Comparison of EDTA and DTPA on Cadmium Removal from Contaminated Soil with Water Hyacinth

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ABSTRACT

This study compared the effect of EDTA and DTPA on cadmium removal from soil by water hyacinth. In this study EDTA and DTPA were used at 3 concentrations 0.5, 1 and 2 mg/L. We collected the samples 4 times: after 20, 40, 60 and 80 days after application to analyze the cadmium concentration in plants by using USEPA method. The results show that the cadmium accumulated in roots more than in shoots. With DTPA of1 mg/L we found that the cadmium concentration was highest. Additionally, the EDTA at 2 mg/L showed cadmium concentration was highest. The comparison of EDTA and DTPA showed that DTPA can remove more cadmium than EDTA. The results show that water hyacinth grows better in EDTA than in DTPA. Thus, the higher cadmium removal might be caused by the better growth rate. At the end of the experiment it was found that DTPA was most suitable for increasing the cadmium removal capacity of water hyacinth and is a suitable phytoremediation technique to help clean contaminated sites.

Keywords : EDTA; DTPA; Sediment; Cadmium Removal Capacity; Phytoremediation

INTRODUCTION

Nowadays, increasing industrial pollution causes many negative effects on environmental quality. These effects are critically important due to their potential damage on human health and the life cycle of plants and animals. Hazardous waste contamination is one of the many increasing problems stemming from industrial activities such as mining. These activities result in hazardous materials being released into soil, water, sediment and groundwater.

Mae Sot District, Tak Province, Thailand was found to have high levels of cadmium contaminationin the stream sediment in Mae Tao creek. It was measured at 6.07 to 33.93 mg/Cd per kg of sediment and 11.66 to 65.22 mg of Cd/L of sediment [1]. Many researchers have studied this problem and searched for methods to reduce the cadmium concentration in this area [2, 3].

Remediation technology has many techniques to clean up heavy metal contamination in water, soil and sediment. These techniques include in situ physical and chemical processes (soil flushing, solidification and stabilization), thermal processes (verification), ex situ physical and chemical processes (soil washing, chemical reduction and oxidation), and other processes such as excavation and off-site disposal [4]. However, most of these treatments are rather costly [5]. Thus, the removal of heavy metals by plants has been recommended due to its relatively low cost and high efficiency. This method is called phytoremediation and uses plants to reduce, remove, degrade or immobilize contaminant toxins in soil, sediment, sludge and ground water [6-8]. Plants used can treat for various contaminants for example, heavy metals, inorganic waste, pesticides, solution, explosives, petroleum oils, hydrocarbon compounds, polycyclic aromatic hydrocarbon compounds and wastewater from garbage heap [7]. This technology is interesting and appropriate to the economic situation of Thailand.Phytoremediation is environmentally friendly. The use of plants is a natural process that reduces the need for additional chemical substances. Plants can uptake the metals from contaminated soil and accumulate them in the roots and later translocate the material to the shoots and leaves. The plants have the metabolism to degrade and reduce the pollutant using dehalogenase and oxygenase enzymes. This pollutant can then be removed by harvesting the above ground tissue of the plant then and incinerating or burying the harvest [9, 8]. The metal can be reclaimed from the ash which further reduces hazardous waste and generates recycling revenues. Phytoremediation technology has been receiving attention lately as an innovative and cost effective alternative to the more established treatment methods used at hazardous waste sites [4, 7]. Phytoremediation is a biological treatment technology, which uses selective plants for clean upof heavy metal contaminated soil and water.

In this research, *Eichhorniacrassipes* (Mart.) *Solms*. (water hyacinth) was studied to determine its ability to reduce the heavy metal in soil. *Eichhorniacrassipes* is not only generally found in the studied area but it also grows easily in every area of Thailand. It is a monocot weed plant species and tends to have high levels of xylem and phloem which may lead to increased uptake of heavy metals.

