Phytoremediation of Cd, Ni and Cr by *Scindapsus Pictus Var Argyaeus* in Industrial Sludge

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ABSTRACT

This research focused on the ability of plants to hydroponically treat digested industrial sludge contaminated with chromium (Cr), cadmium (Cd) and nickel (Ni). Analysis were conducted using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to measured the content of heavy metals. The anaerobic sludge was obtained from the wastewater treatment lagoon located near rubber factory wastewater treatment plant. *Scindapsus Pictus Var Argyaeus* species was planted in hydroponic pots placed under transparent roof to simulate the natural environment. The pots were applied with 6.05 mg and 13.50 mg digested dried industrial sludge. The study was also to investigate the effect of pH and conductivity (EC) in the phytoremediation processses along the rhizosphere of *Scindapsus Pictus Var Argyaeus*. Generally the absorption of heavy metals by *Scindapsus Pictus Var Argyaeus* was in the order of Ni > Cr > Cd. The species could be able to remove 66% (3962 mg/kg DWplant^{-1})Ni, 19% (89 mg/kg DWplant^{-1}) Cd and 53% (396 mg/kg DWplant^{-1}) Cr from the hydroponics. The main factor of phytoremediation by the application with 6.05 mg and 13.50 mg sludge in this study were at pH 6.73±0.80 ; EC, 2.80±0.92 µS/cm and pH 6.80±0.67 ; EC, 3.20±1.44 µS/cm respectively.

Keyword: heavy metal, phytoremediation, industrial sludge, rhizosphere and hydroponic

INTRODUCTION

The final disposal of sewage sludge in Malaysia has become an important issue owing to public resistance and the limited area of land available. The most effective strategy is to reduce the quantity of sludge produced by various industrial processes. If this reduction is unfeasible, then the reuse of sludge in phytoremediation treatment systems should be considered. Recently, phytoremediation has emerged as an alternative to the engineering-based methods. In this new approach, plants are used to absorb contaminants from the sludge and translocate them to the shoots (Hale, *et al*., 2001). Pollutants are then removed by harvesting the aboveground tissue for subsequent volume reduction (i.e., ashing) and storage. Plant species are selected for phytoremediation based on their potential to evapotranspire subsurface water, the degradative enzymes they produce, their growth rates and biomass yield, the depth and distribution of their root zone, and their ability to bioaccumulate metals as contaminants (Burken and Schnoor, 1996).

Major parameters controlling heavy metal uptake by crops are its concentration in hydroponics, nutrients and pH. Roots withdraw substances from the hydroponics, but they also release substances influencing nutrient availability (Jauert, *et al*., 2002). The rhizosphere, the first few millimeters of medium in contact with the roots, may have a pH up to 2 units higher or lower than the medium directly around it, which can significantly affect the uptake of most plant nutrients. Plants experiencing an iron deficiency generally increase the hyrogen ions output into the rhizosphere to acidify the medium and release organic acids. Nitrogen tend to acidify their rhizosphere because they take up more cations of ammonium than anions of nitrate, which is counterbalanced by acidify of pH (VanLoon G.W. and Duffy, S.J., 2005). Jauert, *et al*. 2002 has suggested that the most important factor for the uptake of cationic heavy metals from sludges by plants is the pH of the medium in which they are growing. Elemental sulfur, added to soils contaminated with cadmium and planted with common mustard *(Sinapis alba* L.), was shown to acidify the soil and make the cadmium more available to the plant. The previous study also showed that when high levels of sulfur were added the pH dropped significantly and plant growth was inhibited. At pH 5 to 5.5 optimum plant growth was achieved, but was accompanied by significantly increased levels of cadmium uptake (Jauert, *et al*. 2002). In the study reported here, the effect of rhizosphere pH and electrical conductivity on heavy metal uptake in hydoponic solution was investigated.

