ESTEEM

ACADEMIC JOURNAL VOLUME 1. 2003 • ISSN: 1675-7939

Universiti Teknologi MARA Pulau Pinang

ESTEEM

Volume 1, December 2003

CONTENTS

The Fate Of Heavy Metals In A Stabilization Pond System Treating Household Wastewater

Lim Boon Tik
Jabatan Sains Gunaan UiTM Cawangan Pulau Pinang Kampus Bukit Mertajam
Tel : 04-3823400, Fax : 04-3802000, E-mail : Lim765@p.pinang.itm.edu.my

Abstract

The waste stabilization pond system in Taman Kota Permai, Seberang Perai Tengah, Penang consisting of two facultative ponds in parallel and a maturation pond connected to each of them in series is being used to treat domestic sewage. This study investigates the removal efficiency of trace metals (Zn, Cu, Pb, and Cd) and their speciation in this stabilization pond system.
The percentage of the removal of the dissolved heavy metal concentrations throughout the treatment path from the raw sewage to the final effluent was for zinc (79%), copper (63%), lead (73%) and cadmium (66%). The removal efficiency of these heavy metals was found to be most obvious in the facultative ponds. The mean percentages of the removal of these heavy metal concentrations in these ponds were zinc (65%), copper (50%), lead (64%) and cadmium (49%).
Trace metals species are differentiated utilizing anodic stripping voltammetry (ASV) and their labilities towards ammonium form chelex resin in successive column and batch procedures. Species are classified as being ASV-labile, moderately labile, slowly labile and inert. It was observed that there was some reduction in the percentage of ASV-labile species and moderately labile species along the treatment path. However, there was an increase in the percentage of the other two species. This phenomenon could be due to the formation of complexes with organic matters.

Keywords: STABILIZATION POND, SPECIATION, LABILITIES, TRACE METALS

Introduction

Stabilization ponds have been used for sewage treatment in places where sufficient land is normally available and temperature is most favorable for their operation. In Malaysia, the ponds system is popularly used to treat palm oil mill effluent, rubber factory waste and domestic waste prior to their discharge into watercourses. Evaluation of the performance of this type of treatment system by Asairinachan (1979) and John (1984) generally shows that it is effective in reducing, among others, the BOD and suspended solids in the effluents. However, very few information regarding the efficiency of the removal of heavy metals in this system had been reported. Kaplan *et al.* (1987) studied a waste stabilization pond system treating domestic wastewater and found that a decrease in the total concentrations of Zn, Cu, Pb and Cd was attained during the various stages of treatment. However, the percentages of heavy metals in the dissolved fraction were found to increase along the treatment path. Heavy metals are transition elements in theperiodic table. The most important feature which distinguish heavy metal from other toxic pollutants are that they are not biodegradable and that, once they have entered the environment, it will remain forever in the environment and may transform into other physico-chemical forms once it react with other chemicals in the environment. The potential toxicity of a heavy metal is controlled by their physico-chemical form.Sewage treatment ponds may receive effluents from both domestic and industrial sources, as well as intermittent influxes of storm water runoff from nearby areas. All these sources produce effluents contaminated with heavy metals and some portions of these metals will pass through the treatment process to be discharged to surface waters (Lester *et al.*, 1979).

If there is a trend towards the greater use of sewage treatment ponds to treat industrial effluents, a better understanding of the role of treatment processes in metals abatement (Brown & Lester, 1979) is warranted The efficiency with which a sewage treatment pond system retains influent metals will depend upon the physico-chemical forms of the metals and their response to the physical and biological treatment processes. Therefore, knowledge of the metal speciation may go along way in understanding the variability in the treatment efficiencies.

The objectives of the this project are:

(a) to determine the removal efficiency of trace heavy metals (Cd, Cu, Pb and Zn) in a stabilization pond system treating domestic wastewater.

(b) to study the speciation of the heavy metals along the treatment path. The speciation scheme proposed by Figura and McDuffie (1980) was adopted in this study with some modifications.

Materials And Method

The Stabilization Pond System

The stabilization pond system for this study is located in Taman Kota Permai , Seberang Perai Tengah, Penang, Malaysia. It consists of two facultative ponds operating in parallel and a maturation pond connected to each of them in series (Fig.1). Domestic waste from the neighboring residential areas is channeled into the ponds for treatment. The effluent from the maturation pond is discharged through two outlets into the Juru River. The hydraulic retention time of the two facultative ponds was estimated to be 46 days whereas that of the maturation pond was 11 days.

