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Co-composting of eggshell waste in self-heating reactors: monitoring and end product quality

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Abstract

Industrial eggshell waste (ES) is classified as an animal by-product not intended to human consumption. For reducing pathogen spreading risk due to soil incorporation of ES, sanitation by composting is a pre-treatment option. This work aims to evaluate eggshell waste recycling in self-heating composting reactors and investigate ES effect on process evolution and end product quality. Potato peel, grass clippings and rice husks were the starting organic materials considered.

The incorporation of 30% (w/w) ES in a composting mixture did not affect mixture biodegradability, nor its capacity to reach sanitizing temperatures. After 25 days of composting, ES addition caused a nitrogen loss of about 10 g N kg⁻¹ of initial volatile solids, thus reducing nitrogen nutritional potential of the finished compost.

This study showed that a composting mixture with a significant proportion of ES (30% w/w) may be converted into calcium-rich marketable compost to neutralize soil acidity and/or calcium deficiencies.

Keywords: Industrial eggshell waste, composting, self-heating potential, soil improver

1- INTRODUCTION

There are millions of hen eggs that are broken every day in food plants. The eggshell (ES) is usually seen as a waste from this industry, whose production can represent from 0.03 to 0.12 of the mass of the egg products obtained from eggs (Russ and Meyer-Pittroff, 2004).

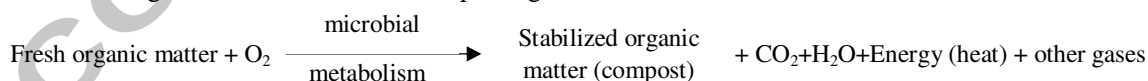
In 2011, European countries produced about 10 600 million ton of eggs from which about 30% was diverted to egg breaking processing (Agra CEAS Consulting Ltd, 2008; FAO, 2012). Since ES represents 11% of the total egg weight (Meski et al., 2011), the annual production of ES in Europe may ascend to 350 million ton.

The adequate handling and disposal of this waste has been considered a challenge for the food industry in what concerns environmental protection, due to not only the large amounts generated but also to its potential for microbial proliferation or growth of pathogens (Russ and Meyer-Pittroff, 2004).

Suitable management strategies have not been well established for ES and disposal in landfills has been traditionally used (Tsai et al., 2008). However, recycling and recovery should be investigated to avoid the waste of resources.

In accordance with Regulation (EC) N° 1069/2009 of the European Parliament and the Council, the ES is nowadays classified as an animal by-product (ABP) not intended to human consumption. ABP are categorized into three categories, which reflect the level of risk to public and animal health arising from those wastes, and for each category, a list of disposal and use alternatives is imposed in that Regulation. ES is included in the inventory of Category 3, and in this case composting prior to soil incorporation is an alternative to disposal/use, in order to reduce spreading risk of pathogens to the environment and human health.

Composting may be defined as a process of biological decomposition and stabilization of organic substrates, under aerobic conditions, that allows development of thermophilic temperatures, as a result of biologically produced heat (Haug, 1993), for human and plant pathogens inactivation. It can transform organic matter of animal or vegetal origin into a final product that is stable, free of pathogens and plant seeds, rich in humus and beneficial for recycling of soil organic matter and nutrients. A generalized equation of composting follows:



Nowadays, there is a renewed attention concerning composting and its application is not limited to a farm context but is broadened to municipal and industrial frameworks. In this scope, composting has been identified as an environmentally sound alternative, for tailoring the recovery of waste organic matter and nutrients to suppress soil deficiencies (Farrell and Jones, 2009).

Due to the high nutrition content of ES, namely in calcium, its recycling by composting seems quite interesting. In fact, the application of enriched calcium compost to soils deficient in this nutrient may

constitute an option to promote ES recycling into a value-added product and consequently recover a natural resource contained in this ABP.

In a composting process the major energy input is due to the organic content of the initial mixture (Haug, 1993). Since ES is mainly an inorganic material with about 94% (w/w) CaCO_3 (Tsai et al., 2008), it may be expected that the energy released from organic decomposition may not be sufficient to rise the temperature of the composting matrix to the thermophilic range adequate for pathogen inactivation. Consequently, composting of ES with other materials should be considered to upsurge the energy input for the process, aiming to satisfy sanitizing requirements for ES (70°C for 1 h) (Commission Regulation (EU) N°142/2011)."

Nevertheless to the authors' best knowledge, eggshell composting in significant quantities (higher than 20% w/w) is scarcely addressed in literature. Kemper and Goodwin (2009) tested windrow composting of animal litter with eggshell, unfinished compost and clay subsoil, in the presence of an inoculant to aid humus build up. The maximum temperatures achieved were 65°C, but after eleven weeks the end product compost was still immature. Quina et al. (2013) studied the feasibility of composting industrial eggshell waste and others ABP (horse and chicken manure) using the indigenous microbial population of the mixture. The temperature profiles attained maximum values of 50°C, but mature composts with adequate properties for agronomic applications were obtained after 50 days. Even so, composting tests involving industrial eggshell waste with other wastes, namely from the food industry are still lacking in the literature.

The main aim of this work is to examine the feasibility of promoting eggshell waste recycling in self-heating composting reactors, to ensure proper sanitation and to investigate the effect of eggshell on the evolution of composting processes and on the quality of the end products. Potato peel (PP) (from the food industry), grass clippings (GC) and rice husks (RH) were the organic materials considered to ensure a balanced initial composting mixture.

2- MATERIALS AND METHODS

2.1 - Self heating composting reactors

Experiments were performed in a system of three self-heating reactors (SHR) with 0.7 m high and 0.48 m diameter, and isolated with a rubber-based elastomer (Aeroflex MSR) to reduce heat losses. The air is uniformly distributed across a perforated acrylic plate located at the bottom of the reactors. Airflow was supplied by a compressor, and measured through a meter E4K-4BR, Kytola Instruments. Temperature was monitored on-line using a thermocouple type K (Bresimar Automação) located at the center of the composting mixture to record its value every 10 min, by using a datalogger module (Virtual HMI CSMSTRSX, Redlion).

The exit gases were removed through an orifice at the top cover of the reactors, conducted to a water trap before analyzing oxygen concentration (v/v) with a gas sensor, XLS1047, XLlogger. On average the oxygen concentration was measured four times a day.

The reactors were equipped with a balance for monitoring the mass reduction due to organic matter degradation. The weight of the reactor content was always recorded after drainage of eventual leachates produced.

