



REMOVAL OF HEAVY METALS (Cu, Ni, Zn, Pb, Cd) FROM COMPOST BY MOLASSES HYDROLYSATE

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Abstract. This study aimed to remove heavy metals (Cu, Ni, Zn, Pb, Cd) from composts using molasses hydrolysate, produced from molasses by-product of the sugar industry. Batch experiments were conducted to examine the effects of differing experimental conditions on the removal of heavy metals, according to contact time and solid–liquid ratio. Batch experiments achieved removal efficiencies of 66% for Cu(II), 52% for Ni(II), 57% for Zn(II), 51% for Pb (II), and 77% for Cd(II) at 60 minutes and 1:12.5 solid–liquid ratio. Column experiments achieved removal efficiencies of 91% for Cu, 86% for Ni, 99% for Zn, 61% for Pb, and 99% for Cd at 0.55 mL/minute flow rate and a solid–liquid ratio of 1:12.5 g/mL. Producing large quantities of highly acidic and heavy metal contaminated solution, compost with low pH, and decreasing some parameters' concentrations of compost such as C, TKN, total P are the disadvantages of suggested technology.

Keywords: batch experiments, column experiments, compost, extraction, heavy metal, molasses hydrolysate.

Introduction

Composts include high proportions of stable organic matter and nutrients, and are therefore used as organic conditioners in agriculture. Besides these positive characteristics, composts can also include inorganic and organic pollutants. Municipal solid waste (MSW) composts may contain high concentrations of toxic trace elements, especially when mechanically-sorted organic fraction is used for their production rather than separately-collected waste-streams. Many previous studies have found that the amount of heavy metals in composts is an important factor in limiting their agricultural use (Ciba *et al.* 2003; Núñez *et al.* 2007; Akram Qazi *et al.* 2009; Farrell, Jones 2010; Saha *et al.* 2010; Paradelo *et al.* 2011). There are many sources of heavy metals in compost, e.g. household dust, batteries, plastics, paints, inks, bodycare products, medicines and household pesticides. In relation to the application of composted residuals to soil, the main elements of concern include: Zn, Cu, Ni, Cd, Pb, Cr and Hg because they are potentially present in compost at concentrations that may exceed the background levels in the receiving soil. The presence of heavy metals in composts is the main cause of adverse

effects on animal and human health (Hseu 2004; Businelli *et al.* 2009; Farrell, Jones 2009; Smith 2009; Achiba *et al.* 2010; Chen *et al.* 2010; Paradelo *et al.* 2011). To prevent the pollution of soil or groundwater by heavy metals from compost, many countries such as Belgium, Canada and Germany have established standards for heavy metal contents in compost. Table 1 lists the maximum permissible limits stipulated by various countries for the heavy metal content of composts.

A review of the literature indicates that the heavy metal content of composts can be reduced using physical and chemical processes prior to composting, or the addition of zeolites during the composting process (Veeken, Hamelers 2003; Casado-Vela *et al.* 2007).

Molasses is a by-product of sugar production. In previous studies, molasses has been used for various industrial fermentations as a cheap source of carbon and nutrients (Ren *et al.* 2006; Li *et al.* 2007; Hsiao *et al.* 2009; Park *et al.* 2010). In addition, molasses has been used as an external carbon source for denitrification and for biodiesel production (Karatay, Dönmez 2010).

In the removal of heavy metals from solid matters such as soil and sediment, complexing agents that do not

Table 1. Maximum permissible limits stipulated by various countries for the heavy metal content of composts (mg/kg dry compost) (<http://www.compostnetwork.info/index.php?id=10>)

Heavy metal	Germany	Belgium	Canada	France	Sweden
Cu	150	100	100	–	150
Zn	400	1000	500	–	500
Mo	–	–	5	–	5
Co	–	–	34	–	25
Cd	2	5	3	8	3
Ni	50	50	62	200	50
Pb	200	600	150	800	150
Hg	1	–	0.8	8	3
Cr	150	150	210	–	150
As	–	–	13	–	–
Se	–	–	2	–	–

produce toxic by-products at the end of decomposition should be used in order to prevent secondary pollution following treatment. Natural chelating agents such as sugar acids and hydroxycarboxylic acids can meet such a need. When oxidized under acidic conditions, molasses – which is rich in carbohydrates – produces a hydrolysate that includes natural chelating agents (Bipp *et al.* 1998).

The present study examines the suitability of chelating agents for treating heavy metals in compost, as these reflect the successful application of sugar acids and hydrolysates with sugar acid contents for the decontamination of heavy metal-loaded soils and waste incineration residues (Bipp *et al.* 1998).

The objective of the present work is to develop an inexpensive and effective chelating agent for the removal of heavy metal ions from compost. In this regard, the study investigated the removal of five heavy metals (Cu(II), Ni(II), Zn(II), Cd(II), and Pb(II)) from compost both in batch and column systems, using hydrolysate of industrial by-product molasses. The use of molasses hydrolysate is a new approach for metal removal from compost.

