Column Washing of Cadmium from Soil and Sludge by a Mixture of $Na_2S_2O_5$ and Na_2EDTA

Chompoonut Chaiyaraksa and Natchatheeya Sriwiriyanuphap
Department of Chemistry, Environmental Chemistry Program, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520, Thailand

Abstract

Washing of cadmium contaminated soils and sludge, which are hazardous materials, using a mixture of 0.1 M $Na_2S_2O_5$ and 0.01 M Na_2EDTA was investigated in the column mode. Initial Cd concentration in soil and sludge was 500 mg kg^{-1}. The amount of sample packed in the column was 9.25 g. The washing solution was pumped with a flow rate of 1.2 ± 0.1 ml min^{-1} through the column. Every 5 mL of leachate was collected to analyze the removed Cd concentration. The sequential extraction was conducted to study what form of Cd was removed. Linear regression was performed to determine what soil and sludge parameters had the greatest influence on the washing. The silt content (0.002-0.02 mm in particle size) in soil was found to be the main factor for the washing. The lower the silt content, the higher the removal efficiency. The soil washing efficiency was in the range of 23-36%. The removed Cd was mostly in exchangeable form. The sludge washing efficiency was about 7%. The predominant forms of the removed Cd were reducible form and exchangeable form.

Keywords: soil remediation, sludge washing, cadmium, sodium metabisulfite, sodium EDTA

1. Introduction

Numerous industrial practices, such as battery processing, electroplating processing, and plastic stabilization processing, have resulted in cadmium contamination of soils and sludge [1]. Technologies available for treating metal contaminated sludge and soils include solidification/stabilization and vitrification [2]. Recently, researchers try to develop soil washing techniques where soil-bound contaminants are transferred to the liquid phase by desorption and solubilization. Factors affecting heavy metal retention by soils include pH, cation exchange capacity (CEC), particle size distribution, natural organic matter, minerals and the presence of other inorganic contaminants [3-6]. Several washing solutions have been investigated such as water, organic solvents, chelating agents, surfactants, and acids. Hessling et al. (1990) washed contaminated soils by various solutions. Their results showed that an EDTA solution was far superior to tap water or an anionic surfactant solution [7]. Reed et al. (1996) studied the flushing of a Pb (II) contaminated sandy loam using 0.1 N HCl, 0.01 M EDTA, and 1 M $CaCl_2$ in the column mode. They found that lead removal efficiencies for HCl, EDTA, and $CaCl_2$ were 85%, 100%, and 78%, respectively. The final soil pH for HCl was near 1, raising the concern of increased contaminant mobility, decreased soil productivity and adverse changes in the soil's chemical and physical structure due to mineral dissolution [8]. Removal of many metals by reaction with chelating reagents is efficient but the cost of chelating reagents such as EDTA was high [9]. $Na_2S_2O_5$ is an inexpensive reducing agent, which has been extensively used to treat different metal contaminated waste [10]. Abumaizar and Smith studied the batch and column washing of metals contaminated silky sand. They found that a mixture of 0.1 M $Na_2S_2O_5$ and 0.01 M Na_2EDTA provide an economically optimum solution for cadmium and zinc removal [11].

The aim of the study was to evaluate the potential of soil and sludge washing for removing cadmium contamination using a mixture of 0.1 M $Na_2S_2O_5$ (reducing reagent) and 0.01 M Na_2EDTA (chelating reagent). The experiments were carried out in column mode. The effect of soil and sludge compositions was investigated. The study also focused on the form of cadmium that was removed by the solution.

2. Materials and Methods

2.1 Soil and sludge samples

Soils were sampled from 4 provinces; Bangpra sub-district, Sriracha district, Cholburi province, Kudnokplao sub-district, Meung district, Saraburi province, Klonghok sub-district, Klongluang district, Patumthani province, Loomkao sub-district, Klogsumrong district, and Lopburi province at 2 different depth levels: 0-15 cm (topsoil) and 15-32 cm (subsoil). Sludge, which is a hazardous material, was from General Environmental Conservation Co.Ltd. (GENCO), Samaedum, Bangkhoon-tien district, Bangkok Metropolis.

