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Heavy Metal Reduction in Plant Using Soil Amendment

C. Chaiyaraksa, T. Khamko

***Abstract*—**This study investigated the influence of limestone and sepiolite on heavy metals accumulation in the soil and soybean. The soil was synthesized to contaminate with zinc 150 mg/kg, copper 100 mg/kg, and cadmium 1 mg/kg. The contaminated soil was mixed with limestone and sepiolite at the ratio of 1:0, 0:1, 1:1, and 2:1. The amount of soil modifier added to soil was 0.2%, 0.4%, and 0.8%. The metals determination was performed on soil both before and after soybean planting and in the root, shoot, and seed of soybean after harvesting. The study was also on metal translocate from root to seed and on bioaccumulation factor. Using of limestone and sepiolite resulted in a reduction of metals accumulated in soybean. For soil containing a high concentration of copper, cadmium, and zinc, a mixture of limestone and sepiolite (1:1) was recommended to mix with soil with the amount of 0.2%. Zinc could translocate from root to seed more than copper, and cadmium. From studying the movement of metals from soil to accumulate in soybean, the result was that soybean could absorb the highest amount of cadmium, followed by zinc, and copper, respectively.

***Keywords*—**Heavy metals, limestone, sepiolite, soil, soybean.

I. Introduction

THAILAND is currently promoting a wide range of industrial development. The industries use many chemicals and these substances contaminate in the environment. Heavy metals such as zinc, copper, cadmium are one of these chemicals. They are considered to be highly toxic in the environment [1]. Heavy metals cannot be decomposed by microorganisms so they cannot be removed easily from the environment [2]. Plants grow in the contaminated soil will absorb heavy metals and will affect the growth of the plant. The yield of the plant can reduce. In addition, the crop product will be contaminated and will affect the health of consumers [3]. There are many ways to treat contaminated soils, such as soil washing [4], phytoremediation [5], vitrification [6], and biological treatment [7]. Addition of modified materials to the soil is an interesting alternative because it is an easy and cheap method. Modified materials can reduce the movement of heavy metals in the soil by means of sorption, precipitation and ion exchange [8]. There are various types of soil modified materials such as phosphate material [9], zeolite [10], organic matter [11], and limestone [12], [13]. Yuebing et al. experimented to evaluate the efficacy of bentonite, sepiolite, and phosphate in fixing contaminated cadmium in soils. They found that soil modifiers can reduce cadmium concentration in roots, leaves, seeds of rice [14]. Liang et al. (2014) added sepiolite and palygorskite to cadmium contaminated soil. The results indicated that sepiolite could reduce cadmium concentration in rice to below 0.18 mg/kg [15]. Sun et al. studied the effect of soil improvement using sepiolite. The results showed that when adding 1% sepiolite, the concentration of cadmium in the edible portion of spinach was lower than 0.2 mg/kg fresh weight [16]. This study investigated the properties of limestone and sepiolite for modifying the soil. At present, soybeans receive special attention. It is a major economic crop of the country. The government has encouraged soybean cultivation after rice harvesting in the dry season. In this study, limestone and sepiolite were mixed with the soil. The ratio between limestone and sepiolite was varied to find out the suitable ratio for soybean cultivation. The observation was on the weight of seed, plant growth, the heavy metal content in seed, the value of the translocation factor (TF) and the value of the bioaccumulation factor (BAF).

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II. Methodology

A. Soil Sample

The soil used in the experiment was from Amphoe Pho Yao, Chachoengsao Province, Thailand. Ten soil samples from the different location were sampled in the total area of 3.95 acres. All ten soil samples were put together and brought to a laboratory to dry, determined the characteristics and synthesized to contaminate with 1 mg/kg of Cd, 150 mg/kg of Zn and 100 mg/kg of Cu. The synthesized soil was left at room temperature for 1 month to stabilize metals in the soil. The soil pH was measured using a pH meter (Consort, C860). Samples were analyzed for moisture content by drying in oven at 110 ºC and calculating the mass loss, organic matter by Walkley–Black titrations [17], cation exchange capacity (CEC) by ammonium saturation method, particle size by hydrometer, bulk density by core method, electrical conductivity (EC) by conductivity meter, total N by Kjeldahl method, available P by Bray II method, available K, major and trace elements by atomic absorption spectrometry (AAS) (Perkin Elmer, AAnalyst 200) [18].

B. Soil Modifier

Limestone and sepiolite were purchased from Loba Chemie and Sigma-Aldrich, respectively. Their pH, composition, surface area, pore size, and pore volume were determined using pH meter (Consort, C860), X-ray fluorescence spectrophotometer (Siemens, SRS 3400), and Brunauer Emmett teller/Gas adsorption analyzer, respectively

C. Plant Seedling

The soybean (Chiang Mai 60) was selected for planting due to the short harvesting time (about 97 days). A large and not distorted seed was selected and planted seedling into a tray (3 seeds per 1 tray).