Collection of Wastewater Samples

Wastewater samples were collected in pretreated 4 L polyethylene bottles from sampling points A, B and C (Fig.1) with A representing inlets (influent) to the respective facultative pond, B_1, B_2 B_3 and B_4 the outlets (facultative) of the respective facultative pond to the maturation pond and C_1 and C_2 outlets (effluent) of the maturation pond leading to the nearby river. The samples were first centrifuged at 8000 rpm for 20 minutes and the supernatants filtered through 0.45 um membrane filters to be separated into particulate and dissolved fractions. The particulate fraction of each sample consisting of the pellet and the residue was digested with concentrated HNO_3 (AR grade) in Microwave Oven Milestone Model 1200 Mega to near dryness. After cooling to room temperature, the sample volume was made up to 10 mL with de-ionized water.

Moderately labile

This fraction is obtained from the difference between that retained by the Chelex column (Chelex labile species) and that found by direct ASV analysis.

Inert Fraction

The dissolved fraction was acidified and digested and then analyzed for total trace metals. The inert fraction is computed by subtracting the Chelex-labile & slowly labile fractions from the total trace metals.

Quality Assurance

The following were steps taken to ensure quality data:

1. All preparatory works were conducted in class 100 laminar flow clean bench.
2. Deionized water of resistivity 18 è - cm was used to prepare all the solutions.
3. All chemicals used were of AR grade or better.
4. All glass wares and sampling bottles were soaked in acid bath for at least 24 h.
5. Blank was used in all analysis.

Speciation Procedures

A flow chart for the speciation method is presented in Fig. 2.

Total trace metal concentrations

There were determined by Atomic Absorption Spectrophotometer (flame or thermal) after acid digestion.

ASV "labile" fraction

After filtration, direct Anodic Stripping Voltammetry analyses of the samples were performed immediately after addition of 0.5 mL ammonium citrate buffer (pH 3) to 10 mL of sample. Method of standard additions was used for this analysis. Voltammetric measurements were conducted using a Metrohm 693 VA Processor in combination with a Metrohm 694 VA stand (multimode electrode operation with a hanging mercury drop electrode, HMDE, an AgCl/Ag reference and a platinum counter electrode). Instrument settings were: plating time, 360 s; scanning from –1150 mV to 135 mV; scan rate, 20 mV s^{-1}; stripping peak potentials: Zn (-968 mV), Cd (-587 mV), Pb (-400 mV), Cu (-30 mV).

Chelex Labile Species

A 1000 mL portion of the filtered sample was passed through a column of Chelex 100 resin in ammonium form to collect the Chelex labile trace metal fraction. The resin from the column was then eluted with 60 mL 2.5M HNO_3 followed by deionised water to a volume of 100 ml. before analysis for the trace metals.

Slowly Labile Species

A volume of 250 mL of the effluent that had passed through the Chelex column was collected in acid pretreated 400 mL beakers. After addition of 2 g of ammonium form Chelex 100 resin, the mixture in the beakers capped with parafilm and stirred for 72 h. Then the resin containing the slowly labile fraction was separated through a fritted column. The resin from batch procedures was eluted with 15 mL 2.5 M nitric acid, followed by de-ionized water to a volume of 25 mL and analyzed for the trace metals.

Result And Discussion

Total Trace Metal Removal

Table 1 showed the mean total concentrations of Zn, Cu, Pb, and Cd and the percentages of their removal determined at various stages of treatment. This phenomenon could be caused by the following processes in the stabilization ponds, namely, complexation, adsorption and co precipitation brought by organic and inorganic ligands in the domestic wastewaters. The mean total concentrations were observed to decrease along the treatment path and the most significant removal of metals was achieved in the facultative ponds. For Zn and Pb, the facultative pond itself appears to remove more than 60%

of these metals. Overall, the treatment system was able to achieve the removal of 79, 73, 63 and 66% for Zn, Pb, Cu and Cd, respectively.

Removal of Labile Species

The mean concentrations of labile species (ASV labile and moderately labile) at the various stages of treatment are presented in Table 2. The data show that there was marked reduction in the percentages of labile species along the treatment path. According to Florence (1986), labile species has been found to correlate well with the toxic fraction of a metal. Thus, the potential toxicity of the effluent had been greatly reduced before it was discharged into Juru River.

