Removal and Speciation of Heavy Metals in a Stabilization Pond System Treating Domestic Wastewater

Lim B.T., Seng C.E.*and Lim P.E.

School of Chemical Sciences, Universiti Sains Malaysia, 11800, Penang, Malaysia
*Corresponding author. Tel.: +604-653-3888 ext.3550; fax: + 604-657-4854
E-mail address: ceseng@usm.my (Seng C.E.)

Abstract : This study was conducted to investigate: (1) the removal efficiencies of Zn, Pb, Cu and Cd in a stabilization pond system treating domestic wastewater, (2) the speciation patterns of dissolved metals distinguished according to their detectability by anodic stripping voltammetry (ASV) and their lability towards Chelex resin along the treatment path and (3) the speciation patterns of particulate metals among five operationally defined host fractions, namely exchangeable, carbonate, reducible, organic-bound and residual. The results show that total metal removal efficiencies of 88, 79, 90 and 70 % for Zn, Pb, Cu and Cd, respectively, were achieved. There was a shift to the dissolved fraction for all the metals along the treatment path. For all the four dissolved metals, the less labile species formed the predominant fraction in their speciation patterns before and after treatment. The speciation patterns of particulate metals show that most of Zn, Pb, Cd, Fe and Mn were found in the reducible fraction whereas Cu was mainly associated with the organic fraction. Relatively little variation in the speciation patterns along the treatment path was observed indicating that the same mechanisms were at work for removing the metals from the dissolved to the particulate phases. Environmental significance of the metals in terms of potential bioavailability and remobilizability has been greatly reduced due to the treatment.

Keywords : Stabilization ponds, heavy metals, removal, speciation

Abstrak : Kajian ini dijalankan untuk mengkaji (1) kecekapan penyingkiran Zn, Pb, Cu dan Cd dalam sistem kolam penstabilan yang mengolah air buangan domestik, (2) corak penspesiesan logam terlarut yang dibezakan mengikut kebolehan mengesan oleh voltammetri pelucutan anod (ASV) dan kelabilannya terhadap resin Chelex di sepanjang lintasan pengolahan, dan (3) corak penspesiesan logam dalam zarahan di antara lima pecahan yang menjelaskan berbagai operasinya, iaitu, boleh disalingtukarkan, karbonat, boleh diturunkan, terikat kepada organik dan residu. Keputusan menunjukkan bahawa kecekapan penyingkiran logam total masing-masing ialah 88, 79, 90 dan 70 % untuk Zn, Pb, Cu dan Cd telah tercapai. Terdapat satu perpindahan kepada pecahan terlarut bagi semua logam yang dikaji di sepanjang lintasan pengolahan. Untuk semua empat logam terlarut, spesies yang kurang labil menjadi pecahan dominan di dalam corak penspesiesannya sebelum dan selepas pengolahan. Corak penspesiesan bagi logam dalam zarahan menunjukkan bahawa sebahagian besar Zn, Pb, Cd, Fe dan Mn berada dalam pecahan yang boleh diturunkan, manakala kebanyakan Cu dihubungkan dengan pecahan organik. Secara relatifnya, perubahan kecil didapati dalam corak penspesiesan di sepanjang lintasan pengolahan menunjukkan bahawa mekanisme yang sama dilakukan untuk penyingkiran logam daripada fasa terlarut kepada fasa zarahan. Signifikan persekitaran bagi logam secara biotersediaan potensi dan remobilisasi telah banyak dikurangkan disebabkan oleh pengolahan.

Introduction

Waste stabilization ponds have been recognized as a very efficient and low cost system for the treatment of domestic and agro-based industrial wastewaters particularly in the tropical and sub-tropical climates. This kind of treatment system depends entirely on natural processes. Its principal disadvantage is the requirement of a relatively large land area. In Malaysia, the pond system is popularly used to treat palm oil mill effluents, rubber processing factory and domestic wastewaters prior to their discharge into watercourses. In evaluating the performance of this kind of treatment system, Asairinachan [1] and John [2] showed that such system was effective in reducing, among others, the oxygen demand and suspended solids in the effluents. Kaplan et al. [3] studied the fate of heavy metals in waste stabilization ponds treating domestic wastewater. Their results showed that the percentages of dissolved Zn, Cu, Pb and Cd, as opposed to the

particulate fraction, increased along the treatment path but the percentages of anodic stripping voltammetry (ASV)-labile metal species decreased significantly. Lim *et al.* [4] studied the distribution of Zn, Ni, Cu and Pb along the treatment path of wastewater in a stabilization pond system treating a mixture of sewage and piggery wastewater. Their results were generally in agreement with the findings of Kaplan *et al.* [3] in that the Chelex resin-labile metal species decreased along the treatment path.

