

Characteristics And Leachability Studies Of Heavy metals In Dumping Yard Of Solidwaste Treatment Plant

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Abstract

Using acid digestion (AD), multiple extraction procedure (MEP), toxicity characteristic leaching procedure (TCLP), and equilibrium leach test (ELT), Cd, Cr, Cu, Pb, Ni, and Zn were leached from fresh and partially decomposed municipal solid wastes. By fractionating the heavy metal ions into exchangeable, acid extractable, oxidisable, reducible, and residual fractions, Sequential Extraction (SE) tests were carried out to assess the mobility of the metal ions. The order of the tests' decreasing extraction efficiencies was AD > MEP > TCLP > ELT. Except for Ni, less than 45% of the metal content was in a form that was bioavailable (exchangeable and acid extractable). The levels of total and TCLP extractable metals were within the TCLP regulatory limits and USEPA composting standards, respectively.

Key words: Solid waste, heavy metals, leaching tests, mobile fraction, TCLP

INTRODUCTION

Municipal Solid Waste (MSW) is typically dumped in open areas without source separation in underdeveloped nations. The environment in MSW dumpsites contains more heavy metals due to the co-disposal of home hazardous waste, such as batteries, paint residues, ash, treated woods, and electronic trash (Pare et al., 1999).

To evaluate the risk that landfills pose to the environment and human health, MSW management experts frequently need to interpret data on metal leachability (Scott et al., 1990). Leaching tests are frequently used to evaluate the worst-case environmental situation in which the samples' constituent parts become soluble and mobile. Numerous leaching techniques, such as acid digestion, TCLP, ELT, SE, and MEP, have been cited in the literature to extract soluble components from solid matrix (Hesbach et al., 2001). Many of these are regulatory techniques that are required to characterize materials, while others have organization approval for proving conformity with specific requirements. The majority of these tests concern hazardous waste. The procedures vary depending upon the number and particle size of leached materials, the kind and volume of leachant solutions and the leachant delivery period (Kim, 2002). The United States Environmental Protection Agency (USEPA) established the Toxicity Characteristics Leaching Procedure (TCLP), which is frequently used to categorize hazardous solid wastes and assess the worst leaching circumstances in a landfill setting (USEPA, 1986). The Multiple Extraction Procedure (MEP) is a technique created to imitate the leaching that occurs when acid rain repeatedly falls on an unsanitary landfill (Testing Methods, Canada, 1986). According to Prudent et al. (1996), the equilibrium leach test (ELT) is designed to assess the maximum leachate concentration under benign conditions.

The chemical nature of the metals determines their mobility and toxicity when they are present in landfills. According to reports, the majority of the metal included in MSW is present in inert form, making it improbable for the metal to undergo chemical reactions in landfills but instead to leach from the waste bed (Tessier et al., 1979). It is well known that the amount of heavy metals in solid wastes has a significant impact on how harmful they are (Lottermoser, 1985).

For the assessment of reclamation and hazardous potential of the reclaimed waste, when it is utilized as compost for agricultural purposes, knowledge of heavy metal content, their species, and the leachability at various environmental conditions from the dumpsite is a prerequisite. Assessment of the species of metal ions allows for the assessment of the sustainability of mined waste as compost or cover material since the effect of heavy metals is determined by their form of existence (Norvell, 1984). Therefore, fractionating the metal content into exchangeable, acid extractable, reducible, oxidisable, and residual fractions will allow for a more accurate assessment of the contamination potential of landfills due to heavy metals. For this reason, the Tessier approach is frequently utilized (Tessier, 1979). Due to the creation of an oil film on the top, failing to remove the oil and grease from the wastewater could result in major water pollution issues in the nearby water bodies. As soon as the formation begins, it degrades the oxygen level, which has a detrimental effect on aquatic life and vegetation. The oxygen cannot enter the internal system of water bodies because of this oil layer. When DO becomes anaerobic, its effects degrade. AAS was used to determine the presence of the heavy metals by adding 2ml aquaregia to the effluent sample.

MATERIALS AND METHODS

Municipal Solid Waste Substrates

During the administration-organized awareness week on source segregation of solid waste, fresh municipal source-segregated waste was sampled at a Corporation waste pickup location. To assess the degree of decomposition (VS and Carbon content), partially decomposed solid waste samples were taken from an open dumpsite and analyzed (APHA, 1999). The physical composition of representative samples was manually sorted and weighed separately for each component to determine its percentage distribution. They were then dried in the shade, homogenized, grounded, and kept for later examination. The dried samples' chemical makeup, including its level of carbon and ammonia-N, was also examined.