Biological activity of the composting mixture was assessed by calculating oxygen uptake rate (OUR) defined as (Barrena et al., 2009):

$$\text{OUR (g O}_2 \text{ kg VS}^{-1} \text{ h}^{-1}) = \frac{Q \times \Delta O_2 \times 31.98}{1000 \times V_g \times X_{VS}} \quad (1)$$

where Q (L h⁻¹) is the airflow rate, ΔO_2 (mL L⁻¹) the difference in oxygen concentration between the inlet and the outlet airflow, 1000 is the conversion factor from mL to L, V_g (L mol⁻¹) the volume of one mole of gas at inlet conditions, 31.98 (g mol⁻¹) is the molecular weight of O₂, and X_{VS} (kg) the weight of the organic matter of the composting mixture.

The profile of organic matter reduction observed during experiments was fitted to a first-zero kinetic model (Tosun et al., 2008):

$$\frac{X_{VS}}{X_{VS0}} = \frac{X_{VSr}}{X_{VS0}} \exp(-k_r t) + \frac{X_{VSs}}{X_{VS0}} k_s t + \frac{X_{VSs}}{X_{VS0}} \quad (2)$$

where $\frac{X_{VS}}{X_{VS0}}$ is the fraction of remaining organic mixture in the mixture at day t , $\frac{X_{VSr}}{X_{VS0}}$ and $\frac{X_{VSs}}{X_{VS0}}$ are

the fraction of rapidly and slowly biodegradable organic matter fraction, respectively and k_r and k_s are the rapid and slow rate constants (day⁻¹), respectively. After fitting, the obtained equation was used to quantify instantaneous X_{VS} . Cumulative OUR was calculated by numeric integration of the instantaneous OUR values recorded during composting.

2.2 – Materials and experimental design

Potato peel (PP) was gathered at a Portuguese industry of potato chips, rice husk (RH) was provided by a rice husking factory and grass clippings (GC) were obtained from a garden maintenance service from a national football stadium. Materials were used in composting experiments immediately after their collection.

Grass clippings were sieved through a 5 cm mesh, in order to obtain a homogenous material in size and shape. The other materials did not require any specific treatment.

To select a composting mixture with an adequate biodegradability level to drive the process into thermophilic conditions, three formulations were tested (Table 1) involving PP, GC and RH as

ingredients. Since PP is a very wet material (~85% moisture) and with low inter-particle volume of voids available for oxygen diffusion, RH was added as structural and drying amendment material. Free air space (FAS) of initial mixtures was predicted according to a model based on the ingredients proportions and described elsewhere (Soares et al., 2013).

Each blend was prepared by weighing the components according to the pre-defined proportions indicated in Table 1, for a total load equivalent to a volume of 99 L. The ingredients were mixed thoroughly for 20 min, before loading the SHR.

The initial airflow rate was 7.5 L min^{-1} , and afterwards it was manually adjusted to guarantee an outlet oxygen concentration in the range of 5 to 15% (v/v). Composting experiments lasted 25 days and the content of the reactors was homogenised in a daily basis. Samples were taken for analysis on day 0, 4, 11, 18 and 25.

The eggshell was collected at a national industry of pasteurized liquid eggs and boiled eggs and immediately preserved at -12°C until further use. Before starting the experiments, the ES was defrosted for 24 h at room temperature. The main properties of ES are indicated in Table 2.

2.3 – Analytical methods

2.3.1 – Moisture, pH, electrical conductivity and equivalent CaCO_3

The moisture content was determined as the loss in weight after samples were dried in an oven at 105°C to constant weight. The pH and electrical conductivity (EC) were measured in water extracts obtained with a solid to liquid ratio of 1:5 (v/v) for 1 hour. pH was measured directly in suspensions, but in the case of EC, filtration was performed and the contribution of water, glassware and filter paper (blank essay) was subtracted.

The calcium carbonate content was assessed by dissolving a 1 g dry basis of compost in 50 mL 0.5 N HCl (with heat) and back-titrating to pH 7 with 0.25N NaOH (McGinnis et al., 2011).

2.3.2 – Organic matter and carbon content

The organic matter content was considered equal to the weight loss after dry incineration (VS) of 2.5 g of sample (dried at 105°C). Incineration was conducted in a muffle furnace at 550°C for at least 4 h, until differences between two successive weighings were less than 0.01g. Organic carbon content was determined with a Carbon-Sulphur Analyzer (Leco Instruments, model SC-144 DR), where the sample was oxidized to carbon dioxide by heating at 550°C , in the presence of an infrared detector for C-CO_2 quantification.

2.3.3 – Nitrogen species and losses

Kjeldhal nitrogen content ($\text{N}_{\text{Kjeldhal}}$) was quantified on 0.50 g of dried ground sample by mineralization within a strong acid medium (sulfuric acid 98%), followed by steam distillation and then titrimetric determination with HCl (Tremier et al., 2005). N-NH_4^+ was extracted with KCl (2M) (1:10w/v) and N-NO_3^- with water (1:10 w/v) for 2 h. Mineral nitrogen concentration was determined by colorimetry with a segmented continuous flow analyzer (Skalar SAN Plus) using a method based on the modified

Berthelot reaction for N-NH_4^+ and promoting the reaction with sulfanilamide and N-1-naphthyl ethylenediamine dihydrochloride for N-NO_3^- (Sanchez-Monedero et al., 2001; Doublet et al., 2010).

The organic nitrogen content (N_{org}) of the samples was calculated by Eq (3):

$$N_{\text{org}} = N_{\text{kjeldhal}} - N_{\text{NH}_4^+ \text{ air-dried}} \quad (3)$$

where $\text{N}_{\text{kjeldhal}}$ is the sum of organic nitrogen compounds and free-ammonia of air dried sample and $\text{N-NH}_4^+ \text{ air-dried}$ refers to ammonia content of air dried samples.

Loss of nitrogen during process evolution, N_{losses} , was expressed in $\text{g N kg}^{-1} \text{ VS}_{\text{initial}}$, and estimated according to the equation proposed by (Zeng et al., 2012a)

$$N_{\text{losses}} = \alpha_3 + \beta_3 \times [N_{\text{bio}} + (\text{NH}_4^+)_{\text{initial}}] \quad (4)$$

where $\alpha_3=0.213$, $\beta_3=0.913$, N_{bio} is the organic nitrogen decomposed ($\text{g N kg}^{-1} \text{ VS}_{\text{initial}}$) and $(\text{NH}_4^+)_{\text{initial}}$ is the ammonia content in the composting matrix ($\text{g N kg}^{-1} \text{ VS}_{\text{initial}}$).