In urban areas, pond systems may receive wastewater from both domestic and industrial sources, as well as intermittent influxes of storm water runoff from nearby areas. Some of these wastewaters are contaminated with heavy metals, a portion of which may pass through the treatment system and be discharged to watercourses. It is therefore of importance to evaluate the efficiency of metal removal and to understand the removal mechanisms in the waste stabilization pond system. To achieve that, a more comprehensive knowledge of the metal speciation in both the dissolved and particulate phases along the treatment path of the stabilization pond system is warranted. To date, such information is still lacking. Heavy metals chosen for this study were Zn, Pb, Cu and Cd as they are common pollutants found in urban areas.

The objectives of the present study are to investigate: (1) the removal efficiencies of Zn, Pb, Cu and Cd in a stabilization pond system treating domestic wastewater, (2) the speciation of dissolved metals along the treatment path based on four operationally-defined fractions, namely ASV-labile, moderately and slowly labile as well as inert to Chelex-100 cation exchange resin and (3) the speciation of particulate metals along the treatment path using a sequential leaching technique which identifies the metal among five operationally-defined host fractions, namely exchangeable, carbonate, reducible, organically bound and residual.

Materials and methods

The Stabilization Pond System

The stabilization pond system for this study consists of two facultative ponds operating in parallel and a maturation pond connected to each of them in series (Fig.1). The depths of the facultative and maturation ponds are 2.04 and 1.55 m, respectively. At the influent flow rate of 4.42×10^3 m^3/day, the hydraulic retention time of the two facultative ponds is estimated to be 46 days whereas that of the maturation pond is 11 days. Domestic wastewater
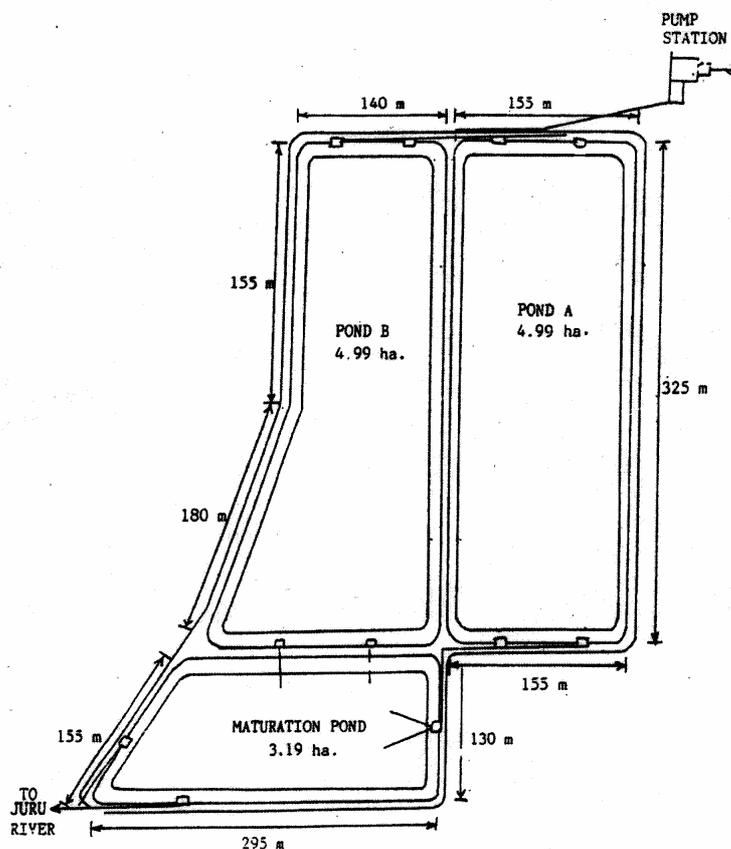

Figure 1 : Layout and dimensions of the stabilization pond system

from the neighbouring residential areas is channeled into the ponds for treatment. The effluent from the maturation pond is discharged through two outlets into the Juru River. Performance evaluation has shown that the BOD removal efficiency attained by the facultative ponds varied within the range of 40 – 83 % and the quality of the final effluent from the pond system consistently complies with the effluent standards prescribed under the Malaysian Environmental Quality (Sewage and Industrial effluents) Regulations 1979. The mean pH increased from 6.43 for the influent to 6.92 for the facultative pond effluent and 7.36 for the final effluent whilst the mean dissolved oxygen level also increased from 1.8 to 4.2 mg/L.

