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First

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Use of organic acids in the composting of municipal solid waste: a pilot-scale study

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Compost made from municipal solid waste (MSW) contains heavy metals that can interfere with the use of organic amendment in soil. In order to find effective ways to reduce the potential risk of heavy metals, we have investigated a novel approach by use of organic acid during MSW composting. Citric and oxalic acid dissolutions $(0.25 \text{ mol} \cdot 1^{-1})$ were used at determined ratios (kg dried MSW: cm³ acid). Cr and Ni concentrations were similar in compost, independent of acid contribution. By contrast, Cu concentrations decreased by 63% (at citric acid ratio 1:15), 65% (at citric acid ratios 1:20 and 1:40) and 83% (at oxalic acid ratio 1:40); furthermore, Pb concentrations reduced by 71% (at citric acid ratios 1:20 and 1:40 and at oxalic acid ratio 1:40) and Zn concentrations reduced by 67% (at citric acid ratios 1:10 and 1:20) and 70% (at oxalic acid ratio 1:40). The total metal mass decreased by an average of 12% in the compost fraction, whereas the total percentage of the residual fraction increased by an average of 20%. The acid addition in the studied ratios improved compost quality without negatively influencing biostabilization.

Keywords: composting; heavy metals; speciation; citric acid; oxalic acid

Introduction

The total production of municipal solid waste (MSW) has considerably increased in recent years. Statistical reports indicate that approximately 290 million tonnes of waste per year are generated in Europe [1]. The European regulations advocate for the exploitation of the content resources in these wastes and the reduction of mass destined to landfill [2]. MSW composting is a way to meet these commitments. The biostabilized compost (low microbiological activity), which is free of pathogens, can be used as a fertilizer and as amendment for soils and sediments [3–5].

However, the application of MSW compost is not exempt of risks. Heavy metals, such as Cr, Cu, Ni, Pb and Zn, can be found in all compost. Their concentrations and the chemical forms could sometimes be a handicap for compost use in soils [6]. The European policy [7,8] and, specifically, the Spanish regulation [9] for compost use are based on total heavy metal concentrations. We are interested in the study of the treatments that contribute to minimizing the metallic content with the purpose of extending the applicable quantity of compost.

Some techniques, such as bioleaching [10,11], supercritical fluid extraction [12,13], mineral adsorption [14], electroremediation [15] and the extraction with chemical agents [16,17], for heavy metals removal are used in a solid matrix, such as soil, sludge and sediment. From these techniques, chemical extraction is the most economically viable and efficient [18,19]. Numerous studies have investigated heavy metals removal in sludge using inorganic acids, such as sulfuric acid (H₂SO₄) [20,21], hydrochloric acid (HCl) [21,22] or nitric acid (HNO₃) [21–23]; using organic acids such as citric acid (C₆H₈O₇) [21–23], oxalic acid (H₂C₂O₄) [23] or acetic acid [21–23]; using chelating agents such as EDTA (ethylenediaminetetraacetic acid) [24]; and using inorganic chemicals such as ferric chloride (FeCl₃) [25]. In addition, others studies have evaluated the remediation of soils and sediments using hydrochloric, nitric and citric acids [26], EDTA [26,27] or calcium chloride (CaCl₂) [28]. It has been concluded that organic acids, in less extreme pH conditions, are effective to extract most of the metals; in addition, considering that they are biodegradable reagents, their use entails a lower environment impact.

Despite the extensive bibliography, there is no information available on the use of chemical agents during composting of MSW. The aim of this study has been to investigate the effect of the addition of organic acid dissolutions (citric acid, oxalic acid) on the concentration, speciation and fate of heavy metals during a pilot-scale examination of composting of MSW. The study has been focused to determine if the use of these acids in a determined ratio (kg dry waste: cm³ acid) reduced metallic toxicity in compost without affecting negatively biodegradation and stability evolutions. The availability of the metals has been evaluated with the European Community Bureau of Reference (BCR) speciation test and the percentage of metallic

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fraction with an end fate to compost with a mass balance has been determined.

Materials and methods

Characteristics of MSW

MSW was obtained from Cordoba's Recovery and Composting plant (southern Spain). In this plant, the pretreatment system for MSW is manual triage for the biggest wastes, followed by mechanical triage with a rotary drum. In addition, metallic wastes are put out by an electromagnet. Particle-size fractions smaller than 80 mm are composted. At the end process, particles smaller than 10 mm (compost fraction) are removed. The separation process is comprised of a rotary drum sieve and a densimetric table, at the end of composting process. The larger fractions are dumped.

In this pilot-scale study, fresh MSW fractions smaller than 80 mm are composted. They are composed of 52% food waste, 20% glass, 14% paper, 5% plastics and 9% other materials (in dry weight).

