The sorption distribution coefficient of lead and copper on the selected soil samples from Selangor

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Abstract— The sorption of heavy metals (i.e. Pb and Cu) in soils from Selangor was investigated using batch equilibrium test (BET). The test was conducted in two systems, i.e. single and mix solutions. The sorption isotherms from BET were well described by the Langmuir equation which then used to calculate the sorption parameters, i.e. distribution coefficient (K_d) and maximum adsorption capacity (A_m). The Langmuir sorption equation was chosen according to the experimental data that are fitted to the equation (i.e. based on their linear regression values, r^2). The study has revealed that different soils have different sorption capacity for different heavy metals. The K_d values are proportional to the sorption capacity of soils. Soil with high sorption capacity possesses higher K_d value. The sorption of Pb and Cu in single solution is higher than in mix solution, due to competition for sorption sites among heavy metals in mix solution. The K_d values for Pb in single solution ranging from 36.18 – 334.48 L/g and for Cu is 9.29-66.19 L/g. In mix solution, the K_d values for Pb and Cu are smaller ranging from 23.13-31.79L/g and 3.95-18.53 L/g respectively.

Keywords: sorption, heavy metals, distribution coefficient, maximum adsorption capacity, Langmuir

Abstrak— Penjerapan logam berat (iaitu Pb and Cu) dalam tanah di Selangor dikaji dengan menggunakan ujian penjerapan berkelompok (BET). Ujian ini dilakukan dalam dua sistem berbeza; iaitu sistem larutan tunggal dan campuran. Isoterma penjerapan dari ujian BET boleh diperjelaskan lagi menggunakan persamaan Langmuir yang kemudiannya digunakan untuk mendapatkan parameter penjerapan, iaitu pemalar taburan (K_d) dan kapasiti penjerapan maksima (A_m). Persamaan Langmuir dipilih kerana ianya berpadanan dengan hasil ujian yang diperolehi (berdasarkan nilai regrasi garis lurus r^2). Kajian ini menunjukkan tanah berbeza mempunyai keupayaan penjerapan yang berbeza untuk logam berat yang berbeza. Nilai K_d adalah berkadar langsung dengan keupayaan penjerapan. Tanah berjerapan tinggi mempunyai K_d yang juga tinggi. Penjerapan logam Pb dan Cu dalam larutan tunggal adalah lebih tinggi dari larutan campuran, ini disebabkan oleh perebutan kepada tapak perlekatan logam-logam tersebut dalam larutan campuran. Nilai K_d untuk Pb dalam larutan tunggal berjulat 36.18 – 334.48 L/g dan untuk Cu berjulat 9.29-66.19 L/g. Dalam larutan campuran, nilai K_d untuk Pb dan Cu adalah lebih kecil berjulat dari 23.13-31.79L/g dan 3.95-18.53 L/g.

INTRODUCTION

The behaviour of heavy metals in soils has been extensively studied and published during the past 20 years (Anderson & Christensen, 1988; Antoniadis & McKinley, 2000; Wan Zuhairi, 2003a; 2003b). Many researchers have applied the mathematical models on the adsorption data to calculate the partition (distribution) coefficient (K_d). The K_d is an important input parameter in contaminant transport modeling to model the contaminant flow in groundwater (i.e. such as under the landfill sites). The K_d reflects the contaminant sinks, i.e. the contaminants are adsorbed on to the active soil components such as clay minerals, carbonates, and organic matter. The sorption processes slow down (i.e. retard) the movement of pollutants in soils. K_d is a very important parameter that needs to be correctly quantified. It is used in computer transport models such as the MODFLOW computer program. This paper highlights the determination of K_d values of some selected soils samples from active landfill sites in Selangor. The soil samples were subjected to 24 hours of shaking with heavy metals (HMs) in two separate systems (i.e. single solution and mix solution). In

addition, this paper describes the competitive sorption among heavy metals and its effect on the K_d values.