Collection of Samples

Samples were collected in 4 L acid-washed polyethylene bottles from the inlets to the respective facultative pond and combined to form a composite sample of equal proportion (influent). Similarly, composite effluent samples were formed from samples collected from the 4 outlets of the facultative ponds and the 2 outlets of the maturation pond, respectively. The samples were first centrifuged at 8000 rpm for 20 min and the supernatants filtered through 0.45 µm membrane filters to be separated into particulate and dissolved fractions. A total of 10 sets of samples were collected for the determination of total dissolved and particulate metal concentrations as well as for the speciation study of dissolved metals. For the speciation of particulate metals, 6 sets of samples were collected for this study. The sampling periods encompassed the wet and dry seasons.

Determination of Total Dissolved and Particulate Metal Concentrations

Exactly 40 mL of the filtrate was digested in Teflon bomb with 5 mL concentrated HNO_3 using a microwave digester (Milestone mls 1200 mega) and the digested sample was analyzed for the total dissolved metal concentration using graphite furnace AAS (Perkin Elmer SIMAA 6000).

The membrane filter after filtration together with the residue after centrifuging were dried in an oven at 103 °C for 24 h. A known weight of the particulate was digested in Teflon bomb with 5 mL 30 % H_2O_2 and 5 mL 65% HNO_3 using a microwave digester and the digested sample was analyzed for the total particulate metal concentration using graphite furnace AAS.

Speciation Study of Dissolved Metals

Trace metals species in the dissolved phase were differentiated utilizing ASV and their labilities towards ammonium form of Chelex resin in successive column and batch procedures [5]. Briefly, an aliquot of the filtered sample was set aside for the determination of ASV-labile metal species by differential pulsed ASV using a Metrohm 693 VA processor in combination with a Metrohm 694 VA stand (multimode electrode operation with a hanging mercury drop electrode, a AgCl/Ag reference and a Pt counter electrode). The remaining sample was passed through a column packed with the ammonia form of the Chelex-100 resin of 50-100 mesh size following the procedure described in Riley and Taylor [6]. The difference between the Chelex-labile and ASV-labile species gives the moderately labile species. Effluent from the resin column was shaken with the Chelex resins for 72 h to determine the slowly labile and inert metal species using the batch procedure [5]. The concentrations of Chelex-labile, moderately and slowly labile as well as the inert metal species were determined using graphite furnace AAS.

Speciation Study of Particulate Metals

The sequential extraction scheme (Fig. 2) generally follows that of Tessier *et al.* [7] except that 1.0 M ammonium acetate instead of 1.0 M magnesium chloride at pH 7.0 was used as the extraction reagent for the exchangeable fraction due to lower matrix effect posed by the former reagent in the AAS determination. This procedure was developed for the partitioning of particulate metals into the exchangeable, carbonate, reducible, organic/sulphide and residual fractions. About 0.2 g of particulate samples in triplicates were weighed accurately and put through the sequential extraction procedure in acid-washed 50 mL polyethylene centrifuge tubes with screw-on caps. Each successive extraction was then separated by centrifugation at 3000 rpm for 30 min. All extracts were stored in acid pre-washed polyethylene bottles for trace metals determinations.

