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Sorption characteristics of cadmium in a clay soil of Mae Ku creek, Tak Province, Thailand

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Abstract. Mae Sot is a district in Tak province, the northern part of Thailand where has encountered with cadmium (Cd) contaminated in soils. Exposure of Cd can lead to severe health effect, for examples, bone softening, osteoporosis, renal dysfunction, and Itai-Itai disease. This study aims at elucidating sorption behavior of Cd in the contaminated soil collected from Mae Ku creek, Mae Sot district, Thailand. Batch sorption experiment was conducted in order to investigate sorption characteristics of Cd onto the contaminated soil. The soil sample taken from the study area consists of 26% sand, 16% silt 58% clay, which categorized as a clay soil, based on USDA classification. Soil pH is slightly alkaline (pH~7.7) and organic matter in the soil is 2.93%. The initial concentration in the batch sorption experiment was in the range from 0- 200 ppm. The result from the batch sorption experiment showed that soil sample can adsorb Cd up to 173.5 ppm and the sorption behavior of the soil sample can be well described by Freundlich isotherm, indicating the multilayer sorption (R^2 = 0.9964), with Freundlich constants of 0.312 and 1.760 L g^{-1} for 1/n and K_f, respectively.

1. Introduction

Cadmium (Cd) is a heavy metal, which typically occurs with zinc (Zn), lead (Pb), and copper (Cu) mineral. Cadmium contamination in the environment can cause by fuel combustion, human activities such as mining and using fertilizers. Moreover, natural also causes Cd contamination, for examples, stream transportation or volcanic eruption. Exposure pathway of Cd can come from ingestion of contaminated food and water as well as inhalation of cadmium fume from industry or smoking cigarette can also lead to Cd exposure [1]-[4].

Mae Sot is a district in Tak province, the northern part of Thailand which has been encountered Cd contamination in soil. Simmons [5] studied Cd concentration in soil sample in paddy field in Ban Pha Te, Phatat Pha Daeng sub-district, Mae Sot, Tak Province, which Cd concentration in soil samples varied from 0.5 to 284 mg kg^{-1}, some samples excess the background concentration of Cd in Thailand (0.002- 0.14 mg kg^{-1}) [6]. Moreover, Simmons et al. [5] analyzed 15 soil profiles from 0-75 cm. depth

from the ground surface. As a result, it showed that distribution of Cd mostly high in 0-30 cm. depth, accounting for 88.84% of total Cd concentration in soil profile, indicated that the source of contamination may come from suspended sediment from Mae Tao creek where flows through Phadaeng zinc mine where people in the study area used as irrigation water for crops. Akkajit and Thongcumpou [7] investigated fractionation of Cd and other metals (Cu, Fe, Mn, Pb, and Zn) that related for bioavailability by using BCR sequential extraction. The result showed that Cd has highest proportion of exchangeable form (BCR1), compared with other metals as follows: Cd (29.9%) > Mn (27.7%) > Zn (25-27%) > Pb (2.6%) > Cu (less than 0.5%) >Fe (0.05%). Similarly, Kosolsakul [6] studied fractionation of Cd in Baan Mae Tao Mai, Phrathat Phadaeng sub-district, by using BCR and Tessier sequential extraction. The result showed that Cd in BCR 1 fraction had the highest proportion (approximately 67%-84%) compared with other fractions and higher BCR 1 was found in the high Cd concentration areas. The result from Tessier sequential extraction showed that Cd in the study area had Cd associated with the carbonate phase (T2) more than the exchangeable phase (T1). The higher Cd concentration contaminates, the higher proportion of T2 becomes, whereas the proportion of T1 does not change significantly.

Even though there are many studies, which investigated about leaching potential of Cd from contaminated soils in Mae Sot District, the study of the sorption behavior of such contaminated soils in the site are still lacking. The sorption plays an important role in controlling the migration of contaminant, influenced by many parameters, such as pH, clay content, and organic matter (OM) [8]. As a result, the batch sorption experiment was carried out in order to elucidate sorption behavior of the contaminated soil in the study area.

