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# Effects of Natural Zeolites on Bioavailability and Leachability of Heavy Metals in the Composting Process of Biodegradable Wastes

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Additional information is available at the end of the chapter

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## Abstract

The bioavailability and leachability of heavy metals play an important role in the toxicity of heavy metals in the final compost followed by land application. This chapter examines the effects of natural zeolite on bioavailability of heavy metals (Zn, Cu, Mn, Fe, Ni, Pb, Cd, and Cr) in the form of water soluble and diethylenetriaminepentaacetic acid (DTPA) extractable. The toxicity characteristic leaching procedure (TCLP) test was performed to examine the leachability of heavy metals. Water solubility, DTPA extractability, leachability, and most bioavailable fractions were reduced during agitated pile composting (APC) and rotary drum composting (RDC) of water hyacinth with zeolite addition. The addition of the natural zeolite (clinoptilolite) during the composting process led to an increase in Na, Ca, and K concentrations and significantly reduced the water solubility and DTPA and TCLP extractability of heavy metals. The addition of an appropriate amount of natural zeolite during the composting process enhanced the organic matter degradation, thereby increasing the conversion into the most stabilized organic matter and reducing the bioavailability and leachability of heavy metals.

**Keywords:** Heavy metals, bioavailability, speciation, natural zeolite, composting, water hyacinth, sewage sludge

## 1. Introduction

Wastewater treatment plants are increasing worldwide due to urbanization and subsequent increases in sewage sludge production. The management of large quantities of sewage sludge generated from water treatment is a critical problem. Therefore, to overcome the undesirable impacts of the disposal of organic wastes such as water hyacinth and sewage sludge on the environment, it is essential to reduce the volume of these wastes and successfully reuse them as a source of organic matter and nutrients.

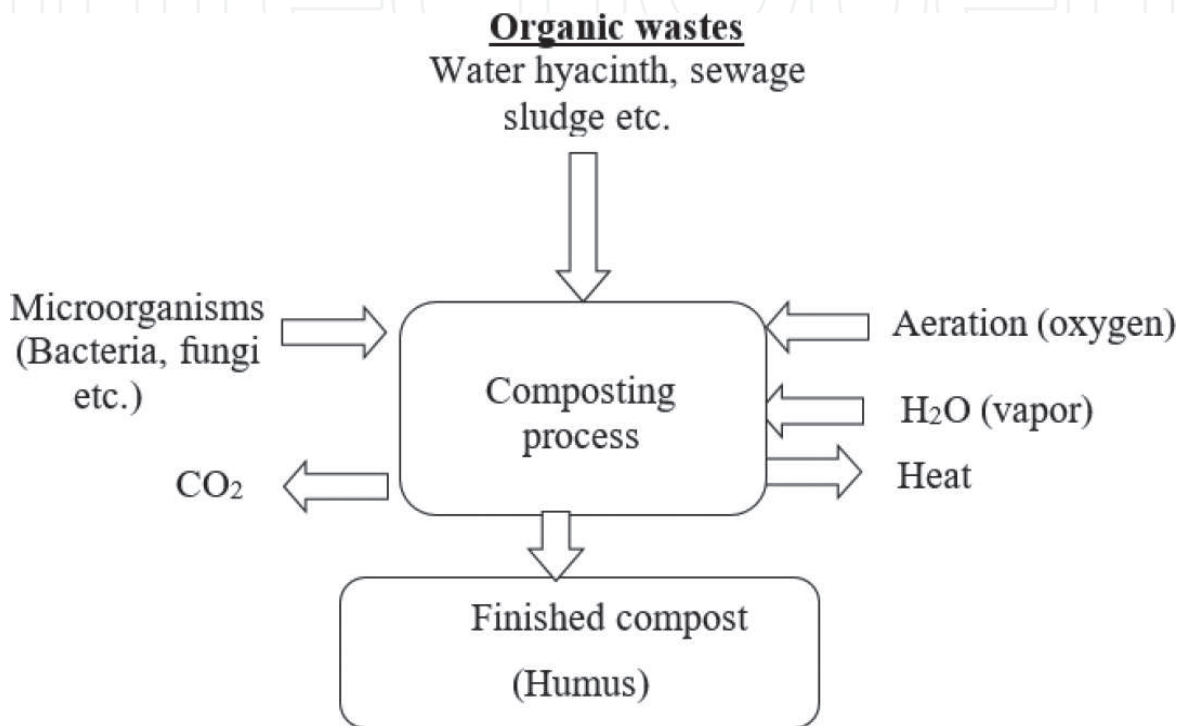
Composting is highly an economical method for the handling and final disposal of biodegradable wastes because it is helpful for material recycling and disposal [1, 2]. Water hyacinth (*Eichhornia crassipes*) is a commonly used plant for phytoremediation and constructed wetlands due to its high growth rate and great accumulation of inorganic and organic pollutants [1]. Therefore, the composts prepared from water hyacinth and sewage sludge may contain higher concentrations of heavy metals [3, 4]. The presence of nonbiodegradable and toxic heavy metals in the compost normally prevents its reuse in land applications. If compost with a high concentration of heavy metals is applied to soil, the accumulation of heavy metals in the plants and subsequently the food chain poses a risk to animal and human health [4, 5].

The total concentration of heavy metals measured from compost samples digested with strong acids can indicate the possibility of metal pollution, but cannot specify information related to the bioavailability of heavy metals [5, 6]. The bioavailability of any element specifies the fraction of the element's total content that is easily soluble in an aqueous system, and hence is freely available to plants and soil microorganisms. Water-soluble metals are biologically more dynamic and consequently have a significantly higher risk of contaminating the environment [4, 7]. The diethylenetriaminepentaacetic acid (DTPA)-extractable fraction of metals is a supplemental approach to determine the bioavailable fractions of heavy metals in the compost and soil applied with compost [8]. The toxicity characteristic leaching procedure (TCLP) is applied to evaluate the leaching potential of toxic heavy metals present in waste materials and compost. Heavy metals can be leached from compost and soil amended with compost, and hence pollute groundwater and surface water [9]. The leachability of a metal can be distinguished as the ratio of the quantity of the heavy metal leached from the TCLP test to its total concentration. The TCLP test is commonly used to assess the leachability of heavy metals in compost and whether the compost is hazardous or not [10].