METHODOLOGY

1) Soil preparation: Soil samples were collected at a depth of 0-30 cm at a site in Mae Sot district, Tak province, Thailand. The soil properties are shown in (table 1).

2) Pots preparation: 21 pots (30 cm. x 35 cm. high) were washed with 10% nitric acid solution twice, and then rinsed with distilled water.

3) Chelating agent preparation: Ethylenedinitrilo-tetraacetic acid (EDTA) and Diethylenetriamine-pentaacetic acid (DTPA) were diluted in deionized water to obtain concentrations of 0.5, 1 and 2 mg/L., Five kilograms of Cadmium contaminated soil were added to each pot. The chelating agent was applied in 3 concentrations:

3.1) Experiment set 1; control pot without added chelating agent and using contaminated soil.

3.2) Experiment set 2; the addition of EDTA at 3 doses of 0.5, 1 and 2 mg/L and using contaminated soil.

3.3) Experiment set 3; the addition of DTPA at 3 doses of 0.5, 1 and 2 mg/L and using contaminated soil.

Table 1 Soil properties.

Soil properties	Methods	Value	Unit
pH	1:1 soil/water ratio	7.6	
Conductivity	1:1 soil/water ratio	0.18	dS/m
Soil moisture	% moisture = (wet weight - dry weight) x 100 / wet weight	8	%
Organic matter	$K_2Cr_2O_7$ digestion	2.56	%
Nitrogen	Kjedahl	0.13	%
Phosphorus	Molybdenum blue	8.33	mg/kg
Potassium	Digested with Na_2CO_3	56	mg/kg
CEC	Ammonium acetate	7.4	meq/100g
Soil texture	Hydrometer method	loam	
Cd	US EPA-3052	44.64	mg/kg

4) *Eichhorniacrassipes* preparation: Water hyacinths (4 plants per 1 pot) were selected from an uncontaminated area in the Bangpakong River, Nahmuang Sub-District, Muang District, Chachoengsao Province.

5) Planting and maintenance: A rotator machine was placed in each pot and the water level in each pot was maintained at 10 L until the end of the experiment.

6) Sample collection:

6.1) Water samples were collected from each pot in 100 ml bottles. The bottles had 2 or 3 drops of 65% nitric acid added to analyze total cadmium.

6.2) Soil samples were collected from each pot in 100 g lots and stored in zip lock bags. The soil samples were oven dried at 103^{o}C for 2-3 days to a constant weight and used to determine dry matter yield. It was crushed to pass through a 2 mm sieve to determine the total cadmium concentration.

6.3) Plant samples were collected, washed with tap water twice and rinsed with distilled water before being separated into 2 parts: roots and shoots. These samples were oven-dried at 70^{o}C for 2-3 days to get a constant weight and to determine dry matter yield.

7) Sample analysis:

7.1) Water samples were analyzed for total cadmium using USEPA method 3051A [11] All samples were made up to 50 ml with deionized water and preserved at $4^{o}C$ until analysis. The digested solution was analyzed by Atomic absorption spectrometer (AAS).

7.2) Soil samples and plant samples were analyzed for total cadmium using USEPA method 3052 [10]. The sample was made up with 50 ml of deionized water and preserved at $4^{o}C$ until analysis. The total digested solution was analyzed by Atomic absorption spectrometer (AAS).