Soils and sludge were dried, passed through 12 mesh sieve and kept in plastic containers at room temperature for analyzing the physical and chemical characteristics, such as pH, bulk density (D_b), surface area, cation exchange capacity (CEC), organic matter (OM), moisture content (MC), particle size distribution, Al_2O_3, Fe_2O_3, MnO_2 and metal methods. Autosorb-l (Quantachrome) was used to analyze surface area. An X-ray fluorescence spectrophotometer (Phillips PW2400) was used for Al_2O_3, Fe_2O_3, and MnO_2 analysis. Metal concentrations were analyzed by an atomic absorption spectrophotometer (AAS) (Shimadzu AA-680). Other methods were performed according to the procedures described by Carter [12].

Five hundred milligrams per kilogram of Cd contaminated soil and sludge was synthesized by adding standard cadmium nitrate solution into soil and sludge in a plastic container. Then, they were mixed for homogeneity, and left at room temperature for 3 months. After that, they were dried between 103-105°C. Then the contaminated samples were brought for column washing.

Both samples of soil and sludge, before and after washing, were extracted by sequential extraction [13] for studying the ratio of Cd in different forms that were removed from soil and sludge.

2.2 Column washing [11]

The column was made of plastic with an inner diameter of 2 cm and a total length of 7 cm. The column was divided into 3 parts. The middle part was packed with the sample of soil or sludge, at the amount of 9.25 g. The upper and lower parts were filled with glass beads as shown in Figure 1.

A mixture of 0.1 M $Na_2S_2O_5$ and 0.01 M Na_2EDTA (300 ml) was prepared and poured into a plastic beaker. The washing solution was pumped with a flow rate of 1.2 ± 0.1 ml min^{-1} through the lower part of the column. The washing solution that came out of the top part of column was collected and analyzed for pH. The pH was adjusted to 2 with 1:1 HNO_3 and the analyzed Cd concentration was analyzed by AAS. The percentage of Cd that was removed from the sample was calculated. All experiments were conducted in triplicate.

2.3 Batch washing [11]

A two gram dry sample was placed into a 60-ml plastic container. The washing solution, which was a mixture of 0.1 M $Na_2S_2O_5$ and 0.01 M Na_2EDTA, was added into the sample. The ratio of sample weight to the volume of washing solution was 1 g: 2.5 ml. The sample was shaken at room temperature for 2 hours by a horizontal shaker at a shaking rate of 175 rpm, and then centrifuged at the rate of 4,000 rpm. The aliquot was filtered through 0.45 μm filter paper using vacuum filtration. The pH of the filtrate was adjusted to 2 with 1:1 HNO_3. The Cd concentration was analyzed by AAS. The percentage of Cd that was removed from the sample was calculated. All experiments were conducted in triplicate. Further experiments were carried out by changing the ratio of sample weight to the volume of washing solution from 1 g: 5 ml to 1 g: 7.5 ml.

3. Results and Discussion

Physical and chemical characteristics of soils and sludge are shown in Table 1 and Table 2.

3.1 Column washing

The results of finding Cd removal efficiency from soil samples that are sampled from 4 provinces sampled vs. washing solution is presented in figure 2a-d. The washing solution used was a mixture of 0.1 M $Na_2S_2O_5$ and 0.01 M Na_2EDTA. $Na_2S_2O_5$ has two types of duty:

1. $Na_2S_2O_5$ reduces Cd^{2+} to Cd^{+}, which is not a stable form, and can be removed from soil easily. Cd^{+} can then be oxidized with oxygen becoming Cd^{2+}. This makes a complex compound with EDTA.
   $Cd^{+}+O_2+2H_2O \rightarrow 4\ Cd^{2+} + 4OH^{\cdot}$
2. $Na_2S_2O_5$ weakens the bond of Cd-soil attachment. This makes Cd casy to remove from soil and stay in the water phase. Cd thus can form a complex compound with Na_2EDTA more easily. This a complex compound is in water-soluble form. The mechanism is as the equation :
   $Me + L \leftrightarrow MeL$
   When Me = metal cation
   L = ligand anion

