after 7 PV of leaching. This indicates the soil was capable of retaining Cu until 2 PV. However, further leaching in soil columns resulted in the release of Cu via leachate. The soil slightly achieved the breakthrough curve at C_i/C_o 0.90 i.e. after 7 PV of leaching.

Chromium (Cr)

The migration profile of Cr shows that Cr concentration decreased gradually until the depth of 5.0 cm before increasing to the depth of 7.0 cm (Fig. 2). The highest concentration was observed at the top part of the soil column i.e. 694 ppm and the lowest concentration was at the depth of 5.0 cm i.e. 425 ppm. This indicates that the retention of Cr occurred in the top of soil column. Migration of Cr through the soil column after the carrying capacity is reached was then observed. The relative concentration (C_i/C_o) shows that Cr is significantly retained until 2 PV of leaching (Fig. 3). At this stage, it indicates the exchange of Cr with the cation in the soil surface, where the soil shows the high carrying capacity. Further leaching found the C_i/C_o is immediately increased from 0.04 at 2 PV of leaching to 0.83 at 7 PV of leaching. This indicates the achievement of breakthrough curve where the C_i/C_o was about 0.82.

Nickel (Ni)

The migration profile of Ni shows the concentration of Ni was within 213 ppm and 468 ppm. The concentration of Ni decreased gradually with the depth (Fig. 2). The breakthrough curves of Ni in samples after 7 PV of leaching show the gradual increase of Ni from 1 PV until 7 PV of leaching (Fig. 3). The high C_i/C_o slightly achieved the breakthrough curve after 7 PV i.e. 0.98.

Lead (Pb)

Based on the migration profile, it is noted that the retention of Pb was high at the depth of 1.0 cm and slightly decreased through the bottom part of soil column (Fig. 2). The range of Pb concentrations was within 278 ppm and 562 ppm. The breakthrough curve of Pb shows significant retention of Pb at the first 3 PV of leaching due to the soil having high capacity to exchange Pb from the solutions (Fig. 3). The values of C_i/C_o also show immediate increase from 4 PV of leaching to 6 PV of leaching ($C_i/C_o = 0.939$), before maintaining at 7 PV of leaching.

Zinc (Zn)

The migration profiles of Zn shows the concentration of Zn were within 257 ppm – 496 ppm (Fig. 2). High retention of Zn was at the depth of 1.0 cm with the concentration of 496 ppm was observed. It is also noticed that Zn gradually decreased from the depth of 3.0 until the 7.0 cm. The pattern of migration profile of Zn is similar with those for Cu and Pb in the soil column. The breakthrough curve of Zn in Figure 3 shows the relative concentration (C_i/C_o) of Zn has increased immediately from the first 3 PV of leaching, which indicates the high mobility of Zn through the soil column. After 4 PV of leaching the Zn concentration in the leachate was slightly maintained. Hence, the breakthrough curve was achieved at C_i/C_o about 0.80.

Mass Balance Calculations

The mass balance calculations for Cu, Cr, Ni, Pb, and Zn samples are summarized in Figure 4. All heavy metals in the soil samples show significant migration from the contaminant solution through the soil columns. The concentration of Cu, Cr, Ni, Pb, and Zn released (C_i) were 0.53 g/l, 0.37 g/l, 0.39g/l, 0.30 g/l and 0.52g/l respectively. On the other hand the percentages of Cu, Cr, Ni, Pb, and Zn retained (C_R) were 51% g/l, 61% g/l, 54%, 64% and 45% respectively. The result indicates that Zn is more mobile compared to the other heavy metals, followed by Cu, Ni, Cr and Pb. It is also found that the deviation of the amount retained (C_R) and amount of acid digestion (C_T) was less than 26%. The lowest deviation is shown for Zn, which was 18.4% and the highest was 25.5% for Pb. The high value of Pb from soil acid digestion (C_T) in comparison with calculated soil retained (C_R) might be due to the inaccuracy of sample preparation and analysis of the soil samples.