MATERIALS AND METHODS

Seed sources and sludge

In the processing of latex, ammonia is used to maintain the latex in liquid form which was applied directly to the latex before undergoing other process in the factory. The reactions between trace elements such as heavy metals from wastewater with ammonia liquid produces a precipitate in the form of sludge (Inseong Hwang, 2000). Sludge contamination is more persistent and may remain for long periods of time by binding strongly to sludge particles. The sludge used in the study was obtained from a wastewater treatment lagoon treating wastewater from a rubber factory. These plants species were collected from a wild population growing in a field. The plants were chosen because they are locally available. In order to get the seeds, the dry seed heads were crushed to release the seeds. The seeds were grown in a pots of soil which were placed in a greenhouse. The size of the pots are 20 cm x 40 cm high. The plants were watered three times a week.

Preparation of Pots and Plants

The pots were arranged and placed in a greenhouse illuminated with natural light. Two 11 cm diameters hydroponic polypriplyne pots were stacked on top of each other. The top pot is perforated at the bottom is where the plant was housed so that the roots can grow and obtained its nutrient from the bottom pot. The bottom pot hold 250 mL when filled to a depth of 10 cm. When appropriate, sludge was added to the hydroponic solution as digested sludge. Washed sand was filled on the base of small pots to support the plants during grow. Oxygen was allowed within roots zone for organic mineral to stimulate aerobically (Burken, *et. al*., 2001). The pots were wrapped in aluminium foil to prevent algae growth and organic photolysis (Aitchison, *et al*. 2000). There were five replicates of each treatment. The species was grown in pots containing a nutrient solution composed of; 6.0 mM KNO_3, 4.0 mM $Ca(NO_3)_2$, 0.1 mM $NH_4H_2PO_4$, 1.0 µM $MgSO_4$, 25 mM $CaCl_2$, 12.5 mM H_3BO_3 and 250 ml diionized water (Ebbs, *et al*, 2001). The pH was adjusted to approximately 5.5 with HCl and KOH (Zavoda, *et al*., 2001). The pots were applied with 6.05 mg and 13.50 mg industrial sludge as digested dried industrial sludge, which have trace metals elements to provide the proper micronutrients for different plant growth needs. Only aqueous phase are involved in absorption of roots in hydroponics.

The plants, *Scindapsus Pictus Var Argyaeus* were grown hydroponically to study their ability to accumulate biologically and tolerate the content of heavy metal in the medium. Through mechanisms of direct uptake and accumulation of contaminants in root cells in rhizosphere zone, and the release and exudation of enzymes stimulates microbial activity in the aqueous media (Chen. 2001). All plants were grown and maintained for 28 days in the hydroponic (Qian, *et al*., 1999). The heavy metals concentrations and the volume of medium were checked every four days. The concentration of metals were analysed by using a Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). After 12 days, plants were transferred to 250 mL of fresh hydroponic solution which contain nutrient and digested sludge for second application. The pH and electrical conductance of hydroponic medium were determined at each sampling to study rhizosphere pH and electrical conductance (EC) trends. Uptake of metals into shoots of plants was influenced by pH and EC. The reduction of heavy metals concentrations was monitored every four days.

Plant digestion

At the end of the treatment period, whole of 4 weeks old plants were harvested. The plants were removed from the pots and the roots were rinsed in warm deionised water to remove liquids of the hydroponic medium. Then the whole segment of plants were soaked in a 100 mM $CaCl_2$ solution to remove any cell wall associated with free space heavy metals (Jauert, *et al*. 2001). Plants used for metal analysis were dried in a convection oven for 24h at 105^{o}C until a constant weight was obtained. After drying, the plants were ground up using a M20, IKA-WERKE grinder for heavy metals analysis. Approximately 1 g of dried plants were weighed and placed in Anton Paar teflon tubes for digestion. Ten milliliter of concentrated nitric acid was added to each tube (Andersen dan Kisser, 2004). After the digestion, the marbles were removed and the excess acid was allowed to evaporate. The samples were then analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Model Perkin Elmer, Elan 9000). Reagent blanks and internal standards were used where appropriate to ensure accuracy and precision in the analysis.