With this metal extraction process, reaction of complexation will have to compete with the following processes:

1. Metal hydroxide and carbonate formation
2. Surface complexation and precipitation on soil particles

By graphing the soil from 4 provinces for topsoil and subsoil the results reveal that Cd removal to increased rapidly at the beginning of washing. After continuing the washing, the Cd removal % remained constant. The percentage of washed Cd from soils that come from Cholburi province and Saraburi province increased rapidly when using washing solution betweer 0-50 ml. Washing solutions could wash Cd from soil that come from Patumthani province, Saraburi province, Lopburi province and Cholburi province at the depth level of 0-15 cm, 19.73%, 23.04%, 25.81% and 29.48%, respectively. For the depth level of 15-32 cm, Cd could be washed 25.53%, 29.13%, 32.32% and 32.37%, respectively. The Cd removal efficiency from subsoil (15-32 cm) was higher than from topsoil (0-15 cm), due to the higher CEC and the percentage of clay in subsoil.

From the statistical regression analysis using program SPSS Version 9.01 with the confidence level of 95%, the silt content in soil was shown to be the main factor for Cd removal. Cadmium was washed from soil more, if the soil had a in low percentage of silt (Figure 3). Soil from Cholburi province in both depth levels, and soil from Lopburi province at the depth level of 15-32 cm revealed a low silt percentage, in the range of 4.27-7.83%. The percentage of washed Cd was at 29-32%. Soil samples from both Saraburi province and Patumthani province at both depth levels and from Lopburi province at depth level of 0.15 cm, revealed a high percentage of silt,int the range of 16.04-20.34%. The percentage of washed Cd was very low, approximately 19-29%.

The percentage of washed Cd from 4 different types of soil was rather low. This may be due to 2 reasons; Firstly, the washing in column mode takes a long time. This creates an opportunity for Cd to become precipitated as hydroxide or carbonate or sulfide. Secondly, in The washing solution process, there already is an excess of cadmium ion. This allows reversible reactions. This causes Cd ion to be removed from soil with more difficulty.

The Cd removal efficiency from sludge in column mode is presented in figure 2e. The percentage of washed Cd increased rapidly at washing solution volume of 0-50 ml. Cd was washed from sludge at 5.01% when using 50 ml of washing solution. When continuing the washing, Cd was removed more, but not very much. The highest percentage of washed Cd was 7.12%. The percentage of washed Cd in sludge was very low, compared to the 4 types of soil. This may come from 4 reasons; Firstly, the organic matter in sludge is high, thus the opportunity of $Na_2S_2O_5$ to weaken the bond of Cd - soil attachment is less. Secondly, pH in the sludge is high (pH 8.04), thus most of Cd in sludge will be in Cd hydroxide form. Na_2EDTA then cannot be substituted for hydroxide to form a stable complex compound. Even though Cd ion in cadmium hydroxide can be redissolved into the solution and form a complex with EDTA, the reaction rate will be very slow. Thirdly, the washing in column mode will take a long time, so Cd has an opportunity to become a metal hydroxide or carbonate or sulfide. This is a barrier for Cd to form a stable complex compound with EDTA. The last reason is that other metals in the sludge such as chromium (table 2), may compete with Cd, to form complex compounds with EDTA in the experimental pH range. (pH 6-7) [14]

3.2 Sequential extraction

Figure 4a shows the sequential extraction results before removing Cd from 4 types of soil samples in both depth levels. It reveals that 43.3-71% of all Cd was in exchangeable form and 6.7-49.2% of all Cd was in the residual form. It was also found in other forms, but very little.