2. Methodology

2.1. Sample collection

The topographic map of study area was derived from the Royal Thai Survey Department (RTSD) in 2006. Cadmium concentration map [7], and types of soil map derived from the Land Development Department (LDD) in 1988 were together considered in order to assign the sampling point in the study area. After soil sampling spot was selected, field observation was done to collect the soil sample. Before collecting soil samples, top soil was removed to the desired depth. Then, based on LDD soil sampling method, the soil sample was collected by mixing 1 kg of 5 sub-sampling spots within 10 m of the radius in sampling spot in order to get soil sample as the representative soil in the interesting spot. all of the sampling spots were collected at particular depth around 15 cm depth from the ground surface. After that, this sample was dried at 60^{o} C and sieved through 2 mm sieve.

2.2. Soil properties

The proportion of sand, silt, and clay of the soil sample in the study area was analyzed by using hydrometer. Based on ASTM 422 method, soil particle analysis was carried out. 50 g of soil sample of < 2 mm grain size, was put into 1,000 cm^3 deionized water with the dispersal agent (4% Sodium Hexametaphosphate) in the plastic cylinder. The solution was shaken to make soil suspension well mixed, and then placed the 152H hydrometer in to the solution. The measurement of hydrometer was recorded at specific time periods as follows: 8, 15, 30 min and 1, 2, 4, 8, 16, 24, 36, 50 hr in order to analyze for soil particles size [9].

For organic matter measurement, the Walkley and Black procedure was done. One gram of soil sample was mixed with 10 ml of 0.1 N Potassium Dichromate ($K_2Cr_2O_7$) and 15 ml of concentrated sulfuric acid, and leave it for 30 min After that, the solution was filled with 50 ml deionized water and cooled down the solution temperature. Five drops of O-phenantholine were added into the solution, then tritrate the solution with ammonium iron (II) sulfate hexahydrate ($Fe(NH_4)_2(SO_4) \cdot 6H_2O$; FAS) to finally determine organic matter [10].

2.3. Batch sorption experiment

In this study, the batch experiment was performed in order to investigate adsorption coefficients, which can describe sorption behavior of the soil sample. One gram of soil sample was put into a

polypropylene bottle with 20 ml of Cd solution, which varied the Cd concentration from 0 to 200 ppm (0, 25, 50, 75, 100, 150, 200 ppm), based on our preliminary of this soil type. Moreover, the pH value of soil solution was adjusted to 7 by using NaOH and HNO_3 and ionic strength was adjusted to 1-5 mM by adding $CaCl_2$ in order to adjust solution condition as same as surface water [11]. Then polypropylene bottles were shaken by orbital shaker with 200 rpm at room temperature for 24 hours to let Cd sorption reaches an equilibrium condition. After that, soil solution was filtered by using Whatman no. 42 filtered paper and analyzed for residue Cd concentration from filtered solution by using AAS (Analytic Jena).

In order to explain sorption behavior of soils, these sorption isotherms were applied to describe sorption behavior as follows: Linear isotherm, Freundlich isotherm, and Langmuir isotherm. The calculation of these isotherms is showed in Eqs. 1-3, respectively.