RESULTS AND DISCUSSION

Rhizospehere pH and Conductivity

Aqueous medium with sludge content of 6.05 mg shows range of pH values between 5.54 to 8.23 whilst the 13.50 mg medium shows range of 5.48 to 7.85 as shown in Figure 1. The electrical conductance of 6.05 mg medium and 13.50 mg medium shows a decline pattern from day 1 to day 28 of the experiment. There was a reduction in solution volume when the contaminant uptake by plants. When metals-salts, acids or basic are dissolved in hydroponics or water, they can exist as ions and the solutions are electrolytes. The conductivity of medium decreased as the cationic metal of rhizosphere decreased in the unsaturated medium (Ebbs, *et. al*, 2001). The plants with the lowest rhizosphere pH had the highest total of metal-hidrogen bonding in medium was also seen within conductivity value.

For the pots of 6.05 mg of industrial sludge, between day 24 and 28 there was reduction of conductivity from 2.25 µS/cm to 1.04 µS/cm although the rhizosphere pH increased between 6.58 and 7.05. At the same period the absoption of Cd and Cr were 43554 ng and 12143 ng respectively while no absorption for Ni. Figure 3 shows that 19305 ng Cr was absorbed where the pH 7.3 – 8.23 and conductivity, 2.73-2.43 µS/cm during the experiment at 8 and 12 days (Figure 1) during the first application of sludge. While no absorption for Cd and Ni elements at the same period as in Figure 2 and 4. Figure 3 shows that 24094 ng of Cr was absorbed where the pH 6.34-6.58 and conductivity was 3.24- 2.25 µS/cm during the experiment at day 20 and 24, but no absorption for Ni and Cd elements at the same period as shown in Figure 2 and 4. Between day 4 and 8 shows only Cd and Cr were absorbed by the plant with values of 16442 ng and 82556 ng respectively with pH range of 7.3 to 8.23 and the reduction of conductivity from 2.73 to 2.43 µS/cm.

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Figure 1: The pH and electrical conductivity of hydroponic medium which contain 6.05 mg and 13.5 mg of industrial sludge in 28 days.

The application of 13.5 mg of industrial sludge, between day 4 and 8 shows the reduction of conductivity from 5.32 µS/cm to 4.15 µS/cm although the rhizosphere pH increased between 6.45 and 7.32. At the same period the absoption of Cr and Ni were 19239 ng and 1971540 ng respectively while no absorption for Cd as shown in Figure 2. Figure 3 shows that 3167 ng Cr was absorbed where the pH increased from 6.29 to 7.02 and conductivity was 0.56-2.08 µS/cm during the experiment between day 24 and 28 (Figure 1) in the second application of sludge. While no absorption for Ni and Cd elements at the same period as in shown Figure 2 and 4. Figure 2,3 and 4, shows that Cd,Cr and Ni were involved in absorption except for day 4 to 8 and day 24 to 28. But the Cr metal were absorbed by plant continuously for day 0 to 28 in Figure 3