Pilot-scale composting process

Five piles (1.5 m height, 1.5 m width, 1.0 m length) of 100 kg each were obtained from a fresh MSW pile (2.0 m height, 2.0 m width, 3.0 m length) of 500 kg. These piles were composted on sheets of inoxidizable steel $(2 \text{ m} \times 2 \text{ m})$ during 55 days. All experimental piles were turned with a manual spade and irrigated at 10, 20, 35 and 45 days. Before each turning, the moisture content in the pile was determined by a portable moisture meter (MB 45, DHAUS) and all piles were irrigated up to 40% moisture, since this is considered within the acceptable range for composting [3,29]. Temperature measuring was carried out at 50 cm depth from the surface and the centre of the pile. The temperature was determined by a sensor (PT-100) and data logger (Testo 175-T2). The temperature reached values between 45 and 60° C at the more active stage (10–35 days) and between 27 and 34°C at the end of the composting process.

There were five pilot-scale composting processes: a control experiment without acid addition, three experiments with citric acid addition ($pK_a = 3$, tricarboxylic acid) and the last experiment, as a comparison, with oxalic acid ($pK_a = 1.25$, carboxylic acid). All acid dissolutions were at 0.25 M. The acid addition was always performed after irrigation, at 10, 20 and 35 days. Table 1 presents the experiment ratios (dry waste kg: cm³ acid).

Sampling procedure and mass balance

Sampling was realized at 0, 10, 20, 35, 45 and 55 days of the composting period. To obtain a representative sample, sampling was carried out in several sites of the experimental pile and at different depths (25.0, 50.0 and 75.0 cm). The biowaste sample was sieved with an inoxidizable steel sieve with mesh size of 50 mm to obtain 2 kg sieved material. It was then divided into two parts. One part (about 100 g) was sieved with sieve mesh size of 10 mm and the sieved material was immediately used in the respiration activity test; the other part was dried at 105°C to a constant weight and, after, it was crushed with a blade mill (ORTO-ALRESA) for the rest of the analysis.

The mass balance of the composting process was determined by weighing of the fractions: fresh MSW, biowaste at 55 days, compost and reject.

Methods of analysis

The pH was measured in aqueous extract with a substrate to water ratio of 1:25 [30]. Organic matter was determined by multiplying the result obtained in the analysis with potassium dichromate from the oxidizable organic carbon [31] by the Waksman coefficient (1.72). The Volatiles Solids (VS) content of the MSW was determined based on its weight loss after combustion at 550°C for five hours [30]. Stability was evaluated by measuring of the maximum Specific Oxygen Uptake Rate (SOUR_{max}) of a 1 g sample in a liquid suspension at 30°C. The SOUR_{max} determination was realized by patented respirometer according to the method described by Chica et al. [32] and founded on Lasiridi and Stentiford [33].

The heavy metals (Cr, Cu, Ni, Pb, Zn) were analysed by flame atomic absorption spectrometry (A Analyst 300, Perkin Elmer, USA) after the waste sample was incinerated at 550°C in a muffle furnace for four hours and after HCl digestion [6]. The analyses were carried out in triplicate and a *t*-test was performed using STADVISOR software.

The speciation of heavy metals in the fresh MSW and compost was studied using the sequential extraction procedure proposed by BCR, which harmonizes previous methods [34–36]. Heavy metals were classified by four fractions: exchangeable ions and metal carbonates (EXCH); metals associated with iron and manganese oxides (FeMnOX); metals bound to organic matter (OMB); and metals associated to crystal structures (residual, RESI). Table 2 shows the steps of the BCR method to extract the different

Table 1. Ratio (kg dry waste: cm³ acid).

Control experiment	Experiment 1*	Experiment 2*	Experiment 3*	Experiment 4**
Without acid	1:15	1:20	1:40	1:40

*Composting with citric acid addition. **Composting with oxalic acid addition.

Table 2. Sequential chemical extraction procedure.

	EXCH	FeMnOX	OMB	RESI
Extractant	40 ml CH ₃ COOH 0.1 M	40 ml NH ₂ OH· HCl 0.1 M	10 ml H ₂ O ₂ 8.8 M	5 ml HCl (37%) 15 ml HNO ₃ (35%)
Stirring time	16 hours	16 hours	1 hour	
Centrifugation (3000 rpm)	40 minutes	40 minutes		
Heating			1 hour at 85°C	3 hours at 150°C
Reactive			50 ml CH ₃ COOHNH ₄ 1.0 M at pH 2	
Stirring time			16 hours	
Centrifugation (3000 rpm)			40 minutes	40 minutes

fractions. Metal species were analysed using the atomic absorption. In all cases, the differences between the total content of each metal calculated from the sum of the four fractions and the total content obtained by incineration and digestion of the sample were less than 15%.

Results and discussion

Evolution of organic matter, pH and SOUR_{max}

The changes in dry organic matter content of MSW during composting are presented in Figure 1(a). During the active stage (10–35 days), the percentages of dry organic matter content were reduced by between 18–20%. After that, they decreased continuously and finally reached around 35%.

