

Article

Composting as an Alternative for the Treatment of Solid Waste from the Kraft Pulp Industry

Marcia Zambrano Riquelme ^{1,*}, Dante Rodríguez-Luna ², Francisco Javier Alcalá ^{2,3} , Olga Rubilar ¹, Marysol Alvear ⁴ , Francisco Encina-Montoya ⁵  and Gladys Vidal ^{6,7} 

- ¹ Departamento de Ingeniería Química, Universidad de La Frontera, Temuco 4811230, Chile
² Facultad de Ingeniería, Instituto de Ciencias Químicas Aplicadas, Universidad Autónoma de Chile, Santiago 8910060, Chile
³ Departamento de Desertificación y Geo-Ecología, Estación Experimental de Zonas Áridas (EEZA-CSIC), 04120 Almería, Spain
⁴ Departamento de Ciencias Químicas y Recursos Naturales, Universidad de La Frontera, Temuco 4811230, Chile
⁵ Nucleus of Environmental Studies, Catholic University of Temuco, Temuco 4781312, Chile
⁶ Environmental Engineering & Biotechnology Group (GIBA-UDEC), Environmental Science Faculty & EULA-CHILE Center, Universidad de Concepción, Concepción 4030000, Chile
⁷ Water Research Center for Agriculture and Mining (CRHIAM), ANID Fondap Center, ANID/FONDAP//15130015, Victoria 1295, Concepción 4030000, Chile
* Correspondence: marcia.zambrano@ufrontera.cl; Tel.: +56-45-232-5472

Abstract: The increasing industrial pulp production has led to a negative growth of the associated solid wastes, thus making necessary alternative ways of handling them in suitable sanitary landfills to minimize adverse effects on the environment and well-being of people. Solid waste treatment prior to its disposal is a target to minimize pollution of the natural resources (air, soil, water) due to accidental leaching. This paper aims to determine better experimental conditions in the container to develop an optimal composting design for pulp solid wastes. For this, an experimental methodology is introduced. This paper presents the results about the influence of independent control variables (grits addition and composting process time) on dependent variables (chemical and biological), for which a composting design was used, and a face-centered central composite factor was applied. The results showed mature compost over 60-day treatment, with the following experimental observations (i) the grits addition did not decrease the pH in the first stage of the composting process; and (ii) the microbial activities were high during the active stage of the composting progress and evolved to stable, lower values together with a proper trend of $N-NH_4^+$ and $N-NO_3^-$ at the end. Grits addition of around 6% is the optimal experimental amount to use for the composting process of the secondary sludge from the Kraft mill industry. In conclusion, treating secondary sludges and grit residues from the Kraft mill industry to produce compost is feasible and sustainable. This action reduces the environmental pollution risk (evidenced by soil pH change and possible water pollution) and improves the soil assimilation capability of inorganic micronutrients and organic compounds after application. Thus, the controlled waste reuse will pass from a negative input to the environment to a positive, sustainable solution, which can be used as a soil-nutrient improver in agriculture.

Keywords: grits; composting process; kraft mill; soil improver



Citation: Zambrano Riquelme, M.; Rodríguez-Luna, D.; Alcalá, F.J.; Rubilar, O.; Alvear, M.; Encina-Montoya, F.; Vidal, G. Composting as an Alternative for the Treatment of Solid Waste from the Kraft Pulp Industry. *Agronomy* **2023**, *13*, 1099. <https://doi.org/10.3390/agronomy13041099>

Academic Editor: Sung-Cheol Koh

Received: 13 March 2023

Revised: 4 April 2023

Accepted: 7 April 2023

Published: 12 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In South America, the pulp and paper activities in Argentina, Brazil, Chile, Colombia and Uruguay are of key importance in the global context, currently covering 11% of the global pulp production and 33% of the global pulp exports. Today, South American chemical commerce pulp capacity could theoretically add another 30 million tons based on already announced projects; no other world region is adding whatever is close to

such capacity [1]. Regarding the country's capability, in 1990, Chile was the 10th pulp producer in the world market with a total production of 0.6 million Air Dry Tone (ADT), whereas in 2000 was the 6th producer with 1.8 million ADT. In 2010, Chile became the 4th world producer with 4.5 million ADT, followed by Brazil, Canada and the United States of America [2]. Chile and Uruguay have increased by more than 16 million tons, so no other similar regions have recorded a similar increase [3].