Leaching Procedures

On samples of fresh and mining waste, leachability experiments were performed utilizing acid digestion, MEP, TCLP, ELT, and SE. Table 1 provides a summary of the extraction processes' specifics. Reagent preparation was done with double-distilled water. Heavy metal analysis was performed on the extracts after 0.45-micron filtration and storage in polythene bottles. Cd, Cr, Cu, Ni, Pb, and Zn were measured using a vario-6 atomic absorption spectrophotometer (Analytical Jena, Germany) with D2 background correction. Ar was used as the carrier gas for the study utilizing the electrothermal atomization technique (PSS, 2001). Spiked samples were used to validate the analytical results. Triplicate measurements were used to check the accuracy of the findings, and discussions were based on the average values.

RESULTS AND DISCUSSION

Solid Waste Characteristics

Table 1 shows the composition of the mined and fresh wastes used for the leaching investigations. The two samples differ significantly from one another. Food trash, paper, textiles, garden waste, leather, and wood made up 86% of the fresh waste sample, whereas just 27% of the mining garbage was biodegradable, with the remaining 63% consisting of soil and other fine fractions. High moisture content was present in the fresh MSW (58–62%). Ammonia-N made up about 18 to 20 g/kg of the fresh waste, which had a carbon content of 280 to 320 g/kg. The mined waste had a moisture level of 28 to 30%, and as volatile solids made up 30% of the total solids, the remaining

70% are likely to be fixed solids. It demonstrates that the majority of the fine fraction in the mined trash was not biodegradable, which is further supported by the meager amount of total organic carbon (60–110 g/kg) that was available. The waste's ammonia-N content was 0.2–0.3 g/kg.

Total Metal Contents by acid digestion

Table 2 depicts the concentrations of Cd, Cr, Cu, Ni, Pb, and Zn in fresh and mining wastes. The amounts of Cd, Cr, and Pb in the mining waste were twice as high as those in fresh waste samples, which had higher Zn and Cr levels. This might be explained by the mine waste's high inorganic concentration (70%). The main source of heavy metal content in fresh and mined MSW is the mixing of biomedical, home hazardous waste, and automotive waste. When waste is stabilized, the total bulk is decreased without changing the amount of heavy metals present. As a result, the partially decomposed mining waste contains a higher percentage of metals than the fresh trash.

Similar results with higher concentration of heavy metals in old solid waste samples than the fresh waste samples were also reported in literature (Jain et al., 2005), but Ni in the fresh waste was more than that in the mined waste. A similar investigation in Thailand revealed the following metal contents in the mined waste substrates: Cd - 1 to 3.5 mg/kg, Cr - 0.6 to 210 mg/kg, Cu - 150 to 350 mg/kg, Pb - 310 to 350. Indian compost quality criteria were compared to the metal content of mining waste (MoEF, 2000), and the results showed that Cr (>50 mg/kg), Ni, and Pb (>100 mg/kg) exceeded the limitations. The co-disposal of household hazardous waste with MSW may be to blame for this. The levels of Cu (300 mg/kg), Cd (50 mg/kg), and Zn (1000 mg/kg) were below the MoEF's thresholds. Compost Cd, Cr, Cu, Pb, Ni, and Zn concentrations were significantly below the designated levels as compared to USEPA quality guidelines.

Multiple Extraction Procedure

Table 3 depicts the Cd, Cr, Cu, Ni, Pb and Zn in extracts from the fresh and mined waste substrates using multiple extraction procedure. Higher concentrations of Cr, Cu, Ni, Pb and Zn were evident in extracts from fresh waste than that of mined wastes. Pb was the predominant metal followed by Zn, Cr, Ni, Cu and Cd. Higher concentrations of Pb and Zn in MEP extracts may be attributed to the interaction of the elements with acetic acid which is reported to enhance the solubility (Esakku et al., 2003). The long-term leachability was maximum for Zn i.e. 20 and 80 mg/kg from the fresh and mined waste, respectively.

Toxicity Characteristics Leaching Procedure

The amounts of Cd, Cu, Cr, Pb, Ni, and Zn in TCLP extracts of fresh and mining wastes are shown in Table 3. When the findings were compared to the USEPA's regulatory standards, it became clear that neither the fresh nor the mined wastes were dangerous in nature in terms of their Cd, Cr, and Pb levels (which were 1, 5, and 5 mg/L, respectively). The TCLP extractable metal levels were within the legal limits, according to similar research on mined solid waste samples from a Thai dumpsite (PSS, 2000).

Equilibrium Leach Test

The concentrations of Cd, Cu, Cr, Pb, Ni, and Zn in ELT of fresh and mining wastes are shown in Table 4. In comparison to fresh garbage, mining waste has higher concentrations of metals other than Pb. Dumpsite leachate, with the exception of Ni (Table 4), had lower metal contents than ELT extracts of fresh and mining wastes. For Cd, Cr, Cu, Ni, Pb, and Zn, the Indian requirements for landfill leachate dumping into inland surface water are 1, 2, 3, 1, and 5 mg/L, respectively (MoEF, 2000). It was discovered that the metal content of the ELT extracts of fresh and mined waste substrates was below the disposal standards. These findings are consistent with the low levels of leachable metals reported in previous leachates (Goumans et al., 1991; Robinson, 1995; and Revans et al., 1999) as well as the fine fractions of dumpsite soils (Esakku et al., 2003).