2.3.4 – Stability and germination tests

The compost stability was determined as described by Paradelo et al.(2012): about 25 g of compost was pre-incubated overnight at 25°C, and then transferred into 1-L Mason jar, containing 20 mL of 0.5 M NaOH in a 50 mL beaker. The jar was sealed and incubated at 37 °C. The CO_2 evolved by microbial respiration was daily measured by titration of the residual NaOH with 0.5 N HCl. The mean respiration rate of compost, expressed as $\text{mg C-CO}_2 \text{ g C}^{-1} \text{ d}^{-1}$, was obtained from a three days monitoring.

In the germination tests, 5 mL of sample water extract (1:10, dry weight: v) were placed in a petri dish containing 10 seeds of *Lepidium sativum*. Three replicates per sample were incubated at 25 °C in dark conditions for 48 h. After this period, the number of germinated seeds and their root length were measured. A control test was prepared with deionized water (Komilis & Tziouvaras, 2009).

Germination index (GI) was calculated by Eq.(5) as a percentage of a control experiment (with deionized water):

$$\text{GI} (\%) = \frac{\text{RSG} \times \text{RRG}}{100} \quad (5)$$

where RSG is the relative seed germination (%) and RRG the relative root growth (%).

2.3.5 – Humic and fulvic carbon fractions

Extractable carbon (C_{ext}) was measured in a 0.1 M NaOH compost extract (1:20, w/v) and the fulvic acid carbon (FCA) was quantified in the same extract, after precipitation of the humic acids at pH 2 and 4 °C overnight. The dissolved carbon content was measured in a Shimadzu TOC-500A (Cayuela et al., 2006). The humic acid carbon content (HAC) was calculated by subtracting fulvic acid carbon to the extractable carbon.

2.3.6 – Heavy metals and calcium content

Metals (Cd, Cr, Cu, Pb, Zn) and Ca content was quantified by flame atomic absorption spectrometry (Perkin Elmer – 3000) after *aqua regia* extraction according to European standard EN 13650:2001.

2.3.7 – Free air space

FAS of the composting mixtures during aerobic biodegradation was calculated according to Eq. (6) (Adhikari et al., 2009):

$$FAS = \left(1 - \frac{BD}{PD}\right) \times 100\% \quad (6)$$

where BD is the wet bulk density (kg m^{-3}) and PD is the wet particle density of the mixture (kg m^{-3}). The parameter BD was determined by weighing the reactor content and calculating the mixture volume and PD was estimated based on the procedure defined by Adhikari et al. (2009). Additionally, during composting monitoring, FAS was also quantified by a theoretical approach proposed by Richard et al. (2004):

$$FAS = \left(1 - BD \times \left(\frac{1 - DM}{D_w} + \frac{DM \times OM}{PD_{OM}} + \frac{DM \times (1 - OM)}{PD_{ash}}\right)\right) \times 100\% \quad (7)$$

where BD is the wet bulk density (kg m^{-3}), DM the fraction of dry matter, OM the fraction of organic matter in dry basis, D_w the density of water (kg m^{-3}), PD_{OM} the particle density of organic matter (1600 kg m^{-3}) and PD_{ash} the particle density of ash (2500 kg m^{-3}).

2.4 – Statistical analysis of data

In what concerned organic matter mineralization during composting evolution, differences between mixtures with and without eggshell were estimated using one way ANOVA and Tukey test at a p-value (significance level) of 5%.

Statistical analyses, model fitting and numeric integrations were performed in software Matlab (Version 7.8.0.347, Math- works, USA).

3- RESULTS AND DISCUSSION

3.1 – Selection of a composting mixture composition

It is well established that the self-heating capacity of a composting mixture depends on the heat production rate during the microbial breakdown of organic materials. This parameter can be considered as linearly dependent on the oxygen consumption rate (Barrena et al., 2006) and determines the extent to which easily biodegradable organic matter has decomposed (Barrena et al., 2011). In fact, also according to Scaglia et al. (2000) higher demand of oxygen per unit of organic matter can be understood as higher release of heat produced by biodegradation, if heat losses by evaporation, conduction and convection are kept low. To categorize the biological activity of organic mixtures and thus establish a comparison of the potential self-heating capacity, Barrena and co-

workers proposed three main categories based on the rate of oxygen consumption (Barrena et al., 2011):

- i) high biodegradable (respiration activity higher than 5 mg O₂. gVS⁻¹ h⁻¹);
- ii) moderate biodegradable (respiration activity within 2 to 5 mg O₂. gVS⁻¹ h⁻¹) and
- iii) low biodegradable (respiration activity lower than 2 mg O₂. gVS⁻¹ h⁻¹).

In the scope of this work, the selection of the initial mixture for subsequent composting of eggshell was performed on a high self-heating based concept, meaning that finding the composting mixture with higher oxygen consumption per unit of organic matter during thermophilic activity was study prime goal.

For each mixture tested in the reactors SHR₁ to SHR₃, whose properties were indicated in Table 1, Fig. 1a) shows the temperature and airflow profiles and Fig. 1b) depicts the OUR evolution, over 25 days of composting trials.

For each mixture tested in the self-heating reactors 1 to 3 (SHR₁ to SHR₃), whose properties were indicated in Table 1, Fig. 1a) shows the temperature and airflow profiles and Fig. 1b) depicts the OUR evolution over 25 days of composting trials

The results reveal that regardless of the mixture composition, temperature profiles have the expected behaviour over time, where the three classic phases are well observed (Zhu, 2006). Indeed, a short initial phase is visible due to the activity and growth of mesophilic organisms that increase the temperature within the first 24 h of composting. Then, the thermophilic phase (T>40°C) was developed and lasted about 7 days, promoting degradation of materials, while non-thermo-tolerant organisms were inhibited. Finally, the mesophilic activity arose once again and determined the temperature profile, reflecting the depletion of readily biodegradable components. The maximum temperatures achieved were 61.9, 60.4 and 57.5°C for SHR₁ to SHR₃, respectively.

Differences between mixtures were also observed in terms of time/temperature relations for thermal inactivation of pathogens. In accordance to Haug (1993), most common pathogens and parasites present a minimum threshold of 55°C during 10 to 60 min of exposure for thermal inactivation. In this study, SHR₃ presented a lower exposure period of 5 consecutive hours to 55°C, while for SHR₁ and SHR₂ that period attained 81 and 68 hours, respectively. Nevertheless, none of the mixtures tested attained the criteria of temperature exposure (70°C for 1 h) imposed by Commission Regulation (EU) N°142/2011 now in force, which might be a consequence of excessive aeration (high airflow rates).