1. Materials and methods

Compost samples used in this study were obtained from Istanbul Solid Waste Recycling and Composting Facility, operated by Istanbul Metropolitan Municipality (Turkey).

1.1. Characterization of compost samples

Distilled water was added to the compost samples at a 5:2 ratio (e.g. 10 mL distilled water/4 g sample) to determine the pH values of the samples. After being mixed by a magnetic mixer for 10 minutes, pH values were read using a pH meter (Jenway 3040 Ion Analyzer).

A compost sample (1 g) was dried in a drying oven at 105 Celsius for 24 hours. The compost samples were

weighed before and after drying in order to calculate moisture content, as follows (Methodenbuch zur Analyse von Kompost 1994):

$$\text{Moisture}(\%) = \left[(M_1 - M_2) \times 100 \right] / M_1 \quad (1)$$

In this equation: M_1 refers to compost weight before drying (gram) and M_2 refers to compost weight after drying (gram).

To determine the amount of heavy metals (Cu, Ni, Zn, Pb, Zn, Cd) and other elements (Ca, Na, Mg, K, P) in the compost samples, a screened fresh compost sample was dried at 105 °C and ground to a grain size of 0.25 mm. Then, a compost sample of 1–2 g was placed into an Erlenmeyer flask; 10 mL 1:1 (volume/volume) water and nitric acid was added to perform the decomposition process. Following the completion of the decomposition process, the sample was cooled; subsequently, 5 mL hydrogen peroxide, 5 mL concentrated hydrochloric acid and 5 mL water were added; the sample was then re-heated to evaporate the acids. After cooling, the sample was diluted with distilled water and filtered by using a 0.45- μ m membrane filter. The resulting solution was analyzed to determine the presence and concentration of various elements (Methodenbuch zur Analyse von Kompost 1994; AWWA 1995). Samples were analyzed using an ICP-MS (Inductively Coupled Plasma-Mass Spectrometer, Thermo-Elemental ICP-MS-X Series).

To detect the weakly-bound parts of the metals, 1 L distilled water was added to 100 g (dry-weight) compost sample, which was agitated in a horizontal orbit agitator for 24 hours at 160 cycles/minute (Bipp *et al.* 1998). The liquid phase was then filtered with a 0.45- μ m membrane filter. The amount of heavy metals in the filtrate was determined via a Flame Atomic Absorption (Unicam 929 AA) spectrometer.

The percentages of C, H, N and S in the compost samples were determined using an elemental analyser. Before being sent for elemental analysis, samples were dried at 50 °C for 24 hours and ground to a fine powder in a quartz mortar. The equipment specifications were as follows: Thermo Finnigan Flash EA 1112 Series Elemental Analysis device, temperature: 900 °C; mobile gas He; burning gas O₂.

The Total Organic Carbon (TOC) in the compost samples was determined (using a Shimadzu, TOC-V CSH device, with solid sample modul for Total Organic Carbon Analyzer; SSM-5000 A).

Orthophosphate amounts were determined spectrometrically with SM 4500-P E:2005 (ascorbic acid) method. TKN values were determined with SM 4500-Norg B:2005 (Macro-Kjeldahl) method (AWWA 1995).

To determine the types of heavy metals in the compost, samples were analyzed using an XRD (X-Ray Powder Diffraction, Rigaku D/Max-2200/PC XRD) spectrometer.

Prior to analysis, samples were dried at 50 °C for 24 hours and then ground to a fine powder in a quartz mortar.

A Scanning Electron Microscope (SEM) (JSM 5600 model) was used to determine the morphological structure of the compost samples (before and after the extraction process).

1.2. Preparation of molasses hydrolysate

A 5-g sample of molasses was dissolved in 20 mL HNO₃ (30%) for the preparation of molasses hydrolysate. The solution was then heated to 85 °C for 4 hours. The mixture was allowed to cool and then filtered (Bipp *et al.* 1998).

1.3. Detection of organic acids in molasses hydrolysate

The types of organic acids in the molasses hydrolysate were determined using a HPLC (High Pressure Liquid Chromatography) (SHIMADZU Class-Vp 5.0). The equipment and column specifications were as follows: Shimadzu UV detector (214 nm); Column, ACE C18, 250×4.6 mm internal diameter; column temperature: 35 °C; flow rate, 0.8 mL/minute; injection, 10 µL; mobile phase, 0.2 M KH₂PO₄ (pH: 2.4 with orthophosphoric acid); duration of analysis, 30 minutes.

1.4. Batch experiment method

In the batch experiments, molasses hydrolysate was used without any dilution or pH adjustment process (at its original pH of ≤1). A sample of 30 mL molasses hydrolysate was added to each 5-gram compost sample (dry-weight) to determine the effect of contact time on the efficiency of heavy metal removal. Samples were then agitated at 160 cycles/minute. Contact times (t) were set at 5 minutes and 24 hours.

To determine the effect of the solid–liquid ratio on the efficiency of heavy metal removal, molasses hydrolysate was added to each compost sample until a solid–liquid ratio of 1:2.5–1:75 g/mL was achieved. Samples were then agitated at 160 cycles/minute. Contact times were set at 30 minutes and 1 hour.