Zeolites are natural hydrated aluminosilicate minerals with a three-dimensional framework structure tetrahedrally coordinated to  $\text{SiO}_4$  and  $\text{AlO}_4$  [1, 11, 12]. The aluminum ion occupies the center of the tetrahedron of four oxygen atoms. However, the isomorphous replacement of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  produces a negative charge in the lattice. The  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  are exchangeable for balancing the net negative charge and are commonly exchanged with particular cations (cations of Pb, Th, Cd, Zn, Mn, and  $\text{NH}_4$ ) in aqueous solutions [1, 13]. Natural zeolite has been applied broadly for decreasing the mobility and bioavailability of heavy metals in water hyacinth and sewage sludge composting because of its sorption and exchangeable properties for heavy metals [13, 14]. It can uptake heavy metals that are present in the composting mass in easily available fractions, and exchange with Na and K [15].

## 2. Composting process

Composting may be defined as a biological breakdown and stabilization of organic substrates, under conditions, which allowed progress of thermophilic temperatures due to heat produced during the degradation of waste biologically. The final product is stable and free from pathogens, and can therefore be applied for land application [16]. **Figure 1** shows the outline of composting process.



**Figure 1.** Outline of composting process.

### 2.1. Factors affecting the composting process

The carbon to nitrogen ratio (C/N ratio) can be a crucial factor in the composting process. To determine the optimal C/N ratio is important for optimizing the composting [17]. C/N ratios between 30 and 50 are favorable for the aerobic composting process. At lower C/N ratio, ammonia can be lost and biological activity is also affected, whereas at higher C/N ratio nitrogen may be a limiting nutrient [18]. The particle size of composting materials should be minimized to ensure efficient aeration and easy decomposition by the bacteria, fungi, and actinomycetes. Therefore, waste materials should be shredded into small pieces between 25 and 75 mm prior to composting [18]. Moisture content is another significant factor affecting the composting process, as moisture greatly disturbs the physical and chemical properties of waste biomass in sequence of the degradation of organic wastes [19]. The moisture content should be in the range between 50 and 60% in the composting process. The optimum moisture content is generally considered approximately 55% [18]. Aeration is an important factor for both microbial growth and gas emission in the composting process [20]. The aeration rate

strongly affects microbial activity, substrate degradation rate, and temperature variation in the composting processes of organic wastes [21]). Rasapoor et al. [21] reported that low and medium aeration rates increased the concentration of total nitrogen (TN), which drastically decreased the C/N ratio and lengthened the thermophilic phase. The artificial air supply is generally sustained at 1–2 m<sup>3</sup>/day/kg of volatile solids. A temperature increase is an indicator of microbial activities in the process of composting, and thus temperature change can be measured as a suitable parameter to regulate the status of composting processes [22, 23]. Temperature can affect the nature of microorganisms and the rate of decomposition of organic wastes [23]. Lin [24] reported that when the temperature was about 65°C, total coliforms dropped. López-Real and Foster [25] reported that the application of 55°C for only 3–4 days completely eliminated all pathogens. Stentiford [26] stated that the composting temperature must be maintained between 55 and 65°C for the inactivation of total pathogens. The pH is another important parameter for the composting process. The pH can be affected during the composting process due to the production of short-chain organic acids from the feedstock since the early phase of the composting process [27]. The short-chain organic acids and ammonia are maintained in a pH range of 4.9–8.3 [28]. Lower pH decreased microbial activity, thus hindering the growth of composting reaction [27]. However, high pH (>8.5) caused nitrogen loss in the form of ammonia [18].

### 3. Heavy metals in the composting process

Heavy metals (mg/kg)	Sewage sludge	Municipal solid waste	Water hyacinth
Zn	233	278 ± 22	297.8 ± 3.0
Cu	62	410 ± 26	103.3 ± 0.8
Mn	59.9	–	1105.0 ± 27.5
Fe	3768	–	13300 ± 30
Ni	23	44 ± 7	235.8 ± 1.8
Pb	101	325 ± 24	1537.0 ± 12.5
Cd	0	3.3 ± 0.4	83.8 ± 1.3
Cr	44.03	52 ± 9.2	279.0 ± 1.3

**Table 1.** Heavy metals concentration (mg/kg) in the final compost of different wastes.

The availability of metals in the final compost is the one of the major sources of soil pollution. Heavy metal pollution in the soil is mainly caused by Cu, Ni, Cd, Zn, Cr, and Pb [29, 30]. Some heavy metals (Fe, Zn, Ca, and Mg) have been reported as having a bioimportance to human being and plants. However, some others (As, Cd, Pb, and methylated forms of Hg) have been reported to have no known bioimportance in human biochemistry and physiology, and their consumption even at very low levels can be toxic to living organisms [31]. **Table 1** illustrates

the total concentration of metals (Zn, Cu, Mn, Fe, Ni, Pb, Cd, and Cr) in the final compost of different wastes. The total metal contents are increased in the final compost due to the reduction of organic matter and release of CO<sub>2</sub> during the mineralization process [4]. The total metal concentration found after strong acid digestion of final compost is useful as an overall pollution indicator but provides no useful information about the bioavailable fractions and chemical speciation of metals [5, 6].

#### 4. Heavy metals bioavailability

The bioavailability of heavy metals depends on different extractable fractions rather than on the total metal concentration. Therefore, the bioavailability of heavy metals provides more important evidence of metal toxicity [32]. Even if the heavy metals concentration in sewage sludge or compost is far below the regulation limit, the long-term land application of compost with background heavy metals concentration can increase the content and accumulation of the heavy metals in the soil [10].