However, according to Fig. 1a) the heat removal by convection may have been lower for SHR₃ in comparison with SHR₁ and SHR₂, because the air flow rate applied by kg of VS was smaller in the former case. Therefore differences found in terms of time/temperature exposure should be attributed to the biodegradability of the organic matter in the starting material. The lower capacity of mixture SHR₃ to achieve and maintain higher temperatures is also observable in OUR profile. According to Fig. 1b) the maximum OUR reached in SHR₃ ranged the interval characterized by moderate biodegradability as

indicated by Barrena et al. (2011), which points out a smaller availability of biodegradable organic matter. This is probably due to the presence of higher amounts of rice husks that contain significant levels of recalcitrant organic matter. In addition, also biodegradability of the potato peel may play a role owing to the presence of compounds like lignin and phenolic substances (Ezekiel et al., 2011) that are rather resistant to degradation and their rate of disappearance is not as fast as that of polysaccharides (Said-Pullicino et al., 2007).

For the mixtures SHR₁ and SHR₂ the maximum OUR reached the level of “high biodegradability”, but the OUR cumulative values for thermophilic phase ($T > 40^{\circ}\text{C}$) were 432 and 624 g O₂ kg⁻¹ of organic matter for SHR₁ and SHR₂, respectively. This means that the SHR₂ mixture is characterized by a higher thermal energy to drive the composting process into thermophilic temperatures and induce pathogen elimination as required for eggshell recycling by composting.

However, high biodegradable mixtures may impair composting because when materials decompose quickly, pores between particles are reduced and gas transfer conditioned (Albuquerque et al., 2008). Therefore, FAS was quantified according to Eq (6) and (7) and pore space evolution during composting is presented in Fig. 2a)-b).

In general, FAS calculated by Eq. (6) is slightly lower than quantification provided by the theoretical approach proposed by Richard et al. (2004), Eq. (7), with relative errors ranging between -1.6 to -8.9%. Nevertheless, FAS evolution during composting was similarly described by the two equations used in this study, and both emphasized that SHR₂ undergoes a more prominent reduction of FAS during the most active phase of biodegradation (the initial 7 days of compost). But the proportion of rice husk in mixture SHR₂ allowed to maintain FAS far above 30%, which is commonly considered to be the limiting value (Huet et al., 2012). Thus, it was considered that the higher biodegradability of SHR₂ places no restriction on the pore volume. Therefore, the SHR₂ mixture was selected for further experiments.

3.2 – Co-composting of industrial eggshell in a pre-selected organic mixture

To investigate the effect of eggshell (ES) waste on composting process evolution, two mixtures were tested: SHR₂-0%ES constituted by the mixture previously selected from reactor SHR₂, and SHR₂-30%ES involving 30% (w/w) of ES and 70% (w/w) of SHR₂.

In these experiments, a working reactor volume of 105 L was used, and the starting airflow was set to 3.5 L min⁻¹, equivalent to 0.5 L min⁻¹ kg⁻¹ of initial organic matter. The air volumetric rate was adjusted over time, and homogenization and sampling procedures followed the methods aforementioned.

3.2 1– Temperature profiles and self-heating capacity

The profiles shown in Fig. 3a) demonstrate that in both mixtures there was rapid increase in temperature, mainly due to microbial metabolism favored by the presence of readily available organic substances. The reaction temperature reached about 70°C and remained above that value for 18 consecutive hours for SHR₂-0% ES and 8.7 successive hours for SHR₂-30% ES, and thus fulfilling the minimum time and temperature sanitizing requirements of 1 h at 70°C, proposed by Commission Regulation (EU) N°142/2011. The incorporation of 30 % of ES did not significantly affect the biodegradability of the mixture. Indeed, OUR profiles remained near to the high biodegradable level (even slightly higher than without eggshell) and their cumulative values for the thermophilic phase were also identical (Fig. 3 b)): 545 g O₂ kg⁻¹ VS (7.6 days with T>40°C) and 566 gO₂ kg⁻¹ VS (7 days with T>40°C) for SHR₂-0%ES and SHR₂-30% ES, respectively. This unexpected similarity between mixtures is also supported by the identical organic matter content in starting mixtures, namely 7.6 kg and 7.3 kg of VS for SHR₂-0%ES and SHR₂-30% ES, respectively.

Although it was expected that the incorporation of ES in the mixture SHR₂ could change the global amount of organic matter available for degradation, that did not occur because ES is a high density material (763 kg m⁻³) which increased SHR₂ bulk density from 245 kg m⁻³ to 323 kg m⁻³.

Consequently, the amount of organic matter for SHR₂-30% was nearly identical to SHR₂-0%, once the initial working volume of the reactors was kept constant.

Moreover, by reducing the air flow initially fed to the mixture SHR₂ from 1.3 to 0.5 L min⁻¹ kg⁻¹ of initial organic matter, a significant increase in the maximum temperature was attained (from 60.4°C to 72.8°C, Fig. 1a) and Fig. 3a)). These findings indicate that the mixture was sensitive to the flow rate of air with respect to removal of heat by convection during composting. Regarding biodegradability, the maximum OUR reached was slightly reduced in the early stage of the process (5.3 to 4.8 g O₂ kg⁻¹ VS h⁻¹, Fig. 1b) and Fig. 3b)), probably due to an initial limitation in oxygen concentration during that stage, but that change was determinant to reduce convective heat losses, and therefore attain the desired the sanitation temperatures needed for ES treatment. Nevertheless, seeding of the initial mixture would be a worthwhile option to evaluate in future studies. In fact, the addition of adequate inoculants could enhance global biotransformation (reaction rates) with consequent reduction of the mixture susceptibility to the air convective effects.

3.2 2– Moisture content, pH and physical changes

To provide the necessary substrates and nutrients for microbial activity during composting, the moisture content should be in the range from 50% to 70% (Ahn et al., 2008). Indeed, high levels of humidity are harmful for efficient composting development, since it leads to a decrease of the air void volume available (free air space) for oxygen movement.

The moisture content, pH and FAS profiles for the mixtures tested are presented in Fig. 4a)-b). From these results it is clear that the incorporation of ES in the SHR₂ reduced the initial moisture content from 68 to 53% and during the process these values remained relatively unchanged without any external water correction. The reactors used were not equipped with a gutter and therefore part of the water vapor lost from composting mixture, by evaporation, was allowed to condense on the reactors top cover and drop back to the solid matrix, maintaining moisture content in the range shown in Fig.4. In particular, the mixture SHR₂-0%ES had a relatively high moisture content, but the rice husk used as bulking/amendments agent allowed to maintain FAS values (Fig. 4) well above 30%. In addition, the mixture with 30% ES presented a lower FAS available in the organic matrix, as a result of the higher bulk density of the eggshell material. Nevertheless, the air void volume was kept relatively stable.