RESULT AND DISCUSSION

1) Growth rate of water hyacinth

In our study, we looked at the effect on growth rate of water hyacinth in the cadmium contaminated soil caused by the addition of chelating agent EDTA and DTPA in 3 concentration levels;: 0.5, 1 and 2 mg/L (ppm) and compared the effects of using EDTA and DTPA to increase cadmium removal from contaminated soil in Mae Sot District, Tak Province, Thailand. First, we selected 2 week old water hyacinth plants of the same size (25-30 g). The results show that the water hyacinth grew well in all EDTA sets, but most especially with the addition of 2 mg/L (ppm). In the DTPA set, results show the water hyacinth growth rate increased with the various DTPA concentrations as shown in figure 2. From figure 1 and 2 we see that the water hyacinth growth tended to increase over time. The finding that was related with Ariganon (2007)[12]. She studied the effects of 5 kinds of chelating agent and organic acid (DTPA, EDDS, oxalic acid, citric acid and gallic acid) to increase the copper, zinc and nickel uptake capacity in *Ruelliatuberosa* (Burm.f.) Hochr. She reported that the chelating agent did not show phytotoxicity and did not effect the growth rate in plants. This also relatesto German et al. (2003)[13]. They studied the effects of EDTA and EDDS in increasing lead, zinc and cadmium uptake capacity in *Juncea* (L.) Czern. They found the application of EDTA at 3 and 5 ml/kg soil did not effect the dry weight of *Juncea* (L.) Czern.

2) Effect of EDTA and DTPA procedure

2.1) Effect of EDTA on cadmium uptake by water hyacinth

Figure 3 and 4 demonstrate that the accumulated cadmium uptake by roots and shoots tended to increase over time. These results show the EDTA increased cadmium removal capacity of water hyacinth. The cadmium accumulation in roots was higher than in shoots at 98.45 and 13.37 mg/kg dry weight of plant, respectively, at the EDTA concentration of 2 mg/L(ppm)and 80 days growth timeas show in figure 3 and 4. This uptake capacity by roots of water hyacinth related with Jean et al. (2008) [14]. They studied the effects of EDTA and Citric acid to increase Chromium and Nickel uptake capacity in *Darura Inno*xia. *Darura Innoxia*was grown in contaminated soil and EDTA was appliedat 1 mm/kg soil and Citric acid at 1, 5 and 10 mm/kg soil. They found that the two chelating agents caused positive effects on the chromium and nickel accumulation in the root of *Darura Innoxia.*

The uptake capacity in shoots (stem and leaf) of water hyacinth related with Hernandez et al. (2006) [15]. They studied the effects of EDTA on increased uptake capacity of lead, zinc and cadmium in *Cynaracarduncylus*.They found that EDTA can increase the uptake of heavy metals in plants. The heavy metal accumulation in stems and leaves was greater than in roots. This also relates to Wongtanet, J. and Parkpain, T. (2008) [16]. They studied the phytoremediation of lead from water. *Hydrocotyleumbella*, *Pityrogrammacalomelanos* and *Pandanusamaryllifolius* Roxb. were used in the experiment. The result of EDTA additions showed that the accumulation of lead was increased in roots and stems of *Hydrocotyleumbella*, *Pityrogrammacalomelanos* and *Pandanusamaryllifolius* Roxb equal to 19, 31.7 and 3.2 µg/g, respectively. The non-EDTA set the accumulation of lead in roots and stems of *Hydrocotyleumbella*, *Pityrogrammacalomelanos* and *Pandanusamaryllifolius* Roxb were11.4, 17.4 and 2.4 µg/g, respectively.

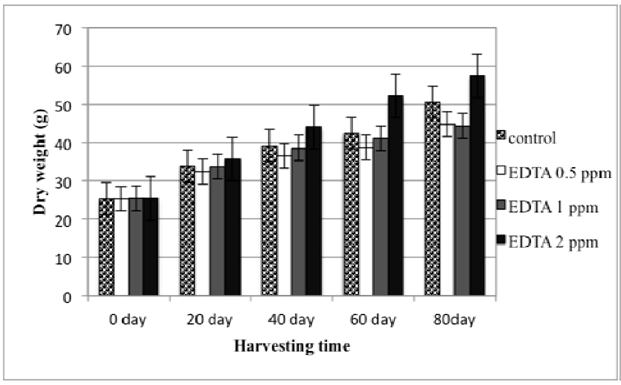

Figure 1. Growth rate of water hyacinth in EDTA additions set.