Distribution of Various Trace Metal Species Along The Treatment Path

The distribution of the mean concentrations of various species for Zn, Pb, Cu and Cd are shown in Table 3.**Zinc**The lability of Zn was found to decrease along the treatment path as seen from the decrease of the percentages of ASV species.

The decrease was most marked in the facultative ponds. . The decrease in lability might be due to complexation of the metal by hydrous oxides (Benjamin and Leckie, 1981) and humic type substances (Gamble *et. al*, 1980) . The formation of high molecular weight compounds increases the percentages of non chelex labile species (slowly labile and inert) as observed in Table 3.**Lead**Table 3 shows that the change in the percentages of ASV labile Pb was relatively small along the treatment path. This was also shown by the inert fraction of the metal. More marked changes were observed for the moderately labile and slowly labile species especially in the facultative ponds.**Copper**For copper, the results are in good agreement with the findings of previous workers (Figura and McDuffie, 1980; Kaplan *et. al.* 1987; Lim *et. al.* 1991). The mean concentrations of ASV labile Cu species in raw and treated sewage were very low as compared to those of other metals. According to Lerman (1973) and Laxen (1981), the labile Cu ions are known to be easily chelated or complexed by organic substances like NTA that are abundance in the domestic sewage. There were relatively little changes in the distribution patterns of the various species along the treatment path.
CadmiumIt is observed that the percentage of moderately labile species decreased sharply as it entered the facultative pond and finally the maturation pond. The sharp drop in percentage is mainly due to complexing activity of the organic compounds in the sewage. This observation agreed very well with the findings of previous workers in a study of Cd toxicity in soft and highly organic pond water (Giesy *et. al.* 1977). Gardiner *et. al.* (1974) demonstrated that humic compounds and suspended muds have the ability to adsorb ionic cadmium strongly. As a result, the percentages of slowly labile and inert species in the facultative ponds and maturation pond increased due to the formation of Cd compounds with bigger molecular weight These two species together made up 69, 75 and 79% of total species in influent, facultative ponds and effluent respectively.**CONCLUSIONS**The results showed that the absorption and co precipitation process in the stabilization pond system in Taman Kota Permai, Penang could remove 79, 73, 63 and 66% of Zn, Pb, Cu and Cd, respectively in the dissolved fraction of domestic wastewaters. The percentages of Chelex labile species (ASV and mederately labile) were found to decrease along the treatment path while percentages of non chelex labile species (slowly labile and inert) increased along the treatment path. This phenomenon could be brought about by organic and inorganic ligands through the complexation process.

Acknowledgement

Associate Professor Dr. Seng Chye Eng and Professor Dr. Lim Poh Eng.IRPA short-term grant (grant no: 305/PKIMIA/622110) from Universiti Sains Malaysia, Penang, Malaysia.

References

Asairinachan K. (1979) *Sewage Treatment- Practical Systems:* Symposium On New Development in Effluent Treatment Technology, *Penang.*

Benjamin M.M. and Leckie J.O. (1981) *Multiple Site Absorption of Cd, Cu, Pb, and Zn on Amorphous Iron Oxyhydroxide.* J. Colloid Interf. Sci., ***79****: 209-221.*

Brown M.J. and Lester J.N. (1979) *Metal Removal in Activated Sludge: The Role of Bacterial Extracellar Polymers.* Water Res., ***13****: 817-837.*

Figura and McDuffie B. (1980) *Determination of Labilities of Soluble Trace Metals in Aqueous Enviromental Samples by Anodic Stripping Voltammetry and Chelex Column and Batch Methods. Anal. Chem., 1433-1439*

Florence T.M. (1986) *Electrochemical Approaches to Trace Element Speciation in Waters: A Review.* Analyst, ***Vol III:*** *489 –505.*

Gamble D.S. Underwood A.W. and Langford C.H. (1980) *Copper (II) Titration of Fulvic Acid Ligand Sites with Theoretical Potentiometric and Spectrophotometric Analysis.* Anal. Chem., ***52****: 1901-1908.*

Gardiner J. (1974). *The Chemistry of Cadmium in Natural Waters (II). The Adsorption of Cadmium on River Mud and Naturally Occuring Solids.,* Water Res., ***8*** *, 157 –164*

Giesy J.P. Leversee Jr. G.J. and Williams D.R. (1977) *Effects of Naturally Occurring Aquatic Organic Fractions on Cadmium Toxicity to* Simocephalus Serrulatus *(Daphnidae) and* Gambusia Affinis *(Poeceliidae).* Water Res., ***11****:1013 – 1020.*