1.5. Continuous system

A glass column of 4.5 cm inner diameter and 45 cm height was used in the experiments. A fiberglass filter of 0.45 µm was located at the bottom of the column. Glass beads of 5 mm diameter were placed in a 4-cm layer on top of the compost to ensure homogeneous distribution of the liquid throughout the column. Moreover, glass beads of 5 mm diameter were placed in a 3-cm layer beneath the compost layer to prevent blocking of the fiberglass filter due to contact with the compost. Liquid was continually maintained above the column to ensure uniform distribution of the extraction solution. Figure 1 gives a schematic view of

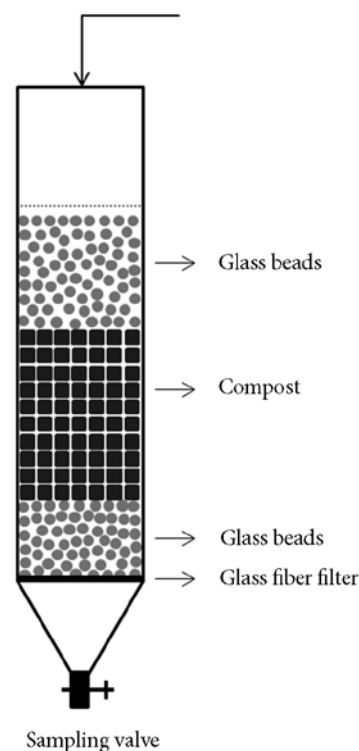


Fig. 1. Schematic view of the column used in the experiments

the column. Solutions were fed into the column (equipped with a tap at the bottom) from the upper part via a peristaltic pump (Watson Marlow 505 DI).

During the continuous studies conducted to produce the capacity curves with molasses hydrolysate, a 40-mL sample was collected from each sample. In the continuous system, the pH of the extraction solution was measured before contacting the compost, and again after leaving the column. Samples collected at the column outflow were filtered using a 0.45-µm membrane filter. After filtration, the pH values of the samples were adjusted to ≤2.0 by adding 1:1 HNO₃ to the filtrates in order to determine the heavy metal contents.

All experiments were replicated and only mean values were presented.

2. Results and discussion

2.1. Organic acids present in molasses hydrolysate

The types and quantities of organic acids detected in the molasses hydrolysate are shown in Table 2. Tartaric, oxalic, malonic, glutaric, formic, p-hydroxybenzoic, malic, 5-sulfosalicylic, fumaric, succinic, benzoic, acetic, lactic, propionic, and L-glutamic acids are important for the mobilization of heavy metals because of their metal chelating and complexing properties (Qin *et al.* 2004; Yang *et al.* 2006; Jing *et al.* 2007; Schwab *et al.* 2008). As can be seen from Table 2, molasses hydrolysate includes organic lactic, malic, citric and fumaric acids. Therefore, the leaching

activity of molasses hydrolysate is based on sugar acids rather than on nitric acid. Similarly, Bipp *et al.* (1998) reported that the leaching activity of molasses hydrolysate is largely determined by the concentration of sugar acids.

Table 2. Types and quantities of organic acids detected in molasses hydrolysate

Organic acid	Concentration (mg/L)
Lactic acid	3850
Malic acid	1120
Citric acid	90
Fumaric acid	20
Quinic acid	Not detected

2.2. Characterization of the compost samples used in the experiments

Results obtained from the characterization of the compost samples are listed in Table 3. Also, these samples' structures were examined by XRD, SEM and IR analysis. Moreover, the experiments of compliance with the plant (phytotoxicity experiments) have been conducted to determine the plant growing characteristic of the compost samples. The authors presented those results in their other studies (Ozbas 2008; Ozbas *et al.* 2011).

The heavy metal contents (Cu, Zn, Pb, Ni, Cd) of the compost samples (Table 3) used in the present study were compared with the maximum permissible limits given in German compost standards (Table 1). In this comparison, it was observed that the Cu, Ni, and Zn levels of the experimental samples would need to be reduced by 66%, 40% and 56%, respectively. Pb and Cd contents were within permissible limits (Pb < 200 mg/kg, Cd < 2 mg/kg).

2.3. Amounts of weakly-bound heavy metals

The study examined the amounts of weak-bound heavy metals within the compost, which could be easily dissolved and released into the environment (Bipp *et al.* 1998; Moutsatsou *et al.* 2006). The results are shown in Table 4.

The water-soluble fraction of heavy metals is the easiest part to extract. It is also the most active part that can be absorbed biologically and therefore has the highest toxicity potential (Núñez *et al.* 2007). As seen in Table 4, the amount of weak-bound heavy metals (except for Cd) within the metal composts did not exceed 3%; 30% of Cd was found to be composed of weak-bound metals.