Micro structural study

The result of scanning electron photomicrograph original soil samples are shown in Figure 5. It indicates the appearance of sub angular like shaped of quartz mineral and layered of kaolinite minerals. The microstructures of soil sample after leaching test at the depth of 1.0 cm are illustrated in Figure 6. The dark spot background in the photomicrograph indicates the presence of pore spaces. The formation of pore space was due to the washed out of fine particles to the bottom part of soil columns. At the mean time, fine particles clogged the pore spaces at the bottom part of the column thus slightly reducing the permeability. The alterations and rearrangement of layered minerals in the bottom part (at the depth of 8.0 cm) of soil sample is observed. This indicates the low pore space of the soil, which reduced the permeability.

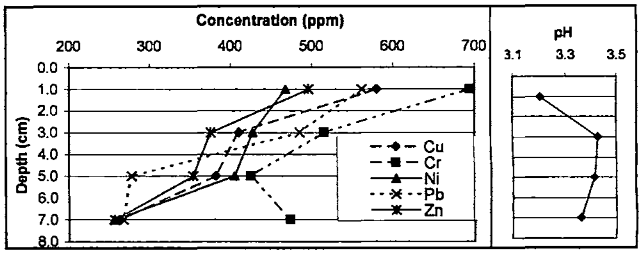

Figure 2. pH value and migration profile of Cu, Cr, Ni, Pb, and Zn after leaching 7 pore volume of contaminant through the soil samples.

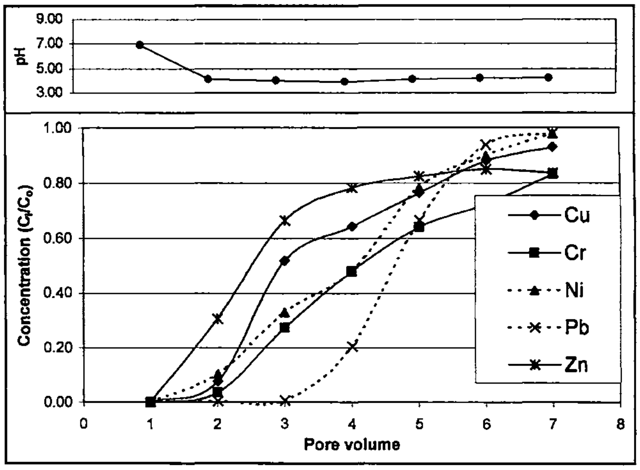

Figure 3. pH value and concentration of Cu, Cr, Ni, Pb, and Zn in leachate after leaching 7 pore volume.

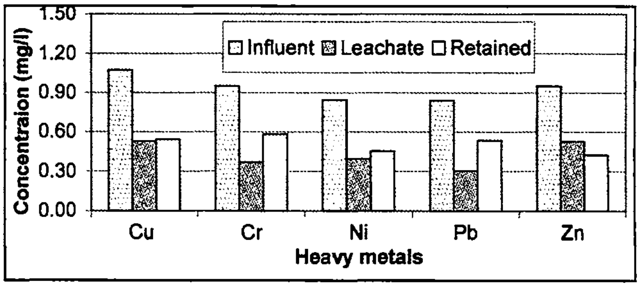

Figure 4. Mass balance calculations of heavy metals based on soil retained and leachate concentration.

CONCLUSIONS

1. The leaching cell conducted on soil samples shows that Cu, Cr, Ni, Pb, and Zn are mostly retained at the top part of the leaching columns i.e. at the depth of 1.0 cm. It is also noted that all of heavy metals decreased with the depth of the soil profiles. The leachate analysis indicated that all of the heavy metals except Pb achieved the breakthrough curves at the first 4 PV of leaching excepted for Pb. The breakthrough curves for Pb was achieved after 5 PV of leaching. It can be concluded that in this research, based on the breakthrough curves and mass balance calculation, the mobilisation or the migration of heavy metals varied. The data obtained indicate that Zn has high mobility followed by Cu, Ni, Cr, and Pb.
2. After leaching 7 pore volume of solution the microstructure at the top part of the soil columns shows the formation of micro cracks, high pore spaces and the forming of channels. For the bottom part, it shows tight structure with low pore spaces and low form of channel. As a result the stabilised soil is maintained before permeability decreased.