MATERIALS AND METHODS

Five samples were collected from active landfill sites in Selangor namely weathered metasediments from Puchong (AHQ), Sungai Sedu clay (SSC), Sungai Sedu Lateritic soil (SSL), Taman Beringin soil (TBL) and Ampang Pechah weathered graphitic schist (APS) (Figure 1). Most of these soils have been used as natural soil liner under the landfill sites to prevent leachate from polluting the groundwater. Soil samples were air-dried, ground and sieved to obtain aggregates that are less than 2 mm. Batch equilibrium test (BET) was undertaken by mixing 4 g of soil with 40 mL of known concentration of heavy metal solution in the centrifuge tubes (Wan Zuhairi, 2000, 2003a, 2003b; Wan Zuhairi *et al*. 2004). In this study, nitrate salts of Pb and Cu were used as a test solution. Nitrate salts were chosen because nitrate has poor ability to complex metallic cations (Msaky & Calvet, 1990). The test was carried out in two separate systems, i.e. single-solution and mix-solution.

In mix-solution, four heavy metals were mixed together, i.e. Pb + Cu + Ni + Zn to study the effect of competition between heavy metals in soil. The soil-solution system was then shaken for up to 24 hours to achieve equilibrium and to allow the contaminant to react with the soil particles. After that, the tube was centrifuged and the supernatant was analysed for equilibrium concentration (C_{aq}) using Atomic Absorption Spectrophotometer (AAS). The concentration of heavy metals adsorbed onto the soil solution (Cads) was then calculated using the formula as follows:

$$C_{ads} = \frac{(C_o - C_{aq}) \cdot V}{(M \times 1000)} \quad (1)$$

Where:

C_{ads} = The amount of contaminant removed from solution (mg/g)

C_o = The concentration of contaminant in the solution before mixing with soil (mg/L)

C_{aq} = The equilibrium concentration of contaminant left in the solution after the experiment (mg/L)

V = Volume of solution in the centrifuge tubes (40 mL)

M = Mass of soil in the tubes (4 g)

The sorption data (C_{ads}) was then plotted with C_{aq} to determine the sorption response curves (i.e. sorption isotherms). The sorption data are modeled according to the shapes of sorption response curves. There are three models that have been widely used to represent the response curves; namely linear, Freundlich and Langmuir models. The decision to select the best model is based on the pattern of the sorption curves.

Sorption can be defined as the interaction of a contaminant with a solid (Piwoni & Keeley, 1990). The sorption data were nicely fitted using the Langmuir equation which is given by equation 2 below. According to Harter and Baker (1977), the Langmuir equation has become well established in summarizing a mass of adsorption data from the batch experiment:

$$C_{ads} = \frac{K_d \cdot A_m \cdot C_{aq}}{1 + K_d \cdot C_{aq}} \quad (2)$$

Where C_{ads} and C_{aq} are as explained above. A_m is maximum sorption capacity of the soil and K_d is partition (distribution) coefficient. According to USEPA (1999), the Langmuir equation can be rearranged into a linear form as shown in equation 3, after substituting 1/B with K_d. Then, by plotting C_{ads} on the y-axis and (C_{ads}/C_{aq}) on the x-axis, one can determine the value of –B as the gradient of the slope and the value of A_m at the intercept:

$$C_{ads} = -B\,(C_{ads}/C_{aq}) + A_m \quad (3)$$

K_d is given by $K_d = -1/B$. The K_d parameter is very important in estimating the potential for the adsorption of dissolved contaminants in contact with soil. As typically used in fate and contaminant transport calculations, the K_d is defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium.

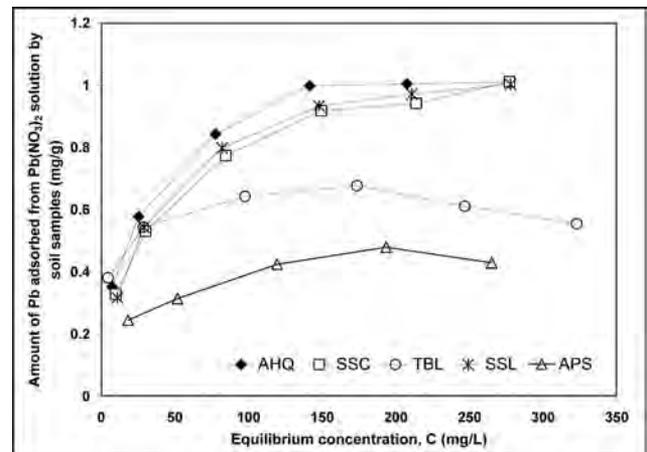
Figure 1: The sampling stations in Selangor.

