Extraction of Lead from Mine Tailings using Fruit and Vegetable Waste Leachate and Edia

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ABSTRACT: The ability of simulated fruit and vegetable waste leachate of different ages to extract lead (Pb) from mine tailings was investigated. Leachate was produced from two column reactors containing fruit and vegetable waste. The results showed a high extraction ability (60 – 70%), but with some fluctuations in levels, for leachates produced during the first 50 days, with a pH of lower than 5.0, while the leachate produced during days 364 to 434, (pH 6 - 8), showed no ability to extract Pb. These periods were the initial phase and acidogenesis phase, respectively. When suitable conditions occurred, the degradation process changed to a methanogenesis phase, where some Pb extraction abilities were observed, but at a much lower degree (<10%) than the initial-phase leachate. However, methanogenesis and associated humic substance (HS) production did not go to completion in these ferments, and so remain uncharacterized for Pb extraction ability. The high dissolved organic carbon (DOC) level and especially the low pH in the leachate likely affected the Pb extraction ability. As expected, EDTA showed a very high extraction ability, ranging from 61 to 75% of the total available Pb in the tailings, which was higher than most (but not all) of the simulated leachate abilities.

Key words: Dissolved organic carbon, extraction, leachate, lead, Pb

INTRODUCTION

Mining activities create a potential risk to the environment because of the release of heavy metals. When mine wastes (waste rock dumps, tailings and slags) are disposed of without any environmental control, they may cause soil and groundwater contamination. The type of contaminants and their concentration in the environment depend on their initial concentration in the mining areas, the nature of the mineral and the local soil and other factors including water pH. This environmental problem, and its effect on human health, is of concern. Heavy metals, such as zinc (Zn), lead (Pb) and cadmium (Cd), are highly persistent in soil, with residence times of thousands of years. Excessive accumulation of heavy metals can cause serious effects on the soil, ecosystem functions and is a health risk to animals and human beings. Among such heavy metals, Pb is one of the most common contaminants in the environment and has chronic toxicity.

A number of techniques have been developed to remove heavy metals from contaminated sites, including *ex-situ* washing with physical-chemical methods and *in-situ* phytoextraction. In the *ex-situ* washing methods, chelating agents or acids are used to enhance heavy metals removal. Ethylenediaminetetraacetic acid (EDTA) is the most commonly used chelate because of its strong chelating ability for different heavy metals. Besides chelating chemicals, dissolved organic carbon (DOC) in the leachate also shows the ability to form complexes with heavy metals. Indeed, water-soluble organic matter may play a significant role in enhancing heavy metal leaching to groundwater.(1)

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In landfills, waste can produce leachate containing DOC, a product of the anaerobic degradation process. Aoyama(2) studied the chemical composition of water soluble organic matter during the decomposition of different types of plant residues, and noted that organic carbon in the extract tended to decrease with time, with decreases in the fulvic acid (FA) fractions but increases in the humic acid (HA) fractions. Although heavy metals are less soluble in the neutral pH phase, they can be solubilized in an acidic leachate and DOC. The complexion ability of DOC is primarily related to its content of functional groups, such as carboxylic and phenolic groups. Previous studies have revealed that the leachate pH was the major factor in controlling the Pb leachability,(3) where leached Pb concentrations increased as the pH changed to extremely low or high values.

Thailand generates over 39,240 tons/day of municipal solid waste (MSW) and more than 40% of this is food waste (Pollution Control Department, Ministry of Natural Resources and Environment, 2003) should be a number, and is not in the refs anyway. The majority of organic waste in Thailand is fruit and vegetable waste, especially that from markets, and is relatively free of contaminants, compared to street collected, household or industrial wastes. Food waste, including fruit and vegetable waste, contains a high level of organic carbon, is rich in organic matter and has a high water content, resulting in a high degree of biodegradation, a high yield of biogas and a large volume of produced leachate.

According to the leachate's extraction or complexation ability for heavy metals, these natural occurring substances may be used instead of EDTA for bioremediation purposes. There are studies on the leaching of heavy metals from mine tailings or soil using DOC from many sources.(4,5) However, there is no investigation of the extraction of Pb from mine tailings using a simulated leachate derived from fruit and vegetable waste. Due to the high level of fruit and vegetable waste in Thailand and also their degradation properties, simulated leachates can be generated in a bioreactor at the same time as biogas production. The objective of this study was to evaluate the ability of simulated landfill leachate derived from the anaerobic fermentation of fruit and vegetable waste to extract Pb from mine tailings, and to compare this across leachate ages and with the commercial complexing agent EDTA as a reference comparison.

MATERIAL AND METHODS

Mine Tailing Preparation

Akra mine tailing was collected from the Akra Gold Mine, Phichit province, Thailand. The Akra gold mine is located at Phichit province, in the northern region of Thailand, which is approximately 280 km away from Bangkok. The mine tailing was contaminated with Zn, Cd, Cr and Pb in varying concentrations due to the differing geology and mining activities.

After collection, the mine tailings were air dried, then ground and sieved through a 10 mesh sieve. EPA Method 3052(6) was used to analyze the metal contents in the mine tailing samples. A tailing sample of 0.5 g was transferred into a fluorocarbon microwave digestion vessel with 10 mL nitric acid and digested for 10 minutes. The sample was cooled and the supernatant diluted with 50 mL deionized water. The supernatant was then filtered through Whatman filter paper (No. 42), and then analyzed using an inductively coupled plasma optical emission spectroscopy (ICP-OES). The sand, silt and clay contents were characterized using a standard sieve and sedimentation method.(7) The mine tailing pH was measured in distilled water at a 1:1 (v/v) ratio of mine tailing to water.(8) The cation exchange capacity (CEC) was determined using a 1 M NH_4OAc (pH 7) solution extraction method,(9) and the organic matter content was estimated by the Walkley and Black method.(10) All glassware used for dilution, storage and experiments were cleaned with a non-ionic detergent, thoroughly rinsed with tap water and soaked overnight in a 10% (v/v) HNO_3 solution and finally rinsed with ultra pure quality water prior to use.