Heavy metals in compost and soil amended with compost are commonly separated into two fractions: (i) inert fraction expected as the nontoxic fraction and (ii) the labile fraction, which is supposed to be possibly toxic [33]. To determine the availability of heavy metals, only the labile fraction has been considered bioavailable. The bioavailable fraction can diverge from one metal to another and from one receptor to another. The bioavailability of heavy metals for plants and microorganisms in soil/compost depends on the composition of the different components of soil/compost, such as carbonates, (oxy) metal hydroxides, organic matter, and silica [4, 33].

The heavy metal bioavailability has been considered one of the most critical problematic parameters for the agricultural application of compost [34]. The mobilization of pollutants depends on three factors: their mobility, concentration, and solubility in the compost/soil [33]. The solubility depends on the chemical composition of the leachate in equilibrium with the material; this chemical composition is influenced by the variation of pH that moves the redox equilibrium to predominant forms [33]. Heavy metals are generally present in their hydroxide forms with low solubility at a higher pH. However, at low pH, metals are available in their cationic forms, which are highly soluble and available for plant uptake. There are two types of complex in metal complexation reactions with soil particles: soluble and insoluble. At pH 9, the solubility of Cu is increased due to the formation of soluble complexes [4].

### 5. Effects of natural zeolite on the bioavailability of heavy metals during the composting process

#### 5.1. Experimental analysis

The details of waste materials are as follows: control (water hyacinth 90 kg + sawdust 15 kg + cattle manure 45 kg), zeolite 5% (control + zeolite 7.5 kg), zeolite 10% (control + zeolite 15 kg),

and zeolite 15% (control + zeolite 22.5 kg) during the agitated pile composting (APC) and rotary drum composting (RDC) of water hyacinth [12, 13]. Water-soluble heavy metals were determined after extraction of 2.5 g of sample with 50 ml of distilled water (sample:solution ratio = 1:20) at room temperature for 2 h in a shaker agitated at 100 rpm [4]. DTPA-extractable metals were attained by mechanically shaking 4 g of ground sample (screened through a 0.22-mm sieve) with 40 ml of 0.005 M DTPA, 0.01 M  $\text{CaCl}_2$ , and 0.1 M (triethanolamine) buffered to pH 7.3 at 100 rpm [4]. The standard TCLP method according to the US EPA Method 1311 [35] was applied to the solid samples in order to determine the potential leachability of the heavy metals. A 5 g sample of compost (size less than 9.5 mm) with 100 ml of acetic acid at pH  $4.93 \pm 0.05$  (pH was adjusted by 1 N NaOH) (sample: solution ratio =1:20) was taken in 125 ml reagent bottle and kept at room temperature for 18 h in a shaker at  $30 \pm 2$  rpm. An atomic absorption spectrometer (AAS) (Varian Spectra 55B) was used to analyze Zn, Cu, Mn, Fe, Ni, Pb, Cd, and Cr concentrations in different extracted solutions.

## 5.2. Total concentration of heavy metals

The total content of heavy metals attained after strong acid digestion is an indicator of compost contamination but cannot provide useful information on the bioavailability of heavy metals in the compost and compost-amended soil [36]. The total concentration of heavy metals was determined during the APC and RDC of water hyacinth with natural zeolite. The total concentration of metals was increased during the APC and RDC process of water hyacinth with natural zeolite (**Table 2**) due to the reduction of organic matter and release of  $\text{CO}_2$  during the mineralization processes [12, 13]. In the APC process, the total concentration of Zn, Cu, Mn, Pb, and Cd was increased highest in control as compared to the zeolite treatments; however, the total concentration of Fe, Cr, and Ni was increased highest in 5, 10, and 15% zeolite treatments, respectively [12]. In the RDC process, the total concentration of Cr, Cd, Zn, Mn, Fe, and Pb was increased highest in 5% zeolite treatment. The total concentration of Ni and Cu was increased highest in 10% zeolite treatment and control, respectively [13]. The total concentration of Zn and Ni was increased with increasing amount of natural zeolite addition in the APC process; however, the concentration of these metals was reduced with an increasing amount of natural zeolite in the RDC process of water hyacinth. In the RDC process, the percentage increase of metals was reduced with an increasing amount of natural zeolite due to the reduction in efficiency of the composting process. A higher addition of natural zeolite in the RDC process could hold the high amount of moisture that reduced the microbial activity [13]. Zorpas et al. [37] reported that the heavy metals contents were greatly decreased by approximately 100, 17, 31.7, 35.1, 24.0, 60.0, 56.7, and 47.9% for Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, respectively, in the process of composting of sewage sludge with zeolite. Zorpas et al. [38] concluded that the addition of 25% (w/w) zeolite in compost is adequate to eliminate around 12–60% of the heavy metals during sewage sludge composting. Sprynskyy et al. [14] reported that the addition of 9.09% clinoptilolite to the sludge reduced the total concentration of metals to around 11–51%. The increases in the concentration of heavy metals in the composting process were mainly because of the losses of mass [37].

Composting methods	Days	Total concentration of heavy metals							
		Control	NZ (5%)	NZ (10%)	NZ (15%)	NZ (0%)	NZ (5%)	NZ (10%)	NZ (15%)
		Zn (mg/kg)				Cu (mg/kg)			
APC	0	161.1	277.0	282.5	236.5	31.0	94.8	161.3	134.4
	30	297.8	297.5	306.5	289.7	103.3	128.4	186.4	149.1
RDC	0	147.3	213.9	218.9	240.0	70.5	80.1	88.1	108.8
	20	155.1	290.1	276.0	273.9	91.6	96.7	100.4	115.4
		Mn (mg/kg)				Fe (mg/kg)			
APC	0	573	499	453.3	483	7.92	16.0	21.4	18.5
	30	1105	652.5	780.1	685.5	13.3	30.2	29.0	26.3
RDC	0	538	475	492	531	11.0	19.90	21.1	21.1
	20	668	652	588	620	14.1	31.30	31.5	24.0
		Ni (mg/kg)				Pb (mg/kg)			
APC	0	187.3	225.7	192.0	184.0	872.5	830.0	842.5	832.5
	30	235.8	277.2	243.8	277.5	1537.5	1292.5	1097.5	1004.5
RDC	0	239.5	222.3	244.0	267.3	958	977.0	1037	1032.0
	20	243.5	256.3	285.0	300.7	1111	1209.0	1268	1100.0
		Cd (mg/kg)				Cr (mg/kg)			
APC	0	43.8	56.8	53.3	56.0	257.0	73.0	75.8	87.8
	30	83.8	81.8	68.5	78.5	279.3	115.0	124.3	116.8
RDC	0	51.5	72.4	75.7	75.8	59.3	60.5	76.2	93.9
	20	60.7	91.2	93.9	78.7	76.3	83.5	91.2	105.1

