Mobility of cadmium in granitic soil using batch and mini column tests

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Abstract: This paper highlights the physico-chemical properties of granitic residual soils and the effectiveness of using batch and column tests to study the migration and sorption of heavy metal (Cadmium) through compacted soil layer. Granitic residual soil was taken from Broga, Selangor and this material has undergone physical-chemical tests conducted based on British Standard Method, BS1377 (1990). For sorption analysis, batch and mini column infiltration tests were conducted according to USEPA (1992) and Antoniadis et al. (2007) methods, respectively. For batch test, results showed that \( K_d \) values for both single and mixture solutions were fitted to Linear equations \( (R^2 \geq 0.8) \). For Langmuir Isotherm, only mixture solution \( (K_F=0.0015 \text{ L/g}; R^2=0.9353) \) was fitted to the isotherm while for Freundlich Isotherm, only single solution \( (K_F=0.0137 \text{ L/g}; R^2=0.9266) \) was fitted to the isotherm. The curve of adsorbed heavy metal concentration, \( q_e \) versus equilibrium concentration, \( C_e \) showed that the sorption of Cd was increased with the equilibrium concentration, until at one point the sorption was decreased. The adsorption capacity, \( q_{max} \) and distribution coefficient, \( K_d \) of single solution (maximum adsorption, \( q_{max}=1.10 \text{ mg/g}; K_d=0.0062 \text{ L/g} \)) were higher compared to mix solution (maximum adsorption, \( q_{max}=0.12 \text{ mg/g}; K_d=0.0022 \text{ L/g} \)). For mini column infiltration test, different G-force (ranged from 230-g to 1440-g) and different types of solutions (single and mixture solutions) were studied in this research. The breakthrough curves showed the concentration of Cd has become higher with the increasing of G-force. The sorption capacity in single and mixture solutions could be ranked as 230-g>520-g>920-g>1440-g. The increasing of G-force also reduced the \( K_d \) values. The \( K_d \) values for single solution were also higher compared to mixture solution due to zero competition for adsorption of metals thus, \( K_d \) values increased. The comparison between batch and column infiltration has also been studied in order to know the better sorption analysis. In both single and mixture solutions, \( K_d \) in batch test showed higher values (single solution, \( K_d=6.2 \text{ L/kg} \) and mixture solution, \( K_d=2.2 \text{ L/kg} \)) compared to all \( K_d \) values in column infiltration test. Results demonstrated that mobility and sorption of Cd were highly depended on physical and chemical properties of the soil. Study also showed that both sorption test have different effects on mobility of heavy metals through soils. The column infiltration test gave the exact values of \( q_{max} \) and \( K_d \) compared to the batch test since the condition of columns method applied were similar to the natural soil conditions.

Keywords: Granitic residual soils, cadmium, sorption, batch test, mini column infiltration test

INTRODUCTION

Cadmium can be contaminated to the environment through variable amounts from natural and anthropogenic activities (Khan et al., 2017). Human activities such as agricultural, domestic waste, municipal sewage, industrial effluent, mining activities, and landfill introduced the heavy metals (Cd) to our natural environment (Vega et al., 2006; Kwon et al., 2010). These contaminants can be dispersed into the aquatic system, effected on living organisms, accumulated in marine food chain and affected human health through consumption of contaminated seafood (Thongraar et al., 2008; Kwon et al., 2010). Nowadays, there are many ways to treat the contaminated heavy metals such as precipitation, oxidation, reduction, solvent extraction, electrolytic extraction, dilution, adsorption, electro-dialysis, filtration, flocculation, sedimentation, evaporation, osmosis, ion-exchange, chelation, biosorption and many more (Kwon et al., 2010). However, adsorption is the most common method because of its low cost and efficient absorbents for removing heavy metals (Lukman et al., 2013). Through geotechnical centrifuge, the migration of contaminant in soils can be assessed (Antoniadis & Mckinley, 2000; Kumar, 2006; Alshaebi et al., 2010). Centrifuge leaching test has shown a great prospect to be used as an experimental study for reactive contaminant transport process in fine grained soils. This research investigated the chemical-physical properties of granitic residual soils and the effectiveness of using batch and column tests to study the migration and sorption of heavy metal (cadmium) through compacted soil layer. According to Tanchuling et al. (2003), contaminant in a batch test was completely dispersed in particle soil system while in column test, contaminant was leached through a normal consolidated clay layer; where not all the soil particle surfaces interacted with contaminants. Through the migration of heavy metals, the contamination and the capacity of soils to retain the heavy metals can be assessed.