Figure 1(b) shows the profile of the pH values of MSW with composting time [37]. At control treatment, the pH value increased from 5.8 to 8.2 in the first 20 days and it was maintained at around 8.0 value. In the case of the experiments with acid, after the 10 first days, pH 7 was maintained up to end of the period. The pH conditions were satisfactory in all experiments (range of optimum environments for microorganisms) [3].

Figure 1(c) presents MSW stability evolution. It shows SOUR_{max} values at 0, 20, 35 and 55 days. The experimental results can be adjusted to a decreased exponential equation type [SOUR_{max} = $a \cdot exp(-b \cdot t)$] where (t) is the composting time, (a) the initial value of SOUR_{max} and (b) is a kinetic coefficient linked with the speed with which the



Figure 1. Variation in the dry organic matter content of MSW, pH and SOURmax during composting.

waste increases its stability [38–40]. The values of these parameters are detailed in Table 3; they show that the stability was similar in all the cases, with the exception of the experiment with oxalic acid, which shows a slightly

superior maximum absolute b value. This may be because in the pile with oxalic acid, the maximum temperature was slightly superior. The composting process accelerates decomposition of organic matter, especially in the stages

Table 3. Adjustment parameters SOUR_{max} to first-order kinetics.

	Control experiment	Experiment 1	Experiment 2	Experiment 3	Experiment
a	30.901	33.406	32.833	32.128	30.269
-b	0.022	0.021	0.020	0.019	0.031
2	0.912	0.857	0.813	0.961	0.950
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, <u> </u>		10	days Control		
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0	10 20 30 days	40 50	0 10	20 30 davs	40 50
	Experiment 3			Experiment 4	
	_ — •	 <u> </u>	·	.	
	Cu	Cr N		Dh -	-

Figure 2. The variation of NC of each metal during composting.

with high temperature [41]. In general, SOUR_{max} dramatically decreased from initial 31.08 mgO₂/gVS \cdot h to around 10 mgO₂/gVS \cdot h after 55 days, reflecting the improvement in MSW stability.

The development of the composting at neutral pH conditions, as a consequence of the acid addition, has not negatively affected stability evolution.

Evaluation of total heavy metals contents during composting

The metal concentration during composting divided by the metal concentration at the beginning is the Normalized Concentration (NC). Evaluation of the NC for each metal is represented in Figure 2. NC was similar in all experiments for the Cr and Ni cases. Nevertheless, in comparison to the control experiment, NC decreased drastically for Cu, Zn and, to a lesser extent, Pb in the experiments with acid.

In the control experiment and at 35 days, the NC values of Cu, Pb and Zn were 6, 1.6 and 2.8, respectively, and the NC values of Cr and Ni were 1. After 55 days of biostabilization, the NC values for Cu, Pb and Zn were 8, 3 and 9.5, respectively, while the NC value for Cr was 0.9 and the NC value for Ni was 2. The reason is that NC

depends on not only the organic material degradation, but also, in a determined way, the pH and the presence of humic substances [42,43]. Cu, Zn and Pb are bound up phenol and carboxylic groups in a stable way, which are in the molecular structures of humic and fulvic acids. These compounds are concentrated in the particle-size fractions that form part of the sample to analyse. In addition, the sorption of these metals with humic acids increased to pH 8 [44–48].

The evolutions of NC of Cu, Cr and Zn were similar in all experiments with citric acid addition, independent of the used acid ratio. However, in the cases of Pb and Ni in experiment 3 (ratio 1:40), NC values were slightly higher than NC values in the experiments 1 (ratio 1:15) and 2 (ratio 1:20) during composting. After the composting process, the NC average values of Cr and Ni were similar to the control experiment; however, in the case of Cu, Pb and Zn they were 2.2, 1.2 and 3.1, respectively. These values were lower than control experiment values. This it is due to the fact that acid proton occupies the active places of the humic substances. At pH ranges 5–7, the maximum complexing capacity decreases due to the protonization of the humic systems' amino groups [49,50].

In the experiment with oxalic acid, the results obtained were similar to the experiment with citric acid (1:40)

Table 4. Total concentrations of heavy metals in fresh MSW, MSW at 55 days, compost and reject.