Batch metal extraction procedures

Simulated leachate

Simulated leachate was generated from two bioreactors (A and B) loaded with fruit and vegetable waste. The reactors were operated in batch mode at room temperature (30-38 ^{o}C) under anaerobic conditions. Fruit and vegetable wastes were prepared to the same composition as the representative waste from the Si-Mum Muang Market, Thailand,(11) and is shown in Table 1. The fruit and vegetable wastes were shredded by hand into 1 - 2 cm pieces (strips or squares) and mixed together to enhance the homogeneity of waste. The shredded waste was mixed with 1 L of anaerobic digested sludge, obtained from wastewater treatment plant of the Utility Business Alliance Co., Ltd. The reactors were operated for 519 days with the addition of alkali (NaOH 5 M) after day 200 in order to increase the alkalinity and pH for methanogenesis bacteria. The pH of the recycled leachate was adjusted to neutral pH (7.0) with NaOH (5 M) three times per week before introduction back into the reactors. Simulated leachate samples were collected from both reactors regularly and were used as test extracting agents. Leachate samples collected at the same times were used as representatives of the same landfill phase but note that they exhibited different properties and extraction abilities. Prior to the extraction ability measurement, leachate samples were filtered through 0.45 µm membrane filter (Whatman) and defined as DOC. Mine tailings were suspended in each leachate samples at a (w/v) ratio of 1:20 (1 g tailings to 20 ml leachate) and shaken for 24 hours in a shaker at 200 rpm at room temperature.(12) After that, suspensions were centrifuged in polypropylene tubes at 10,000 rpm with 20 cm radius of the rotar for 10 minutes in order to separate the solid residues (pellet) from the leachate (supernatant). The extraction experiments were done in triplicate. Deionized water was used as blank in the metal extraction step and also in the analyzing step. The above leachate supernatant was then filtered through No. 42 Whatman filer paper before further analysis. Lead concentrations in the extracting agents (leachate and EDTA) were analyzed by Flame Atomic Absorption Spectrometry.

Table 1. Synthetic waste composition.

Fruits and vegetables	Total wet weight (kg)	Percentage (wet weight)
Chinese White cabbage	0.937	12.5
Morning Glory	0.8625	11.5
Egg plant	2.3625	31.5
Kale	0.75	10.0
Cow Peas	0.9375	12.5
Water mimosa	0.225	3.0
Cabbage	0.225	3.0
Chinese Cabbage	0.15	2.0
Bitter Cucumber	0.1875	2.5
Banana	0.375	5.0
Orange	0.4875	6.5
Total	7.5	100.0

Si-Mum Muang Market waste composition (11)

Ethylenediaminetetraacetic Acid (EDTA)

Extraction of metals from mine tailing was performed using two concentrations of aqueous EDTA solution as an extracting agent. EDTA was prepared by dissolving the reagent grade in deionized water to 0.04 and 0.1 M. The evaluation of its Pb extraction ability followed the same mixing ratio and extraction time as that for the simulated leachate described above, in order to be able to directly compare their extraction abilities. Likewise EDTA solution was analyzed for the amount of Pb extracted by Flame Atomic Absorption Spectrometry.

Sequential extraction method

The sequential extraction procedure of Tessier *et al.*(13) was employed. This method partitions the heavy metals into four operationally defined chemical fractions: acid-soluble fraction, reducible fraction, oxidizable fraction and residual fraction, as follows.

Step 1:- Acid-soluble fraction-bound to carbonates

Three 0.5 g dry sediment samples were each placed into a 50 mL polypropylene centrifuge tube to which 20 ml of 0.11 mol/L of acetic acid was added, capped and then shaken at 30 rpm for 16 hr at room temperature. The extract was separated from the solid phase by centrifugation at 3000 rpm (20 cm rotar radius) for 20 min. The supernatant was decanted and stored in a refrigerator at 4℃ prior to analysis. The residue was washed with 10 mL of deionized water, shaken again for 15 min and then centrifuged for 20 min at 3,000 rpm (20 cm rotar radius). The supernatant was then removed leaving the pellet for the second step extraction.

Step 2:- Reducible fraction-bound to Fe and Mn oxides

To the residue (pellet) from step 1 was added 20 ml of 0.5 mol/L hydroxylamine hydrochloride pH 1.5 (adjusted with 2 mol/L HNO_3), the tube capped and shaken at 30 rpm for 16 hr at room temperature. The extract was separated from the solid phase by centrifugation and decantation as described for step 1 and stored at 4 ^{o}C. The solid residue was washed as in step 1 ready for step 3.

Step 3:- Oxidizable fraction-bound to organic matter and sulfides

To the residue from step 2 in the centrifuge tube was added 5 mL of 8.8 mol/L H_2O_2 (pH of 2 - 3), the tube covered and digested at room temperature for 1 hr followed by 1 hr at 85 ^{o}C in a water bath with occasional shaking for 30 min. Next the tube was uncapped and left to reduce the volume to around 2 - 3 mL. Another 5 mL of 8.8 mol/L H_2O_2 was added, the tube covered was and maintained at 85 ^{o}C for 1 hr before uncovering and the volume reducing to almost dryness. After cooling, 25 mL of 0.1 mol/L ammonium acetate pH 2 (adjusted by concentrated HNO_3) was added to the residue and the tube was shaken for 16 hr at room temperature. The extract was separated from the solid phase by centrifugation and decantation as described above and stored at 4 ^{o}C.