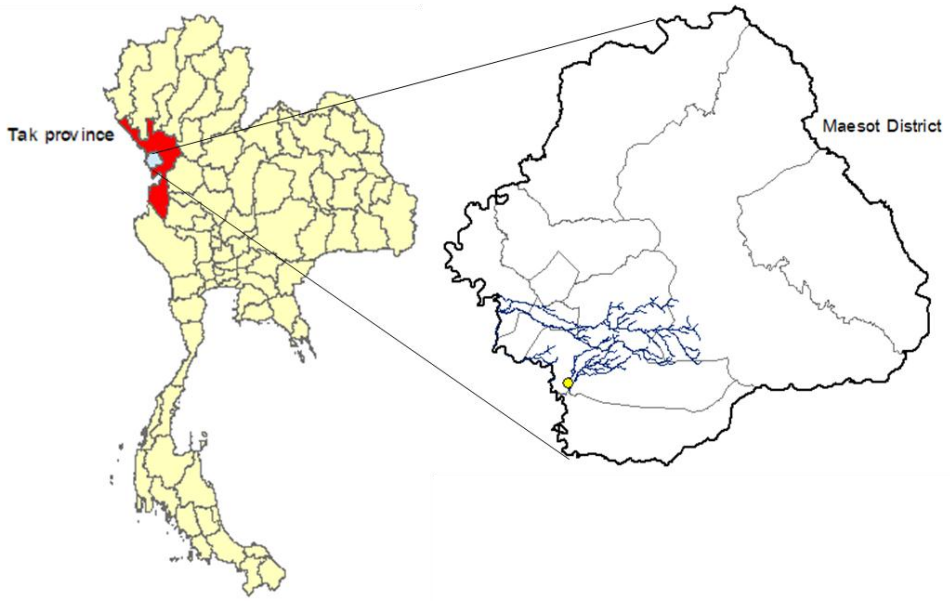
$$Q_e = K_d C \tag{1}$$

$$Q_e = K_f C_e^{1/n} \tag{2}$$

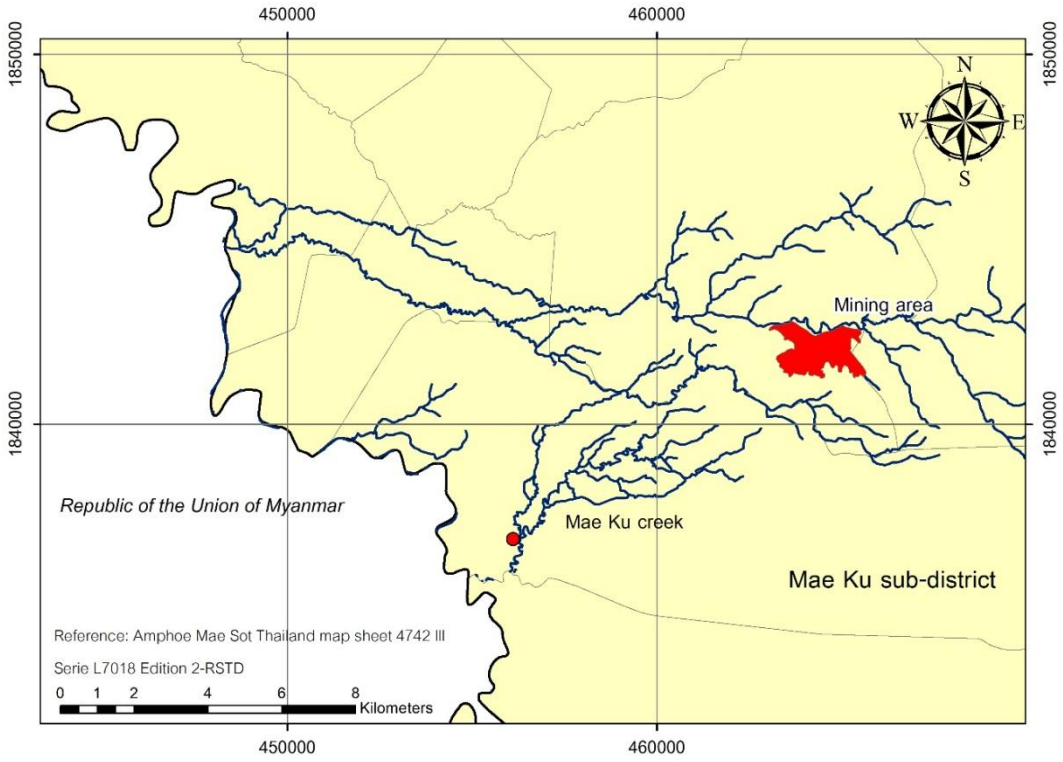
$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

Where Q_e is the concentration that sorbed in sorbent (mg kg^{-1}), Q_m is maximum sorption capacity (mg g^{-1}), C_e is the concentration of Cd in solution at equilibrium (mg l^{-1}), K_f is Freundlich sorption coefficient (L g^{-1}), K_L is Langmuir sorption coefficient (L g^{-1}), K_d is linear coefficient (L g^{-1}), n is Freundlich exponent (-).