Quality Assurance of Data

All reagents used were at least of analytical grade. Ultrapure water of resistivity 18 MΩ cm was used in this study for the blank and the preparation of standard solutions. All glassware and plastics ware used for the experiments were previously soaked in 10 % nitric acid (v/v) and rinsed with de-ionized water. Preparatory work was performed in a Class-100 laminar flow clean bench.
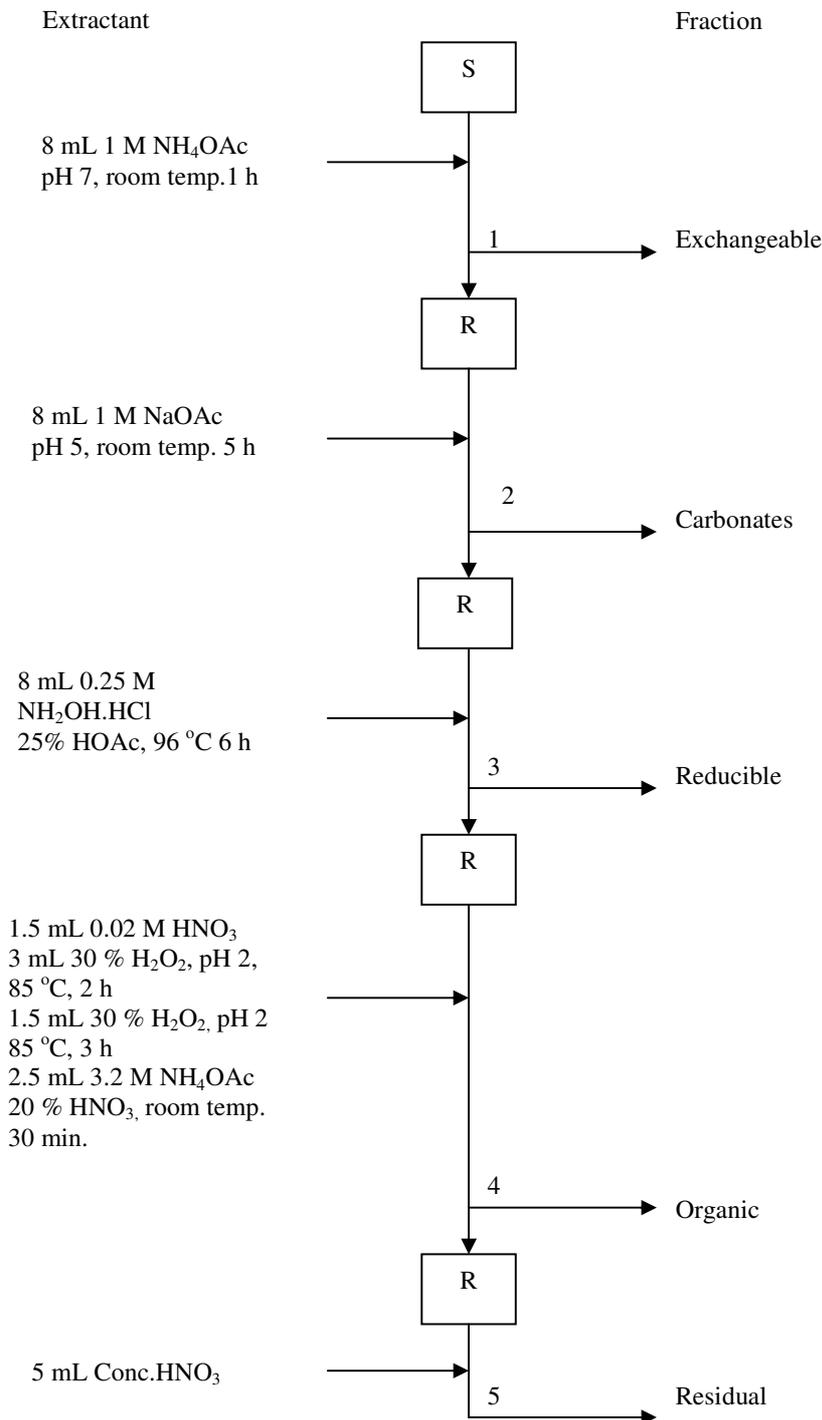
Extractant   Fraction

Figure 2 : Sequential extraction scheme for the speciation of particulate metals

Results and discussion
Removal of heavy metals along the treatment path

        The mean dissolved and particulate Zn, Pb, Cu and Cd concentrations and their percentages of removal at the various stages of treatment are shown in Table 1. For all the metals studied, the mean dissolved and particulate metal concentrations were observed to decrease, respectively, along the treatment path and the most significant removal of metals appeared to occur in the facultative ponds. For Zn, Pb, Cu and Cd, the cumulative removal efficiencies for dissolved metals were 79, 73, 63 and 65 %, respectively, whereas those for particulate metals were 94, 92, 94 and 97 %, respectively. The

total metal removal efficiencies were 88, 79, 90 and 70 % for Zn, Pb, Cu and Cd, respectively. The metal removal efficiencies observed in this study were much higher than those reported in Kaplan *et al*. [3] probably because of the longer retention time. In terms of the distribution of the metals between particulate and dissolved fractions, more Zn and Cu, respectively, 60 and 88 %, were found in the particulate fraction of the influent. In contrast, more Pb and Cd, respectively, 65 and 84 %, were found in the dissolved fraction. Nonetheless, there was a drastic shift to the dissolved fraction for all the metals due to sedimentation and other particulate metal removal processes along the treatment path, particularly in the facultative ponds because of the relatively longer retention time. Thus, the percentages of Zn, Pb, Cu and Cd in the dissolved fraction of the final effluent had increased to 69, 86, 44 and 99 %, respectively.