2.4. Batch studies

2.4.1. The effects of contact time on extraction of heavy metals

Experiments were conducted using molasses hydrolysate to determine the effects of contact time on efficiency of heavy metal removal. The pH of molasses hydrolysate

Table 3. Characterization of compost samples (Ozbas 2008; Ozbas *et al.* 2011)

Parameter	Value	
	Before extraction	After extraction
pH	8±0.01	2±0.01
Moisture content (%)	15±1.1	NM
Bulk density (g/100 ml)	33.530±2.16	NM
C (%)	19.75±2.11	12.95±2.01
H (%)	2.485±0.002	2.14±0.001
N (%)	1.84±0.0012	1.29±0.0010
S (%)	-	-
C/N	10.73±1.03	10.04±1.03
Conductivity (µs/cm)	4.61±0.0014	6.31±0.0015
TKN (%)	1.34±0.0011	0.3±0.0001
Total P (mg/kg dry compost)	0.007±0.00001	0.0026±0.00001
PO ₄ -P (mg/l)	22.6±1.01	47±2.01
Ca (mg/kg dry compost)	0.088±0.0012	0.0181±0.0010
Na (mg/kg dry compost)	0.004±0.00021	0.0045±0.00021
Mg (mg/kg dry compost)	0.007±0.0003	0.0039±0.0003
K (mg/kg dry compost)	0.015±0.00014	0.0155±0.00014
TOC (mg/kg dry compost)	197012±2.44	85547±1.34
Cu (mg/kg dry compost)	440±1.01	40±0.01
Ni (mg/kg dry compost)	83.22±0.22	6±0.02
Zn (mg/kg dry compost)	903±2.01	5±0.01
Pb (mg/kg dry compost)	151.8±0.12	57.6±0.02
Cd (mg/kg dry compost)	0.695±0.01	-

±SD (Standard deviation)
NM: Not measured

Table 4. Results obtained at the end of extraction with distilled water (n = 3)

	Cu	Ni	Zn	Pb	Cd	pH, before extrac.	pH, after extrac.
Heavy metals removed from compost (mg/kg-dry compost)	13.2 ±0.01	0.332 ±0.03	10.15 ±1.1	3.26 ±0.01	0.195 ±0.01	5	7.45
Removal (%)	3 ±0.01	0.40 ±0.02	1.12 ±0.01	2.15 ±0.12	28.13 ±2.11		

±SD (standard deviation)

Table 5. Extraction efficiencies at different contact times using non-diluted molasses Hydrolysate (%) (mcompost = 5 g; Vsolution = 30 mL; pH ≤ 1, for each contact time n = 3)

Contact time (minutes)	Heavy metal removal (%)				
	Cu	Ni	Zn	Pb	Cd
5	26.75 ±2.12	32.34 ±2.12	46.25 ±2.13	31.25 ±1.14	43.00 ±2.33
10	27.68 ±2.11	32.88 ±2.00	48.75 ±2.42	33.13 ±2.12	43.22 ±2.23
15	31.69 ±1.58	36.50 ±2.44	51.25 ±1.22	33.75 ±2.16	51.62 ±1.12
30	56.25 ±1.22	67.06 ±2.00	78.75 ±2.56	54.31 ±1.32	72.81 ±1.25
45	38.90 ±2.44	38.93 ±2.44	64.38 ±2.01	39.72 ±2.43	88.38 ±3.06
60	35.50 ±2.13	36.25 ±2.24	57.13 ±1.54	34.28 ±2.12	51.11 ±1.11
180	35.35 ±2.34	36.25 ±2.23	55.00 ±1.34	33.23 ±2.14	48.50 ±2.50
240	33.39 ±2.24	40.56 ±1.16	51.25 ±1.12	32.50 ±2.13	48.12 ±2.12
1440	42.34 ±1.23	41.50 ±1.16	63.38 ±2.02	30.00 ±1.14	45.83 ±2.16

±SD (standard deviation)

was ≤ 1 before the extraction, and increased to around 2 after extraction at 5–1440 minutes contact times (Table 5). The reason for this increase may be that the pH of the compost was 8, and that the pH of the solution in contact with the compost increased as a result of the neutralization reactions. Experimental data are given in Table 5, which shows that the highest removal efficiencies for all heavy metals except Cd were obtained at 30 minutes contact time (56% Cu, 67% Ni, 79% Zn, 54% Pb). The highest removal efficiency for Cd was obtained at 45 minutes contact time (88%).

2.4.2. The effects of solid–liquid ratio on extraction of heavy metals

Contact times of 30 minutes and 1 hour were used to determine the effect of the solid–liquid ratio on removal efficiency. The efficiency of heavy metal removal at specific solid–liquid ratios is shown in Table 6 (t = 30 minutes) and Table 7 (t = 1 hour).

The results show that removal efficiencies improved as the amount of the molasses hydrolysate increased (solid–liquid ratio decreased). Accordingly, the extraction method reduced the heavy metal concentrations to within specified limits at 1 hour contact time and 1:12.5 g/mL solid–liquid ratio (66% Cu, 52% Ni, 57% Zn, 51% Pb and 77% Cd removal efficiencies. See Table 7).