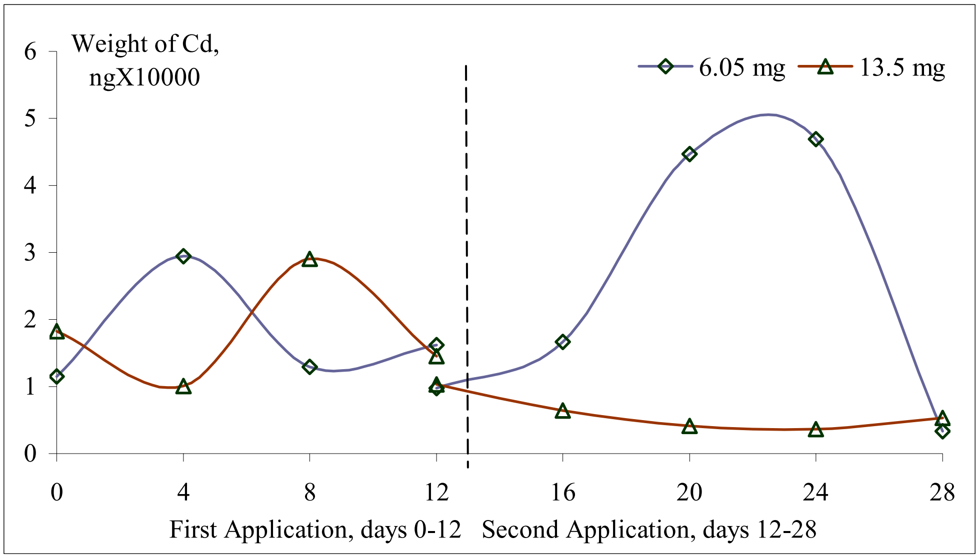

Figure 2 : The variation of Cd in hydroponic medium planted which contains with 6.05 mg and 13.5 mg of industrial sludge within 28 days.

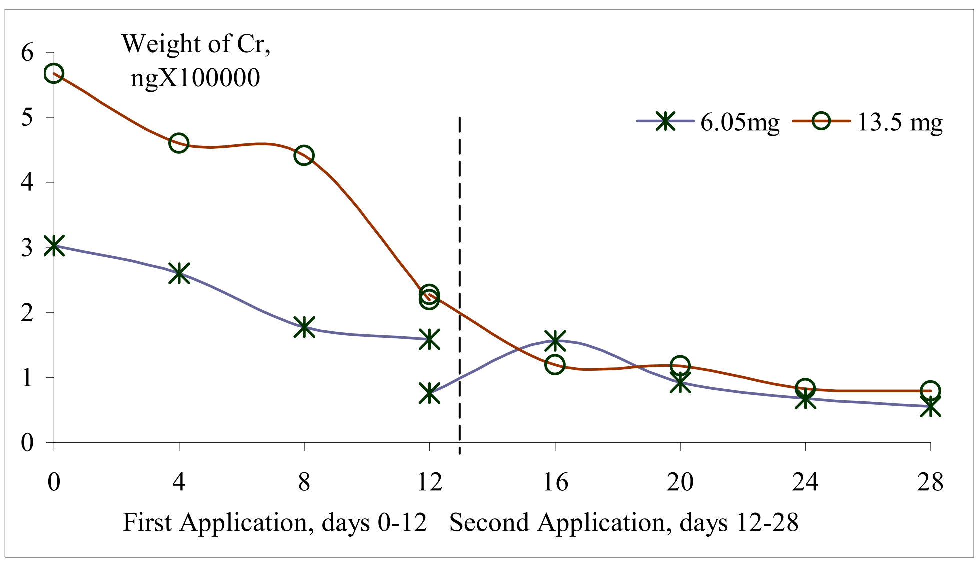

Figure 3 : The variation of Cr in hydroponic medium planted which contains with 6.05 mg and 13.5 mg of industrial sludge within 28 days.