Note: NZ-natural zeolite; control: water hyacinth (90 kg), sawdust (15 kg), cattle manure (45 kg); zeolite 5% (control + zeolite 7.5 kg); zeolite 10% (control + zeolite 15 kg), and zeolite 15% (control + zeolite 22.5 kg).

**Table 2.** Effects of natural zeolite on concentration of total heavy metals during the water hyacinth composting.

### 5.3. Water solubility of heavy metals

The water-soluble fraction of heavy metals in the compost was lower than their total concentration, which is the most toxic fraction in the final compost [39]. **Table 3** shows the changes in the water solubility of the heavy metals during the APC and RDC processes. The water solubility of the metals (percentage of total metal) was decreased by approximately 80.0% for Zn, 76.7% for Cu, 83.1% for Mn, and 100% for Cr in the APC process [40]. However, during the RDC process of water hyacinth, the water-soluble fraction of the heavy metals was decreased (percentage of total metal) by approximately 71.3% for Zn, 79.1% for Cu, 78.3% for Mn, 76.8% for Fe, and 89.4% for Cr. The highest reduction of water-soluble Zn, Cu, Mn, and



Composting methods	Days	Water-soluble metals concentration							
		Control	Zeolite 5%	Zeolite 10%	Zeolite 15%	Control	Zeolite 5%	Zeolite 10%	Zeolite 15%
		Zn (mg/kg)				Cu (mg/kg)			
APC	0	3.38	3.59	1.49	1.42	1.12	1.73	1.77	1.60
	30	1.25	0.87	0.46	0.59	0.92	0.55	0.49	0.97
RDC	0	2.28	2.542	1.57	1.368	2.28	1.703	1.825	2.512
	20	1.264	0.991	0.725	0.9125	1.09	0.49	0.435	1.691
		Mn (mg/kg)				Fe (mg/kg)			
APC	0	8.50	10.89	3.80	2.90	16.14	15.28	9.11	8.89
	30	12.68	3.65	1.11	1.29	75.08	9.92	3.65	6.59
RDC	0	9.99	3.29	3.34	1.965	19.32	21.55	31.09	47.79
	20	3.36	0.98	0.965	1.25	20.28	10.715	10.8	37.57
		Cr (mg/kg)				Ni, Pb and Cd (mg/kg)			
APC	0	2.07	0.43	0.62	0.73	ND	ND	ND	ND
	30	0.54	ND	ND	0.38	ND	ND	ND	ND
RDC	0	1.69	1.605	1.725	0.76	ND	ND	ND	ND
	20	0.4	0.235	0.3325	0.64	ND	ND	ND	ND

Note: ND-not detected; control: water hyacinth (90 kg), sawdust (15 kg), cattle manure (45 kg); zeolite 5% (control + zeolite 7.5 kg); zeolite 10% (control + zeolite 15 kg), and zeolite 15% (control + zeolite 22.5 kg).

**Table 3.** Effects of natural zeolite on water solubility of heavy metals during water hyacinth composting.

Cr was observed in 5% zeolite treatment, whereas a higher reduction of Fe was observed in 10% zeolite treatment [41]. The water-soluble fractions of Ni, Pb, and Cd were not found in the APC and RDC processes. The addition of zeolite significantly reduced the water-soluble Cu, Mn, Fe, and Cr contents during the composting water hyacinth composting process. In the APC process of water hyacinth with natural zeolite, the highest reduction in water-soluble concentration of Zn was found in control. However, the highest reduction in water-soluble fraction of Zn, Cu, Mn, Fe, and Cr was observed in 10% zeolite treatment [40]. In the RDC process, the highest reduction in water-soluble fraction of Zn, Cu, Mn, and Cr was observed in 5% zeolite treatment; however, the highest reduction in Fe was observed in 10% zeolite treatment. The poor reduction in water solubility of metals was observed in 15% zeolite treatment likely due to the higher addition of zeolite, which could hinder the composting process by absorbing water content leading to the clumping of compost biomass [41]. Water-soluble fractions of Ni, Pb and Cd were not found in all zeolite treatments during the APC and RDC processes of water hyacinth [40, 41]. The highest reduction in water solubility of metals was achieved in 10% zeolite treatment during the APC process; whereas in the RDC process

of water hyacinth the highest reduction was observed in 5% zeolite treatment. Stylianou et al. [42] reported that during the sewage sludge composting process, decomposed organic matter plays an important role in releasing water-soluble heavy metals, which increases the availability of their exchangeable forms that can uptake by natural zeolite through ion exchange process.