Table 6. Results of specific solid–liquid ratios (t = 30 minutes; pH ≤ 1; 1:5–1:75 solid:liquid ratios, for each solid:liquid ratio n = 3)

Solid: liquid ratio (g/mL)	Heavy metal removal (%)					pH, after extrac.
	Cu	Ni	Zn	Pb	Cd	
1:5 (0.2)	38 ±2.62	51 ±1.52	41 ±1.53	25 ±2.11	72 ±1.20	2
1:6 (0.166)	50 ±1.41	53 ±1.54	57 ±1.51	48 ±1.57	73 ±1.25	2
1:10 (0.1)	51 ±1.53	53 ±1.54	64 ±1.82	54 ±1.34	95 ±1.16	2
1:12.5 (0.08)	53 ±1.54	67 ±2.00	67 ±2.00	58 ±1.64	98 ±2.54	2
1:25 (0.04)	53 ±1.54	73 ±2.65	78 ±2.56	61 ±1.16	99 ±0.03	1
1:50 (0.02)	55 ±1.62	80 ±3.06	84 ±3.14	62 ±1.15	99 ±0.03	1
1:75 (0.0133)	56 ±1.62	97 ±2.65	88 ±3.04	63 ±2.16	99 ±0.03	1

±SD (standard deviation)

Table 7. Results of specific solid–liquid ratios (t = 1 hour; pH ≤ 1; 1:2.5–1:75 solid:liquid ratios, for each solid:liquid ratio n = 3)

Solid: liquid ratio (g/mL)	Heavy metal removal (%)					pH after extract.
	Cu	Ni	Zn	Pb	Cd	
1:2.5 (0.4)	32 ±2.0	31.5 ±2.42	48 ±1.57	22 ±2.11	40 ±1.02	2
1:5 (0.2)	33 ±2.62	34 ±2.13	49 ±1.65	31 ±1.11	45 ±2.42	2
	55 ±1.54	36 ±2.44	53 ±1.24	34 ±2.12	51 ±1.12	
1:6 (0.166)	56 ±1.22	50 ±1.028	54 ±1.34	48 ±2.52	76 ±2.08	1
1:10 (0.1)	66 ±2.00	52 ±1.28	57 ±1.54	51 ±1.11	77 ±2.54	1
	72 ±2.15	78 ±2.56	89 ±3.06	52 ±1.28	85 ±3.06	
1:25 (0.04)	73 ±2.08	95 ±1.16	90 ±3.06	57 ±1.48	98 ±0.06	1
1:50 (0.02)	73 ±2.0	95 ±1.15	98 ±1.06	70 ±2.08	99 ±0.18	1
	77 ±2.08	99 ±1.16	99 ±1.06	99 ±2.08	99 ±0.18	

±SD (standard deviation)

2.5. Continuous system experiments conducted with molasses hydrolysate

Batch experiments showed that the highest efficiency of heavy metal removal from the compost was obtained at 1-hour contact time and 1:12.5 g/mL solid–liquid ratio.

Under these conditions, 100 mL (33.53 gr) compost was fed into the column and 420 mL molasses hydrolysate solution was passed through the column in 1 hour, at a flowrate of 1.66 mL/minute.

Following the extraction process, the molasses hydrolysate solution had a pH of 2. Under the conditions mentioned, the required removal efficiencies were not achieved for any of the metals other than Cd. Therefore, contact time was increased to 3 hours (0.55 mL/minute flowrate). The targeted removal efficiencies (66% for Cu, 40% for Ni and 56% for Zn) were exceeded using molasses hydrolysate at 1:12.5 g/mL liquid-solid ratio at 3 hours contact time and 0.55 mL/minute flowrate (91% Cu, 86% Ni, 99% Zn, 61% Pb and 99% Cd). The solution had a pH of 1 after the extraction. When the experiment was repeated with less solution (1:10 g/mL), the targeted heavy metal removal efficiencies could not be achieved. The pH of the solution was measured as 1 after the extraction. The results obtained from the column experiment with molasses hydrolysate are listed in Table 8. It was found that 3 hours contact time (0.55 mL/minute flowrate) and 1:12.5 g/mL solid-liquid ratio provided appropriate conditions for the removal of targeted heavy metals with the column method.

Studies were made at 1:12.5 g/mL solid-liquid ratio at 0.55 mL/minute flowrate in order to draw capacity curves. During the study, a 40-mL sample was collected from each test. Figure 2 shows the capacity curves obtained from the column for molasses hydrolysate.