Figure 2: The amount of Pb removed by various soil samples per unit weight of clay soil from single nitrate solution (soil to solution ratio is 1:10).

RESULTS AND DISCUSSIONS

Adsorption isotherms

The sorption curves in Figure 2 were plotted between the amounts of Pb adsorbed from the Pb single-solution against concentration of Pb left in the solution. All curves show a non linear shape and according to Msaky & Culvet (1990), the shape of adsorption isotherms depend on several factors and is not always linear. The sorption curves show that the amount of Pb adsorbed by all soil samples increased with the increasing amount of Pb used in the experiment, especially at lower concentration of initial Pb. This is in accord with the findings of McLaren et al. (1981) who stated that at low concentration the sorption of metals are essentially linear. According to Mohamed et al (1992) at low concentration, clay particles tend to disperse due to the full development of the diffuse double layer, therefore clay particle surfaces in contact with the solution at the maximum. The sorption increases until a certain points where the sorption becomes constant. This phenomenon is due to
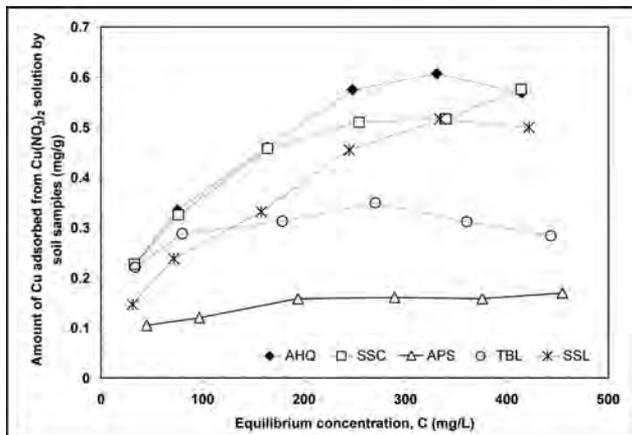
Figure 3: The amount of Cu removed by various soil samples per unit weight of clay soil from single nitrate solution (soil to solution ratio is 1:10).

Figure 4: The amount of Pb removed by various soil samples per unit weight of clay soil from mix nitrate solution (soil to solution ratio is 1:10).

Figure 5: The amount of Cu removed by various soil samples per unit weight of clay soil from mix nitrate solution (soil to solution ratio is 1:10).

the sorption capacity of soil is higher at lower concentration, resulting more Pb is adsorbed. This also indicates that the sites for adsorption on this soil are still available at lower concentration. When the sorption sites become saturated with Pb, the sorption decreases with further increasing of Pb in the solution. All sorption curves show linear pattern at lower concentration, and become constant, i.e. reach the maximum adsorption (A_m) with increasing concentration of Pb. The sorption curves that are plotted close to y-axis indicate higher sorption capacity compared to curves which are located near x-axis. Therefore, from the sorption curves in Figure 2, one can say that AHQ soil has higher sorption capacity compared to SSL, SSC, TBL, and APS. Based on Figure 2, the sorption capacity for all soils can be ranked as follows: AHQ>SSL>SSC>TBL>APS.

Similar observations were observed for Cu as shown in Figure 3. It is interesting to note a contrasting sorption curve of SSL, where the amount sorbed increases with the increasing concentration of Cu in the solution (i.e. linear sorption). Other soils show similar sorption curves as for Pb where the sorption capacity increases and become constant when the concentration of Cu increases. Except for TBL, the sorption of Cu by these soils can be ranked as AHQ>SSC>TBL>APS.

Figures 2 and 3 show that AHQ is far better to adsorb Pb and Cu compared to APS soil. The differences in sorption by these soils are due to variation in their physico-chemical properties as reported elsewhere by Wan Zuhairi (2000, 2001, 2003a,b) and Wan Zuhairi *et al* (2004).

The affinity for sorption is also varied where Pb is adsorbed higher compared to Cu. According to Buchter *et al* (1989), the relationship between soil properties and adsorption parameters exist in a group of soils with different characteristics. Harter & Baker (1977) also stated that the adsorption maxima of soils are well correlated with the chemical, mineralogical and/or physical properties.