Step 4:- Residual fraction that is strongly associated to the crystalline structures of the minerals

The residue from step 3 was digested in a 3:1 (v/v) mixture of concentrated HNO_3 to HF. The metal content of the residue from Step 4 was determined using a microwave-assisted acid digestion procedure.(6) Digests were centrifuged at 3,000 rpm (20 cm rotar radius) for 10 min to clear the supernatant which was then analyzed by ICP-OES.

Analysis of the volatile fatty acid (VFA) levels and composition in the leachate

Volatile fatty acid (VFA) concentrations in leachate samples were analyzed by using standard methods for the examination of water and waste water #5560C So state how you did it what standards used etc.

RESULTS AND DISCUSSION

Mine tailing physical and chemical properties

The physical and chemical properties of the Akra mine tailings are shown in Table 2.

Table 2. Physical and chemical properties of the Akra mine tailing samples used in this study.

Properties	Akra mine tailing	
pH		5.5
Texture	Sand (%)	54.8
	Silt (%)	34.0
	Clay (%)	11.2
Organic Matter (%)		1.04
Cation exchange capacity (cmol/kg)		1.9
Metal content (mg/kg)	Pb	59.83
	Zn	209.24
	Cd	2.16
	Mn	1583
	Cr	54.83
	Ni	9.27

Pb extraction ability and simulated leachate ages

The amount of Pb extracted from the mine tailings using the two simulated leachates with respect to the varying ages of the leachates are presented in Figure 1 as the % Pb extracted of the total amount available (Table 2). Referring to Table 2, the initial concentration of Pb in Akra mine tailing was 59.83 mg/kg. It can be seen from Figure 1 that Pb extraction (%) from mine tailing by simulated leachate ranged from 0% to nearly 70%. The Pb extraction ability of the simulated leachates were very high during the first 140 days of bioreaction but tailed off from almost 70% extraction ability in the first 50 days of anaerobic fermentation to only 20% by day 196. The leachates from reactor A and reactor B showed the same trend as each other. The highest Pb extraction by leachate A (39 mg/kg) was with the 42 day old sample, while that for leachate B was slightly higher (41 mg/kg) at an earlier time point (day 7). In both reactors, during these periods the pH values were very low (<4.5) and the DOC values of the leachates were very high (> 11,000 mg/L) compared to the later periods of the fermentation and especially after 375 days.

Since the leachates were acidic during this phase, Pb could have been extracted by a proton induced mechanism. At a low pH, the activity of H^+ is high and tends to displace metals from binding sites. Although the DOC levels were very high, at this very low pH the organic acids, such as acetic acid, are protonated and became weaker complexing agents.(14) Then the extraction ability of the leachate decreased gradually from ~50% at day 140 to 0% by day 363. The pH values ranged between 5.0 and 6.5 and the system remained in an acidogenesis phase until day 396. The leachate showed no Pb extraction ability from day 363 (pH 6.16 - 6.47) to day 433 (pH 7.8 - 8.4). However, at these pH values there might be precipitation of Pb. The Pb extraction ability of the leachate started to increase from 0% on day 433 up to 7 - 9% (day 518). Although the phase of leachate moved from acidogenesis to methanogenesis on Day 396, the pH of the system did not reach 6 until day 342 and 314 for reactor A and B, respectively, and reached pH 7 on days 403 and 412 for reactor A and B, respectively. The extraction ability of the leachate started to increase again at day 447 when the pH was approximately 8.0 - 8.5 and the DOC was 7,906 and 1976 mg/L for reactors A and B, respectively, but the extraction ability was still low. At this range, there was higher generation of humic substances (FA and HA) that is naturally occurring ligands with strong complexing abilities. FA and HA are large molecular weight materials with many acidic functional groups that can form complex with heavy metals.(14) The extraction ability of this leachate, however, was not comparable with the extraction ability of leachates from the first period of fermentation. Though the bioreactors were studied for a long period of time, the degradation process did not reach maturation phase by the end of the experiment. This may require a much longer time for completion of the degradation process, or an earlier starting of buffering the system.