Sequential Extraction

Table 5 shows the percent contributions of the concentrations of Cd, Cr, Cu, Ni, Pb, and Zn that are exchangeable, acid extractable, reducible, oxidizable, and residual for the fresh and mining waste samples. Since cadmium was

found in the least amount—0.0 – 1.91 mg/kg and 0.03 – 3.49 mg/kg, respectively—in fresh and mined waste samples, it's possible that the species of cadmium are not particularly significant in terms of the environment. Sequential extraction might not be sensitive enough to disclose the true situation in comparison to past observations because the total Cd concentration was so low (Esakku et al., 2005). In the fresh and mined waste, the residual proportion of Cr ranged from 70 to 90% of the total metal content. According to Gumgum and Ozturk (2001), remobilization of residually bound metals is uncommon, therefore it's possible that natural conditions would prevent Cr from being released from MSW. Pb bioavailability in fresh and mining waste samples ranged from 20 to 35% of the total Pb concentration. Lead sulphates and phosphates may have precipitated, accounting for up to 50% of the total Pb content in the residual fraction (Lindsay, 1979). In fresh and mining waste, the bioavailability of nickel was 40 and 70%, respectively. The mobility of Ni in the exchangeable and extractable fractions may be hazardous to the environment. From fresh and mined wastes, respectively, about 83 and 70 percent of the Cu was in residual form. Cu's bioavailability in mine waste was limited to a maximum of 20%. Bioavailability of Zn in mine waste was 30%. This pattern matches the conclusions drawn from our past research (Esakku et al., 2005).

The total of the exchangeable and acid extractable fractions is the bioavailable or mobile fraction. Compared to other fractions, mobile metal fractions are more conveniently accessible for environmental purposes. Cd, Cr, Cu, and Zn are considerably below the limitation values according to a comparison of values obtained for mobile fractions with compost quality requirements set by MoEF and US-EPA (Hogland et al, 1997) (MoEF, 2000). Lead and Ni demonstrated mobile fractions that were extremely near the predetermined limits. Ni, Cd, Zn, Pb, Cu, and Cr are the metals that are most readily available from waste substrates for environmental purposes.

Comparison of the leaching tests

Based on the total metal contents recovered with aqua regia for each metal, leachable metal fractions obtained using various leaching procedures were computed, and the results are shown in Table 4. ELT extracts showed relatively low metal fractions compared to the other processes. A maximum of 5% of the total Cd from the fresh waste substrate could be leached away, according to ELT data. Up to 21.4% of the total Ni content in mined waste substrate was recovered using TCLP. The MEP approach was used to extract the most Zn (21.8% of the total) from the mined waste substrate. The greatest mobile fractions of Ni from fresh and mining wastes, calculated as the sum of exchangeable and extractable fractions, were 40.3 and 68.5%, respectively. The findings also suggest that there is a considerable complexation between Cr and solid waste particles and that none of the selected chelating agents is sufficiently effective to remove Cr contamination from MSW. Leaching of heavy metals from compost may be more challenging than from soil, according to prior research (Wasay et al., 2001). Results from the TCLP may be helpful in assessing the risk involved in classifying trash as hazardous or non-hazardous in nature for solid waste management. Results from MEP and ELT can be compared to risk-based water quality regulations or recommendations.

Acid digestion, MEP, TCLP, and ELT all had lower extraction efficiencies than the other tests. The various extraction fluids employed for the tests, such as distilled water for ELT (pH 7.0), sodium acetate buffer for TCLP (pH 5.0), acetic acid and HNO₃ + H₂SO₄ mixture for MEP (pH 3.0), and aqua regia (pH 1) for acid digestion, may be to blame for this. One of the key elements influencing the release of metals seems to be pH. It is well known that metals have a propensity to leach more when the pH level is extremely acidic (Van der Sloot et al., 1997; and Jang et al., 2002). Leaching efficiency will also be impacted by the size of the waste particle, which impacts the surface area exposed to the leaching solution, and the development of metal-organic complexes, as in the case of TCLP extracts (lead acetate). The other influencing parameters in leaching experiments are oxidation-reduction conditions, liquid/solid ratio, and contact time. From the aforementioned findings, it can be inferred that leaching tests can offer useful information regarding the mobility of elements and also enable the evaluation of potential cleanup techniques for solid waste to reduce any negative environmental effects.