Sequential extraction was carried out after washing soil in column mode. The exchangeable form of Cd in the soil from Cholburi province was washed most, at approximately 59% of all forms. (Figure 4b) The reason is that Cd in exchangeable form forms weak bonds with organic and inorganic substances. Thus, $Na_2S_2O_5$ can reduce or pull Cd out easily. For Cd in water-soluble form and reducible form, although there was only small amounts in soil, it was washed entirely. Water in the washing solution dissolves and removes Cd in water-soluble form. Cd in reducible form sticks with Fe_2O_3 and MnO_2. $Na_2S_2O_5$ can reduce Cd in reducible form quite well. Cd in residual form and acid soluble form were removed some but very little, since Cd in these forms will bond with silicate and carbonate in a strong structure, that is difficult to be extracted. Cd in oxidizable form could not be washed at all, due to Cd bonding with sulfide and oxide in soil with various mechanisms such as absorption, complexation and chelation, that is difficult to react with $Na_2S_2O_5$ and Na_2 EDTA.

Cd in soil from Saraburi province, Patumthani province and Lopburi province in exchangeable form were highly removed at approximately 61.7-77.7%. Cd in acid soluble form, reducible form and oxidizable form were washed very little. Cd in water-soluble form, which was present in small amounts, was washed entirely. The amount of Cd in residual form, after being washed, was found higher than before due to the changing of Cd to other forms, especially the exchangeable form changing to the residual form.

For sludge before washing, most Cd was found in reducible form at 60.79% and exchangeable form at 31.21% (Figure 4a). When removing with washing solution, Cd in exchangeable form and reducible form were removed most by approximately 43.64% and 39.56%, respectively (Figure 4b). Although there was only a small amount of Cd in water-soluble form, it was washed entirely. The acid soluble form and oxidizable form were removed very little. The amount of Cd in residual form, after being washed, was found higher than before which can be explained the same as mentioned above.

3.3 Comparison between column washing and batch washing

The percentage of removed Cd from soil and sludge by column washing was lower than batch washing (approximately 39.3-66% and 10.01%, respectively) [15]. The reasons for the lower removal efficiency in column mode are as follows: Firstly, column washing allows a shorter period of time for Cd in soil to react with washing solution compared to batch washing. This decreases the opportunity of Cd to react with the washing solution. Secondly, the shaking method in batch mode allows soil to release some Cd while soil is breaking up into small particles. Thirdly, in batch mode, the contact surface between soil and washing solution is increased due to the breaking up of soil particles. Lastly, in column mode, if packed too tight, the soil sample is pressed tightly, then the washing solution has less chance to touch Cd.

4. Conclusion

From the statistical analysis by program SPSS, version 9.01, it was found that the silt content in soil was the main factor that effected washing of Cd in column mode. The Cd was removed more in soil with low percentage of silt. Cd was removed from soil approximately 22.5-35.5%. The amount of washing solution that was suitable to be used in washing Cd from soils that come from Cholburi province and Saraburi province was 35 ml and 100 ml, respectively. For soil samples that come from Patumthani province and Lopburi province and sludge, the washing solution used was 50 ml. Cd was removed from sludge by only 7.12%.

For all 4 types of soil, before washing, Cd was mostly in exchangeable form, the secondary was residual form. For sludge, Cd was mostly in reducible form and exchangeable form.

Washing Cd from soil in column mode could remove Cd in exchangeable form the most, in the range of 59-77.7%, For sludge, Cd that was in reducible form and exchangeable form were removed at most, 43.64% and 39.56%, respectively.

The Cd removal efficiency from soil and sludge by column washing was lower than batch washing. In terms of the form of extracted Cd, there was no difference between washing in column mode and batch mode.

5. Acknowledgements

Authors would like to express their grateful appreciation to Dr. Suwannee Julyapoon, Dr. Saowapark Sooktrakulvetre and Asst. Prof. Kanitta Tunkananurak for their reading of the manuscript and criticism. We are grateful to Asst. Prof. Dr. Tawan Sooknoi for provision of the pump and for his valuable advice in the experiment on Autosorb-1. We thank Dr. Punnama Siripunnone for her advice in using the X-ray fluorescence spectrophotometer. The authors also wish to acknowledge the staff of the Soil Survey Division, Department of Land Development, for giving us the information about soil in Thailand and soil sampling.