Table 1 : Mean dissolved and particulate metal concentrations (µg/L) at various stages of treatment

Metal		Dissolved	% removed	Particulate	% removed
Zn	Influent	67±9	0	101±12	0
	Facultative pond effluent	24±5	64±10	31±6	69±10
	Maturation pond effluent	14±3	79±5	6.4±1.1	95±5
Pb	Influent	20±3	0	10.7±0.9	0
	Facultative pond effluent	7.3±0.9	64±7	3.1±0.4	71±7
	Maturation pond effluent	5.5±0.8	73±5	0.9±0.1	92±5
Cu	Influent	13±3	0	94±9	0
	Facultative pond effluent	6.4±0.7	50±13	30±3	68±13
	Maturation pond effluent	4.8±0.6	63±8	6.0±0.7	93±8
Cd	Influent	3.7±0.5	0	0.73±0.12	0
	Facultative pond effluent	1.9±0.6	49±13	0.17±0.04	77±13
	Maturation pond effluent	1.3±0.3	65±10	0.019±0.003	97±10

Data based on 10 samples.

Table 2 : Mean metal concentration in particulate (µg/g) at various stages of treatment

Metal	Zn	Pb	Cu	Cd
Influent	1006±119	107±9	941±88	7.3±1.2
Facultative pond effluent	619±121	62±8	601±67	3.5±0.9
Maturation pond effluent	315±56	45±7	299±32	0.92±0.16

Data based on 10 samples.

If the removal of particulate metals along the treatment path were achieved through solely sedimentation process, the particulate metal concentration would be expected to be constant irrespective of the stage of treatment. But this was found to be not the case as shown in Table 2. In fact, the particulate metal concentration decreased progressively along the treatment path indicating that other removal mechanisms were also at work. Walker and Hurl [8] also observed the same trend in the reduction of heavy metals in a storm water wetland and suggested biological assimilation and chemical transformation as the likely removal processes of particulate metal in addition to sedimentation.

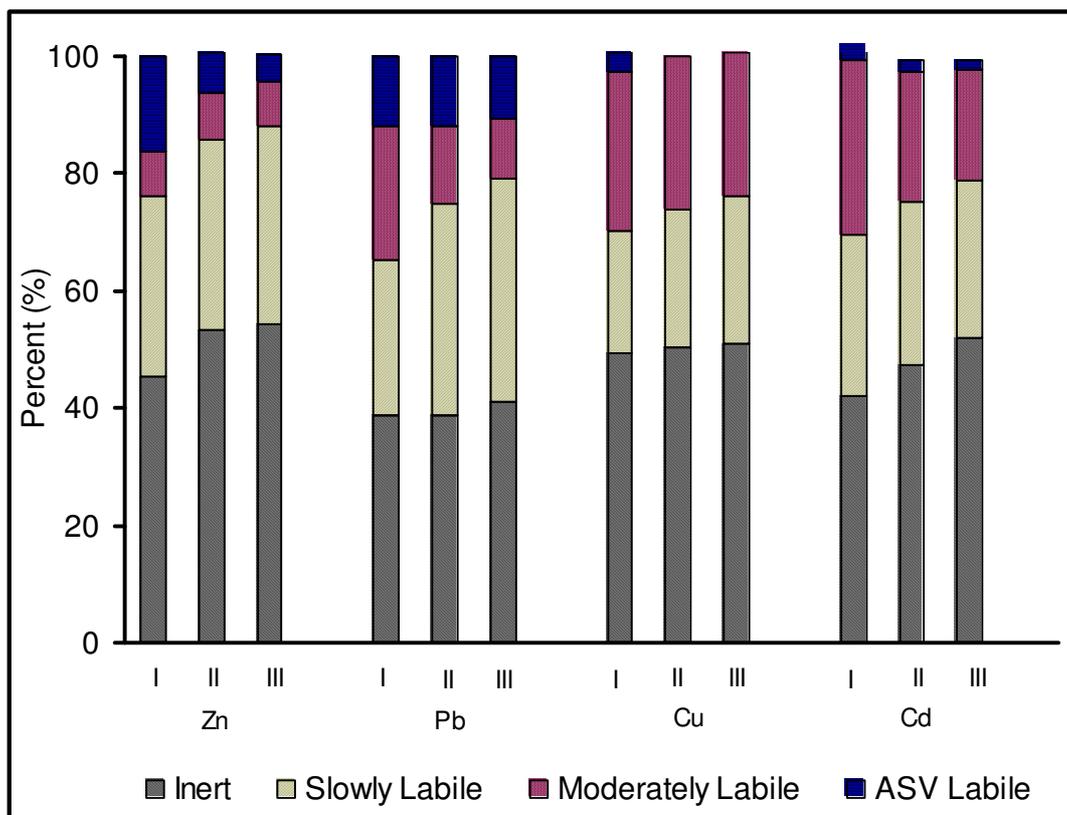*Speciation of dissolved metals along the treatment path*