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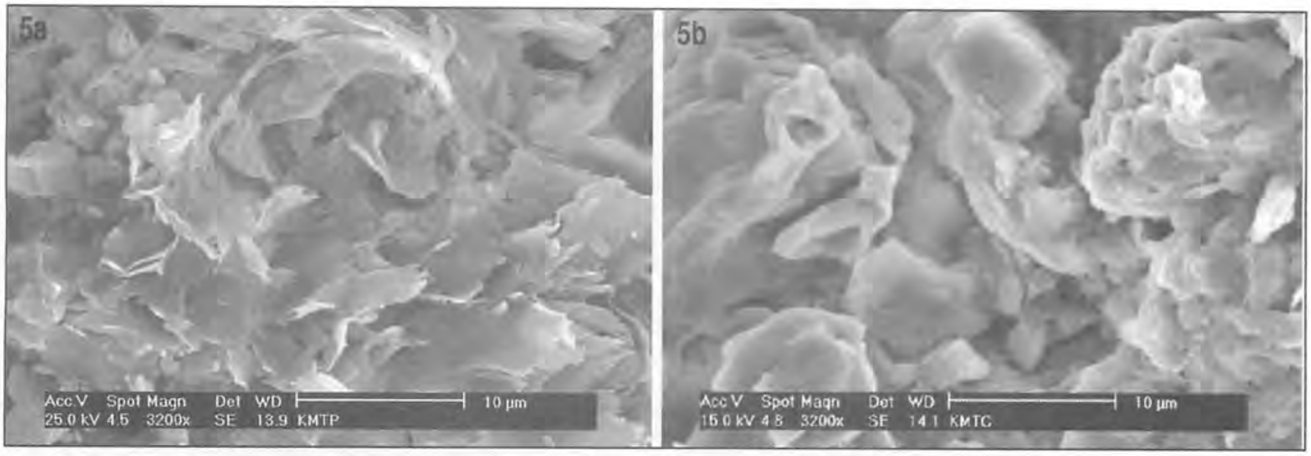

Figure 5. The scanning electron micrographs of clayey soil before leaching test (A) shows the layered of kaolinite minerals and (B) the subangular of quartz mineral.

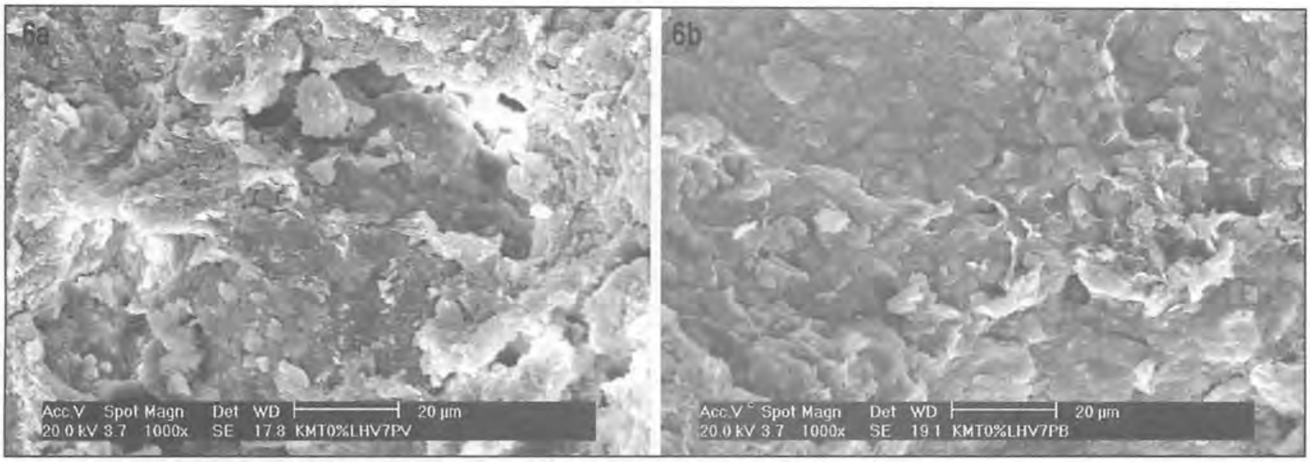

Figure 6. The scanning electron micrographs of clayey soil after leaching test (A) shows the formation of micro crack, enlarge of pore and formation of channels and (B reducing pore space, rearrangement of layered minerals and formation of more packed structure.

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