Sorption behavior of contaminated soil can be defined by the fitting graph with the sorption isotherm. If the graph is fitted well with Freundlich isotherm, the sorption behavior of contaminated soil can be defined as multilayer sorption of ions on a heterogeneous surface. If the graph can be fitted well with Langmuir isotherm, sorption behavior of contaminated soil can be described as monolayer sorption on mono layer surface [12]-[14]. Moreover, the linear sorption isotherm is Freundlich sorption isotherm that Freundlich exponent (n) equivalent to 1 [15].



(a)



(b)

Figure 1. Soil sampling point in Mae Ku Creek, Tak Province, Thailand

3. Result and discussion

3.1. Study area

The soil sample was taken in Mae Ku Creek, Tak province within a range of UTM eastings of 455000 to 460000 and a range of UTM northings of 1835000 to 1840000 as shown in Figure 1. The soil type in the sampling point was classified as Mae Rim series by LDD.

3.2. Soil properties

Physico-chemical properties of the soil from the sampling spot are shown in Table 1.

Table 1. Physico-chemical properties of the soil

Sand (%)	Silt (%)	Clay (%)	OM (%)	pH
26	16	58	2.93	7.7

The soil collected can be classified as a clay soil by USDA soil triangle. The soil pH is 7.7, which is slightly alkaline and the percentage of organic matter in the soil sample is 2.93.

3.3. Batch sorption experiment

Sorption of Cd concentration in the sampling soil is shown in Table 2.

Table 2. Sorption and percent sorption of soil sample

Initial Cd concentration (mg L^{-1})	Cd Adsorption (mg g^{-1})	Adsorption (%)
nd.[a]	nd.	-
21.43	0.43	99.95

44.42	0.89	99.72
68.05	1.35	99.49
88.82	1.76	98.95
128.50	2.53	98.36
173.50	3.42	98.42

[a] nd: not detected

Cd sorption in soil (Q_e) and residue Cd in solution (C_e) from the experiment were plotted and fitted by Freundlich isotherm, Langmuir isotherm, and Linear isotherm in order to get sorption behavior of the soil. The result from the experiment was shown in Figure 2 and Table 2.