#### 5.4. DTPA extractability

It has been considered that DTPA is a chelating agent and generally used for the analysis of metals availability for plants in the soil amended with heavy-metal-contaminated compost or sewage sludge at regular or even higher concentration [43]. In the case of added zeolite, the amount of DTPA-extractable Pb, Cu, and Zn significantly decreased in the composting because of the higher ion exchange capacity [10]. The DTPA extraction efficiency of the metals was decreased by about 56.6% for Zn, 85.4% for Cu, 81.7% for Mn, 78.5% for Ni, and 75.5% for Cr in the APC of water hyacinth with natural zeolite [40]. However, the DTPA extraction efficiency of metals was decreased by about 58.6% for Zn, 81.1% for Cu, 48% for Mn, 52.1% for Fe, 93.2% for Ni, and 77% for Cr during the RDC process of water hyacinth with natural zeolite [41]. A decrease in DTPA-extractable heavy metals were more found in the RDC process than in the APC process (**Figure 2**). DTPA-extractable concentrations of Pb and Cd were not observed during the APC and RDC processes of water hyacinth with zeolite. In the APC process of water hyacinth, the highest reduction in DTPA extractability of Cu and Mn was observed in control; however, Zn, Cu, Ni, Fe, and Cr were reduced in 5 and 10% zeolite treatments in comparison to the control [40]. The DTPA extraction of Zn, Mn, and Fe was increased in control during the RDC process. However, in the zeolite-added compost, the DTPA extractability of Zn, Cu, Mn, Fe, and Cr was reduced significantly. The reduction in DTPA-extractable heavy metal can be attributed as ion-exchange process where metal cations are mainly exchanged with Na, K, and Ca. DTPA-extractable fraction of Pb and Cd were not found in all zeolite treatments during the APC and RDC processes of water hyacinth [40, 41]. A higher reduction in DTPA extraction of Ni was observed in 10% zeolite treatment followed by 5 and 15% zeolite treatments, and control in the APC process of water hyacinth [40]. A decrease in DTPA-extractable metals in the final compost of water hyacinth with zeolite addition can be attributed to the ligneous bulking agent (sawdust) promoting both the formation and complexation ability of humic acid, resulting reduction in bioavailability of heavy metals [41]. The reduction of DTPA extractability of Zn, Cu, Ni, and Cr was also observed by Chiang et al. [10] during the sewage sludge composting with natural zeolite. In the control test, the concentrations of all tested DTPA metals were higher than those in the zeolite treatments. In matured compost product from the control test, the DTPA solution extracted about 65.0, 18.7, 63.2, and 39.5% of the total Zn, Ni, Cu, and Pb, respectively [10]. DTPA-extractable heavy metal reduction is attributed to the mechanism of ion-exchange processes where metal cations are mainly exchanged with Na, K, and Ca during the composting process [11, 15]. Furthermore, the reduction in DTPA-extractable metals at the end of the composting process due to the transformation of organic matter leads to the formation of metal-humus complexes, which make the metals insoluble and thus less easily extractable [44].

Xiong et al. [45] concluded that ligneous bulking agents, especially wood sawdust, promote both the formation and complexation ability of humic acid, which can reduce the bioavailability of heavy metals, thus reducing the pollution risk of heavy metals in the agricultural application of compost.

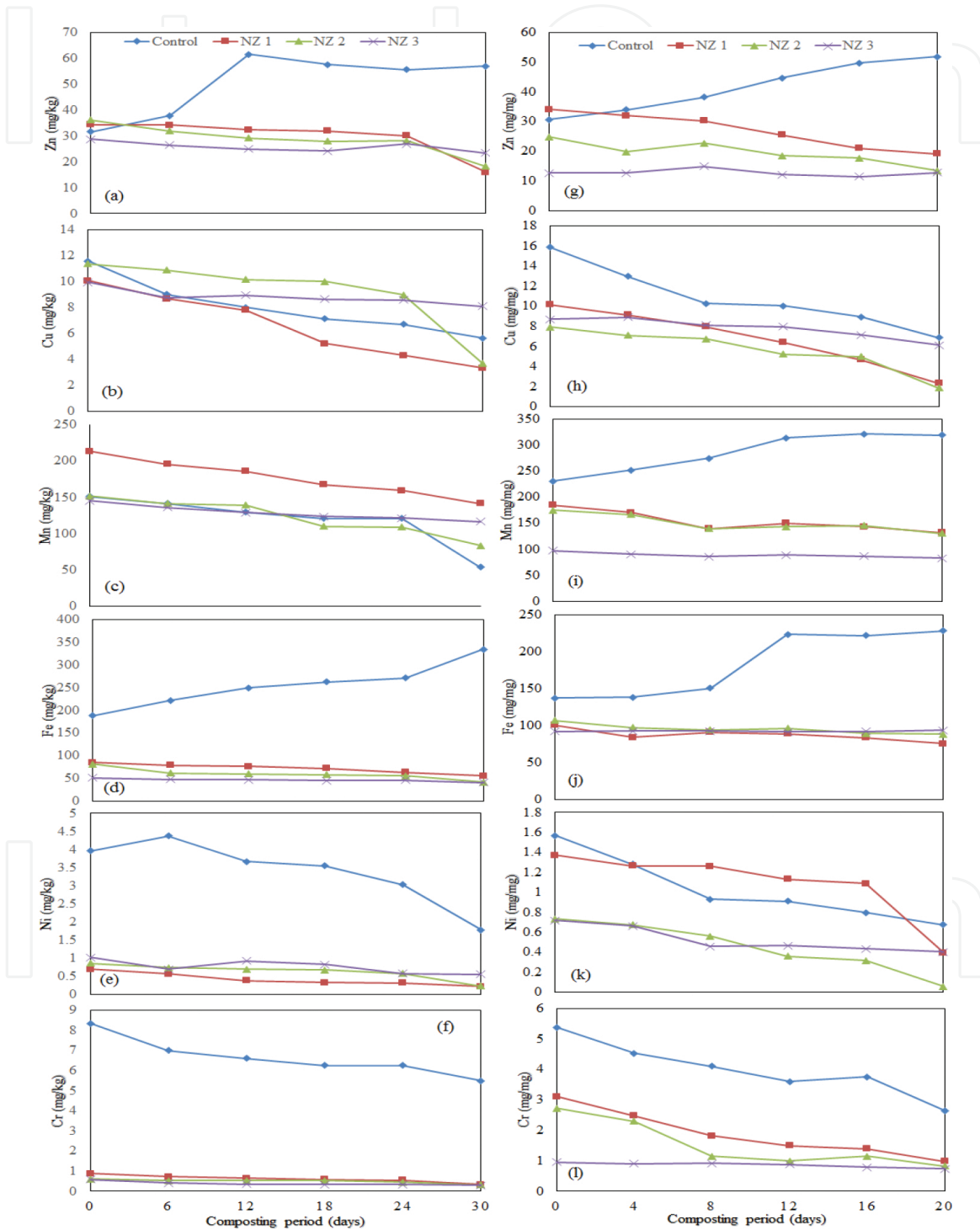


Figure 2. Changes of DTPA-extractable concentration of heavy metals during the agitated pile (a-f) and rotary drum (g-l) composting of water hyacinth (NZ-natural zeolite).