Figures 4 and 5 show the amount of Pb and Cu removed from the mix-solution after 24 hours of shaking in BET. Both figures show similar sorption behaviour as shown earlier by sorption curves in single-solution (Figure 2 and
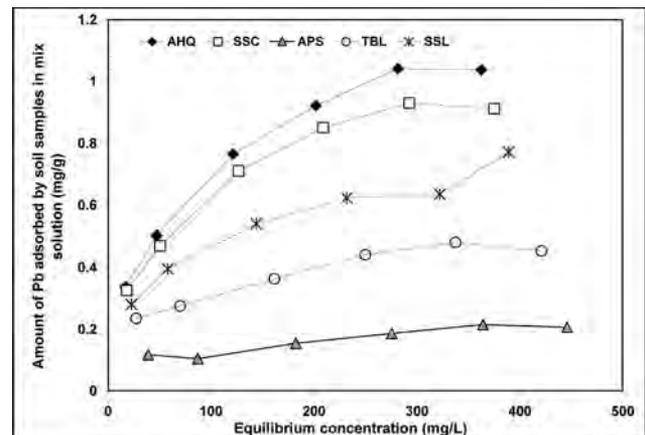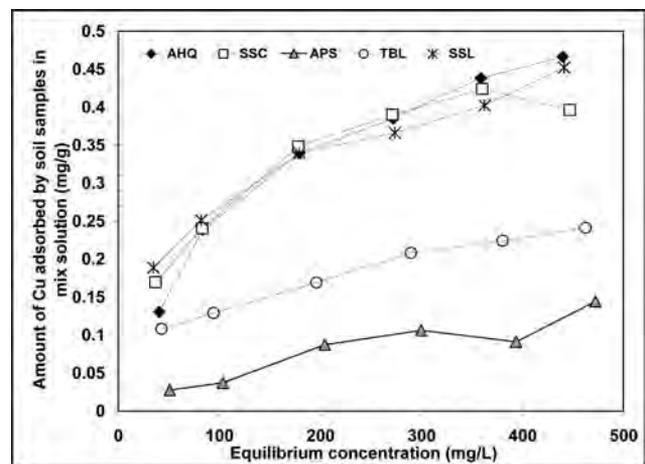
3). The amount of Pb and Cu adsorbed increases with the increasing concentration of Pb and Cu in the mix-solution. The sorption curves are linear at low concentration, and approaching constant sorption at higher concentration, i.e. maximum adsorption is achieved. However, the maximum amount of Pb and Cu adsorbed by all soils in mix solution are relatively low compared to the amount sorbed in single-solution. This is attributed to the competition between heavy metals for sorption sites which are of course rather limited in soils. Heavy metals in mix-solution (i.e. four heavy metals Pb, Cu, Ni and Zn all mixed together) compete among themselves for a place onto to the active soil components (Wan Zuhairi & Abdul Rahim Samsudin, 2005). For example, the maximum Cu being adsorbed in single solution by soil AHQ (Figure 3) is 0.6971 mg/g, whereas in mix solution, the maximum amount sorption is 0.6044mg/g, a decrease of about 13.2%.

Partition (distribution) coefficient, K_d

The sorption data for all samples can be best modeled using the Langmuir equation (i.e. Equation 3). Figure 6 shows the Langmuir plot of Pb in single and mix solution

Table 1: Langmuir isotherm parameters of soil samples.

Soils	Elements	Single solution			Mix solution		
		K_d (L/g)	A_m (mg/g)	r^2	K_d (L/g)	A_m (mg/g)	r^2
AHQ	Pb	62.72	1.053	0.944	23.13	1.112	0.895
SSC	Pb	44.03	1.031	0.942	24.48	0.988	0.895
APS	Pb	53.96	0.479	0.848	29.56	0.202	0.487
TBL	Pb	334.49	0.626	0.812	31.79	0.474	0.772
SSL	Pb	36.18	1.092	0.994	24.48	0.741	0.862
AHQ	Cu	13.95	0.697	0.930	7.16	0.604	0.972
SSC	Cu	16.46	0.627	0.958	14.25	0.480	0.944
APS	Cu	30.52	0.177	0.884	3.95	0.176	0.374
TBL	Cu	66.19	0.332	0.652	15.86	0.249	0.798
SSL	Cu	9.29	0.630	0.908	18.53	0.458	0.887

K_d = Distribution coefficient, A_m = Maximum sorption capacity; r^2 = correlation coefficients

for soil AHQ only. The graphs were plotted between C_{ads} (in y-axis) against C_{ads}/C_{aq} (in x-axis). The linear regression values (r^2) are given as 0.9437 and 0.8949, indicating that the sorption data are best fitted using this model. From the linear graphs in Figure 6, the parameters of K_d and A_m were calculated. Table 1 shows the K_d, A_m and r^2 values for both single and mix solutions for all soil samples. Higher K_d value means that the soil has higher sorption capacity. K_d values represent the retardation of pollutants by soils. Anderson & Christensen (1988) stated that high values of K_d indicate that metal has been retained by the solid through sorption reactions, while low K_d indicate that most metal remains in solution where it is available for transport.