A significant rise in pH was observed in the aqueous extracts of the composting matrix from both reactors over 25 days of operation (Fig. 4). During the first four days of thermophilic activity, pH increased from a neutral range (6.6 and 6.9 for SHR₂-0%ES and SHR₂-30%ES) to an alkaline level near 9. During the composting processes, pH reached a maximum of 9.4 for SHR₂-0%ES and 9.5 for SHR₂-30%ES. Kumar, et al. (2010) observed a similar pattern for green and food waste. The evolution of this variable is often driven by the ammonification, which corresponds to the transformation of organic nitrogen to $\text{NH}_4^+/\text{NH}_3$ (De Guardia et al., 2010).

3.2 3– Organic matter evolution

The extent of organic matter mineralization is shown in Fig. 5, where different letters indicated that differences are statistically significant, according to the Tukey's test with p-value < 0.05. The overall organic reached about 45% at the end of 25 days, which is statistically equal for both processes (with and without ES). However, during the initial 4 to 5 days of the process SHR₂-30%ES seems to favor organic matter degradation since its content was 8.5% lower in comparison to SHR₂-0%ES, and in this case mean values are statistically different. In addition, during the first 4 days of composting, cumulative OUR for the mixture with ES was 13% higher than SHR₂-0%ES (Fig. 3 b), which corroborates the organic matter profile.

3.2 4– Nitrogen dynamics

One of the main transformations of nitrogen during aerobic composting of an organic matrix includes ammonification that leads to the release of ammoniacal nitrogen (De Guardia et al., 2010; Zeng et al., 2012b). Moreover, the total ammoniacal nitrogen can be immobilized as organic nitrogen, accumulated in the compost, emitted as ammonia and/or converted into nitrate and then molecular nitrogen through nitrification and denitrification, respectively. Therefore, during the composting

process, nitrogen can be either kept in the solid matrix, lost through leaching or released as ammonia, nitrous oxide or molecular nitrogen in exhaust gases.

Fig. 6 a)-b) present the content of nitrogen species over time of the mixtures tested (SHR₂-0%ES and SHR₂-30% ES), and Fig. 6c) depicts cumulative nitrogen losses over time. Since no leachates were produced during composting experiments, it was assumed that nitrogen losses by this route were negligible.

In terms of nitrogen species, initial composition of the studied composting mixtures was affected by eggshell incorporation. In fact, due to the protein fibers embedded in the ES (Meski et al., 2011), the organic nitrogen present in the starting composting mixture increased by 45% but the N-NH₄⁺ content was lowered by 15%, when SHR₂-30%ES mixture is compared to SHR₂-0%ES (Fig. 6a)-b)).

As the process started to evolve during the first 4 to 5 days of composting, the organic N concentration decreased by ammonification. However, this did not lead to N-NH₄⁺ build up in the organic matrix (Fig 6a)-b)). In fact, N-NH₄⁺ concentration profiles have also declined, indicating the occurrence of ammonia volatilization associated to the thermophilic period, characterized by higher temperature and pH values. De Guardia, et al. (2008) have also obtained similar results in their studies on nitrogen dynamics during the composting of wastewater sludge and woodchips, concluding that N-NH₄⁺ concentration in the organic matrix was smaller when composting temperatures were higher. Zeng et al. (2012a) have found that ammonification is a key process to N losses during the composting of organic matrices. Thus, in this study it was observed that the N losses sharply increased during the first days of composting, and SHR₂-30%ES was the mixture with higher nitrogen transfer (Fig. 6c)). Indeed, once the temperature started to decrease, the ammonia volatilization hampered the increase of N-NH₄⁺ concentration in the composting mixture and organic nitrogen profile decrease became smoother. An important outcome of this research, according to Fig.6c), is the fact that eggshell incorporation may enhance N losses from organic matrix (1.25 times higher), which is in agreement to the C/N ratio of the tested mixtures: 23 for SHR₂-0%ES and 18 for SHR₂-30%ES. These results are similar to some of those reported in previous studies (Zeng, et al., 2012a).

In what concerns nitrification, it was been accepted that nitrate is nearly absent during thermophilic phase because high temperatures are indicated as adverse to nitrifying bacteria (Sanchez-Monedero et al., 2001). However, recent studies have pointed out that ammoniacal nitrogen oxidation to nitrate is inhibited by intensive organic matter degradation (Zeng et al., 2012b). In this study, the nitrate content became relevant at day 12 for SHR₂-30%ES, when temperatures were close to 25°C, indicating that ammonia-oxidizing bacteria (AOB) activity was enhanced. However, for SHR₂-0%ES no significant nitrate concentration was quantified, yet that does not clearly indicate that the absence of nitrification occurred, because N₂O emissions were not here quantified. Nevertheless, according to Zeng et al. (2012b) several factors may be responsible for the lack of AOB activity, namely slow growth of AOB

(low cell yield), the inhibition by the competitive activities of heterotrophic microorganisms, and the low oxygen transfer rate between air flow and biofilms on the surface of the particles.

3.2 5– Final compost quality

After 25 days of composting in self-heating reactors, solid mixtures were allowed to conclude the maturation phase in small piles that were homogenized and moisture corrected every week, until 144 days of composting. The main properties of the final composts obtained in this study are presented in Table 3. Both composts exhibited alkaline pH and low electrical conductivity (EC). The organic matter (OM) content in the SHR₂-30%ES final product was lower due to the high percentage of eggshell initially incorporated in the mixture (30% in wet basis). In addition, the compost with ES was Ca enriched and presented a significant equivalent content in CaCO₃, meaning that its higher neutralizing capacity can be used to correct soil acidity. The maturity of composts can be confirmed by the low NH₄⁺/ NO₃⁻ ratio (<0.5) and by moderately low respiration rate corresponding to a stable compost (Brinton et al., 1995).

Independently of the presence of ES, composting end-products obtained were phytotoxin-free and therefore safe for soil application, since germination indices were close to 80%. Moreover, the presence of heavy metals was not a limiting factor for the final composts use as soil improvers, since concentration levels were small and below the limits imposed by the European proposed quality criteria for composting end-products (Table 3).

4- CONCLUSIONS

This study constitutes a first insight into the feasibility of co-composting industrial eggshell waste (ES) in self-heating reactors.

Experimental tests showed that ES incorporation did not affect significantly the capacity of the composting mixture to reach sanitizing conditions; however nitrogen losses were enhanced during the first 25 days of composting.

End-product quality assessment showed that finished composts presented physical, chemical and phytotoxic properties adequate for soil incorporation, even when 30% of ES was used in the composting starting mixture.