The speciation patterns are controlled by the processes occurred in the water column such as complexation, coprecipitation and sorption. For example, Kunz and Jardim [9] concluded that complexation was the most important mechanism in controlling copper speciation in raw sewage. Complexation of the metal with ligands such as humic type substances usually leads to the formation of high molecular weight compounds resulting in an increase of the percentages of less labile species (slowly labile and inert). Coprecipitation and sorption are basically scavenging processes involving particulates which remove dissolved metal species from the solution.

Table 3 : Mean concentrations (µg/L) of the metal species at various stages of treatment

	Metal	ASV-Labile	Moderately Labile	Slowly Labile	Inert
Influent	Zn	11±3	5±3	20±4	31±8
	Pb	2.4±0.8	4.6±0.8	6.0±0.9	7.0±1.4
	Cu	0.41±1	3.5±1.4	2.7±0.9	6.3±1.6
	Cd	0.10±0.1	1.0±0.2	1.0±0.2	1.6±0.3
Facultative pond effluent	Zn	1.5±0.9	1.8±0.6	7.8±1.5	13±5
	Pb	0.9±0.13	1.0±0.4	2.6±0.6	2.8±0.5
	Cu	0	1.7±0.2	1.5±0.3	3.2±0.6
	Cd	0.04±0.01	0.4±0.2	0.5±0.2	0.9±0.3
Maturation pond effluent	Zn	0.7±0.4	1.0±0.3	4.7±0.8	8±2
	Pb	0.6±0.2	0.5±0.2	2.2±0.4	2.2±0.8
	Cu	0	1.2±0.3	1.2±0.3	2.5±0.5
	Cd	0.02±0.01	0.2±0.1	0.3±0.1	0.8±0.1

The mean concentrations of the ASV-labile, moderately labile, slowly labile and inert metal species along the treatment path are shown in Table 3 whereas the dissolved metal speciation patterns are depicted in Fig. 3. Fairly similar metal speciation patterns were observed between the effluents from the facultative and maturation ponds for all the metals. In general, the slowly labile and inert species formed the dominant fraction before and after treatment. It was also observed that there was an increase in the less labile fractions at the expense of the more labile fractions along the treatment path. This can partly be explained by complexation process as evidenced by the decreasing complexing capacity along the treatment path with the biggest decrease occurring in the facultative ponds (Table 4). However, this study could not ascertain the dominant process controlling the metal speciation patterns among the processes involved, namely complexation, coprecipitation and sorption.

Figure 3 : Speciation patterns of dissolved Zn, Pb, Cu and Cd along the treatment path(I: influent, II: effluent from the facultative ponds and III: effluent from the maturation pond)