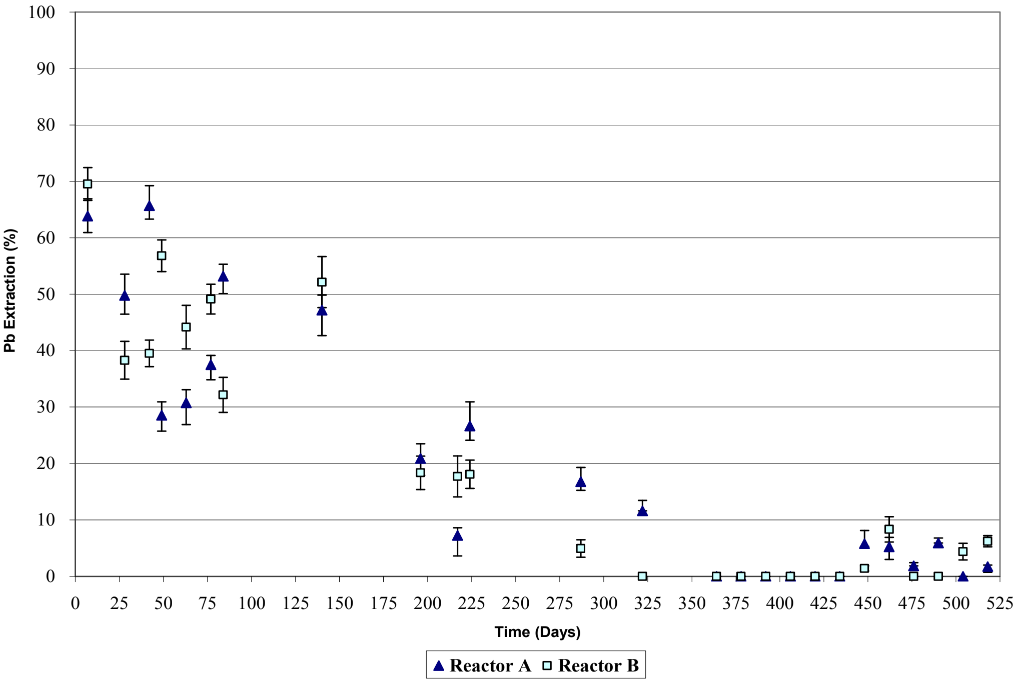

Figure 1. Pb extraction (% of total available Pb) from mine tailings using simulated leachates of different ages.

Pb extraction ability and the simulated leachate DOC levels

After collection, the leachate from both reactors were filtered through a 0.45 µm membrane filter and measured for Total Organic Carbon (TOC). These TOC values of the filtered leachates are herein defined as DOC. The DOC of leachate A ranged from 11,338 to 14,000 mg/L (days 7 to 210) while that for leachate B ranged from 8,615 to 12,550 mg/L in the same time period. The DOC of both reactors remained stable at approximately 12,000 – 14,000 mg/L for the first 200 days and then after the addition of alkali the DOC slightly increased from 12,000 - 14,000 mg/L at day 200, and to ~16,000 mg/L by day 385. The highest DOC recorded was 16,168 mg/L in reactor A at day 385. After that, the DOC decreased dramatically to 1,662 mg/L by day 509 until the end of experiment (day 525). There was a methanogenesis phase with a high production of methane gas, so the DOC in the leachate was likely to have been converted to methane gas through degradation.

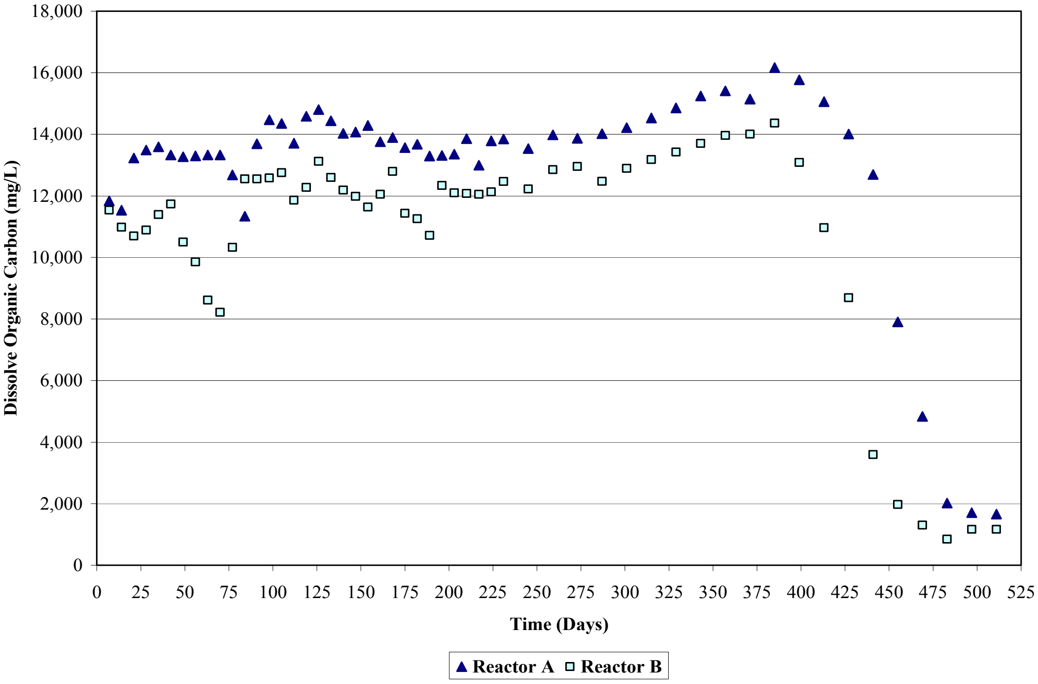

Figure 2. Dissolved organic carbon (DOC) levels in the two leachates with increasing fermentation time.

The graph plotted between the Pb extraction from the Akra mine tailings by the simulated leachate, as the % of the total available Pb in the tailings, and the DOC values in the leachate revealed that the Pb extraction was very low at low DOC values and increased when the DOC values increased up to a limit of <15,000 mg/L (Figure 3). At DOC values of less than 12,000 mg/L, Pb extraction was lower than 10% with several samples from different aged leachates showing no detectable Pb extraction. When DOC values were between 12,000 to 15,000 mg/L, extraction ability ranged from 0 (reactor B only) to nearly 70% Pb extraction. For those cases where the DOC levels were above 15,000 mg /L (reactor A only) no detectable Pb extraction was observed. Some high DOC leachate samples were representatives of low pH leachates (initial and acidogenesis phase), whilst others represent the late acidogenesis phase before going to methanogenesis because DOC remained nearly constant for a long period of time from day 140 to 385.