6. References

[1] Alloway, B.J., Heavy Metal in Soils, 2rd edition, Blackie Academic & Professional, UK, 1995.

[2] LaGrega, M.D., Buckingham, P.L. and Evans, J.J.C., Hazardous Waste Management, McGraw-Hill, Inc, Singapore, 1994.

[3] Reed, B.E. and Cline, S.R., Retention and Release of Lead by a Very Fine Sandy Loam: I. Isotherm Modeling, Separation and Sci. Technol., Vol.29, No.12, pp.1529-1551, 1994.

[4] Van Benschoten, J.E., Reed, B.E., Matsumoto, M.R. and McGarvey, P.J., Metal Removal by Soil Washing for an Iron Oxide Coated Sandy Soil, Water Environ. Res., Vol.66, No.2, pp.168-174, 1994.

[5] Cline, S.R. and Reed, B.E., Lead Removal from Soils via Bench-Scale Soil Washing Techniques, J. Environ. Eng., ASCE., Vol.121, No.10, pp.700-705, 1995.

[6] Van Benschoten, J.E., Associate member, ASCE, Matsumoto, M.R., Associate member, ASCE and Young, W.H., Evaluation and Analysis of Soil Washing for Seven Lead-Contaminated Soils, J. Environ. Eng., ASCE, Vol.123, No.3, pp.217-224, 1997.

[7] Hessling, J.L., Esposito, M.P., Traver, R.P. and Snow, R.H., Results of Bench-Scale Research Efforts to Wash Contaminated Soils at Battery-Recycling Facilities. in: Metals Speciation, Separation and Recovery, Vol. II, Patterson, J.W. and Passino, R. (ed.), Lewis Publishers, Chelsea, Mich., pp.497-544, 1990.

[8] Reed, B.E., Carriere, P.C. and Moore, R., Flushing of Pb(II) Contaminated Soil Using HCl, EDTA and $CaCl_2$, J. Environ. Eng., ASCE, Vol.122, No.1, pp.48-50, 1996.

[9] Allen, H.E. and Chen, P., Remediation of Metal Contaminated Soil by EDTA, Environ. Prog., Vol.12, No.4, pp.284-293, 1993.

[10] Abumaizar, R.J. and Khan, L.J., Laboratory Investigation of Heavy Metal Removal by Soil Washing, J. Air Waste Manage. Assoc., Vol.46, pp.765-768, 1996.

[11] Abumaizar, R.J. and Smith, E.H., Heavy Metal Comtaminants Removal by Soil Washing, J. Hazard. Mater., Vol.B70, pp.71-86, 1999.

[12] Carter, M.R., Soil Sampling and Methods of Analysis, Lewis Publishers, Florida, USA, 1993.

[13] Tessier, A., Campbell, P.G.C. and Bisson, M., Sequential Extraction Procedure for Speciation of Particulate Trace Metals, Anal. Chem., Vol.51, pp.844-851, 1979.

[14] Ringbom, A., Complexation in Analytical Chemistry, John-Wiley & Sons, Inc, USA, 1979.

[15] Sriwiriyanuphap, N., Column and Batch Washing of Cadmium from Soil and Sludge by a Mixture of Sodium metabisulfite and sodium EDTA, KMITL Thesis, Bangkok, Thailand, 2002.

Column Washing of Cadmium from Soil and Sludge by a Mixture of $Na_2S_2O_5$ and Na_2EDTA
Chompoonut Chaiyaraksa and Natchatheeya Sriwiriyanuphap