D. Planting

After applying the mixture of limestone and sepiolite at the ratio of 1:0, 0:1, 1:1, and 2:1 to soil at the amount of 0% (control), 0.2%, 0.4%, and 0.8% ($w_{soil\ modifier}/w_{soil}$), the mixed soil was left for 1 month before planting. When seedling age was 20 days, the plant at the same height was selected to plant in the pot containing those mixed soil (1 plant per 1 pot). The growth of soybean was observed by measuring the height and counting the number of pods every week. The soybean was harvested after 110 days of planting. The shoot, root, and seed were dried, weighed, and analyzed heavy metals content.

E. TF and BAF

$$TF = C_{seed} / C_{root} \quad (1)$$

$$BAF = \frac{C\ \text{metal in dried biomass (mg/kg)}}{C\ \text{metal in the soil (mg/kg)}} \quad (2)$$

C_{seed} = heavy metal concentration in seed, C_{root} = heavy metal concentration in root, $C_{metal\ in\ dried\ biomass}$ = heavy metal concentration in plant, $C_{metal\ in\ the\ soil}$ = heavy metal concentration in soil

III. Results and Discussion

A. Soil Characteristic

The slightly acid low fertility sandy loam soil was sampled to carry out the experiment. The heavy metals concentration was low (Table I). It was synthesized to contaminate with 1 mg/kg of Cd, 150 mg/kg of Zn and 100 mg/kg of Cu.

TABLE I
Soil Characteristics

parameter	value
pH	6.52 ± 0.06
Conductivity (µS/cm)	320.20 ± 5.13
Soil type	Sandy loam
Bulk density (g/cm^3)	1.54 ± 0.05
Moisture (%)	11.74 ± 1.43
OM (%)	5.88 ± 0.39
CEC (meq/100g)	5.94 ± 0.54
Total N (%)	0.0035 ± 0.0008
Available P (mg/kg)	10.94 ± 1.37
Available K (mg/kg)	29.54 ± 2.64
Cu (mg/kg)	6.96 ± 0.92
Cd (mg/kg)	1.83 ± 0.35
Zn (mg/kg)	105.44 ± 2.42

B. Soil Modifier Characteristics

Limestone and sepiolite are basic substances. Limestone has a lower surface area, pore volume and pore size (Table II). The majority of the composition is CaO. Sepiolite has a lower pH. The majority of the composition is SiO_2. Zinc and copper concentration was not high. Cadmium concentration was high. However, the amount of modifier to put in the soil was low, so it would not give much effect to the total concentration of metals in the mixed soil.

TABLE II
Soil Modifier Characteristics

		limestone	sepiolite
Heavy metal	Zn (mg/Kg)	3.39	9.16
	Cu (mg/Kg)	1.29	3.49
	Cd (mg/Kg)	3.09	1.39
composition	CaO (%)	84.20	0.39
	Nd_2O_3 (%)	7.98	
	V_2O_5 (%)	3.69	
	CuO (%)	2.22	
	SiO_2 (%)		58.2
	MgO (%)	1.96	32.30
	MnO (%)	1.18	
	SO_3 (%)	0.45	0.38
	Fe_2O_3 (%)	0.29	0.61
Surface area (m^3/g)		4.06	169.20
Pore volume (mL/g)		0.02	0.50
Pore size (nm)		2.38	5.56
pH		9.44	8.72

C. Planting

After mixing soil modifiers with contaminated soil, the pH increased to 7.13-7.48. The suitable pH for growing soybean is about 6.8 – 8. The higher the amount of the soil modifier, the higher the pH is. After adding the mixture of limestone and sepiolite at the ratio of 1:0, 0:1, 1:1 and 2:1 to soil at the amount of 0.2%, 0.4%, 0.8% ($w_{soil\ modifier}/w_{soil}$), the dry weight of seed was 7.59-8.47, 7.25-14.58, 12.94-21.31 and 8.41-13.65 g/pot, respectively. When adding the mixture of limestone and sepiolite (1:1) at the amount of 0.2% to contaminated soil, the dry weight of soybean was found highest (21.31 ± 3.50 g/pot). Comparing of adding the mixture of limestone and sepiolite at the ratio of 1:1 at the amount of 0%, 0.2%, 0.4%, 0.8% ($w_{soil\ amendment}/w_{soil}$), the stem height and number of pod of soybean growth in 0.2% was the highest (Figs. 1 and 2).