From the capacity curves, it can be seen that molasses hydrolysate initially removed Cd, Zn and Ni, followed by Cu and Pb. Removal efficiency exceeded the 66% target for Cu (91%) when using 200 mL solution (Fig. 2). Zn removal efficiency of 100% (target 54%) was achieved with 120 mL solution. The highest removal efficiency for Cd ($\approx 100\%$) was obtained at 120 mL solution. The target removal efficiency for Ni (40%) was more than doubled (86%) with 120 mL solution (Fig. 2). Examining the change in the pH values during the column studies, it can be concluded that pH value (which was ≈ 1

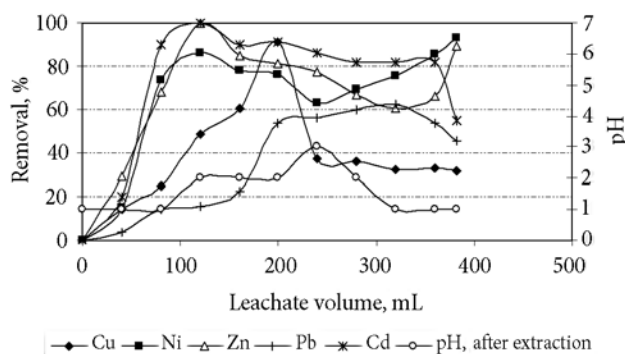


Fig. 2. Capacity curves obtained by using molasses hydrolysate

before extraction) increased as more solution was passed through the column. When 240 mL solution was passed through the column, the pH reached 3 and then decreased to 1 (Fig. 2).

The capacity experiments conducted with molasses hydrolysate indicated that when 200 mL solution was passed through the column (at 1:12.5 g/mL solid-liquid ratio), the removal efficiency exceeded the target levels (91% Cu, 76% Ni, 82% Zn, 54% Pb and 91% Cd).

XRD analysis showed that CdPbO_3 , Cu_2O (cuprite), ZnO , NiCO_3 (gaspeite), and NiO heavy metal compounds were present in the compost samples (Fig. 3).

In a study of composts, Zorpas *et al.* (2000) reported those results:

- the exchangeable fraction was affected by changes in the ionic composition of water;
- the carbonate fraction of the compost was affected by changes in pH value;
- the reducible part was composed of iron and manganese oxides;
- the organic part released metals dissolving under oxidation conditions;
- the residue part was generally composed of primary and secondary minerals;
- metals were attached to the crystallite structure of these minerals.

Peters (1999) reported that metal compounds in samples should be in an exchangeable form, carbonate, or reducible oxide form in order to ensure the removal of heavy metals from solid environments via extraction methods.

Table 8. Results of column experiments conducted with molasses hydrolysate (for each column condition $n = 3$)

Column conditions	Heavy metal removal (%)				
	Cu	Ni	Zn	Pb	Cd
$t = 1 \text{ h}$, $Q = 1.66 \text{ mL/minute}$, $1:12.5 \text{ g/mL}$ solid:liquid ratio	37 ± 2.44	33 ± 2.62	50 ± 1.24	44 ± 2.24	99 ± 0.028
$t = 3 \text{ h}$, $Q = 0.55 \text{ mL/minute}$, $1:10 \text{ g/mL}$ solid:liquid ratio	44 ± 1.57	42 ± 1.57	51 ± 1.24	64 ± 1.82	77 ± 2.54
$t = 3 \text{ h}$, $Q = 0.55 \text{ mL/minute}$, $1:12.5 \text{ g/mL}$ solid:liquid ratio	91 ± 2.5	86 ± 1.336	99 ± 0.29	61 ± 0.16	99 ± 0.18
$\pm \text{SD}$ (standard deviation)					

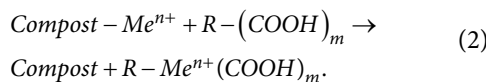
The XRD results for compost samples in the present study indicated that heavy metals were in the form of reducible oxides and carbonates, and were therefore suitable for the extraction method (Fig. 3). The XRD results for compost samples in the present study indicated that heavy

metals were in the form of reducible oxides and carbonates, and were therefore suitable for the extraction method (Fig. 3).

XRD indicated the following heavy metal compounds remaining in the compost samples following extraction: $\text{Cu}_9\cdot 2\text{Si}_{10}\text{O}_{29}\cdot 11\text{H}_2\text{O}$, Cd_2SiO_4 , $\text{NiSO}_4(\text{H}_2\text{O})_7$, PbZnSiO_4 , CuO , $\text{Na}_2\text{Ni}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$, NiO , PbSiO_3 (Fig. 4).

The XRD analysis of various solutions and the post-extraction compost samples showed that the metal compounds that were in the form of reducible oxides and carbonates at the beginning of the experiments (in the compost samples not subjected to extraction) were generally converted into silicium oxides. The metal forms containing SiO were defined as residue in the literature. These metal forms cannot be removed from material via extraction (Peters 1999). Moreover, it was revealed that Ni remaining in the compost after the extraction was converted into SO_4^{3-} (sulphate) compounds in all solutions used in the experiments.