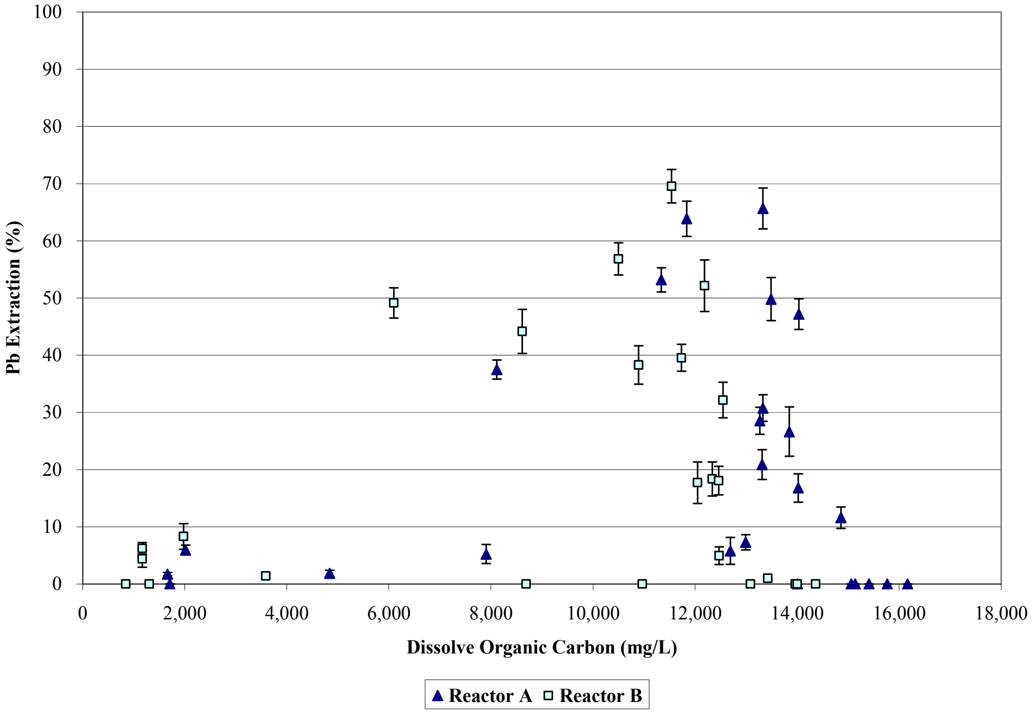

Figure 3. The Pb extraction (% of total available Pb in the tailings) by the simulated leachate and their Dissolved Organic Carbon (DOC) levels.

DOC values were high during the initial and acidogenesis phases of the anaerobic fermentation in both reactors, and exhibited a low pH. Most of the DOC in the low pH leachates was acetic acid, but also other intermediate organic acids were present (data not shown). At a pH of lower than 4.5, the pH had a stronger effect on the Pb extraction ability of the leachate than the DOC level. (where is the analysis, such as PCA or ANOCOVA, to support this statement) With pH values between 5 and 8, the leachate showed no detectable Pb extraction ability even though the DOC values were still very high (12,000 - 14,000 mg/L), because of heavy metal precipitation. At a low DOC, there was a low level of Pb extraction. Low DOC levels in the leachate were representative of samples from the last assayed phase of the fermentation, where the generation of humic substances (HS) was observed (data not shown) Thus, it might be due to a complexation effect of HS that increased the Pb extraction. However, the humification process was still at the beginning step and resulted in small contents of HS being produced. Therefore, it can be concluded that for this kind of leachate, pH showed a stronger effect on the Pb extraction ability of the leachate. Since the degradation process of the system did not reach the maturation phase, humic acid (HA) that could show strong complexing ability, was either not formed or was generated in a very small amount. Thus, there is no evidence either way of any positive effect from a strong complexing agent, such as HA, in this leachate.

Pb extraction ability and simulated leachate pH

The pH of the simulated leachates from different time periods is presented in Figure 4 and the leachate pH as a function of the Pb extraction (% of total Pb available) is presented in Figure 5. The pH values of the two simulated leachates from fruit and vegetable waste were very low in the beginning, being between 3.5 and 3.7. The pH values then slightly increased from 3.5 at day 7 to 4.5 at day 40 and then pH 5.0 at day 67. After that, the pH was stable at around 5.0 until day 200 when it started to gradually rise again. From these pH values, it was suggested that the simulated landfill processes of both reactors were still in the acid phase because pH 5.0 is not suitable for methanogenesis. After alkali addition with NaOH in order to increase the alkalinity of the system (to neutral pH), the pH started to increase gradually from pH 5.0 at day 200 to pH 6.5 at day 380. Finally, the pH increased more rapidly from 6.5 to 8 and then 9 by days 430 and 519, respectively.