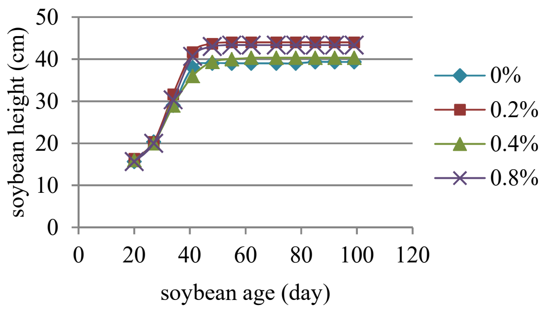

Fig. 1 Soybean height at different age when applying limestone: sepiolite (1:1) to soil at the amount of 0%, 0.2%, 0.4%, 0.8%

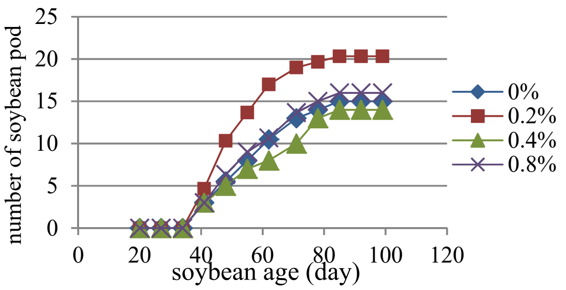

Fig. 2 Number of soybean pod at different age when applying limestone: sepiolite (1:1) to soil at the amount of 0%, 0.2%, 0.4%, 0.8%

Results in Fig. 3 indicated that the heavy metal concentration in seed was lower when adding modifiers to the contaminated soil. By using 1.1 limestone: sepiolite (0.2%), the concentration of heavy metal in seed was not exceeding food standard according to the Notification of the Ministry of Public Health (No. 273), 2003, Re: Food Standards Containing Contaminants (20 mg/kg Cu, 0.8 mg/kg Cd, and 100 mg/kg Zn) [19].

Table III showed the TF value of Cu, Zn, and Cd. This value can inform the ability of metals to move from root to seed. The value in Table III indicated that Cu, Zn, and Cd slightly could transfer from root to seed. Zn could transfer from root to seed at the highest level.