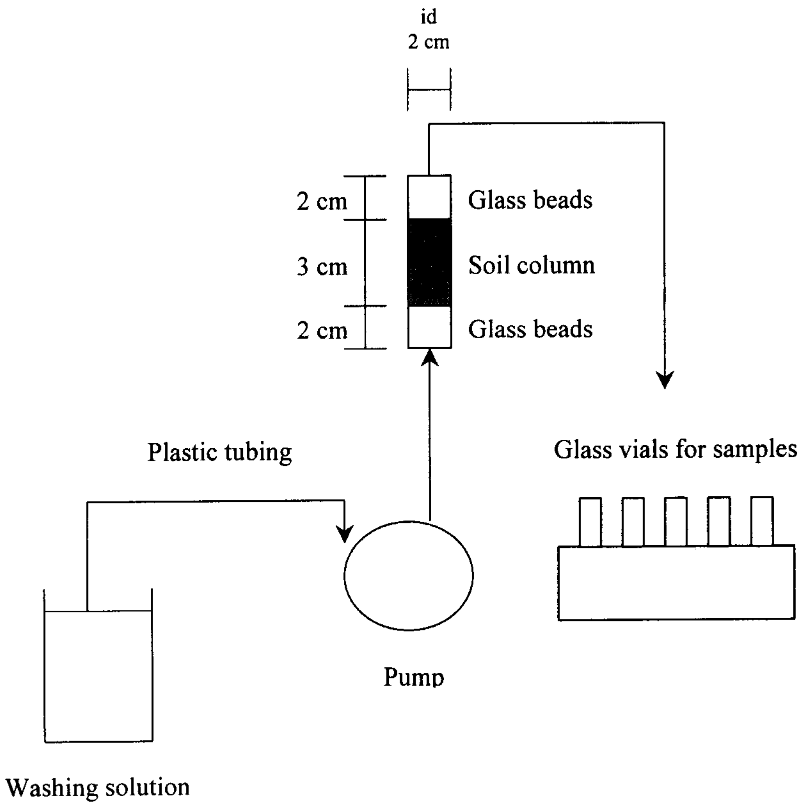
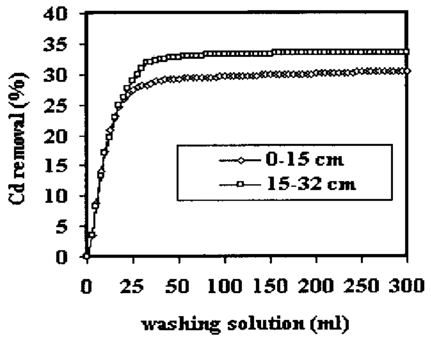
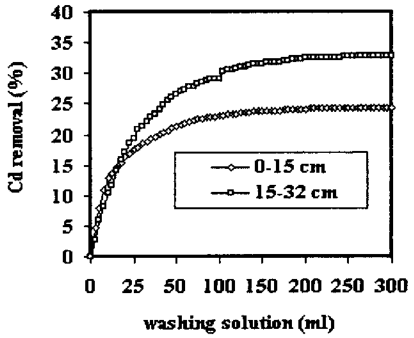


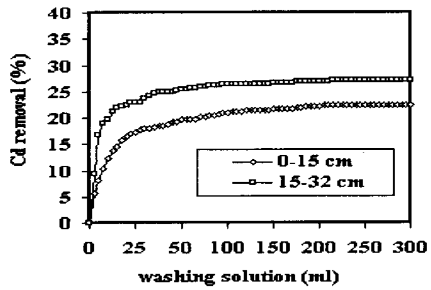
Figure 1 Diagram of soil column for the washing



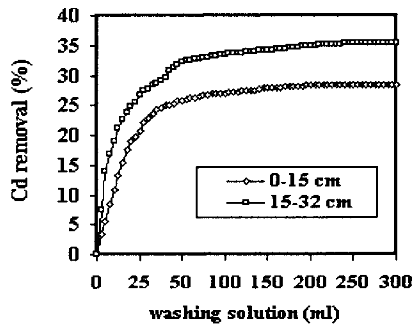
(a)



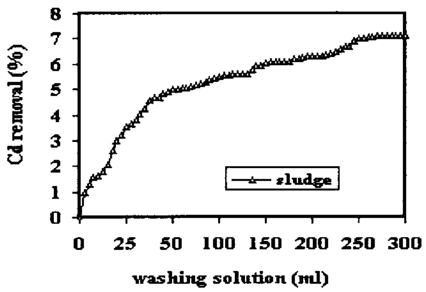
(b)



(c)