### 5.5. Leachability of heavy metals

Contaminants	Threshold (mg/kg)
Arsenic	100
Barium	2000
Cadmium	20
Chromium	100
Lead	100
Mercury	4
Selenium	20
Silver	100

Note: Only applicable to samples that are 100% solid.

**Table 4.** Threshold limits for leachable heavy metals (mg/kg).

The TCLP test is intended to define the mobility of organic and inorganic constituents that are available in liquid and solid wastes [35]. TCLP is used to evaluate the suitability of compost for land application or whether it should be considered a hazardous waste. The procedure is planned to check the leaching possibility of metals in the compost material for agricultural application. The controlling limits for the leached fraction of toxic heavy metals are based on avoiding groundwater pollution through metals, which can create a risk to human health and environment [30]. According to the US EPA [35], the threshold limit for heavy metals contamination in compost is given in **Table 4**. The TCLP-extractable heavy metal concentrations (mg/kg) were in the range of 0.82–3.0, 1.2–3.7, and 12.7–17.9 for Cd, Cr, and Pb, respectively, in the mature compost, confirming that water hyacinth compost was not hazardous to the soil application.

The TCLP-extractable heavy metals were in compliance with the EPA regulatory thresholds limit. **Table 5** shows the variation of leachable heavy metals (Zn, Cu, Mn, Fe, Ni, Pb, Cd, and Cr) during the APC and RDC processes of water hyacinth with natural zeolite. In the APC process of water hyacinth, the TCLP concentration of metals were reduced approximately 61.4% of the total Zn, 72.0% of Cu, 51.4% of Mn, 73.9% of Fe, 64.6% of Ni, 53.3% of Pb, 82.8% of Cd, and 59.7% of Cr in zeolite treatments [40]. In the RDC process of water hyacinth, the leachability of heavy metals was reduced (percentage of total metal) approximately 67.4% for Zn, 52.7% for Mn, 67.0% for Fe, 67.9% for Ni, 71.0% for Cd, and 72.6% for Cr in zeolite treatments. However, the highest reduction in leachability of Cu (73.2%) and Pb (72.4%) was found in the control during the RDC process of water hyacinth [41]. A higher reduction in leachability of metals was observed in zeolite treatments when compared to control in both APC and RDC of water hyacinth [40, 41]. In the RDC process, the highest reduction in leachability of Zn, Mn, Fe, and Ni was observed in 5% zeolite treatment, whereas the reduction of Cd and Cr was observed in 10% zeolite treatment. In the water hyacinth composting with

natural zeolite, the pH of the initial feed mixture was enhanced in comparison to control, which reduced the leachability of heavy metals [40, 41, 46]. Furthermore, the reduction in the leachable concentration of heavy metals might be due to humic substances formed at the end of composting process, which had a capacity to form a complex with metals [1, 47]. The reduction in the leachability of Cu and Pb was not significant in any of the zeolite treatments in comparison to control. Increasing the amount of zeolite addition did not reduce the leachability of metals. The reduction in the leachability of heavy metals was much less in 3% zeolite treatment in comparison to control and 1 and 2% zeolite treatments during the RDC process.

Composting methods	Days	Leaching concentration of heavy metals							
		Control	Zeolite (5%)	Zeolite (10%)	Zeolite (15%)	Control	Zeolite (5%)	Zeolite (10%)	Zeolite (15%)
		Zn (mg/kg)				Cu (mg/kg)			
APC	0	30.39	57.53	42.53	37.22	3.47	7.60	12.0	8.0
	30	28.62	23.855	18.86	25.99	3.50	2.88	4.38	3.58
RDC	0	42.22	50.08	38.15	24.77	6.60	13.18	7.31	6.13
	20	21.27	22.20	21.28	20.99	2.30	7.40	3.60	4.45
		Mn (mg/kg)				Fe (mg/kg)			
APC	0	155.10	283.40	259.50	254.0	141.50	53.45	31.02	27.87
	30	233.80	247.90	216.90	210.55	136.70	26.32	16.44	14.99
RDC	0	205.10	184.10	180.40	140.20	121.70	48.30	27.10	32.80
	20	175.50	119.60	130.0	133.90	63.30	27.40	23.40	24.0
		Ni (mg/kg)				Pb (mg/kg)			
APC	0	10.90	17.60	13.42	9.93	36.50	38.50	37.0	36.79
	30	9.50	7.56	7.60	6.84	32.0	280.0	27.0	29.0
RDC	0	8.60	7.69	5.50	5.33	53.20	26.05	22.05	21.40
	20	3.60	2.80	2.10	3.29	17.0	12.87	12.65	17.80
		Cd (mg/kg)				Cr (mg/kg)			
APC	0	1.50	1.98	1.26	1.35	4.62	6.90	5.70	4.30
	30	1.20	0.49	0.43	0.66	3.82	4.38	4.08	2.78
RDC	0	1.86	1.75	2.95	4.55	6.10	2.53	4.30	2.55
	20	1.02	0.82	1.22	3.01	3.65	1.18	1.41	1.65

Note: Control: water hyacinth (90 kg), sawdust (15 kg), cattle manure (45 kg); zeolite 5% (control + zeolite 7.5 kg); zeolite 10% (control + zeolite 15 kg), and zeolite 15% (control + zeolite 22.5 kg).