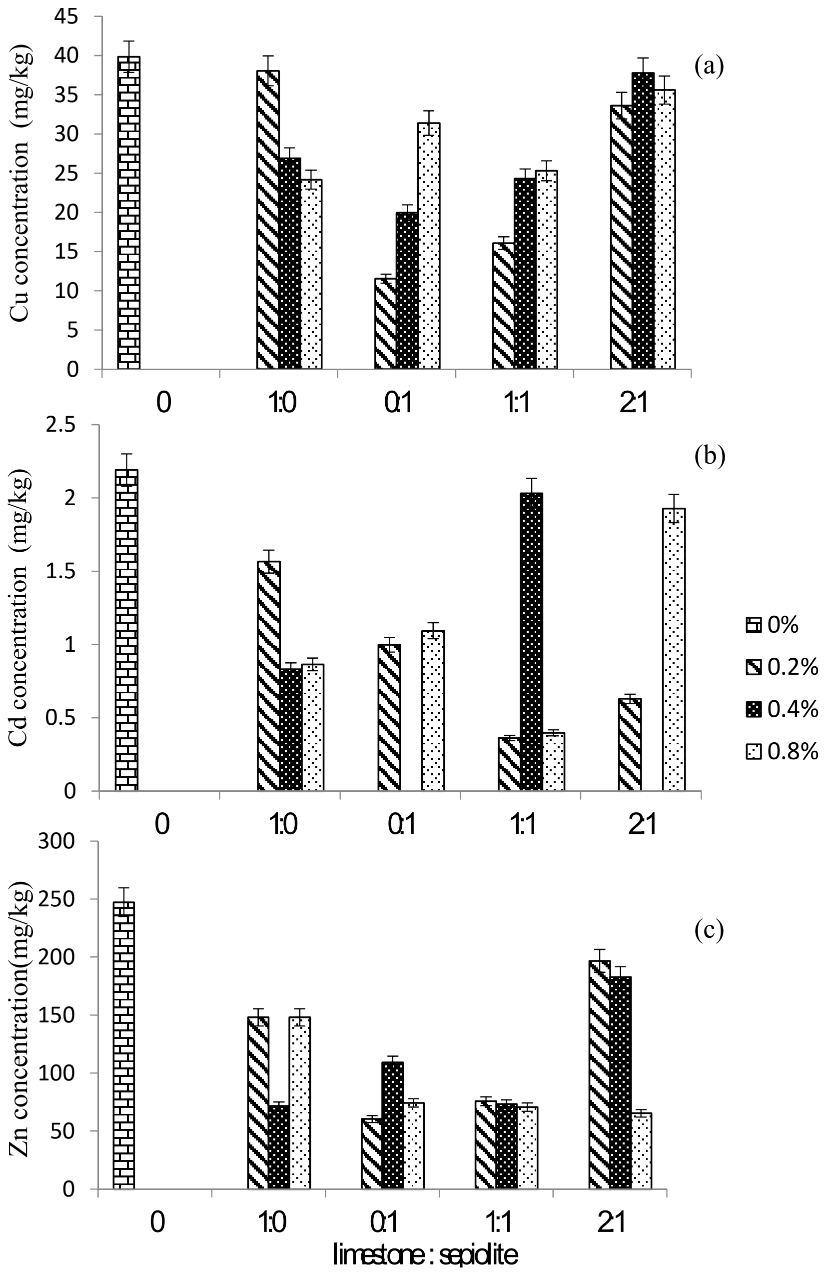

Fig. 3 Metal concentration in seed after applying the mixture of limestone and sepiolite at the ratio of 1:0, 0:1, 1:1 and 2:1 to soil (a) Cu concentration (b) Cd concentration (c) Zn concentration

TABLE III
TF VALUE

limestone: sepiolite, % in soil	Cu	Cd	Zn
Control	0.04 ± 0.00	0.10 ± 0.01	0.13 ± 0.01
1:0, 0.2%	0.08 ± 0.00	0.09 ± 0.01	0.21 ± 0.02
1:0, 0.4%	0.07 ± 0.01	0.05 ± 0.01	0.11 ± 0.02
1:0, 0.8%	0.09 ± 0.01	0.06 ± 0.01	0.27 ± 0.02
0:1, 0.2%	0.09 ± 0.01	0.10 ± 0.02	0.05 ± 0.01
0:1, 0.4%	0.05 ± 0.00	0.00 ± 0.00	0.14 ± 0.01
0:1, 0.8%	0.10 ± 0.02	0.05 ± 0.01	0.16 ± 0.03
1:1, 0.2%	0.21 ± 0.02	0.03 ± 0.03	0.22 ± 0.02
1:1, 0.4%	0.14 ± 0.03	0.11 ± 0.01	0.16 ± 0.04
1:1, 0.8%	0.13 ± 0.02	0.03 ± 0.02	0.15 ± 0.03
2:1, 0.2%	0.11 ± 0.02	0.04 ± 0.01	0.33 ± 0.05
2:1, 0.4%	0.10 ± 0.01	0.00 ± 0.00	0.35 ± 0.04
2:1, 0.8%	0.10 ± 0.03	0.12 ± 0.05	0.12 ± 0.04

Table IV showed the BAF value of Cu, Zn, and Cd. This value can inform the ability of metals to move from soil to plant. From Table IV, the BAF value more than 1 means Cu, Zn, and Cd can highly transfer from soil to plant especially Cd. However, applying 1:1 limestone: sepiolite could reduce such transferring.

TABLE IV
BAF VALUE

limestone : sepiolite, % in soil	Cu	Cd	Zn
Control	2.14 ± 0.00	8.37 ± 0.47	3.69 ± 0.10
1:0, 0.2%	1.33 ± 0.01	6.58 ± 0.89	1.80 ± 0.08
1:0, 0.4%	1.39 ± 0.01	3.10 ± 0.42	1.40 ± 0.02
1:0, 0.8%	1.27 ± 0.00	2.70 ± 0.23	1.83 ± 0.02
0:1, 0.2%	1.34 ± 0.00	3.54 ± 0.53	2.45 ± 0.37
0:1, 0.4%	1.28 ± 0.00	5.71 ± 2.15	1.95 ± 0.03
0:1, 0.8%	1.88 ± 0.02	5.93 ± 0.76	1.54 ± 0.05
1:1, 0.2%	1.36 ± 0.00	2.61 ± 0.20	1.02 ± 0.05
1:1, 0.4%	1.45 ± 0.01	3.56 ± 0.21	1.42 ± 0.02
1:1, 0.8%	1.74 ± 0.01	2.84 ± 0.12	1.65 ± 0.03
2:1, 0.2%	1.39 ± 0.01	6.09 ± 1.14	2.16 ± 0.12
2:1, 0.4%	1.31 ± 0.01	3.12 ± 0.37	2.14 ± 0.05
2:1, 0.8%	1.50 ± 0.05	4.17 ± 0.44	1.93 ± 0.03

IV. CONCLUSION

The amount of Cu, Cd, and Zn in soybean seed grown in unmodified soil were higher than that grown in modified soil. When adding the mixture of limestone and sepiolite (1:1) at the amount of 0.2% to contaminated soil, the dry weight of soybean was found highest and the concentration of heavy metals in seed was not exceeding food standard according to the Notification of the Ministry of Public Health (No. 273), 2003, Re: Food Standards Containing Contaminants. This study confirmed that the addition of limestone and sepiolite to soil successfully could reduce Cu, Cd, and Zn mobility in soil and the potential to move into the biosystem.

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- Immobilization of Cadmium in Soil Using Magnetic Biochar Derived from *Eichhornia crassipes*

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