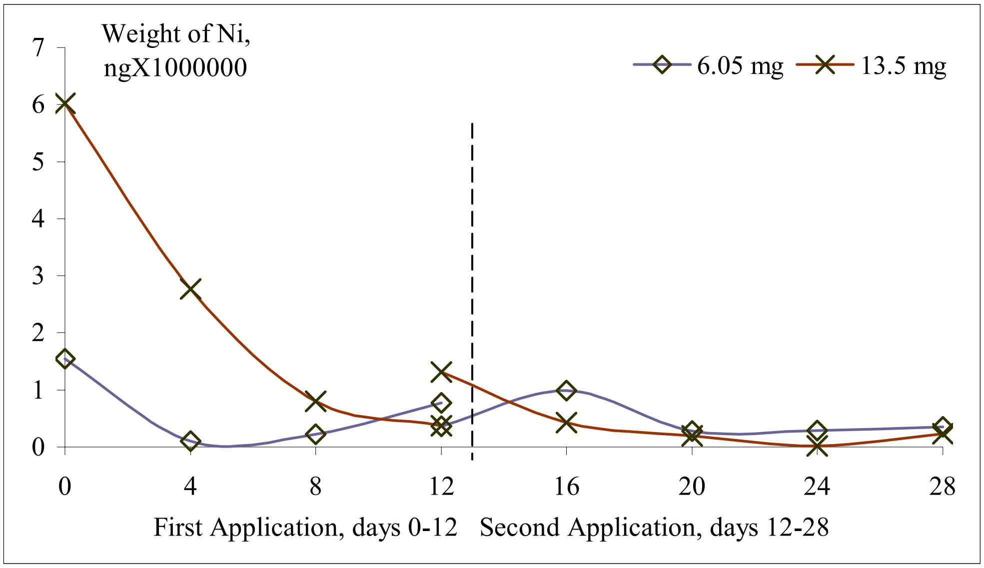

Figure 4 : The variation of Ni in hydroponic medium planted which contains with 6.05 mg and 13.5 mg of industrial sludge within 28 days.

The Accumulation Of Heavy Metals By *Scindapsus Pictus Var Argyaeus*.

The uptake Ni increased as the rhizosphere acidic decreased from 7.1 to 6.63 pH in the hydroponic application of 6.05 mg industrial sludge as shown in Figure 1 and 4. Ni uptake by plant also increased for the 13.5 mg application of industrial sludge at pH of 6.45 and 7.85 are shown in Figure 1 and 4. Compare to the pH in range 6.29 to 7.02, there was no absorption of Ni.

The plant were transferred to 250 ml pots containing 6.05 mg of industrial sludge which consistsed of Ni, 4948394 ng (817916 mg/kg), Cu, 168665 ng (27879 mg/kg) and Cr, 116632 ng (19278 mg/kg) in the first application. After 12 days, the plant were transferred to new 250 ml pots containing 6.05 mg of industrial sludge which consistsed of Ni, 694640 ng (114816 mg/kg), Cu, 115011 ng (19010 mg/kg) and Cr, 111323 ng (18401 mg/kg) in the second application. The amount of heavy metals reduced for the 0-12 and 12-28 days application are shown in Table 1. The total percentage absorption of heavy metals by plant were 40% of Ni, 52% of Cu and 50% of Cr is shown in Table 1.

Under the same condition, the spesies were transferred to 250 ml pots containing 13.5 mg of industrial sludge and consistsed of Ni, 1550260 ng (256241mg/kg), Cd, 11514 ng (1903 mg/kg) and Cr, 302768 ng (50044 mg/kg) in the first application. After 12 days, the plant were transferred to new 250 ml pots containing 13.5 mg of industrial sludge which consistsed of Ni, 6017429 ng (445735 mg/kg), Cd, 18277 ng (1354 mg/kg) and Cr, 567211 ng (42016 mg/kg) in the second application. The amount of heavy metals reduced for the 0-12 and 12-28 days application are shown in Table 1. The total percentage absorption of heavy metals by plant were 66% of Ni, 19% of Cd and 53% of Cr is shown in Table 1.

Table 2 shows that the accumulation of heavy metals recovered from plant tissue was higher than the amount of heavy metals absorbed by plant from pots. According to the results, plants grown on industrial sludge treated hydroponic showed higher amounts of heavy metals and register the highest heavy metals concentration in plant tissues. The components of 13.5 mg sludge, may be even less effective because they potentially solubilize, bind and complex-Cr that plants may not be able to take up, is shown in Table 1. Whereas, Cd accumulation in shoots is driven mainly by mass flow due to the transpiration process. The application of acidic medium could reduce translocation of Cd to the shoots due to the treatment that reduce transpiration and increasing relative humidity around the shoots (Harris and Taylor, 2004). The results of the Ni, Cr and Cd elements analysis of plants showed a differential accumulation of trace elements in plant tissue of species (Table 2). Selection of the appropriate plant species should be based on element concentration in plant tissues if element recovery from harvested plant materials is an important goal of the phytoremediation process.