**Table 5.** Effects of natural zeolite on leaching concentration of heavy metals during agitated pile and rotary drum composting of water hyacinth.

## 6. Conclusions

The addition of natural zeolite (clinoptilolite) during the composting process led to significantly reduce the water solubility, and DTPA and TCLP extractability of heavy metals. The TCLP test proved that the concentrations of all selected heavy metals in control and the concentrations of the heavy metals released from the zeolite-treated compost were below the threshold limits. The highest reduction in the bioavailability and leachability of the heavy metals was observed in zeolite treatments 5 and 10% during the APC and RDC processes of water hyacinth. The addition of natural zeolite at suitable concentration successfully reduced the bioavailable and leachable fraction of heavy metals during the composting process of sewage sludge and water hyacinth. Natural zeolite takes up a significant amount of heavy metals during the composting of organic wastes. Addition of the natural zeolite during the composting process led to the increased Na, Ca, and K concentrations and effectively reduced water solubility and DTPA and TCLP extractability of heavy metals. The optimum percentage of zeolite addition in composting mass could fasten degradation of organic biomass; therefore, it decreased the bioavailability and leachability of the heavy metals during the composting process.

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## References

- [1] Villasenor J, Rodriguez L, Fernandez FJ. Composting domestic sewage sludge with natural zeolites in a rotary drum reactor. *Bioresour. Technol.* 2011; 102(2):1447–1454. doi:10.1016/j.biortech.2010.09.085
- [2] Singh J, Kalamdhad AS. Concentration and speciation of heavy metals during water hyacinth composting. *Bioresour. Technol.* 2012; 124:169–179. <http://dx.doi.org/10.1016/j.biortech.2012.08.043>
- [3] Gupta R, Mutiyar PK, Rawat NK, Saini MS, Garg VK. Development of a water hyacinth based vermireactor using an epigeic earthworm *Eisenia fetida*. *Bioresour. Technol.* 2007; 98:2605–2610. doi:10.1016/j.biortech.2006.09.007
- [4] Singh J, Kalamdhad AS. Bioavailability and leachability of heavy metals during water hyacinth composting. *Chem. Spec. Bioavailab.* 2013a; 25(1):1–14. doi:10.3184/095422913X13584520294651
- [5] Walter I, Martinez F, Cala V. Heavy metal speciation and phytotoxic effects of three representative sewage sludge for agricultural uses. *Environ. Pollut.* 2006; 139:507–514. doi:10.1016/j.envpol.2005.05.020
- [6] Venkateswaran P, Vellaichamy S, Palanivelu K. Speciation of heavy metals in electroplating industry sludge and wastewater residue using inductively coupled plasma. *Int. J. Environ. Sci. Technol.* 2007;4(4):497–504.
- [7] Hsu JH, Lo SL. Effects of composting on characterization and leaching of copper, manganese, and zinc from swine manure. *Environ. Pollut.* 2001; 114:119–127.
- [8] Fuentes A, Llorens M, Saez J, Aguilar MI, Marin ABP, Ortuno JF, Meseguer VF. Ecotoxicity, phytotoxicity and extractability of heavy metals from different stabilised sewage sludges. *Environ. Pollut.* 2006; 143:355–360. doi:10.1016/j.envpol.2005.11.035
- [9] Singh J, Kalamdhad AS. Assessment of bioavailability and leachability of heavy metals during rotary drum composting of green waste (Water hyacinth). *Ecol. Eng.* 2013; 52:59–69. <http://dx.doi.org/10.1016/j.ecoleng.2012.12.090>
- [10] Chiang KY, Huang HJ, Chang CN. Enhancement of heavy metal stabilization by different amendments during sewage sludge composting process. *J. Environ. Eng. Manage.* 2007; 17(4):249–256.
- [11] Yu Y, Shapter JG, Popelka-Filcoff R, Bennett JW, Ellis AV. Copper removal using bio-inspired polydopamine coated natural zeolites, *J. Hazard. Mater.* 2014; 273: 174–182.
- [12] Singh J, Kalamdhad AS. Effects of natural zeolite on speciation of heavy metals during agitated pile composting of water hyacinth. *Int. J. Recycl. Org. Waste Agric.* 2014; 3(55): 1–17.

- [13] Singh J, Kalamdhad AS. Influences of natural zeolite on speciation of heavy metals during rotary drum composting of green waste. *Chem. Spec. Bioavailab.* 2014;26(2):65–75. doi: 10.3184/095422914X13953177945668
- [14] Sprynskyy M, Kosobucki P, Kowalkowski T, Buszewsk B. Influence of clinoptilolite rock on chemical speciation of selected heavy metals in sewage sludge. *J. Hazard. Mater.* 2007; 149:310–316. doi:10.1016/j.jhazmat.2007.04.001
- [15] Zorpas AA, Constantinides T, Vlyssides AG, Haralambous I, Loizidou M. Heavy metal uptake by natural zeolite and metals partitioning in sewage sludge compost. *Bioresour. Technol.* 2000; 72:113–119.
- [16] Haug RT. *The Practical Handbook of Composting Engineering*. Boca Raton: Lewis publishers; 1993. 1 p.
- [17] Adhikari BK, Barrington S, Martinez J, King S. Characterization of food waste and bulking agent for composting. *Waste Manage.* 2008; 28:795–804. doi:10.1016/j.wasman.2007.08.018
- [18] Peavy HS, Rowe DR, Tchobanoglous G. *Environmental Engineering*. New York: McGraw-Hill; 1985. 661 pp.
- [19] Iqbal KM, Shafiq T, Ahmed K. Characterization of bulking agents and its effects on physical properties of compost. *Bioresour. Technol.* 2010; 101:1913–1919. doi:10.1016/j.biortech.2009.10.030
- [20] Guo R, Li GX, Jiang T, Schuchardt F, Chen TB, Zhao, YQ, Shen YJ. Effect of aeration rate, C/N ratio and moisture content on the stability and maturity of compost. *Biore-sour. Technol.* 2012; 112:171–178. <http://dx.doi.org/10.1016/j.biortech.2012.02.099>
- [21] Rasapoor M, Nasrabadi T, Kamali M, Hoveidi H. The effects of aeration rate on generated compost quality, using aerated static pile method. *Waste Manage.* 2009; 29:570–573.
- [22] Tang Z, Yu GH, Liu DY, Xu DB, Shen QR. Different analysis techniques for fluorescence excitation-emission matrix spectroscopy to assess compost maturity. *Chemosphere* 2011; 82:1202–1208.
- [23] Li Z, Lu H, Ren L, He L. Experimental and modelling approaches for food waste composting: a review. *Chemosphere* 2013; 93:1247–1257.
- [24] Lin C. A negative-pressure aeration system for composting food wastes. *Bioresour. Technol.* 2008; 99:7651–7656.
- [25] López-Real J, Foster M. Plant pathogen survival during composting of agricultural waste. In: Gasser JKR, editor. *Composting of Agricultural Wastes*. London: Elsevier Applied Science; 1985. pp. 291–299.