	$(\mathrm{mg}\cdot\mathrm{kg}^{-1})^*$					
	Samples	Cr	Cu	Ni	Pb	Zn
	Fresh MSW	*57 ^a	31 ^a	17 ^a	41 ^a	44 ^a
Control experiment	Be	*49 ^a	247 ^b	34 ^b	123 ^b	419 ^b
•	Co	*36 ^b	315 ^c	23 ^a	110 ^b	540 ^c
	Re	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	359 ^d			
Experiment 1	Be	*54 ^a	72 ^e	34 ^b	68 ^c	145 ^e
1	Со	*43 ^b	117^{f}	28^{a}	117 ^d	182 ^f
	Re	*71°	75 ^e	32 ^b	46 ^a	194 ^f
Experiment 2	Be	*71 ^c	73 ^e	34 ^b	58 ^c	132 ^e
r	Со	*63 ^a	110^{f}	32^{a}	32 ^d	180 ^f
	Re	*56 ^a	82 ^e	34 ^b	51°	139 ^e
Experiment 3	Be	*38 ^b	75 ^e	24 ^a	24 ^d	130 ^e
	Co	*32 ^b	109 ^f	26^{a}	31 ^d	170 ^f
	Re	*31 ^b	83 ^e	24 ^a	17 ^d	109 ^g
Experiment 4	Be	*40 ^b	46 ^a	25 ^a	31 ^d	115 ^g
r	Со	*39 ^b	52 ^a	22^{a}	32 ^d	162 ^f
	Re	*42 ^b	53 ^a	$\frac{25^{a}}{25^{a}}$	25 ^d	121 ^e
	Class A	70	70	25	45	200
Spanish regulations RD 824/2005	Class B	250	300	90	150	500
	Class C	300	400	100	200	1000
	Class 1	100	100	50	100	200
2nd Draft BTB (2001).EC.	Class 2	150	150	75	150	400
	Stabilized Biowaste	600	600	150	500	1500

(Be) MSW before sieve (at 55 days, particle-size fractions less than 50 mm); (Co) compost (particle size smaller than 10 mm); (Re) reject fraction (particle size greater than 10 mm). *Within the same column, data with the same letter do not differ significantly at the 5% level according to significant difference test.

in all the metals, except Cu, where the NC value was lower (1.5).

Heavy metals concentrations $(mg \cdot kg^{-1})$ in fresh MSW, (Be) biowaste at 55 days, (Co) compost and (Re) reject, and significant difference analysis, are shown in Table 4. Practically, the concentration of Ni in compost was similar to its concentration in fresh MSW in all experiments. In the Cr case, its concentration slightly decreased at the end of the composting process. This was probably due to leaching. By contrast, Cu, Pb and Zn concentrations increased in all experiments, significantly so in the control experiment. Among the causes are the organic matter degradation during composting and the concentration of humic substances in fractions of compost (particle size <10 mm). This suggested that the humic fraction had more affinity towards stable complex formation with Cu, Pb and Zn as compared to Cr and Ni [6,42,51–53].

In comparison, in compost of the control experiment, Cu and Zn concentrations decreased by an average of 66%

in the case of Pb, 71% at ratios 1:20 and 1:40. In the experiment with oxalic acid, the reductions in the Pb and Zn concentrations were similar, while that in Cu was greatest (83%). The results obtained are similar to those for others studies on metal concentration reduction in sludge at extreme pH conditions (2–6) using inorganic and organic acid reagents [22,23,54,55].
g. According to the legislation [9], in the experiments with

acid contribution, compost was of better quality (Class B) than compost of the control experiment (Class C). The compost quality is affected by Cu and Zn concentrations to a large extent.

in compost of the experiments with citric acid addition and,

Speciation of heavy metals in the fresh MSW and compost

Figure 3 shows the speciation of heavy metals in the fresh MSW and compost of each experiment. The composting



Figure 3. Heavy metals speciation in the fresh MSW and compost.

process changed the distribution of four fractions of Cr, Cu, Ni, Pb and Zn. In the control experiment, the exchangeable fraction (EXCH, mobile forms) and reducible fraction (FeMnOX) of all metals decreased during composting. The percentage of both fractions were <15% in all metals, except for Zn, which was 30%. The fixed fraction, RESI, of Cr, Ni and Pb (around 65%) and OMB of Cu and Zn (60% and 50%, respectively) dominated in the compost of the control experiment. This could be explained by the fact that humic substances have a stronger complexing ability with Cu and Zn. Composting seems to reduce the mobility of the metals, which considerably reduces the risk of their transfer to the food chain and waters. These results are similar to the ones obtained by authors in studies of composting of biodegradable municipal wastes [22,35,42,56-60].

In the compost of experiments with citric acid, the distribution of different metallic species fractions was similar in the cases of 1 and 2 (ratios 1:15 and 1:20). In the case of experiment 3 (ratio 1:40), the distribution was the same but

Cr

2.1(A)

1.8(D)

0.4(12)

2.9(88)

 -14.3^{***}

2.7

3.3

0.4(22)**

1.4(78)**

 4.8^{*}

was more marked. When comparing with the control experiment, it is observed that (1) the reduction of the EXCH fraction was greatest in the case of Cr and Pb, similar in Ni and lower in Cu and Zn; (2) FeMnOX fraction distributions were similar to EXCH fractions (3); the OMB fraction increases in the Ni case, is remarkably smaller in the Cu and Zn cases (between 20 and 35%, which confirms the acid proton effect) and similar is in the Cr and Pb cases, with the exception of experiment 3, where it seems to decrease; (4) the fixed fraction, RESI, increased by an average of 20%, except in the case of Ni, where it decreased by an average of 20%.