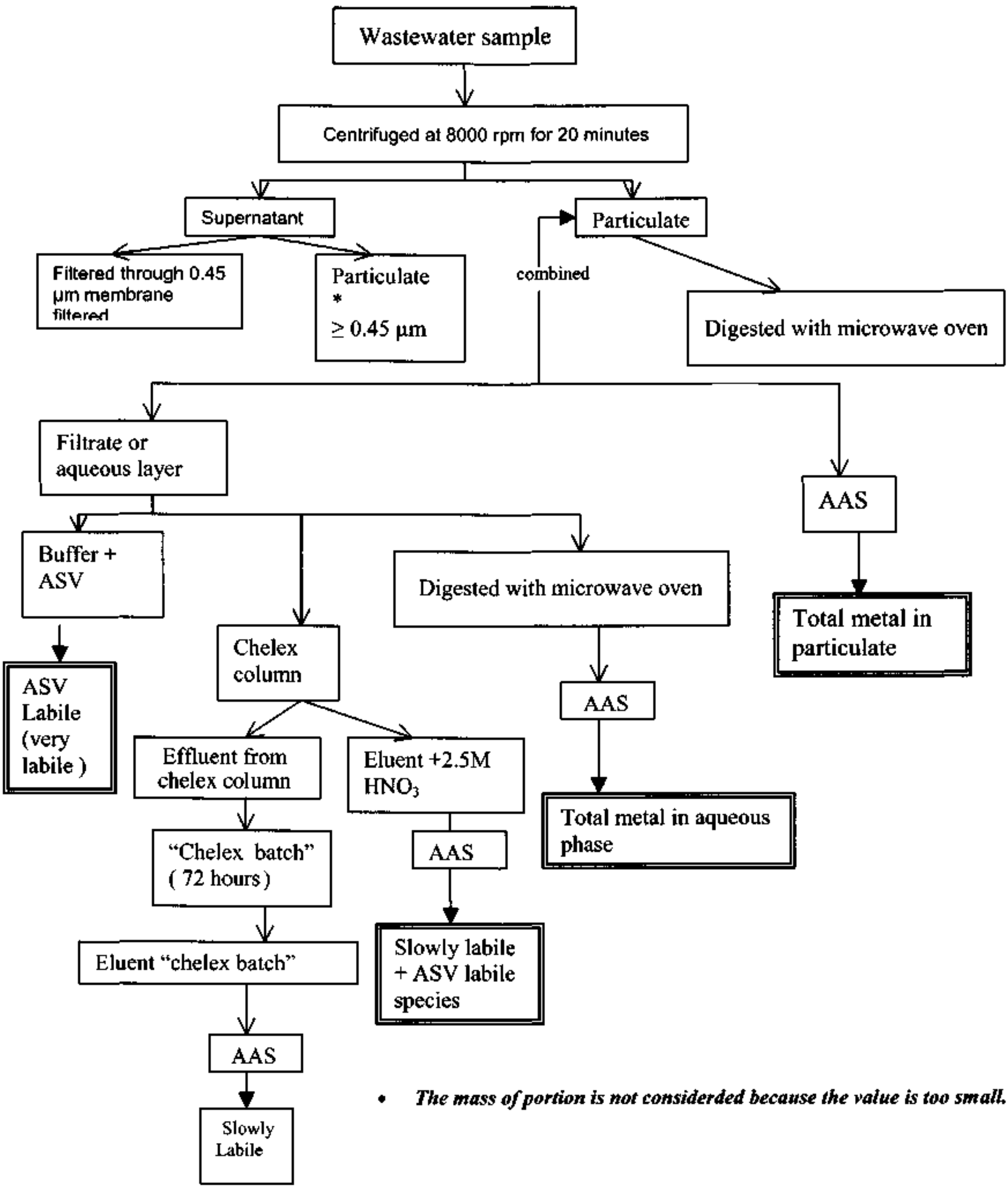
Harrison R.M. and Laxen D.P.H. (1981) *Lead Pollution: Causes and Control.*

Chapman & Hall, ***London.John C.K. (1984)*** *Tackling The Pollution Problems of Agro-based Industries in Malaysia.* Proceeding Asian Chemical Conferences on Priorities in Chemistry in Developement of Asia. *Kuala Lumpur. p.155.*

Kaplan D., Abeliovich. A. and Ben-Yaakov S. (1987) *The Fate Of Heavy Metals In Wastewater Stabilization Ponds.* Water Res. ***21****: 1189- 1194.*

Lim P.E., Leong S.F. and Seng C.E. (1991) *Distribution of Heavy Metals Along Treatment Path of Wastewater in Stabilization Ponds.* Bull. Sing. N. I. Chem. ***19****: 107-112.*

Lester J.N., Harissan R.M. and Perry R. (1979) *The Balance of Heavy Metals Through A Sewage Treatment Works. (I) Lead, Cadmium and Copper.* Sci. Total Envir. ***12****: 13-23.*



- *The mass of portion is not considerded because the value is too small.*

Figure 2 Flow Chart For Wastewater Speciation Scheme.