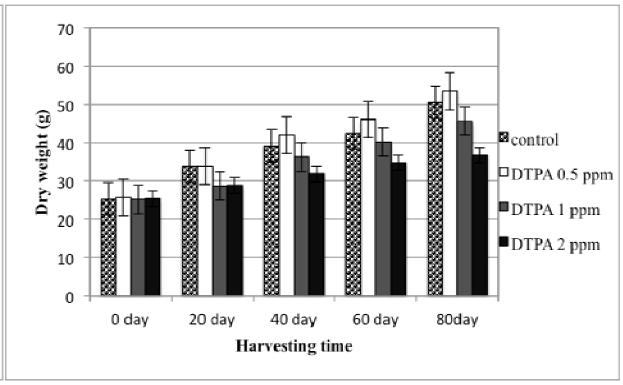

Figure 2. Growth rate of water hyacinth in DTPA additions set.

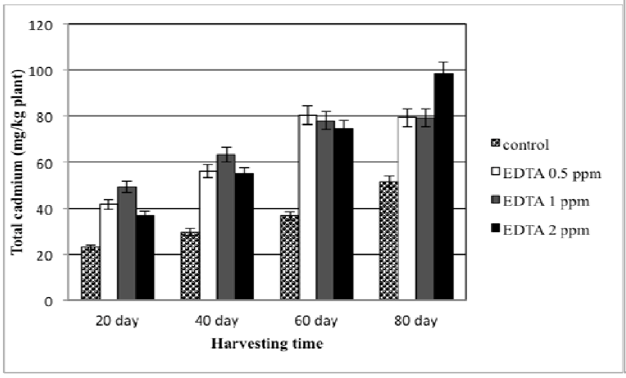

Figure 3. The effect of EDTA on cadmiumuptake byroots of water hyacinth.

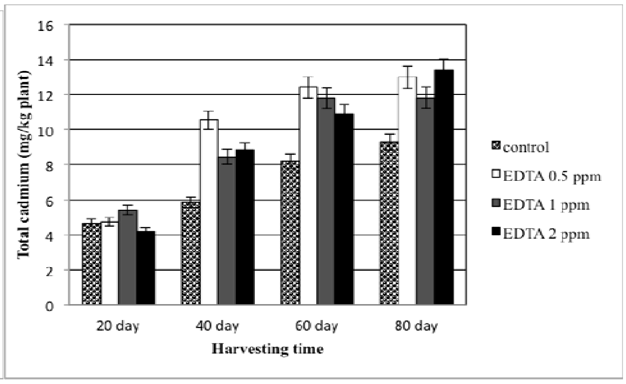

Figure 4. The effect of EDTA on cadmium uptake byshoots of water hyacinth.

2.2) Effect of DTPA on cadmium uptake by water hyacinth

Figure 5 and 6 illustrate that the cadmium removal by roots and shoots tended to increase over time. We found that the DTPA increased cadmium removal. The cadmium accumulation in roots washigher than shoots at 139.25 and 27.02 mg/kg dry weight of plant, respectively, at the DTPA concentration of 1 mg/l (ppm) and 80 days of growth time as shown in figure 5 and 6.

The finding, that DTPA increases the cadmium removal capacity, related with Hua-Yin Zhao et al. (2011) [17]. They studied phytoremediation of lead and zinc mining area soil using two chelators (EDTA and DTPA) to enrich ryegrass. They found that the EDTA and DTPA had great potential for this purpose.