Table 1 shows that correlation coefficients (r^2) are higher than 0.6 except for APS soil in mix solution. K_d values that were calculated from single solution are higher compared to mix solution. The difference between these two K_d values is recorded for up to 90%. This indicates that in single solution, there is no competition for sorption, resulting in higher K_d values (i.e. high amount of heavy metals being adsorbed by soil). Whereas, in the mix solution, there is intense competition for sorption sites, resulting in less being adsorbed and this reduce the values of K_d. The same results were also reported by Frost & Griffin (1977) after comparing the sorption results between pure nitrate salt and high levels of cations in leachate. They discovered that K_d values were high in pure nitrate compared to multi cations in leachate.

One must be extra careful in selecting the K_d values in their transport model. The K_d values for Pb and Cu in single solution obtained from this study ranges from 36.18 – 334.49 L/g and 9.29 – 66.19 L/g respectively. Lower K_d values are recorded from mix solution, ranging from 23.13 – 31.79 L/g for Pb and 3.95 – 18.53L/g for Cu. The highest K_d recorded in this study is for TBL soil, with the K_d values for Pb and Cu are 334.5 L/g and 66.19 L/g, respectively. However, it is somewhat puzzling why these K_d values do not correspond well with the sorption curves in Figure 2 and 3. Perhaps, this particular sorption curve does not fit the Langmuir model.
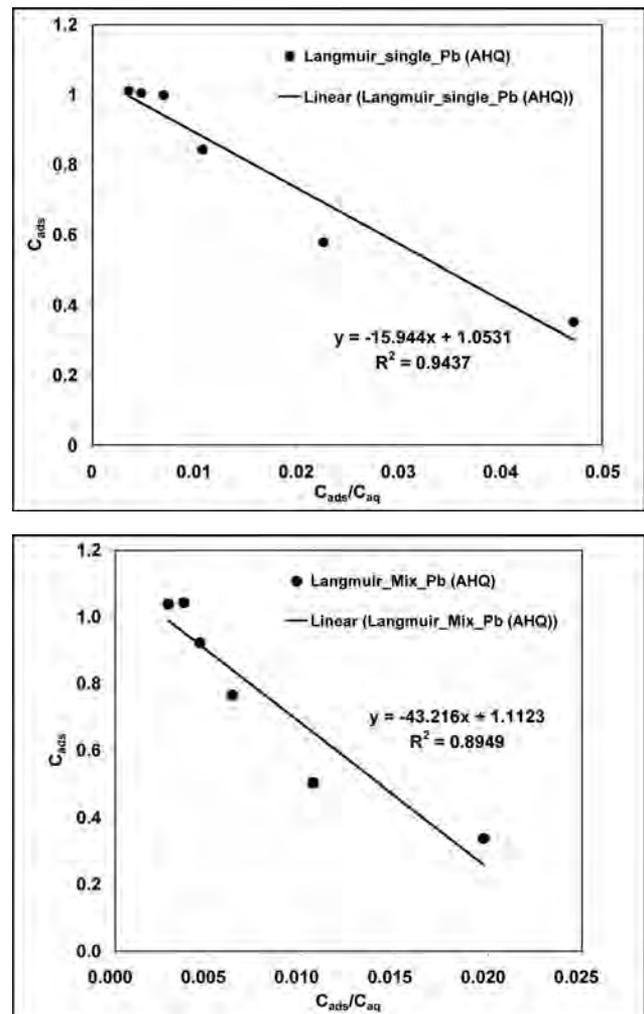

Figure 6: Example of Langmuir plots between Cads against Cads/Caq for Pb in single and mix solutions (only soil AHQ is shown here).