Table 1 : The heavy metals absorption by plant in hydroponic treatment medium

	days	Weight of sludge application to 250 ml of medium pots which were planted with *Scindapsus Pictus Var Argyaeus*					
		6.05 mg			13.5 mg		
		Ni	Cd	Cr	Ni	Cd	Cr
First application, $mgkg^{-1}$	0	256241	1903	50044	445735	1354	42016
	12	127468	2681	26211	27788	1074	16234
	1^{st} Uptake	128773	-778 no uptake	23833	417947	280	25782
Second application, $mgkg^{-1}$	12	59385	1618	12552	97302	765	16873
	28	59214	550	9247	16999	395	5867
	2^{nd} Uptake	171	1068	3305	80303	370	11006
Total uptake, $mgkg^{-1}$		128944	290	27138	498250	650	36788
The uptake from sludge		41%	8%	43%	92%	31%	62%
Heavy metals		Ni		Cd		Cr	
Average of uptake from sludge		66%		19%		53%	

A correlation between a plant's rhizosphere pH and its heavy metals uptake was shown by the results of this study. The results of the trace elements analysis of plants showed a differential accumulation of trace elements in the plant tissue. Interactions between the micronutrients and other divalent cations in plant absorption may partly explain these results. They were antagonistic interaction of B-Cr, B-Ni and Cr-Cd in the absorption of elements by the plant.

Table 2 : Comparison between the uptake of Ni, Cd and Cr from sludge hydroponics medium with the content of heavy metals in plant.

	Weight of sludge applied to 250 ml of medium pots planted with *Scindapsus Pictus Var Argyaeus*					
	6.05 mg			13.5 mg		
	Ni	Cd	Cr	Ni	Cd	Cr
Weight of dried plant	14 gram			9 gram		
Total reduction of heavy metals from sludge hydroponic medium pots, mg	0.39	0.87*	0.082	3.36	4.38*	0.25
The total content of heavy metals in plant, mg	17.20	1.21	2.78	25.12	0.04	1.83

Accumulation of heavy metal in *Scindapsus Pictus Var Argyaeus*, mgkg^{-1} DWplant^{-1}	2416	169	389	5507	8	402
pH factor	6.73±0.80			6.80±0.67		
EC factor, µS/cm	2.80±0.92			3.20±1.44		
The average of heavy metals accumulated mgkg^{-1} DWplant^{-1}	Ni		Cd		Cr	
	3962		89		396	

DW: Dried weight
EC: Electrical Conductivity
*: µg, microgram units.

CONCLUSION

Generally the absorption of heavy metals by *Scindapsus Pictus Var Argyaeus* was in the order Ni > Cr > Cd. Compare with the selectivity of heavy metals was Cd > Ni > Cr by *Helianthus annuus* (dwarf sunflower) (Zavoda, *et al*., 2001), and Cr > Ni > Cd by Indian mustard, Brassica juncea. On the other study, *Myriophyllum Brasiliense Camb*. (parrot's feather) species absorbed the heavy metals from polluted hydroponics was Cr > Cd > Ni (Qian, *et.al.*, 1999).

As seen from Table 1, the uptake of these metals were quite significant. The average uptake measured were 66%, 19% and 53% for Ni, Cd and Cr respectively. These potential percentages of element removal are merely estimates based on data obtained for hydroponically grown plants for 28 days or 1 month per year, but with a salinity level of electrical conductiviy and pH as shown in Table 2, which were tolerated by the species tested. This information data could be important for the use of *Scindapsus Pictus Var Argyaeus* in the phytoremediation of Ni-Cd-Cr-contaminated sludges in hydroponics. Therefore it is recommended that this technology should be considered as viable option for treating metals in hazardous waste .

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