Table 4 : Metal complexing capacity (µM) along the treatment path

Metal	Zn	Pb	Cu	Cd
Influent	7.19	2.37	7.41	0.55
Facultative pond effluent	2.79	0.95	4.5	0.33
Maturation pond effluent	1.64	0.66	3.43	0.23
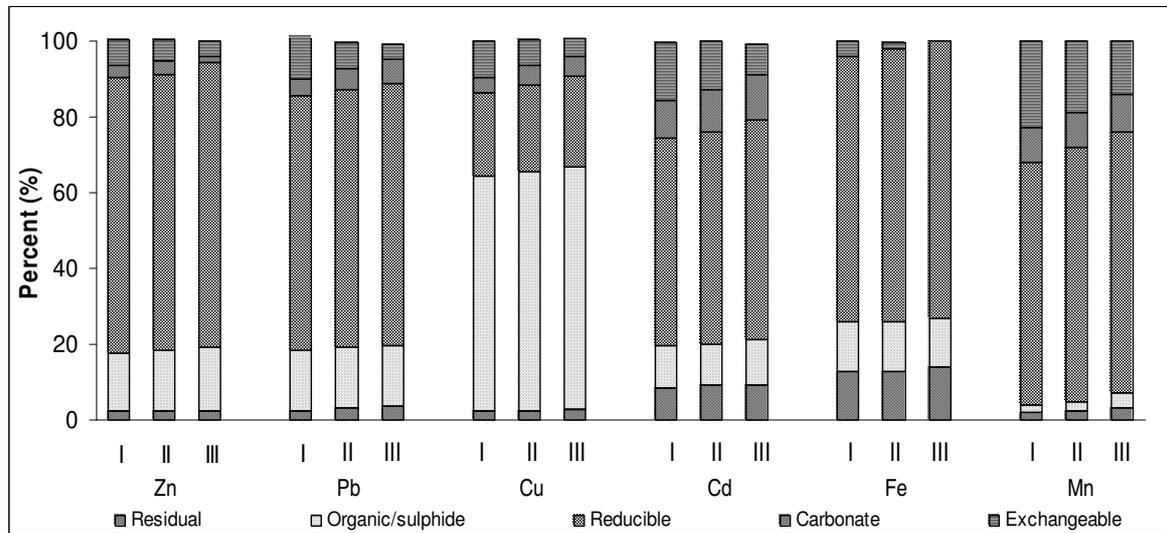
Figure 4 : Speciation patterns of particulate Zn, Pb, Cu, Cd, Fe and Mn along the treatment path (I: influent, II: effluent from the facultative ponds and III: effluent from the maturation pond)

Speciation of particulate metals along the treatment path

Figure 4 depicts the speciation patterns of Zn, Pb, Cd, Cu, Fe and Mn in the particulates of influent as well as effluents from the facultative and maturation ponds. In general, two different groups of speciation patterns were observed, namely, Zn, Pb, Cd, Fe and Mn in one group in which the metals were predominantly found in the reducible fraction and Cu in the other group in which the metal was mainly associated with the organic matter.

The speciation patterns of Zn, Pb, Cd, Fe and Mn show that the reducible fraction was the most important carrier of these metals with >55 % of Zn, Pb and Cd, >60 % of Mn and >70 % of Fe in this fraction. This points to the likely scenario that most of these metals were scavenged by Fe/Mn oxides from solution through processes such as coprecipitation and adsorption [10]. Generally, rather similar speciation patterns were observed along the treatment path for each metal indicating that basically the same binding mechanisms were at work to remove the metals from the dissolved to the particulate phase. Despite similar speciation patterns along the treatment path, a decreasing trend in the percentage of the metal in the exchangeable fraction is still discernable. In this case, the percentage in the exchangeable fraction was found to decrease from 15% in the influent to 8% in the final effluent for Zn, from 11 to 4 % for Pb and from 15 to 8 % for Cd. Thus, the most potentially remobilizable or environmentally available form of the particulate metal was reduced along the treatment path.

The speciation pattern of Cu shows that a majority of the metal (>60 %) was found in the organic fraction. This pattern is typical of Cu in the sediments or suspended particulates [11] and waters [12]. The percentages of Cu found in the reducible fraction at various stages of treatment were 22, 23 and 24 %, respectively, indicating that some of the Cu were scavenged from the solution by Fe/Mn oxides. On the whole, relatively little change in the speciation patterns along the treatment path was observed thus pointing to the same removal mechanisms at work. A decreasing trend in the percentage of Cu in the exchangeable fraction along the treatment path was also observed.