In spite of the inorganic nature of ES, its recycling through composting processes is possible for producing a high neutralizing Ca-rich soil improver.

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Figure 1: Evolution of (a) temperature and airflow rate and (b) OUR composting for SHR₁ to SHR₃ reactors.

Figure 2: Evolution of FAS during composting of SHR₁, SHR₂, SHR₃ a) by Eq (5) b) by Eq (6) (measurements correspond to means of 3 replicates and error bars indicate standard deviation).

Figure 3: Evolution of (a) temperature and air flow rate, (b) OUR and cumulative amount of oxygen consumption during composting of SHR₂ with 0 and 30% ES (w/w).

Figure 4: Evolution of a) moisture content, pH and b) FAS during composting of SHR₂ with 0 and 30% ES (w/w) calculated by Eq. (5).

Figure 5: Organic matter evolution in relation to initial volatile solids content in the organic matrix.

Figure 6: Total nitrogen, organic nitrogen and mineral nitrogen during composting of a) SHR₂-0%ES, b) SHR₂-30% ES and c) cumulative nitrogen losses.

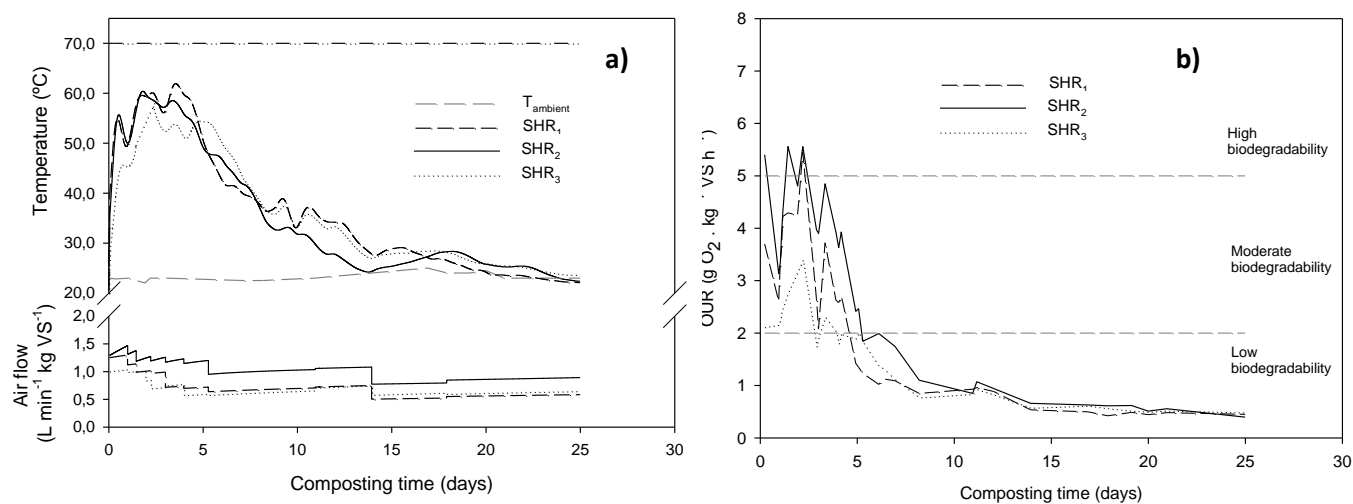


Figure 1: Evolution of (a) temperature and airflow rate and (b) OUR composting for SHR₁ to SHR₃ reactors.

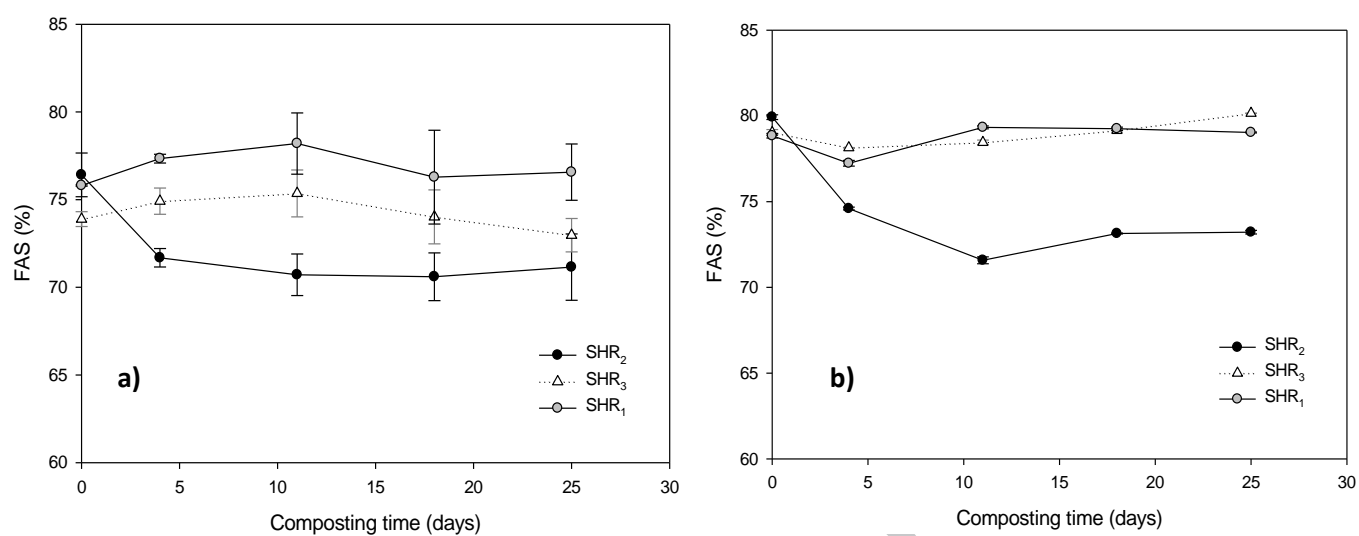


Figure 2: Evolution of FAS during composting of SHR₁, SHR₂, SHR₃ a) by Eq (5) b) by Eq (6) (measurements correspond to means of 3 replicates and error bars indicate standard deviation).