At lower pH conditions, the percentages of Cu and Zn increased in the EXCH fraction, which coincides with the results obtained by other authors for this type of biowaste [35].

The results obtained in the experiment with oxalic acid were similar to the experiment with citric acid (1:40) for all metals, except the case of the OMB-Cu, the distribution

Pb

5.4(A)

5.0(D)

1.0(34)

1.9(66)

-7.4***

3.4

2.9

1.3(26)**

3.7(74)**

3.5*

Content of heavy metals (g)

Ni

 1.4^{*}

1.5(A)

1.8(D)

0.2(13)

1.3(87)

 $+20.0^{***}$

1.7

1.5

0.3(17)**

1.5(83)**

Table 5. Mass content of each metal in the fractions of fresh MSW, MSW at 55 days, compost and reject.

Cu

 2.6^{*}

10.8(A)

3.7(38)**

6.1(62)**

9.8(D)

-9.2***

3.6

4.0

1.0(25)

3.0(75)

[(D-A)/A]	+22.2	+11.1	-11.8	-14.7	+31.9
Experiment 2	2.6	2.4	1.7	2.0	<i>.</i> .
50.5 (Be)	3.6	3.4	1./	2.9	6./
7.7 (Co)	0.5(17)	0.8(19)	0.2(13)	0.2(08)	1.4(19)
42.8 (Re)	2.4(83)	3.5(81)	1.4(87)	2.2(91)	5.9(81)
	2.9	4.3	1.6	2.4	7.3
[(D-A)/A]	-19.4	+26.5	-5.9	-17.2	+8.9
Experiment 3					
67.0 (Be)	2.5	5.0	1.6	1.6	8.7
10.0 (Co)	0.3(14)	1.0(18)	0.3(18)	0.3(23)	1.7(22)
57.0 (Re)	1.8(86)	4.7(82)	1.4(82)	1.0(77)	6.2(78)
	2.1	5.7	1.7	1.3	7.9
[(D-A)/A]	-16.0	+14.0	+6.2	-18.8	-9.2
Experiment 4					
54.9 (Be)	2.2	2.5	1.4	1.7	6.3
8.9 (Co)	0.3(14)	0.5(17)	0.2(15)	0.3(21)	1.4(20)
46.0 (Re)	1.9(86)	2.4(83)	1.1(85)	1.1(79)	5.6(80)
	2.2	2.9	1.3	1.4	7.0
[(D-A)/A]	0.0	+16.0	-7.1	-17.6	+11.1
The mass of fractions	of <50 mm particle size	e taken at 10, 20, 35 a	and 45 days and estima	ted weight loss have b	een considered for
mass balance. *Initial	metal content in the exper-	rimental piles (content of	estimated from analysis	of fractions <50 mm so	ource pile). **Metal
distribution coefficient	t (in %) between the comp	oost and the reject. ***R	elative error (in %) due	to excess $(+)$ or defect	 (-) that is obtained

by adding the metal content of (Co) to (Re), and subtracting the metal content of (Be), which is used as a reference.

Zn

3.7*

18.3(A)

17.7(D)

 -3.3^{***}

7.2

1.6(17)

7.9(83) 9.5

6.3(36)**

11.4(64)**

kg (sample)

Fresh MSW

43.6 (Be)

11.7 (Co)

31.9 (Re)

[(D-A)/A]***

Experiment 1 49.4 (Be)

8.9 (Co)

40.5 (Re)

Control experiment

of which in compost is <10%, remarkably inferior to the distribution in compost of experiment 3 (35%).

In experiments with acid, the RESI fraction predominated in the cases of Cr, Cu and Pb; OMB and EXCH predominated in the cases of Ni and Zn, respectively.

Fate of heavy metals

The mass contents of each heavy metal in the fresh MSW fraction (<50 mm particle size), in the MSW fraction (<50 mm particle size) at 55 days of the composting process (Be), in the compost fraction (<10 mm particle size, Co) and in the reject fraction (particle size between 10 and 50 mm, Re) are presented in Table 5. These results have been obtained multiplying the concentration of each metal (Table 4) with the weight of each fraction (left column in Table 5). The average error percentage is due to the difference between the metal mass in the fraction (Be); the sum of the metals masses in the fractions (Co) and (Re) has been <15%. This is acceptable, considering the physical fractionation methods used and the heterogeneity of biowaste.