As stated by Lee *et al.* (2005), if the organic acid solution has lower hydrogen ion concentration, this solution has a weaker capability for penetrating the solid particles. Citric acid can form complexes with heavy metal ions also. The formation of metal-citric acid complex helps metal solubilization from the solid materials (Lee *et al.* 2005). Heavy metal extraction by organic chelators is based on the affinity of the organic ligand for heavy metals (Gheju *et al.* 2011). As seen in Table 2, molasses hydrolysate contains organic acids such as lactic, mallic, and citric acids. Therefore, it can be said that it reacts with the metals in the compost as an organic acid. This situation was also reported by Bipp *et al.* (1998). Lactic, mallic, fumaric, and citric acids can act as polydentate organic ligands (chelators), because these acids contain carboxylic functional groups. Carboxylic groups might favor the chelating capacity of the organic acid. Metals that form stable complexes with the organic chelator are easily extracted from compost. Thus heavy metal extraction with organic acids takes place due to both their acidic and chelating character, according to Equation (2) (Gheju *et al.* 2011):



Organic chelating extraction is possible only for cationic heavy metals. Cationic heavy metals are electron acceptors (Lewis acids). Lewis acids may combine with a Lewis base (in this study organic chelator) to form a complex (Gheju *et al.* 2011). In this study, the extracted percentage follow the sequence $\text{Cu} \geq \text{Cd} > \text{Zn} > \text{Ni} > \text{Pb}$. The highest removal efficiencies were observed for Cu and Cd. Pb was the most difficult metals to remove from the compost. Similar results (high removal efficiency for Cu and low removal efficiency for Pb) were obtained by authors who have worked

with organic acids (Wuana *et al.* 2010; Zaleckas *et al.* 2012).

Scanning Electron Microscope (SEM) images of the composts were produced both before (Fig. 5) and after extraction (Fig. 6), and showed no important morphological difference between the composts in terms of surface appearance.

2.6. Cost estimation

A solid-liquid ratio of 1:12.5 g/mL (compost/molasses hydrolysate) was found to provide appropriate conditions for the removal of heavy metals using the column method. In Turkey, the known costs are US\$ 0.06 per kg for molasses and US\$ 0.13 per liter for HNO_3 . The cost of HNO_3 and molasses required for the extraction of metals from a tonne of compost is therefore US\$ 2300.

Conclusions

1. Within the batch experiments, an extraction experiment was initially conducted with distilled water to determine the weak-bound parts (which can easily dissolve and diffuse into a liquid environment) of the heavy metals

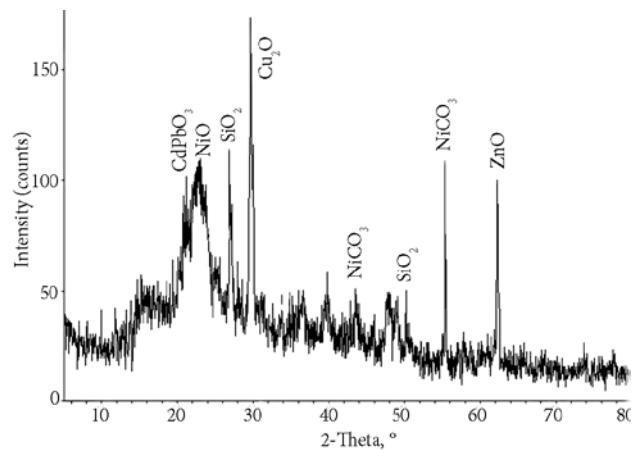


Fig. 3. XRD spectrum of compost sample before the extraction with molasses hydrolysate

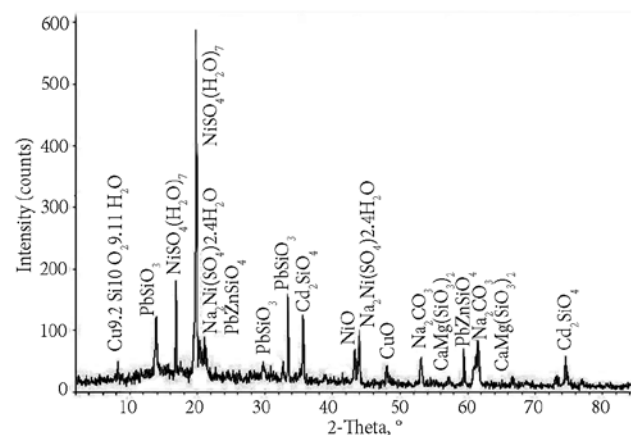


Fig. 4. XRD spectrum of compost sample after the extraction with molasses hydrolysate