Environmental Implications of Heavy Metal Treatment in Stabilization Ponds

The efficacy of the stabilization pond system in treating heavy metals should be assessed not merely on the removal efficiency of total metal but also on the capability of reducing the most potentially environmentally available metal species along the treatment path. Laxen and Harrison [13] recommended that the proportion of Chelex-labile (ASV-labile and moderately labile) fraction in dissolved metals be used as an index of environmental significance since complexation reduces the concentrations of more labile metal species including free metal ions which are known to be more toxic and bioavailable [14]. Correspondingly, the index of environmental significance for particulate metals is the proportion of exchangeable fraction. The values of these indices

Table 5 : Proportions of Chelex-labile fraction in dissolved metals and exchangeable fraction in
particulate metals

	Zn		Pb		Cu		Cd	
	Chelex-labile	Exchangeable	Chelex-labile	Exchangeable	Chelex-labile	Exchangeable	Chelex-labile	Exchangeable
Influent	0.24	0.068	0.35	0.11	0.31	0.099	0.32	0.15
Facultative pond effluent	0.15	0.058	0.25	0.069	0.26	0.066	0.24	0.13
Maturation pond effluent	0.12	0.041	0.21	0.041	0.25	0.046	0.21	0.077

for each metal at various stages of treatment were compared in Table 5. It is evident that, for all the metals studied, sequential treatment in the facultative and maturation ponds has resulted in a greatly reduced potential environmental significance for the final effluent both in terms of dissolved and particulate metals and that the greatest reduction generally occurred in the facultative ponds.

Once the final effluent is discharged into receiving watercourses, the environmental significance of the metals will be affected by the complexing capacity of receiving waters and the extent of release of particulate metals to the dissolved phase. Studies on the impacts of final treated effluent on receiving watercourses have been reported by, among others, Laxen and Harrison [13] and Shi *et al.* [15].

Conclusions

Based on the data obtained, the following conclusions can be drawn:
(1) The stabilization pond system studied could achieve the total metal removal efficiencies of 88, 79, 90 and 70 % for Zn, Pb, Cu and Cd, respectively. Particulate' metals were removed by sedimentation and other processes.
(2) The speciation patterns of dissolved Zn, Pb, Cu and Cd show that the slowly labile and inert metal species formed the predominant fraction before and after treatment.
(3) The speciation patterns of particulate metals show that most of Zn, Pb, Cd, Fe and Mn were found in the reducible fraction whereas Cu was mainly associated with the organic fraction.
(4) For all the metals studied, relatively little change in the particulate speciation patterns along the treatment path was observed indicating that the same mechanisms were at work to remove the

metals from the dissolved to the particulate phases.
(5) Sequential treatment of Zn, Pb, Cu and Cd in the facultative and maturation ponds greatly reduced the potential environmental significance of the final effluent both in terms of dissolved and particulate metals but the greatest reduction occurred in the facultative ponds.

References
1. Asairinachan K. (1979). "Sewage treatment-practical systems", Symposium on new development in effluent treatment technology, Penang.
2. John C.K. (1984). "Tackling the pollution problems of agro-based industries in Malaysia" in Proc. Asian Chemical Conferences on Priorities in Chemistry in Development of Asia. Kuala Lumpur, **155**.
3. Kaplan D., Abeliovich A. and Ben-Yaakov S. (1987) *Wat. Res.,* **21**, 1189- 1194.
4. Lim P.E., Leong S.F. and Seng C.E. (1991) *Bull. Sing. N. I. Chem.*, **19**, 107-112.
5. Figura P. and McDuffie B. (1980) *Anal. Chem.*, **52**, 1433-1439.
6. Riley J.P. and Taylor D. (1968) *Analytica Chim. Acta.* (1968). **40**, 479-483.
7. Tessier A., Campbell P.G.C. and Biso M. (1979) *Anal. Chem.*, **51(7)**, 844-851.
8. WalkerD.J. and Hurl S. (2002) *Ecol.Eng.*, **18**, 407-414.
9. Kunz A. and Jardim W.F. (2000) *Wat. Res.*, **34**, 2061-2068.

10. Hem J.D. (1977) *Geochim. Cosmochim. Acta*., **41**, 527-538.
11. Salomons W. and Forstner U. (1980), *Envir. Technol. Lett.,* **1**, 506-517
12. Smies M. (1983) "Biological aspects of trace element speciation in the aquatic environment" in G. Leppard (ed.), Trace element speciation in surface waters, Plenum Press, New York, **172**.
13. Laxen D.P.H. and Harrison R.M. (1981). *Wat. Res.,* **15**, 1053-1065.
14. Allen H.E., Hall R.H. and Brisbin T.D. (1980) *Environ. Sci. Technol.*, **14**, 441-443.
15. Shi B., Allen H.T. and Grassi M.T. (1998) *Wat. Res*., **32**, 2413-2421.