In the control experiment, metal mass content in the fraction (Be) at the end of the composting period (after 55 days) was similar to the content in fresh MSW in the case of Ni, decreased to half in the case of Cr, and in the cases of Cu, Pb and Zn it increased about five times, two times and six times, respectively, during composting. Cu, Pb and Zn of the fractions of particle size greater than 50 mm (not analysed) seem to be transferred to the fractions of particle size smaller than 50 mm (which are analysed) during composting. This phenomenon may be due to the formation of stable complexes between metal and humic substances that appear during the composting process. The majority of these compounds are concentrated in the particle-size fractions smaller than 1 mm. The formation constants of the complexes of Cu, Pb and Zn are high. This fact avoids that can be to transfer to fractions which are analysed, Cr and Ni present in particle-size fractions greater than 50 mm. [42,53]. The average percentages of metals mass of the (Be) fraction with fate to compost fraction were 37% for the cases of Cu and Zn, and 26%, 22% and 17% for Pb, Cr and Ni, respectively. So, the total metals mass of the (Be) fraction by fate to the (Re) fraction was, on average, 70%.

In the experiments with acid addition, comparing the results with the control experiment, it was evident that mass contents of Cr and Ni in the fraction (Be) at 55 days were similar; by contrast, Cu, Pb and Zn mass decreased by 45–75%, 35–70% and 50–65%, respectively. These results most probably are due to the effect of acid proton, which has already been discussed. In these experiments, the average percentages of metals mass of the (Be) fraction with fate to the compost fraction were similar for all metals and the total metals mass of the (Be) fraction by fate to the (Re) fraction was about 82%.

Conclusions

This pilot-scale study demonstrates that the application of organic acids (citric and oxalic) during MSW composting, at around neutral pH values, does not negatively affect biodegradation and stability evolution. Acid addition at the studied ratios manages to reduce heavy metals concentrations in compost and consequently minimizes their potential risk. Cu, Pb and Zn concentrations decrease by between 60 and 80%, whereas Cr and Ni concentrations are hardly affected by the acid contribution. The results obtained suggest that the acid addition reduces the transfer of Cu, Pb and Zn from large particle fractions to compost. The OMB fraction of these heavy metals decreases considerably. According to the Spanish regulations, acid addition during composting improved product quality.

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References

- Statistical Office of the European Union, Generation of municipal waste, Statistic Report, Brussels, 2008.
- [2] European Commission, Gestión de residuos biodegradables, Directiva 99/31/EC, Brussels, EU, 1999.
- [3] F. Costa, C. García, T. Hernández, and A. Polo, *Residuos Orgánicos Urbanos. Manejo y Utilización*, 2nd ed., CSIC, Murcia, 1995.
- [4] M.J.A. Rijkenberg and C.V. Depree, *Heavy metal stabilization in contaminated road-derived sediments*, Sci. Total Environ. 408 (2010), pp. 1212–1220.
- [5] R. Paradelo, A. Villada, and M.T. Barral, *Reduction of the short-term availability of copper, lead and zinc in a contam-inated soil amended with municipal solid waste compost*, J. Hazard. Mater. 188 (2011), pp. 98–104.
- [6] A. Rosal, Caracterización y mejora de la calidad en el compostaje de residuos sólidos municipales, Ph.D. diss., Universidad de Córdoba, 2007.
- [7] European Commission, Establishing ecological criteria for the award of the community eco-label to soil improvers and growing media, Ecolabel 2001/688/CE, Brussels, UE, 2001.
- [8] European Commission, *Biological treatment of biowaste*, 2nd draft, Brussels, EU, 2001.
- [9] Boletín Oficial del Estado, RD 824/2005 Sobre Productos Fertilizantes, BOE 171, Madrid, 2005.
- [10] C. Solisio, A. Lodi, and F. Veglio, *Bioleaching of zinc* and aluminum from industrial waste sludges by means of *Thiobacillus ferrooxidans*, Waste Manage. 22 (2002), pp. 667–675.
- [11] N. Sabra, H.C. Dubourguier, M.N. Duval, and T. Hamieh, Study of canal sediments contaminated with heavy metals: Fungal versus bacterial bioleaching techniques, Environ. Technol. 32 (2011), pp. 1307–1324.
- [12] C. Kersch, M.J.E. van Roosmalen, G.F. Woerlee, and G.J. Witkamp, *Extraction of heavy metals from fly ash and sand with ligands and supercritical carbon dioxide*, Ind. Eng. Chem. Res. 39 (2000), pp. 4670–4672.
- [13] M.D.A. Saldaña, V. Nagpal, and S.E. Guigard, Remediation of contaminated soils using supercritical fluid extraction: A

review (1994–2004), Environ. Technol. 26 (2005), pp. 1013–1032.