(d)



(e)

Figure 2 Results of Cd removal efficiency after washing of samples

a) soil from Cholburi province b) soil from Saraburi province
c) soil from Pathumthani province d) soil from Lopburi province
e) sludge

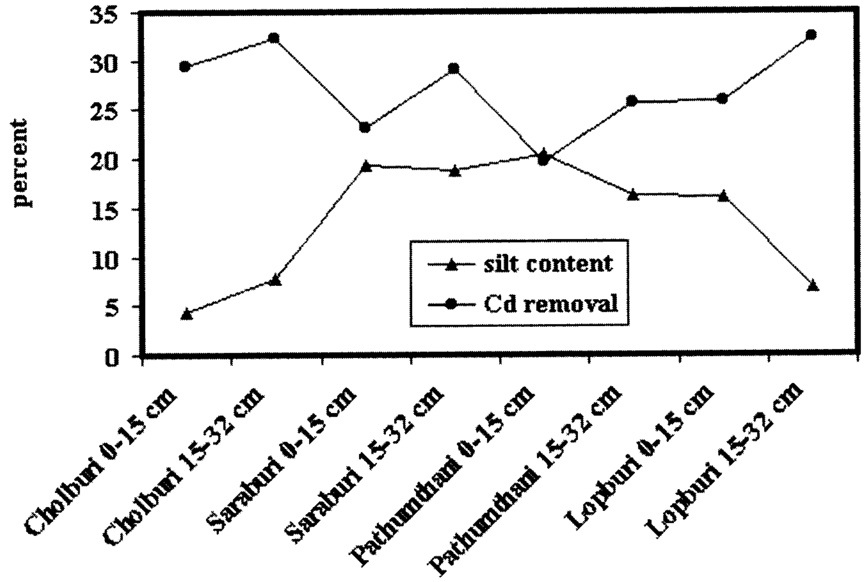


Figure 3 The relationship between the silt content in soil and the Cd removal efficiency

Column Washing of Cadmium from Soil and Sludge by a Mixture of $Na_2S_2O_5$ and Na_2EDTA
Chompoonut Chaiyaraksa and Natchatheeya Sriwiriyanuphap