Antoniadis & McKinley (2000) reported the K_d value for Zn in London Clay as 0.1 L/g (or 98.9 mL/g). Mohd Raihan & Depankar (1998) reported the K_d value of Cd in granitic soil in Malaysia as 0.64 L/Kg (0.64×10^{-3} L/g). The small K_d value reported in their study was due to the small initial concentration of Cd ranging only from 0.1-0.3 mg/L. Anderson & Christensen (1988) reported that the values of K_d for Danish soils range from less than 10 L/kg (0.01 L/g) to more than 1000 L/kg (1 L/g).

It is also interesting to note the values of maximum sorption capacity in soil (A_m). All A_m values reported in Table 1 correspond well with the sorption curves in Figures 2, 3, 4, and 5.

Figures 7 and 8 show the comparison between the K_d values for single and mix solutions. The K_d values are higher in single solution compared to mix solution due to the competition for sorption in mix solution, resulting in the decreasing amount of heavy metals adsorbed. The K_d values of TBL soil for Pb and Cu in single solution are far greater than in mix-solution, probably because the TBL sorption is not well modeled using the Langmuir equation. This argument is well supported using the sorption isotherm curves, where TBL curves were plotted below soils AHQ, SSC and SSL. Further investigation is required to clarify this problem. Others, however, showed acceptable values of K_d.

CONCLUSIONS

The partition (distribution) coefficient, K_d is a parameter that can be used to indicate the sinking of pollutants when they migrate through the environment (i.e. groundwater). This parameter for contaminant transport must be carefully estimated or tested using batch experiments or any other tests. This paper highlights the K_d values of five different soil samples in two different systems, i.e. single and mix solutions. The K_d values obtained in this study varies. The variation in K_d values is due to the variation in the soil's physico-chemical properties, the presence of different types of heavy metals and competition among the heavy metals in the solution. Higher K_d values are recorded in single solution compared to mix-solution. The K_d values for Pb in single solution range from 36.18 – 334.48 L/g and for the range for Cu is 9.29-66.19 L/g. In mix solution, the K_d values for Pb and Cu are smaller, ranging from 23.13-31.79L/g and 3.95-18.53 L/g respectively.

ACKNOWLEDGEMENT

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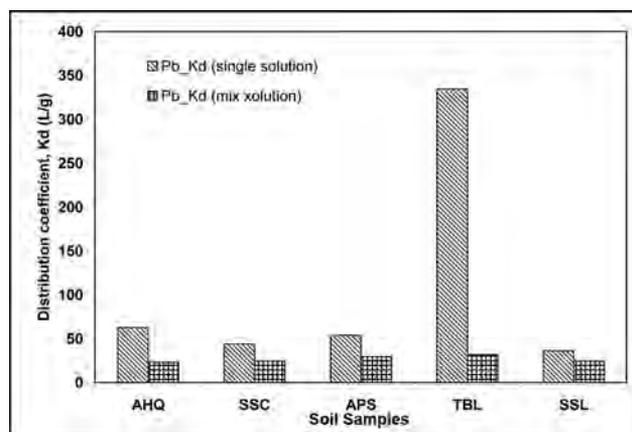

Figure 7: The comparison of K_d values for Pb in single and mix solutions after 24 hours of shaking in BET (soil to solution ratio is 1:10)
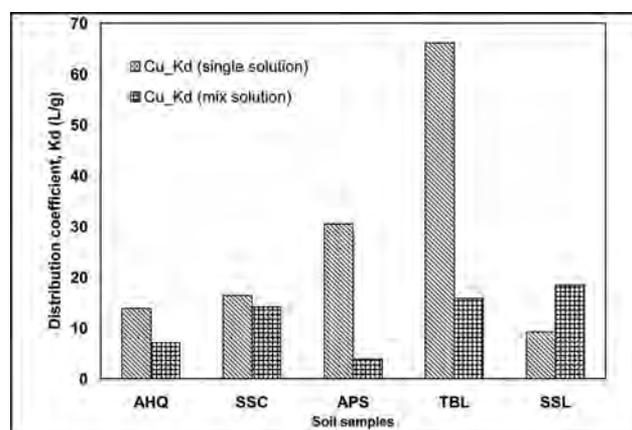

Figure 8: The comparison of K_d values for Cu in single and mix solutions after 24 hours of shaking in BET (soil to solution ratio is 1:10)

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