- [14] J. Villaseñor, L. Rodríguez, and F.J. Fernández, Composting domestic sewage sludge with natural zeolites in a rotary drum reactor, Bioresour. Technol. 102 (2011), pp. 1447– 1454.
- [15] Z. Li, J.W. Yu, and I. Neretnieks, *Electroremediation: Removal of heavy metals from soils by using cation selective membrane*, Environ. Sci. Technol. 32 (1998), pp. 394–397.
- [16] S.W. Paff, B. Bosilovich, and N.J. Kardos, Acid extraction treatment system for treatment of metal contaminated soils, Risk Reduction Engineering Laboratory, Office of Research and Development, EPA/540/R-94/513, Cincinnati, OH, 2004.
- [17] S.F. Chen, C.Y. Huang, and Y.T. Tu, Remediation of soils contaminated with chromium using citric and hydrochloric acids: The role of chromium fractionation in chromium leaching, Environ. Technol. 32 (2011), pp. 879–889.
- [18] R. Ragheaven, E. Coles, and D. Dietz, *Cleaning excavated soil using extraction agents: A state-of-the-art review*, USEPA publication EPA/600/s2-89/034, Cincinnati, OH, 1990.
- [19] S. Babel and D.M. Dancera, *Heavy metal removal from contaminated sludge for land application: A review*, Waste Manage. 26 (2006), pp. 988–1004.
- [20] J.I. Mingot, A. Obrador, J.M. Álvarez, and M.I. Rico, Acid extraction and sequential fractionation of heavy metals in water treatment sludges, Environ. Technol. 16 (1995), pp. 869–876.
- [21] W. Chung-Hsin, K. Chao-Yin, and L. Shang-Lien, *Removal of metals from industrial sludge by extraction with different acids*, J. Environ. Sci. Health 39 (2004), pp. 2205–2219.
- [22] M.M. Marchioretto, H. Bruning, N.T.P. Loan, and W.H. Rulkens, *Heavy metals extraction from anaerobically digested sludge*, Water Sci. Technol. 46 (2002), pp. 1–8.
- [23] A. Veeken and B. Hamelers, *Removal of heavy metals from sewage sludge by extraction with organic acids*, Water Sci. Technol. 40 (1999), pp. 129–136.
- [24] S. Santos, C. Costa, A. Duarte, and H. Scherer, Influence of different organic amendments on the potential availability of metals from soil: A study on metal fractionation and extraction kinetics by EDTA, Chemosphere 78 (2010), pp. 389–396.
- [25] W. Zhiping, Removal of heavy metals from sludge by chemical method, Ph.D. diss., Pathumtani Institute of Technology, 1995.
- [26] K.J. Kim, D.H. Kim, J.C. Yoo, and K. Baek, *Electrokinetic extraction of heavy metals from dredged marine sediment*, Sep. Purif. Technol. 79 (2011), pp. 164–169.
- [27] A. Bermond, G. Varrault, V. Sappin-Didier, and M. Menc, A kinetic approach to predict soil trace metal bioavailability: Preliminary results, Plant Soil 275 (2005), pp. 21–29.
- [28] T. Kowalkowski, H. Tutu, L.M. Cozmuta, M. Sprynskyy, E.M. Cukrowska, and B. Buszewski, Assessment of mobility of heavy metals in two soil types by use of column leaching experiments and chemometric evaluation of elution curves, Int. J. Environ. Anal. Chem. 90 (2010), pp. 797–811.
- [29] T.L. Richard, H.V.M. Hamelers, A. Veeken, and T. Silva, *Moisture relationships in composting processes*, Compost Sci. Utilization 10 (2002), pp. 286–302.
- [30] Anexo VII. Análisis. Métodos Oficiales de los Productos Orgánicos Fertilizantes, Boletín Oficial del Estado, 20 de enero, Spain, 1982.
- [31] UNI 10665, Fertilizers-determination of organic carbon according to Springer-Klee-Titrimetric method, Italy, 1998.