MATERIALS AND METHODS

The material used in this study was granitic residual soil (BGR) taken from Broga, Selangor. Physico-chemical tests were analyzed according to British Standard Method, BS1377 (1990). For sorption, batch and mini column infiltration tests were conducted according to USEPA (1992) and Antoniadis et al. (2007) methods, respectively.
Batch test

This test is used to study the behavior of natural soil (absorbent) through a different initial concentration factor. It also provides a quick method of estimating the contaminant retention capacity of any liner material (Wan Zuhairi & Abdul Rahim, 2007). This method was reported by USEPA (1992a) and Wan Zuhairi, 2003a & 2003b. Soil samples were air-dried and passed through 63 μm sieve. Cadmium nitrate solution, Cd(NO$_3$)$_2$, of single solution was prepared with 10 different concentration 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L, 300 mg/L and 400 mg/L. For mixed solutions, nitrate solution of cadmium, cobalt, zinc, copper, lead and nickel were mixed and diluted into the same concentration of single solution. Nitrate salts were chosen because nitrate has a poor ability to complex with metallic cations (Wan Zuhairi et al., 2008). To perform this test, 4 g of soil sample (absorbent) with 40 ml of metal aqueous solutions (1:10 ratio soil/solution) were added in centrifuge tubes. Samples were shaken at 100 RPM for 24 hours for attaining the equilibrium (Antoniadis & Tsadilas, 2007). After shaking, samples were centrifuged at 1500 RPM for 10 minutes and filtered using 45 μm nitrocellulose membranes. The solutions were analyzed using Couple Plasma Mass Spectroscopy (ICP-MS).

Mini column infiltration test

Standard solution with 500±25 mg/L concentration of cadmium nitrate, Cd(NO$_3$)$_2$, was prepared. Soil sample was weighed, slurried by adding deionized water and was left overnight before transferring to column cell. Sample was centrifuged and compacted soil called ‘mudcake’ layer appeared. 5 ml (equivalent to 1 pore volume) of influent solution of Cd(NO$_3$)$_2$ was added at upper part of column. The cell was centrifuged until all solutions have passed through the ‘mudcake layer’. The effluent solutions were collected. This procedure was continued until 60 pore volumes. For this experiment, different G-force (230-g, 520-g, 920-g and 1440-g) and type of solutions (single and mix solution) were studied.

The concentration of heavy metals absorbed by solution, $q_e$ was calculated using the formula as below:

$$q_e = \frac{(C_0-C_e)V}{W}$$

Where; $C_0$ and $C_e$ are initial concentration and equilibrium concentration respectively (mg/L), $V$ is volume of solution added (ml), $M$ is mass of air-dried soil (g).

Adsorption coefficient, $K_d$ (L/kg) describes equilibrium partitioning of a metal between solid and liquid phases (Antoniadis et al., 2007). $K_d$ values can be determined by following equation $q_e=K_d/C_e$ (Cheyns et al., 2010; Alther, 2002), where $K_d$ is the partition coefficient (L/kg).

**RESULT AND DISCUSSIONS**

**Physico-chemical characteristics**

The physical and chemical characteristic of granitic residual soil is presented in Table 1 and Table 2. Granitic residual soil has coarse grained size where the percentage of sand ranged between 54%-63% while percentage of clay was at ranged of 1%-6%. Granitic residual soil also has an intermediate plasticity index ranged between 9.90 and 11.99. According to Atanassova (1993), coarse grained size of soils exhibited lower tendency adsorption of heavy metals compared to fine grained soils. The pH values for the soils were at pH 5.32-5.54 (acidic). At low pH, heavy metals ions were mobile (Ouhadi et al., 2010) and sorption of heavy metals into soils became less effective. The granitic residual soil also showed the low value of organic matter, specific surface area and cation exchange capacity.

| Physical Characteristics | Particle size distribution: |
|--------------------------|-----------------------------|
| Sand (%)                 | 54-63                       |
| Silt (%)                 | 32-42                       |
| Clay (%)                 | 1-6                         |
| Atterberg Limit:         |                             |
| Plastic Limit (%)        | 38.01-38.69                 |
| Liquid Limit (%)         | 48.50-50.00                 |
| Plasticity Index (%)     | 9.90-11.99                  |
| Specific Gravity         | 2.50-2.59                   |
| Max Dry Density (g/cm$^3$)| 1.64-1.71                   |
| Permeability (m/s)       | 2.08 x 10$^{-6}$            |

| Chemical Characteristics | pH                  | Organic Matter (%) | SSA (%) | CEC (meq/100g) |
|--------------------------|---------------------|--------------------|---------|----------------|
|                          | 5.32-5.54           | 0.39-0.50          | 17.96-21.93 | 0.79-1.35 |