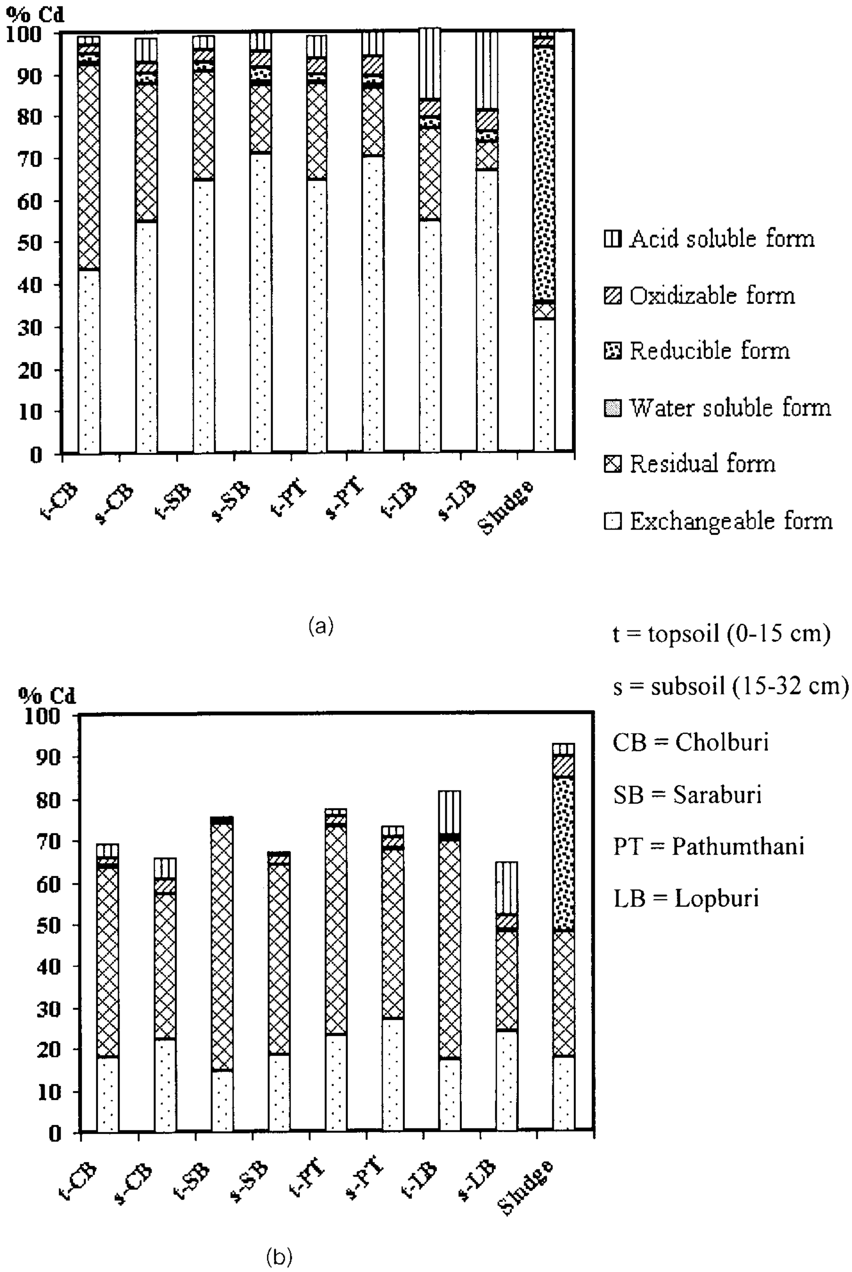


Figure 4 Results from the sequential extraction
a) before sample washing
b) after sample washing

Column Washing of Cadmium from Soil and Sludge by a Mixture of $Na_2S_2O_5$ and Na_2EDTA
Chompoonut Chaiyaraksa and Natchatheeya Sriwiriyanuphap

Table 1 Soil and sludge characterization data

sample	pH 1:1 (w/v)	D_b	Surface area $m^2 g^{-1}$	CEC Meq $100g^{-1}$	OM %	MC %	particle distribution % sand	% silt	% clay	Al_2O_3 %	Fe_2O_3 %	MnO_2 %	Cd mg kg^{-1}
t-CB	5.41	1.42	11.12	0.82	0.68	0.13	92.33	4.27	3.99	3.68	0.46	0.05	nd
s-CB	5.54	1.76	11.12	1.22	0.26	0.18	86.33	7.83	5.10	4.18	0.42	0.03	0.02
t-SB	4.35	1.32	19.41	2.99	0.62	9.55	64.02	19.31	16.74	9.33	1.78	0.02	0.05
s-SB	4.00	1.35	20.44	3.28	0.37	9.94	63.59	18.78	17.51	10.33	1.80	0.02	0.08
t-PT	3.90	1.35	45.26	20.15	2.18	8.65	43.99	20.34	35.82	22.09	5.96	0.09	0.22
s-PT	3.72	1.06	45.74	23.59	1.48	8.92	45.72	16.21	38.05	22.15	5.99	0.09	0.33
t-LB	7.07	1.49	43.00	15.98	2.07	5.31	49.83	16.04	33.50	15.46	5.40	0.16	0.09
s-LB	6.48	1.39	58.54	18.84	0.98	6.71	56.85	6.84	36.13	17.27	5.36	0.12	0.11
sludge	8.54	0.43	37.51	32.76	6.61	16.47	-	-	-	2.07	25.47	0.12	4.77

Remark:		
	nd = non detected	CB = Cholburi
	- = no analysis	SB = Saraburi
	t = topsoil (0-15 cm)	PT = Pathumthani
	s = subsoil (15-32 cm)	LB = Lopburi

Table 2 Data of metals in sludge

Metal	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Concentration (ppm)	5,316.73	1,244.71	6,687.12	315.04	1,946.28	178.92	2,480.86