	Zn	Pb	Cu	Cd
Influent	66.60 ± 8.49	20.42 ± 2.56	12.80 ± 2.86	3.70 ± 0.45
Facultative pond effluent	24.20 ± 5.35 (66%)*	7.30 ± 0.89 (64%)*	6.35 ± 0.71 (50%)*	1.90 ± 0.59 (49%)*
Maturation pond effluent	14.00 ± 2.45 (79%)*	5.50 ± 0.77 (73%)*	4.80 ± 0.56 (63%)*	1.27 ± 0.30 (66%)*

- Numbers in parentheses indicate percentages of removal.

Table 1: Mean total concentration of the metals (µg/l) at various stages of treatment

	Zn	Pb	Cu	Cd
Influent	16.00 ± 3.00	7.20 ± 0.82	3.91 ± 0.85	1.13 ± 0.19
Facultative pond effluent	3.61 ± 0.79 (77.4%)*	1.84 ± 0.40 (74.%)*	1.66 ± 0.22 (58%)*	0.46 ± 0.17 (62%)*
Maturation pond effluent	1.71 ± 0.63 (89.3%)*	1.14 ± 0.27 (84%)*	1.18 ± 0.30 (70%)*	0.23 ± 0.09 (78%)*

* Numbers in parentheses indicate percentages of removal.

Table 2: Mean concentration of labile species of the metals at various stages of treatment (ug/l)

Sample	Metals	ASV Labile	Moderately Labile	Slowly Labile	Inert	Total
Influent	Zn	11 ± 3 (16)*	5 ± 3 (8.0)	20 ± 4 (30)	31 ± 8 (46)	66 ± 8
	Pb	2.4 ± 0.8 (12)	4.6 ± 0.8 (23)	6.0 ± 0.9 (30)	7.0 ± 1.4 (35)	20 ± 3
	Cu	0.41 ± 1 (3.1)	3.5 ± 1.4 (27)	2.7 ± 0.9 (21)	6.3 ± 1.6 (49)	13 ± 3
	Cd	0.10 ± 0.1 (2.7)	1.0 ± 0.2 (27)	1.0 ± 0.2 (27)	1.6 ± 0.3 (43)	3.7 ± 0.5
Efluent From Facultative Ponds	Zn	1.5 ± 0.9 (6.3)	1.8 ± 0.6 (7.5)	7.8 ± 1.5 (33)	13 ± 5 (54)	24 ± 5
	Pb	0.9± 0.13 (12)	1.0 ± 0.4 (14)	2.6 ± 0.6 (36)	2.8 ± 0.5 (38)	7.3 ± 0.9
	Cu	0	1.7 ± 0.2 (27)	1.5 ± 0.3 (23)	3.2 ± 0.6 (50)	6.4 ± 0.7
	Cd	0.04 ± 0.01 (2.0)	0.4 ± 0.2 (21)	0.5 ± 0.2 (28)	0.9 ± 0.3 (48)	1.9 ± 0.6
Final Efluents	Zn	0.7 ± 0.4 (5.0)	1.0 ± 0.3 (7.0)	4.7 ± 0.8 (33)	8 ± 2 (57)	14 ± 3
	Pb	0.6 ± 0.2 (11)	0.5 ± 0.2 (9)	2.2 ± 0.4 (40)	2.2 ± 0.8 (40)	5.5 ± 0.8
	Cu	0	1.2 ± 0.3 (25)	1.2 ± 0.3 (25)	2.5 ± 0.5 (52)	4.8 ± 0.5
	Cd	0.02 ± 0.01 (1.7)	0.2 ± 0.1 (17)	0.4 ± 0.1 (25)	0.6 ± 0.1 (58)	1.2 ± 0.3

* Numbers in parentheses indicate species percentages.

Table 3: Concentration (μg/L) and Percentages of Various Species of Zn, Pb, Cu and Cd along the treatment path