SSA: Specific Surface Area; CEC: Cation Exchange Capacity

**Table 1: Physical characteristics of adsorbent/residual soils.**

**Table 2: Chemical characteristics of adsorbent/residual soils.**

**Batch test**

Heavy metals adsorption capacities can be expressed in relationship between distribution coefficient, $K_d$ and equilibrium concentration, $C_e$. The adsorption isotherm and distribution coefficient ($K_d$) of Cd in single and mixture solutions are summarized in Table 3. According to Wang & Nan (2009), these sorption isotherms provide the sorption behavior of soil suspension when they are at equilibrium with metal solutions. In this study, the Linear equation showed the best fitted for both single and mixture solution ($R^2$ > 0.8). For Langmuir Isotherm, only mixture solution ($K_1$=0.0015 L/g; $R^2$ = 0.9353) fitted to the isotherm while
for Freundlich Isotherm, only single solution ($K_f=0.0137$ L/g; $R^2=0.9266$) fitted to the isotherm.

Figure 1 and Figure 2 show the amount of Cd absorbed by granitic residual soil in single and mixed solutions. The sorption of Cd increases with the equilibrium concentration; indicates that the soil has reached a sorption maximum, until at one point, the sorption decreases. According to Strawn & Sparks (1996) in Carriere et al. (1995) adsorption of heavy metals was fast at the initial concentration but at higher concentrations adsorption became slow (reaction became slower). The adsorption capacity, $q_e$ and distribution coefficient, $K_d$ of single solution (maximum adsorption, $q_e=1.10$ mg/g; $K_d=0.0062$ L/g) were higher compared to mix solution (maximum adsorption, $q_e=0.12$ mg/g; $K_d=0.0022$ L/g). These findings were parallel with agreement reported by Markiewicz-Patkowska et al. (2005). In mixture solution, Cd needs to compete with other metals to obtain active sites in soils, thus it reduces the amount of heavy metal adsorption and subsequently lowering Kd values (Zarime & Wan Zuhairi, 2016).

**Mini column infiltration test**

Mini column infiltration test was conducted to study the migration and the sorption of Cd through granitic residual soil. According to Timms & Hendry (2008), the $K_d$ values conducted using centrifuges in laboratory was approximate the $K_d$ values at field conditions. Result of mini column infiltration test were presented in Figure 3 and Figure 4. Measured breakthrough curves were produced by plotting relative concentrations ($C_e/C_o$) with number of pore volumes (PV). $C_e/C_o$ was a ratio between the concentrations of effluents ($C_e$) with the solution concentrations of heavy metals introduced into column ($C_o$). Both breakthrough curves showed similar trends. The relative concentration of Cd also increased with the increment of pore volumes and at one point it became constant. The breakthrough curve remained constant was due to maximum adsorption capacity has been reached and the surface sorption sites were already saturated with metals (Zarime & Wan Zuhairi, 2014).

Total penetration of Cd occurred when the $C_e/C_o$ value was equivalent to 1.0 ($C_e/C_o=1$). For total penetration that less than 1 ($C_e/C_o<1$), adsorption of heavy metals was high. For both single and mixture solutions (refer Figure 3 and Figure 4), total penetration for 230g and 520g were more than 1 ($C_e/C_o>1$), while for 920g and 1440g were less than 1 ($C_e/C_o<1$). This showed the adsorption of heavy metals for low G-force (230g and 520g) was higher compared to high G-force (920g and 1440g). According to Antoniadis & Mckinley (2000), at high G-force, the relative concentration of effluent became higher due to less interaction time with the soils surfaces. The breakthrough curves showed the concentration of Cd became higher with the increased of G-force. The sorption capacities in single and mixture solutions can be ranked as 230g>520g>920g>1440g.

Based on measured breakthrough curve of single solution (Figure 3), total penetrations for 230g, 520g, 920g and 1440g were at 16PV ($C_e/C_o=0.53$), 18PV ($C_e/C_o=0.54$), 20PV ($C_e/C_o=1.42$), 32PV ($C_e/C_o=1.52$) respectively and after that it has remained constant up to 60PV. While for mixture solution (Figure 4), total penetrations for 230g, 520g, 920g and 1440g were at 14PV ($C_e/C_o=0.90$), 16PV ($C_e/C_o=0.85$), 16PV ($C_e/C_o=1.69$), 6PV ($C_e/C_o=1.69$) respectively and has also remained constant up to 60PV. Total penetrations for all G-force in mixture solution were higher compared to single solution. This showed that in mixture solution, adsorptions of heavy metals were low

![Figure 1](image1.png)  
**Figure 1**: Amount of cadmium, Cd absorbed by granitic residual soil in single solution.