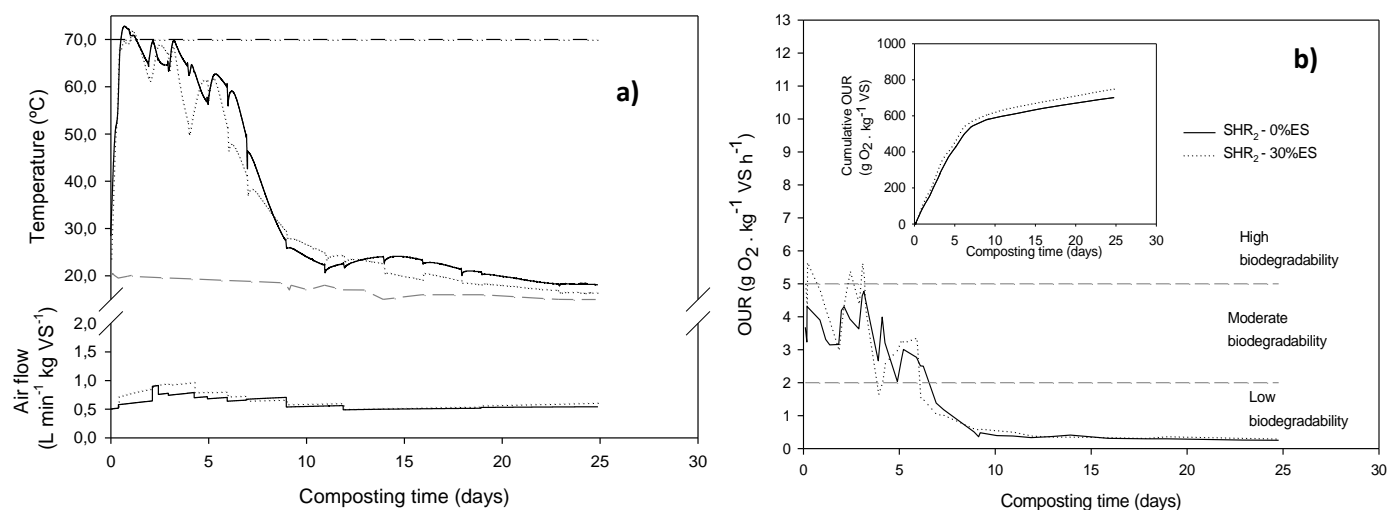


Figure 3: Evolution of (a) temperature and air flow rate, (b) OUR and cumulative amount of oxygen consumption during composting of SHR_2 with 0 and 30% ES (w/w).

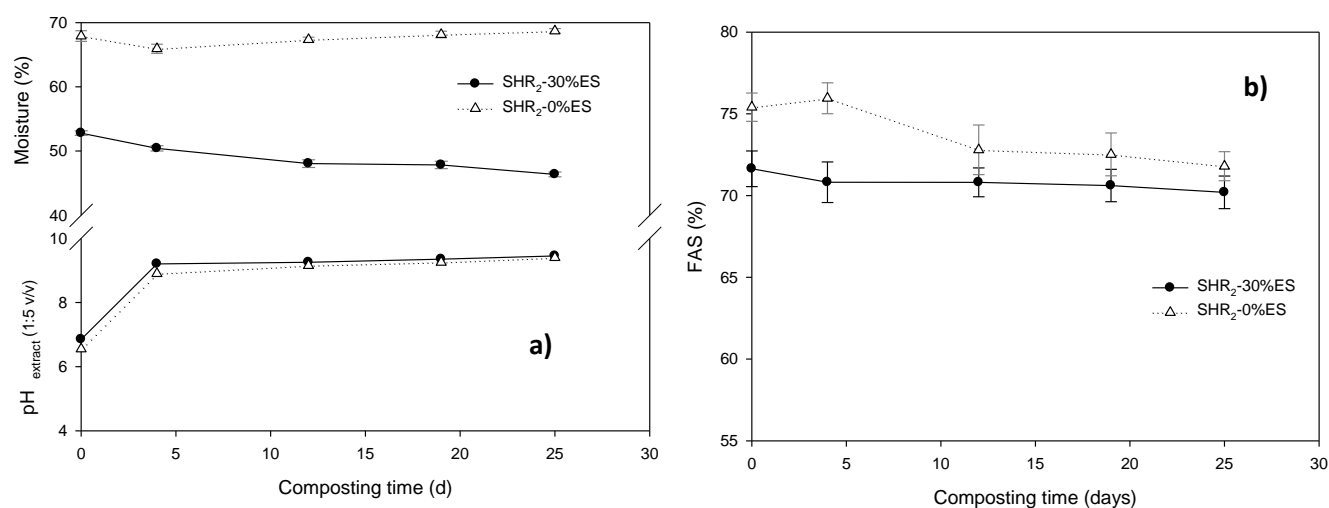


Figure 4: Evolution of a) moisture content, pH and b) FAS during composting of SHR_2 with 0 and 30% ES (w/w) calculated by Eq. (5).

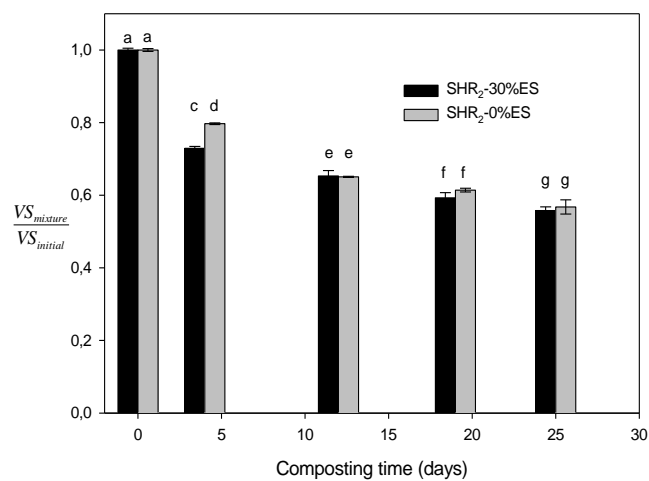


Figure 5: Organic matter evolution in relation to initial volatile solids content in the organic matrix.