CONCLUSIONS

The following conclusion can be drawn based on the results;

- While Cu, Cd, and Zn were well within the permitted limits, the fresh and partially degraded municipal solid wastes had Cr, Ni, and Pb concentrations that were higher than the Indian compost quality guidelines.
- The solid wastes' Cd, Cr, Cu, Ni, Pb, and Zn levels fell short of the USEPA's criteria for compost quality.
- Ni, Cd, Zn, Pb, Cu, and Cr are the metals that are most readily available from the waste substrates.
- The levels of extractable metals in TCLP fell below USEPA-mandated regulatory thresholds.
- ELT samples showed lower metal contents than the allowed levels for disposal of treated leachate in India.
- Acid digest, MEP, TCLP, and ELT all had lower extraction efficiencies than the others.
- Fresh and mined waste samples have less than 45% bioavailability of metals.

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Table 1. Summary of heavy metal extraction procedure

Method	Leachant	Maximum Particle size	Liquid: Solid (L:S) Ratio	Extraction Time (h)	Number of leaching steps	Reference
Acid digest	HCl : HNO ₃ (3 : 1)	-	-	-	-	DIN, 1996
MEP	CH ₃ COOH (for step 1) H ₂ SO ₄ :	2.0 mm	1 : 20	24	1 + 9	USEPA, 1986
	HNO ₃ (60 : 40) (step 2 – 10)					
TCLP		9.5mm	1 : 20	18	1	USEPA, 2001
ELT	Distilled water	150 µm	1 : 4	168	1	ECAEC, 1986
SE	With five different leachants *	150 µm	*	*	5	Tessier et al., 1979

Note: MEP-Multiple Extraction Procedure; TCLP-Toxicity Characteristics Leaching Procedure; ELT- Equilibrium Leach Test; SE -Sequential Extraction; USEPA–United States Environmental Protection Agency; ECAEC–Environment Canada and Alberta Environmental Centre; DIN – Deutches Institute for Normung.
Leachant 1 (Exchangeable). Leachant 2 (Acid Extractable) , Leachant 3 (Reducible), Leachant 4 (Oxidizable), Leachant 5 (Residual)

Table 2. Characteristics of Solid Waste Substrates

S. No.	Particulars	Fresh waste		Mined waste	
		Avg	SD (\pm)	Avg	SD (\pm)
1.	Moisture content (% wet weight)	59	6	30	2
2.	Total solids (% wet weight)	42	5	9	1
3.	Volatile solids (% dry weight)	48	3	30	1
4.	Fixed solids (% dry weight)	50	3	71	1
5.	Carbon (g/kg)	310	22	86	28
6.	Ammonia (g/kg)	19	1	0.	0.2

Table 3. Metals in TCLP extracts of solid wastes

S. No.	Heavy metals	Fresh waste		Mined waste		USEPA standard
		Avg	SD (\pm)	Avg	SD (\pm)	
1.	Cadmium	BDL	0.0	BDL	0.0	1.0
2.	Chromium	0.12	0.01	BDL	0.0	5.0
3.	Lead	0.32	0.10	0.26	0.03	5.0
4.	Copper	3.73	3.70	0.84	0.36	NA
5.	Nickel	0.67	0.06	0.54	0.06	NA
6.	Zinc	0.31	0.08	0.14	0.04	NA

Note: All values are in mg/L; NA – Not applicable; BDL – Below Determination Limit

Table 4. Comparison of ELT metal contents with dumpsite leachate and disposal standards

S.No.	Leachate	Cd	Cu	Cr	Pb	Ni	Zn
1.	ELT-fresh waste	0.02	0.25	BDL	0.35	0.12	0.12
2.	ELT-mined waste	0.02	0.4	0.16	0.32	0.39	0.36
3.	Leachate from DY1	.016	0.42	0.08	0.12	0.42	0.06
4.	Leachate from DY2	0.01	0.12	0.06	0.07	0.49	0.12
5.	Disposal limits* *	1	3	2	1	3	5

Note: All values are in mg/L;

Table 5. Leachable metal contents from solid waste substrates with different leachants

S.No.	Heavy Metals	ELT		TCLP		MEP		SE (Mobile fraction)	
		Fresh	Mined	Fresh	Mined	Fresh	Mined	Fresh	Mined
		waste	waste	waste	waste	waste	waste	waste	waste
1.	Cd	5	2.1	11	1.5	<0.1	<0.1	3.8	35.9
2.	Cr	<0.1	0.4	<0.1	<0.1	1.1	0.5	1.4	11.5
3.	Pb	3.8	1.6	16.6	5.4	11.5	6.0	23.0	33.5
4.	Cu	0.5	0.4	5.3	0.9	9.1	11.1	8.4	17.3
5.	Ni	0.7	3.4	11.7	21.0	3.2	2.6	40.1	68.3
6.	Zn	0.4	0.7	2.8	3.9	16.1	21.9	9.1	32.4

Note: All values are in percentage on weight basis