![Figure 2](image2.png)  
**Figure 2**: Amount of cadmium, Cd absorbed by granitic residual soil in mix solution.

### Table 3: Adsorption isotherm and distribution coefficient ($K_f$) of cadmium, Cd in single and mixture solutions.

| Type of Solutions | Linear Equation | Langmuir Isotherm Constant | Freundlich Isotherm Constant |
|-------------------|-----------------|----------------------------|-----------------------------|
|                   | $K_f$ (L/g)     | $R^2$                      | $K_f$ (L/g) | $1/n$ | $R^2$ |
| Single            | 0.0062          | 0.9130                     | 0.0317 | 4.0519 | 0.1362 | 0.0137 | 0.8344 | 0.9266 |
| Mix               | 0.0022          | 0.8376                     | 0.0015 | 0.1149 | 0.9353 | 0.0145 | 0.5236 | 0.4629 |
Table 4: $K_d$ value in all parameters calculated from the column and batch test.

| Weight (g)/Thickness (mm) | Velocity (RPM)/G-Force | $K_d$ in Single Solution, L/kg | $K_d$ in Mixture Solution, L/kg |
|--------------------------|------------------------|-------------------------------|---------------------------------|
|                          |                        | Single                        | Mixture                        |
| 10                       | 1000/230G              | 0.514                         | 0.777                          |
|                            | 1500/520G              | 23.449                        | 1.079                          |
|                            | 2000/920G              | 0.793                         | 0.420                          |
|                            | 2500/1440G             | 0.981                         | 0.417                          |

**$K_d$ in batch test and mini column infiltration test**

Table 4 also showed the $K_d$ values in all parameters obtained from the column infiltration and batch test. In both single and mixture solutions, $K_d$ in batch test showed higher values (single solution, $K_d = 6.2$ L/kg and mixture solution, $K_d = 2.2$ L/kg) compared to all $K_d$ values in column infiltration test. According to Antoniadis et al. (2007) adsorption of heavy metals in batch test occurred in 'closed system' where it induced the secondary reaction such as precipitation thus, reduced the heavy metals concentration in equilibrium concentration and caused the increment of $K_d$ values. While for column infiltration test, metal sorption was in an 'open system' and no interference occurred thus, the adsorption was continuously leached out of the system. In this case, adsorption of metals ion was higher and decreased the values of $K_d$. However, in certain case, $K_d$ value for mini column infiltration test (G-force; 520g in single solution) showed a higher value ($K_d = 23.449$ L/kg) compared to $K_d$ for batch test ($K_d = 6.2$ L/kg). This observation was due to the presence of the cracks in a ‘mudcakes’ layer. Harter & Naidu (2001) suggested that repetition on experimental work was needed to obtain good values especially when it involved the clay materials.
CONCLUSIONS

This research demonstrated that granitic residual soil has a good retention to absorb Cd. Physical-chemical test and sorption test using mini column infiltration and batch tests have a strong relationship to characterize granitic residual soil and mobility of heavy metal (cadmium) through a compacted soil layer. The comparison between batch test and column infiltration test were important since the different conditions of these two methods were applied. Batch test were occurred in ‘closed system’ and no gravitational forces were applied. In addition, batch sorption isotherms were not always well described by the linear and it gave a wide range of $K_d$ values compared to column test. Through the $K_d$ values, the contamination transport and migration of heavy metals in field can be assessed. The $K_d$ values in batch test also showed about 5 to 30 times higher than the mini column. Results showed that the $K_d$ values for both single and mixture solution were fitted to Linear equations ($R^2 > 0.8$). The adsorption capacity, $q_e$ and distribution coefficient, $K_d$ of single solution were higher compared to mixture solution. Results also showed that the increased of G-force reduced the $K_d$ values. This study concluded that the mobility and sorption of Cd were highly depended on physical and chemical properties of the soil. Study also showed the differences of sorption test which both tests have the effects on mobility of heavy metals through soils. Since the contaminations were very wide issues nowadays, the analysis of the experimental work should carefully be considered especially in adsorption studies.

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