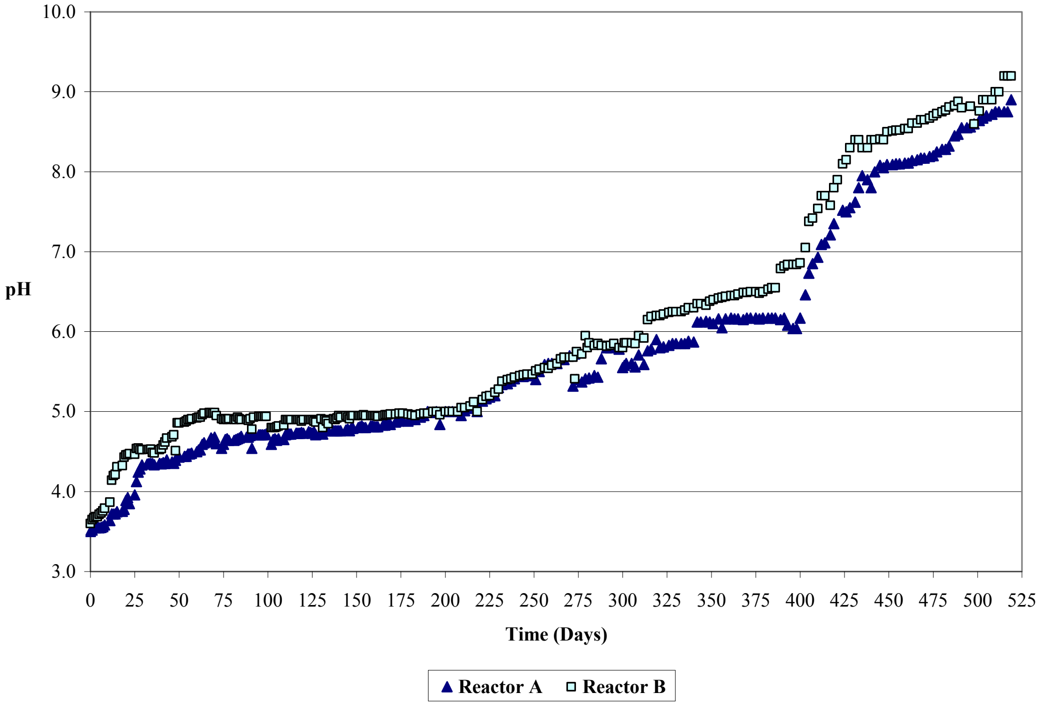

Figure 4. The pH of the two simulated leachates over the course of the anaerobic fermentation.

During the degradation process of the system, the Pb extraction (%) values also changed as a function of the alterations in the leachate pH. From Figure 5, the Pb extraction levels were very high at pH values between 3.5 and 4.5 attaining 65 - 70% at pH 3.5 and 30 – 55% at pH 4.5. When the pH increased from 4 to 6, the Pb extraction efficiency decreased dramatically from 65% at pH 4 to approximately 20% and 0% at pH 5 and 6, respectively, and remained at 0% until the pH value reached 8, where a very low Pb extraction level (<10%) was noted in some cases.

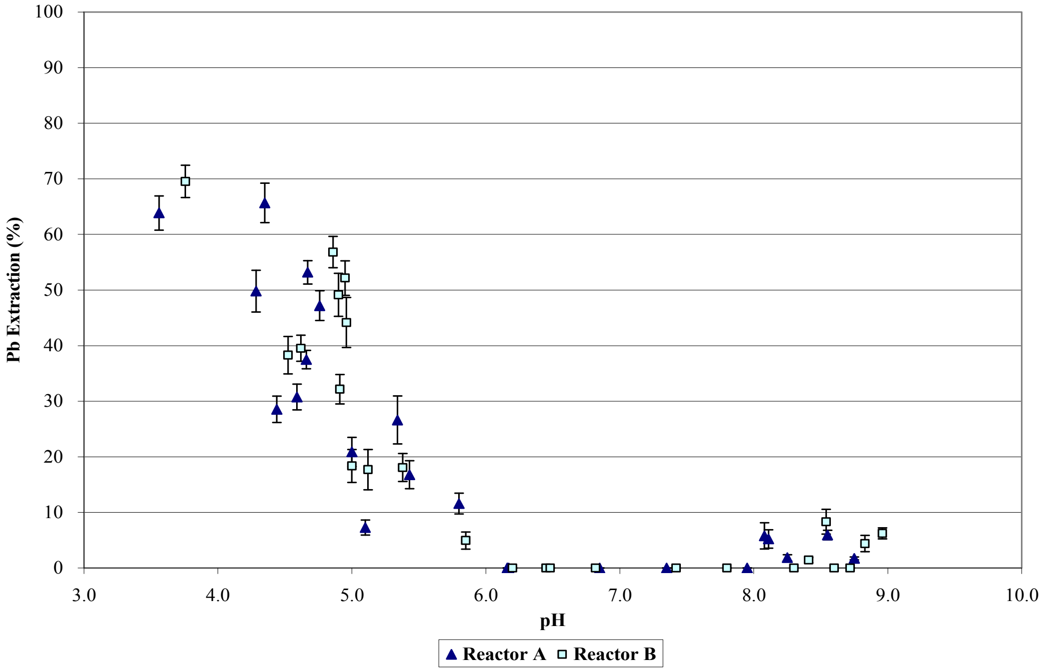

Figure 5. The Pb extraction levels (% of the total available Pb) as a function of the pH value of the two simulated leachates. Data are shown as the mean + 1 SD and are derived from three repeats.

It can be concluded that the Pb extraction ability for Akra mine tailings with simulated leachate was significantly affected by the pH value of the leachate. In addition the very low pH value in the leachate from the initial and acidogenesis phases showed the highest Pb extraction ability. While these leachates at a pH of < 4.5 may be used as extractant, those from the (early) methanogenesis phase, with a pH of between 6 and 8 should not be used as an extraction agent. In addition, the Pb extraction ability of the leachates with a pH of more than 8 (methanogenesis phase) were too low to be of use, especially compared to that obtained from the first phase of fermentation. These results are somewhat similar to those of Impellitteri *et al.*(15) where the Pb extraction was greatest at low (<3) and high pH (>6) values. Pb leaching behavior can be divided into three stages based on the leachate pH: a high alkalinity leaching stage at pH>12, where Pb forms soluble hydroxide anion complexes and leaches out; a neutral to alkaline immobilization stage in the pH range of 6-12, which was characterized by low Pb leachability caused by adsorption and precipitation; and an acid leaching stage at a pH < 6, where the acid neutralizing capacity was totally consumed and therefore free Pb-ion leached out.(16)