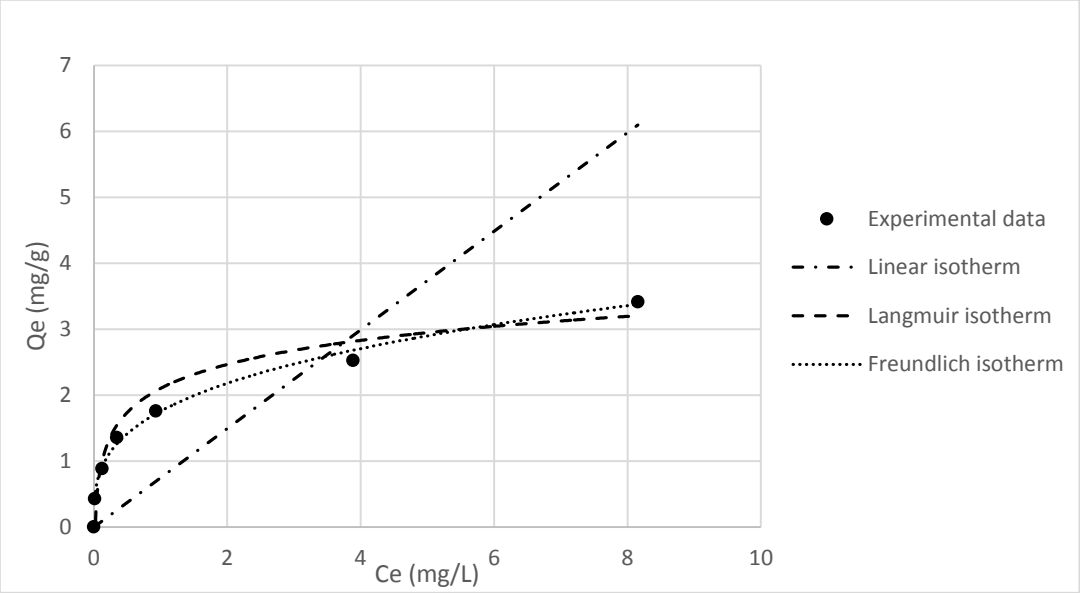


Figure 2. showing experimental data fitted with sorption isotherms

Table 3. Fitted parameters of sorption isotherms

Linear isotherm	**Langmuir isotherm**	**Freundlich isotherm**
$K_d = 0.745$ (L g^{-1})	$K_L = 1.730$ (L g^{-1})	$K_f = 1.760$ (L g^{-1})
	$Q_m = 3.470$ (mg g^{-1})	1/n = 0.312 (-)
$R^2 = 0.2245$	$R^2 = 0.9747$	$R^2 = 0.9964$

As shown in Table 3, it shows sorption of the soil sample in Mae Ku Creek is well fitted with Freundlich isotherm (R^2 = 9964.0), which can be described that Cd ions sorb on the soil surface as multilayer sorption [16].

3.4. Discussion

The result showed that the soil sample has high capability to sorb Cd as shown in Table 2. The sorption ability of the soil sample still exceeds 98 percent, even the initial concentration of Cd is 173.5 mg L^{-1}. The sorption behavior can be described by Freundlich sorption isotherm which is multilayer sorption [17]. Moreover, the sorption behavior of the soil sample has the same sorption behavior as Waleeithikul [17] who also study the sorption behavior of soil in this study area. As compared to Waleeithikul [17], in this study the sample has the percentage of clay higher than that of the previous study, consisting of 64.5% sand, 23.2% silt, and 12.3% clay, classified as a sandy loam soil by USDA. As a result, K_f of the soil sample was 3 times higher than that of the sandy loam soil (0.571 L g^{-1}), while 1/n is lower than that of the sample, indicating that the more preferential sorption of Cd^{2+} onto the clay soil. However, the values of 1/n of both soils were lower than 1, implying that sorption was favorable.

As compared to Karak et al. [18] who studied Cd sorption in a clay soil that has proportion of 18% sand, 34% silt, and 48% clay. K_f of the sample is 7.264 with 1/n equal to 0.466 for Freundlich isotherm (R^2 = 0.965), and K_L equal to 0.027 and Q_m is 84.03 mg g^{-1} (R^2 = 0.844). The results from Freundlich isotherm has higher K_f than the soil sample in the study area (see Table 3). Similarly, both studies showed that sorption behavior can be well fitted by Freundlich sorption isotherm.

4. Conclusion

The study area is located in Mae Ku Creek, Tak Province, that has Cd contamination problem. The soil sample in the study area has 26% sand, 16% silt, and 58% clay with 2.73% OM and soil pH of 7.7. The batch experiment was performed in order to understand sorption behavior of the soil. The batch sorption experiment for the clay soil can be well fitted with Freundlich isotherm (R^2 = 0.9964). As known that the sorption characteristics play an important role in controlling the migration of contaminants, especially heavy metals, therefore, the finding could be used as the representative sorpion of Cd onto clay soil. Moreover, it can be further used for evaluate the groundwater vulnerability map and selected the proper site remediation in the future.

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