- [26] Stentiford EI. Composting control: principles and practice. In: de Bertoldi M, Sequi P, Lemmes B, Papi T, editors. *The Science of Composting, Part 1*. Glasgow: Blackie; 1996. pp. 56–59.
- [27] Beck-Friis B, Smårs S, Jönsson H, Kirchmann H. Gaseous emissions of carbon dioxide, ammonia and nitrous oxide from organic household waste in a compost reactor under different temperature regimes. *J. Agric. Eng. Res.* 2001; 78:423–430.
- [28] Conghos MM, Aguirre ME, Santamaria RM. Biodegradation of sunflower hulls with different nitrogen sources under mesophilic and thermophilic incubations. *Biol. Fertil. Soils* 2003; 38:282–287.
- [29] Karaca A, Cetin SC, Turgay OC, Kizilkaya R. Effects of heavy metals on soil enzyme activities. In: Sherameti I, Varma A, editors. *Soil Heavy Metals, Soil Biology*, vol. 19. Heidelberg: Springer; 2010, pp. 237–265.
- [30] Chiroma TM, Ebewele RO, Hymore FK. Levels of heavy metals (Cu, Zn, Pb, Fe and Cr) in Bushgreen and Roselle irrigated with treated and untreated urban sewage water. *Int. Res. J. Environ. Sci.* 2012; 1(4):50–55.
- [31] Duruibe JO, Ogwuegbu MOC, Egwurugwu JN. Heavy metal pollution and human biotoxic effects. *Int. J. Phys. Sci.* 2007; 2(5):112–118.
- [32] Nair A, Juwarkar AA, Devotta S. Study of speciation of metals in an industrial sludge and evaluation of metal chelators for their removal. *J. Hazard. Mater.* 2008; 152:545–553.
- [33] Yobouet YA, Adouby K, Trokourey A, Yao B. Cadmium, copper, lead and zinc speciation in contaminated soils. *Int. J. Eng. Sci. Technol.* 2010; 2(5):802–812.
- [34] Gupta AK, Sinha S. Phytoextraction capacity of the plants growing on tannery sludge dumping sites. *Bioresour. Technol.* 2007; 98:1788–1794.
- [35] US Environmental Protection Agency Method 1311—toxicity characteristic leaching procedure (TCLP), 1992. 35 pp.
- [36] Cai QY, Mo CH, Wu QT, Zeng QY, Katsoyiannis A. Concentration and speciation of heavy metals in six different sewage sludge-composts. *J. Hazard. Mater.* 2007; 147:1063–1072.
- [37] Zorpas AA, Vassilis I, Loizidou M. Heavy metals fractionation before, during and after composting of sewage sludge with natural zeolite. *Waste Manage.* 2008; 28:2054–2060.
- [38] Zorpas AA, Vassilis I, Loizidou M, Grigoropoulou H. Particle size effects on uptake of heavy metals from sewage sludge compost using natural zeolite clinoptilolite. *J. Colloid Interf. Sci.* 2002; 250:1–4.
- [39] Fang M, Wong JWC. Effects of lime amendment on availability of heavy metals and maturation in sewage sludge composting. *Environ. Pollut.* 1999; 106:83–89.

- [40] Singh J, Prasad R, Kalamdhad AS. Effect of natural zeolite on bioavailability and leachability of heavy metals during rotary drum composting of green waste. *Res. J. Chem. Environ.* 2013; 17: 26–34.
- [41] Singh J, Kalamdhad AS. Uptake of heavy metals by natural zeolite during agitated pile composting of water hyacinth composting. *Int. J. Environ. Sci.* 2014; 5(1): 1–15.
- [42] Stylianou MA, Inglezakis VJ, Moustakas KG, Loizidou MD. Improvement of the quality of sewage sludge compost by adding natural clinoptilolite. *Desalination* 2008; 224:240–249.
- [43] Guan TX, He HB, Zhang XD, Bai Z. Cu fractions, mobility and bioavailability in soil-wheat system after Cu-enriched livestock manure applications. *Chemosphere* 2011; 82:215–222.
- [44] Garcia C, Moreno JL, Hernfindez T, Costa F. Effect of composting on sewage sludges contaminated with heavy metals. *Bioresour. Technol.* 1995; 53:13–19.
- [45] Xiong X, Yan-xia L, Ming Y, Feng-song Z, Wei L. Increase in complexation ability of humic acids with the addition of ligneous bulking agents during sewage sludge composting. *Bioresour. Technol.* 2010; 101:9650–9653.
- [46] Su DC, Wong JWC. Chemical speciation and phytoavailability of Zn, Cu, Ni and Cd in soil amended with fly ash-stabilized sewage sludge. *Environ. Int.* 2003; 29:895–900.
- [47] Wong JWC, Fang M. Effects of lime addition on sewage sludge composting process. *Water Res.* 2000; 34(15):3691–3698.