Pb extraction ability and the volatile fatty acid (VFA) levels in the simulated leachates

The volatile fatty acid (VFA) content of different leachate ages were only measured from day 182 onwards, that is from a few weeks before alkali addition. The VFA of the system remained constant at ~8,000 mg/L as CH_3COOH from day 182 until day 217, and then started to increase from day 224, the same time as the pH started to increase, and reached the highest VFA level (12,825 mg/L as CH_3COOH) at day 385 (Figure 6). Thereafter, as the pH became suitable for methanogenesis bacteria, so the VFA values dramatically dropped to ~1000 mg/L (reactor B) or ~2500 mg/L (reactor A) until the end of experiment. Although the leachates with a high VFA level showed higher extraction abilities than those with a low VFA content, the highest VFA showed the lowest extraction ability. The highest VFA levels were found in the acidogenesis phase but this was as the pH value was getting higher.

The percentage of the total available Pb that was extracted was highest at a high VFA concentration (~8,000 mg/L as CH_3COOH) and a low pH (pH < 5), likely to be because of the pH effect on Pb extraction. At higher concentrations of VFA (>8,000 mg/L as CH_3COOH), the leachate pH also increased to within the precipitation range for Pb. Moreover, VFA was in the acetate form which was not able to form a complex with heavy metals. Therefore, there was no Pb extracted at this range of VFA. At VFA levels lower than 4,000 mg/L as CH_3COOH, there was a generation of HS that could act as a chelating agent to form complexes with heavy metals such as Pb.(17)

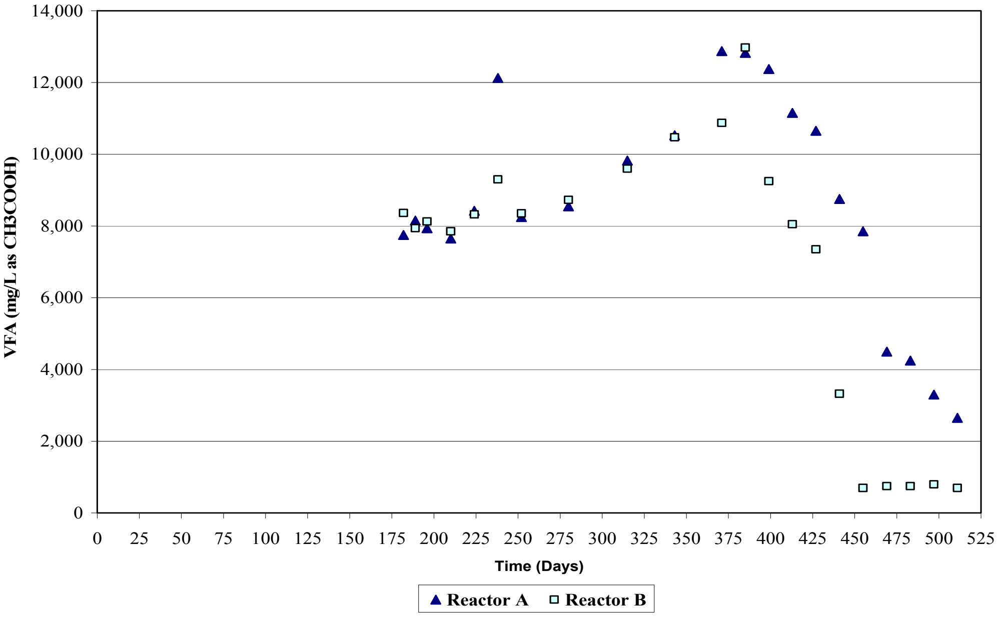

Figure 6. Volatile Fatty Acid (VFA) levels in the two simulated leachates over the course of the fermentation.

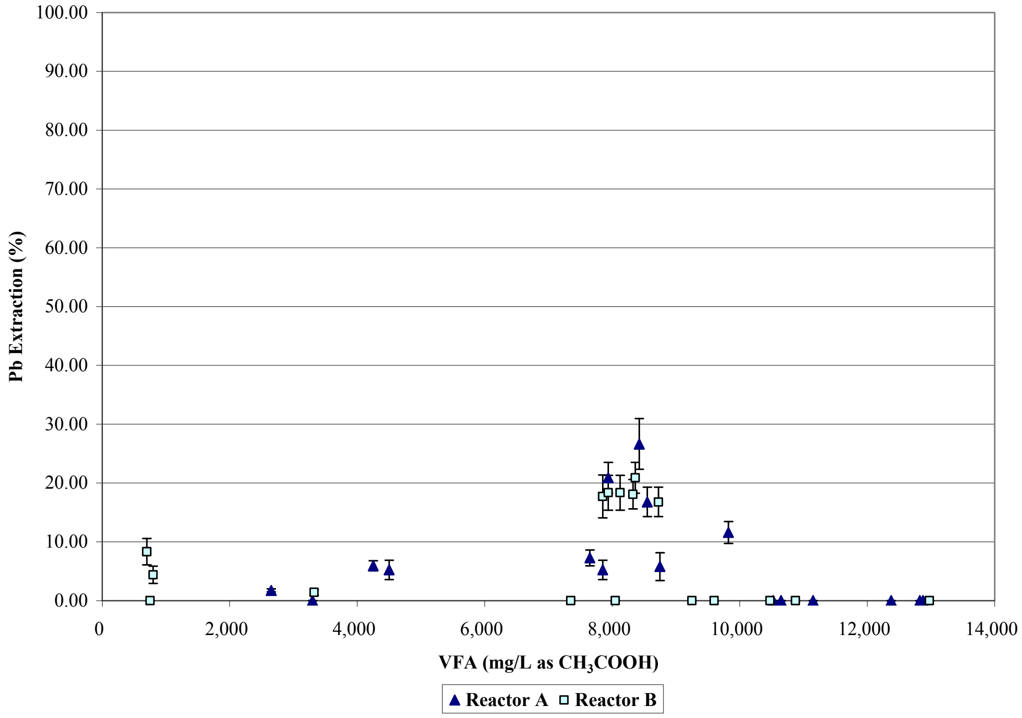

Figure 7. The VFA levels and the degree of Pb extracted (% of the total available amount of Pb) by the simulated leachates.