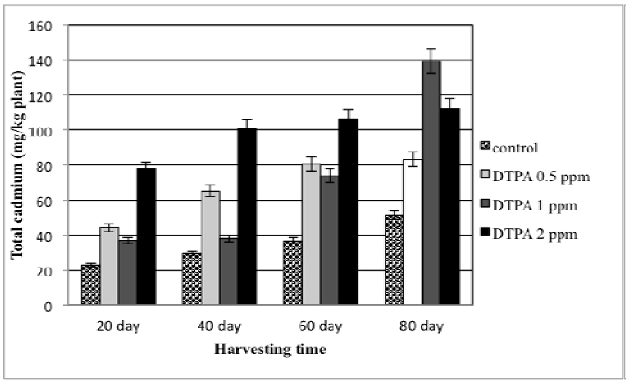

Figure 5. The effect of DTPA on cadmium uptake by roots of water hyacinth.

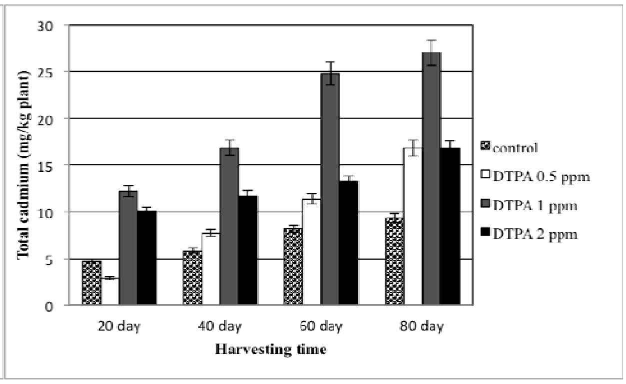

Figure 6. The effect of DTPA on cadmium uptake by shoots of water hyacinth.

2.3) Cadmium accumulation in the soil and water

From table 1, At 20 days, the cumulative amounts of cadmium taken up by the soil amended with EDTA at 0.5, 1 and 2 mg/kg soil, were 89.60, 59.47 and 54.55 mg/kg, respectively, at 80 days the totals were 60.76, 43.63 and 37.82 mg/kg, respectively. The amounts for DTPA were 80.01, 76.14 and 79.91 mg/kg at 20 days and 51.17, 43.33 and 61.77 mg/kg, respectively, at 80 days. The accumulated cadmium in soil tended to decrease over time.

Table 2 shows the concentrations on cadmium accumulate in water tended to decrease over time in the EDTA treated samples. At 20 days, the cumulative amounts of cadmium taken up by the water with EDTA at 0.5, 1 and 2 mg/L, were 12.11, 5.65 and 22.05 mg/L, respectively. At 80 days the amounts were 0.07, 0.06 and 0.07 mg/L, respectively. The amounts for DTPA were 12.38, 11.58 and 11.22 mg/kg at 20 days and 0.07, 0.08 and 0.05 mg/kg, respectively, at 80 days.

These results show that the concentration of cadmium accumulation in water was lower than in soil.

Table 2 The concentration of cadmium accumulation in soil and water.

Days	Soil						Water					
	EDTA			DTPA			EDTA			DTPA		
	0.5 mg/L	1 mg/L	2 mg/L	0.5 mg/L	1 mg/L	2 mg/L	0.5 mg/L	1 mg/L	2 mg/L	0.5 mg/L	1 mg/L	2 mg/L
20	89.60	59.47	54.55	80.01	76.14	79.91	12.11	5.65	22.05	12.38	11.58	11.22
40	78.88	53.60	46.98	74.49	76.92	78.00	0.12	0.11	0.11	0.11	0.11	0.08
60	60.80	52.76	43.04	68.14	75.58	67.68	0.08	0.08	0.08	0.08	0.08	0.08
80	60.76	43.63	37.82	51.17	43.33	61.77	0.07	0.06	0.07	0.07	0.08	0.05

CONCLUSION

The effects of EDTA and DTPA on cadmium removal from contaminated soil using water hyacinth revealed that DTPA can increase the cadmium removal capacity more than EDTA. In addition EDTA can increase the growth rate of water hyacinth more than DTPA. At the end of the experiment it was found that DTPA was suitable for increasing the cadmium removal capacity of water hyacinth and is a suitable Phytoremediation technique to help clean contaminated sites.

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