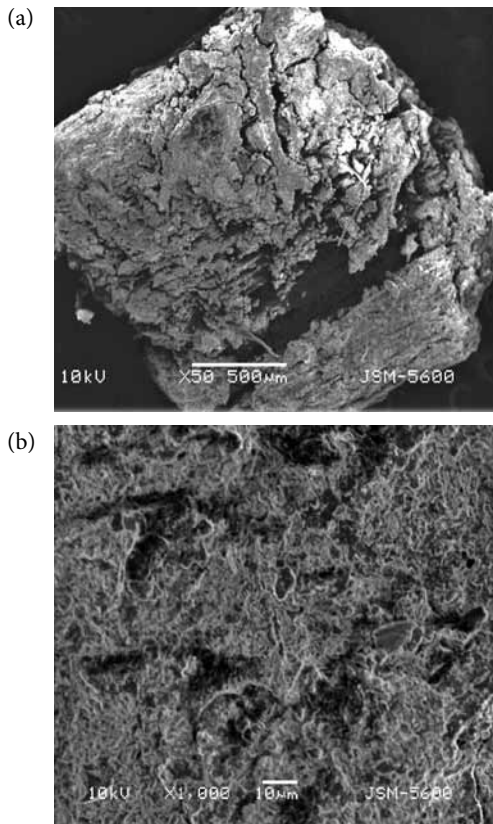


Fig. 5. SEM images of compost samples before extraction

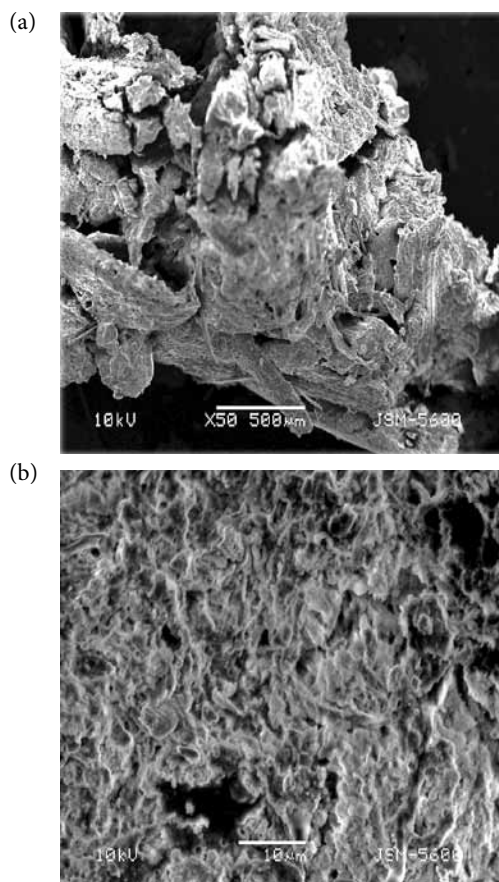


Fig. 6. SEM images of compost samples extracted with molasses hydrolysate

present in the compost samples. The amount of weak-bound heavy metals within the composts did not exceed 3%, except Cd, which was composed of 30% weak-bound metals.

2. The extraction experiments achieved good removal efficiencies. The batch experiments with 1:12.5 g/mL solid–liquid ratio at 1 hour contact time achieved the specified “heavy metal removal efficiency values” for compost standards (removal efficiencies of 66% Cu, 52% Ni, 57% Zn, 51% Pb and 77% Cd).

3. The column experiments used molasses hydrolysate at 1:12.5 g/mL solid–liquid ratio and 0.55 mL/minutes flow rate (33.58 g compost, 400 mL molasses hydrolysate, 3 hours contact time). Capacity curves indicated that molasses hydrolysate initially captured Cd, Zn and Ni, followed by Cu and Pb. The maximum removal efficiencies were 91% (Cu), 83% (Ni), 100% (Zn), 62% (Pb) and 100% (Cd). Target removal efficiencies were achieved for all heavy metals.

4. Comparison of the two methods showed that higher removal efficiencies were achieved for all metals in the column experiments than the batch experiments. Many previous studies in the literature (Mulligan, Wang 2006; Löser *et al.* 2007; Tiwari *et al.* 2007) suggest that the removal efficiencies of different heavy metals can vary between batch and column experiments. The reasons suggested including:

- a) the difference between the complex formation constants;
- b) competition between heavy metals and other metals present in the environment;
- c) the organic bond between the metals and the material to which they are attached.

5. XRD analysis revealed that the metal components remained generally in silicium oxide form in the compost after the extraction experiments. SEM images showed no significant morphological difference between the original (non-extracted) compost samples and the compost samples extracted with molasses hydrolysate.

6. In the removal of heavy metals from solid matter such as soil and sediment, complexing agents that do not produce toxic by-products at the end of decomposition should be used. Natural chelating agents such as sugar acids and hydroxycarboxylic acids can meet such a need. The use of molasses has no impact on the food chain for humans. In addition, as a waste by-product of sugar production, molasses is a low-cost and renewable bioresource. When oxidized under acidic conditions, molasses – which is rich in carbohydrates – produces a hydrolysate including natural chelating agents. Therefore, molasses hydrolysate may have environmental benefits in terms of preventing secondary pollution. The results indicate that it would be appropriate to use molasses hydrolysate for the removal of Cu, Ni, Zn, Pb and

Cd from compost.

7. Producing large quantities of highly acidic and heavy metal contaminated solution, and compost with low pH are the disadvantages of suggested technology. In addition, some parameters' concentrations of compost decreased after the extraction, for example; concentrations of C, TKN, total P.

8. In conclusion, preliminary tests using compost samples from ISTAC, Turkey, showed that molasses hydrolysate has great potential as an alternative natural chelating agent in the removal of heavy metals from compost. Further studies are planned on the reusability or purification of molasses hydrolysate with high metal content, obtained after extraction. Additionally, the compost had very low pH following treatment with molasses hydrolysate. Because of these reasons, further studies will investigate the addition of Ca(OH)₂ (lime) to the compost in order to neutralize the pH prior to use as a soil conditioner.

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