Pb extraction ability of EDTA

The extraction of Pb by the two different concentrations of EDTA is presented in Table 3. EDTA can extract a high level of the total available Pb from the mine tailings in a dose dependent manner. In general, EDTA showed a higher and more stable extraction ability than that of the simulated leachate. However, the leachates with a low pH (initial and acidogenesis phase) showed a comparably or higher degree of Pb extraction.

Table 3. The amount of extracted Pb and the proportion (%) of the total available Pb that was extracted from the mine tailings by EDTA.

EDTA	Pb extracted (ppm)	% Extracted
0.04 M	36.55 ± 2.07	61.09 ± 3.46
0.1 M	45.11 ± 3.26	75.4 ± 5.45

EDTA has a strong complexing ability and forms soluble metal complexes, and so exhibits a higher ability to leach metals in comparison with that of HA. Although HA and FA also form rather strong complexes with metals, their complex metal salts are usually only sparingly soluble in water, which affects their leaching ability.(12)

Fractions of heavy metals

The sequential extraction results of the Akra mine tailings are summarized in Table 4. The release of metals from the contaminated matrix depends not only on the extraction conditions, such as the pH, reagent concentration etc., but also on the modes of metal retention within the soil. Consequently, metal reactivity and behavior towards the extracting solution also depend on the nature of the metal fixation on the matrix particles, which can be operationally measured by application of sequential extraction procedures. Weakly sorbed fractions, such as exchangeable and carbonate can be readily extracted, but an effective extraction of strongly sorbed metals in oxide and residual fractions was not always guaranteed within different types of matrix and contamination sources.

Table 4. The sequential extraction of Pb from the Akra mine tailings in this study, and compared to that derived from two other reports.

Pb (mg/kg)	Fraction 1 Acid-soluble	Fraction 2 Reducible	Fraction 3 Oxidizable	Fraction 4 Residual	Total	Recovery (%)
Pb[(a)]	10.9 ± 1.5	28.5 ± 2.4	7.7 ± 1.2	9.57 ± 1.7	56.64	96
Pb (%)	19.28	50.24	13.59	16.88	100	
Pb in Soil[(b)]	0.093 ± 0.007	21.5 ± 1.2	1.43 ± 0.08	14.8 ± 1.5	37.8	97
Pb (%)	0.25	56.88	3.78	37.83	100	
Pb in Soil[(c)]	3.36 ± 0.74	107 ± 5	9.3 ± 4.2	14.3 ± 1.0	133.96	-
Pb (%)	2.50	79.87	6.94	10.67	100	

(a) This experiment
(b) Data obtained from Zemberyova *et al.*(18)
(c) Data obtained from Cuong and Obbard(19)

Lead was predominantly found in the reducible fraction, in accord with the other two reports.(18,19) Cuong and Obbard(18) used standard reference material (BCR-701) for analysis while Zemberyova *et al.*(19) used soil reference material produced by the Institute of Radioecology and Applied Nuclear Techniques, Kosice, Slovakia. Although the results from this study show some different values from those in the literature, due to different sources, the highest percentage of Pb was found in the reducible fraction. Unlike the soil reference in the literature, the relative proportion of extracted Pb from the mine tailings in this study was higher in the acid-soluble fraction. Acid soluble and reducible fractions of heavy metals including Pb, are more easily leached from their matrix compared with the oxidizable and residual fraction. From Table 4, the combination of acid soluble and reducible fractions is 69.5%, which is essentially the same as the highest level of Pb extractable by the leachate (69.5%). The residual fraction accounted for 16.9%, which means a significant fraction of the Pb can not be easily leached out.

CONCLUSIONS

At a very low pH (initial phase) the simulated leachate of degrading fruit and vegetable waste yields a high Pb extraction ability because of the proton induced effect. However, these anaerobic fermentations did not reach the maturation phase and so only a tiny amount of humic substances (HS) were generated. Thus, the role of HS in these leachates for Pb leaching is unknown. The complexing agent EDTA showed a higher and more stable extraction ability than that of the simulated leachates. However, some leachate extraction results were higher than that obtained with 0.04 M EDTA and only slightly lower than that with 0.1 M EDTA. However, most of the leachates had lower extraction abilities. Although the simulated leachate in the initial phase of degradation showed a high Pb extraction ability, it might not be appropriate for use as an extracting agent because of its unstable properties. Due to the fact that the generation of HS from this kind of waste was low, the improvement of leachate properties or waste compositions to increase HS production should be studied. In addition, the improvement of simulated leachate properties, such as more alkali addition, a temperature control, could be studied to increase the degree of biodegradation for this kind of waste.

ACKNOWLEDGMENT

The authors are grateful for the financial support of The National Center of Excellence for Environmental and Hazardous Waste Management, Chulalongkorn University.

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Received: July 22, 2009
Accepted: November 18, 2009