- [32] A. Chica, J.J. Mohedo, M.A. Martín, and A. Martín, *Determination of the stability of MSW compost using a respirometric technique*, Compost Sci. Utilization 11 (2003), pp. 169–175.
- [33] K.E. Lasiridi and E.D.I. Stentiford, A simple respirometric technique for assessing compost stability, Water Res. 12 (1998), pp. 3717–3723.
- [34] Ph. Quevauviller, A. Ure, H. Muntau, and B. Griepink, Improvement of analytical measurements within the BCRprogramme: Single and sequential extraction procedures applied to soil and sediment analysis, J. Environ. Anal. Chem. 51 (1993), pp. 129–139.
- [35] F. Pedra, H. Domingues, A.B. Ribeiro, A. Polo, and O. Monteiro, *Relationship between Cu and Zn extractable foliar contents and BCR sequential extraction in soil treated with organic amendments*, Environ. Technol. 27 (2006), pp. 1357–1367.
- [36] Q.J. Song and G.M. Greenway, *Trace element availability* in compost, Spectrosc. Eur. 17 (2005), pp. 10–15.
- [37] R. Nogales, F. Gallardo-Lara, and M. Delgado, Aspectos físico-químicos y microbiológicos del compost de basura urbana, Anal. Edafol. Agrobiol. 41 (1982), pp. 1159–1174.
- [38] I.G. Mason and M.W. Milke, *Physical modelling of the composting environment: A review. Part 1: Reactor systems*, Waste Manage. 25 (2005), pp. 481–500.
- [39] I.G. Mason and M.W. Milke, *Physical modelling of the composting environment: A review. Part 2: Simulation performance*, Waste Manage. 25 (2005), pp 501–509.
- [40] M. Dios, Estudio y desarrollo de técnicas respirométricas para el control de la estabilidad del compost, Ph.D. diss., Universidad de Córdoba, 2008.
- [41] H. Miao-miao, T. Guang-ming, and L. Xin-qiang, *Phyto-toxicity and speciation of copper, zinc and lead during the aerobic composting of sewage sludge*, J. Hazard. Mater. 163 (2009), pp. 671–677.
- [42] A. Veeken, Removal of heavy metals from biowaste, Ph.D. diss., Wageningen University, 1998.
- [43] A. Veeken and B. Hamelers, Sources of Cd, Cu, Pb and Zn in biowaste, Sci. Total Environ. 300 (2002), pp. 87–98.
- [44] H. Kerndorff and M. Schnitzer, Sorption of metals on humic acid, Geochim. Cosmochim. Acta 44 (1980), pp. 1701– 1708.
- [45] F.R. Livens, Chemical reactions of metal with humic material, Environ. Pollut. 70 (1991), pp. 183–208.
- [46] N. Senesi, Metal-humic Substance Complexes in the Environment. Molecular and Mechanistic Aspects by Multiple Spectroscopic Approach. Biogeochemistry of Trace Metals, Lewis Publishers, Boca Raton, FL, 1992, pp. 429–496.
- [47] M. Antonelli, N. Calace, D. Centioli, B.M. Petronio, and M. Pietroletti, *Complexing capacity of different molecular* weight fractions of sedimentary humic substances, Anal. Lett. 34 (2001), pp. 989–1002.
- [48] A. Rosal, J.P. Pérez, M.A. Arcos, and M. Dios, La incidencia de metales pesados en compost de Residuos Sólidos Municipales y en su uso agronómico en España, Información Tecnológica 18 (2007), pp. 75–82.
- [49] C. Mantoura, A. Dickson, and P. Riley, *The complexation of metals with humic materials in natural waters*, Estuar. Coast. Mar. Sci. 6 (1978), pp. 387–408.
- [50] P. Alvarenga, P. Palma, A.P. GonÇalves, R.M. Fernandes, A.C. Cunha-Queda, E. Duarte, and G. Vallini, *Evaluation of chemical and ecotoxicological characteristics of biodegradable organic residues for application to agricultural land*, Environ. Int. 33 (2007), pp. 505–513.
- [51] A. Veeken and B. Hamelers, Assessment of heavy metal removal technologies for biowaste by physico-chemical fractionation, India, Environ. Technol. 24 (2003), pp. 329–337.

- [52] E. Perdue and C. Lytle, Distribution model for binding of protons and metal ions by humic substances, Environ. Sci. Technol. 17 (1983), pp. 654–660.
- [53] J.M. García-Mina, Stability, solubility and maximum metal binding capacity in metal-humic complexes involving humic substances extracted from peat and organic compost, Org. Geochem. 37 (2006), pp. 1960–1972.
- [54] D. Wozniak and J. Huang, Variables affecting metal removal from sludge, J. Water Pollut. Control Fed. 54 (1982), pp. 1574–1580.
- [55] J.F. Tyagi, R.D. Auclair, and J.C. Huang, Comparison of acid and microbial leaching for metal removal from municipal sludge, Water Sci. Technol. 26 (1992), pp. 197–206.
- [56] K. Rao and M.V. Shantarain, Concentration and relative availabilities of heavy metals in urban solid wastes of Hyderabad, India, Bioresour. Technol. 53 (1995), pp. 53–55.

- [57] E. Sebasthiar, S. Ammaiyappan, J. Kurian, and P. Kandasamy, Assessment of heavy metal species in decomposed municipal solid waste, Chem. Speciation Biovailability 17 (2005), pp. 95–102.
- [58] Z. Dong-Qing, Z. Hua, H. Pin-Jing, and S. Li-Ming, Effect of bioestabilization on the release potential and speciation of heavy metals in municipal solid waste, Waste Manage. Res. 29 (2010), pp. 406–413.
- [59] T. Paré, H. Dinel, and M. Schnitzer, *Extractability* of trace metals during co-composting of biosolids and municipal solid wastes, Biol. Fertil. Soils 29 (1999), pp. 31–37.
- [60] Y.Y. Liu, T. Mai, M. Uktta, M. Sekine, and T. Higuchi, *Distributions of iron, manganese, copper and zinc in various composts and amended soils*, Environ. Technol. 24 (2003), pp. 1517–1525.