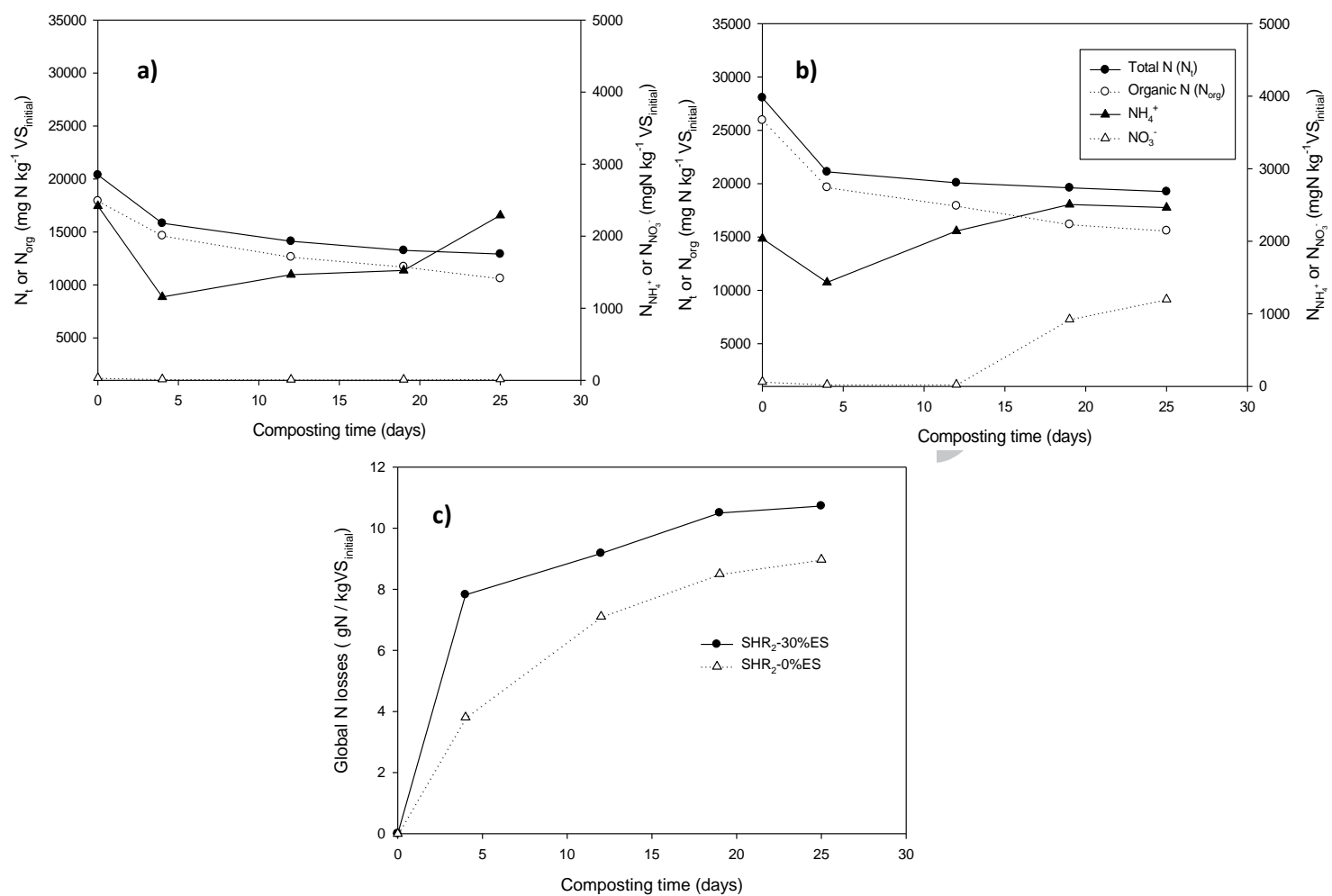


Figure 6: Total nitrogen, organic nitrogen and mineral nitrogen during composting of a) SHR₂-0%ES, b) SHR₂-30% ES and c) cumulative nitrogen losses.

Table 1: Composting mixtures characteristics tested in the self-heating reactors.

	SHR ₁	SHR ₂	SHR ₃
PP (%w/w)	58.7	50.6	66.0
GC (%w/w)	19.4	32.4	8.1
RH (%w/w)	21.9	17.0	25.9
Mixture mass (kg)	23.8	22.7	24.2
Moisture Content (%)±sd	70.5±1.3	69.6±1.5	64.3±1.2
Volatile Solids (VS) (%)±sd	86.7±0.03	85.9±0.03	86.2±0.03
Predicted FAS (%)±pi	73.9±4.2	76.7±4.0	71.0±4.5

SHR: self-heating reactor; PP: potato peel; GC: grass clippings, RH: rice husk, sd: standard deviation, pi: prediction interval

Table 2: Properties of industrial eggshell (mean±standard deviation)

Moisture (%)	pH	Equivalent CaCO_3 content ($\text{g CaCO}_3 \text{ g}^{-1} \text{ dm}$)	Bulk density (kg m^{-3})	FAS (%)	OM ($\text{g VS g}^{-1} \text{ dm}$)	TOC/TN
15.4±0.9	8.3±0.1	89.4±0.2	763±8	59.3±1.7	0.063±0.001	2.1±0.2

Table 3: Main properties of the final composts, after 144 days of composting

Property	SHR ₂ - 0% ES	SHR ₂ – 30% ES
pH	9.3±0.1	8.9±0.1
EC ($\mu\text{S cm}^{-1}$)	846	1028
Equivalent CaCO_3 ($\text{g CaCO}_3 100\text{g}^{-1} \text{ dm}$)	5.0±0.1	61.4±1.7
OM ($\text{g VS g}^{-1} \text{ dm}$)	0.794±0.005	0.285±0.003
TOC/TN	21.0	11.9
$\text{NH}_4^+ / \text{NO}_3^-$	0.1	0.23
GI (%)	75.5±9.1	76.4±10.7
Respiration rate ($\text{mg C-CO}_2 \text{ g}^{-1} \text{ C d}^{-1}$)	5.31±1.1	3.55±0.17
$\text{C}_{\text{HA}}/\text{C}_{\text{FA}}$	0.45±0.02	2.66±0.24
Ca ($\text{g kg}^{-1} \text{ dm}$)	4.0±0.02	222.5±3.23
Cd ($\text{mg kg}^{-1} \text{ dm}$) (limit:1.5)*	0.70±0.01	0.40±0.01
Cr ($\text{mg kg}^{-1} \text{ dm}$) (limit:100)*	12.4±1.0	4.20±0.01
Pb ($\text{mg kg}^{-1} \text{ dm}$) (limit:120)*	12.7±0.01	7.30±0.01
Cu ($\text{mg kg}^{-1} \text{ dm}$) (limit:100)*	8.2±0.20	5.2±0.23
Zn ($\text{mg kg}^{-1} \text{ dm}$) (limit:400)*	47.4±0.3	11.9±0.1

EC: electrical conductivity; OM: organic matter; VS: volatile solids; TOC: total organic carbon; TN: total nitrogen; GI: germination index; HA: humic-like acid; FA: fulvic-like acid; dm: dry matter; * values in brackets represent the limit concentration according to End-of-waste criteria on biodegradable waste subject to biological treatment (3rd draft).

Highlights

- >Eggshell waste (ES) recycling in self-heating composting reactors was investigated
- >Potato peel, grass clippings and rice husks were the starting composting materials
- > ES incorporation did not affect the self-heating capacity of the mixture
- >Nitrogen losses were enhanced by ES during thermophilic period
- >A calcium-rich marketable compost for soil application was obtained