The increase in pulp production implies a growing amount of waste, which is worrying considering the environmental and social implications that this may have. The waste amount generated from pulp production is technology dependent but is estimated to be around 200 kg per ADT [4]. Gavrilescu [5] reported that wastes generated in the Kraft mill fluctuated from 200 to 600 kg per ADT, attending to technology efficiency.

In relation to waste management, the most used current options for their disposal are dehydration, followed by incineration or dumping [6,7]. Sludges from biological wastewater are hard to handle owing to a high presence of microbial community and high humidity content, which is around 99%. The difficulty of finding suitable landfill sites is increasing as urban areas expand [8]. In Europe, for example, landfills have been significantly reduced in recent years as the final disposal of solid waste. Additional alternatives, including pyrolysis, gasification, land spreading, composting and reuse as a building material, are being used, even though more investigation for optimizing the operation is still needed. Gopinathan and Thirumurthy [9] reported that the organic fraction of municipal solid waste and composted pulp mill sludge was a good source of organic matter, phosphorus, nitrogen, and other nutrients, which can be used as additional fertilizer to improve the organoleptic properties of agriculture soils [10,11].

Generation of solid wastes in the pulp and paper industry generates around 45% wastewater sludge (0.2–1.2 kg dry matter (DM) per kg of biological oxygen demand (BOD) removed), 25% ash (what can be used to modify the pH in acid soils [12–14]), 15% wood cuttings and waste, and 15% associated to other solid waste. Wastewater treatment sludge (50–140 kg per ADT) constitutes the substantial solid wastes generated by the pulp and paper industry [15]. In Chile, this type of waste is generally disposed of in sanitary landfills, which are environmentally and sanitary authorized. However, these sites are increasingly scarce due to the conflict this activity poses on the environment, which is regulated by the Environmental Impact Assessment System (EIAS) [16].

The total organic content (TOC) contained in the sludge is around 37% and may have potential positive effects on amending degraded soils [17,18]. Moreover, the alkalinity of grits should help to alleviate the pH decrease during the initial phase of the composting process. Grits are inorganic waste with alkaline pH obtained from the lime slaker classifier of the re-causticizing process [19]. The addition of grits to acid soil increased pH from <5 to values in the 7.4–8.2 range, measured in CaCl_2 [12]. This range is higher than the values observed in a mixture of commercial lime and acid soil since CaO present in the solid wastes is more reactive than industrial CaCO_3 present in the commercial lime. A 10–30% addition of grits to amend soils increased pH and water content, thus improving the chemical availability of nutrients [20,21]. Therefore, composted pine bark has been found to be suitable as a growing substrate for forestry seedlings and other seeds [22]. Bark can improve the tilth, structure, and aeration of soils and increase water absorption. Except for nitrogen, it has a high ion exchange capacity and contains all the nutrients necessary for a good soil organic content.

The focus on biosolids waste management and their products has changed from disposal to its favorable use [23,24]. The non-composted, direct use of pulp mill sludge in agricultural soil may guide to severe negative effects on the crops [25]. The successive application will need periodical monitoring of the optimal amount used and application time spanned to avoid soil and water pollution. Secondary sludge is often difficult to handle (due to the high microbial content and low solid content). The sludge must be dewatered before being deposited in a landfill, in otherwise, soluble nutrients would be subsurface leached, thus contaminating soil and groundwater. The compost obtained

from the combination of composted primary and secondary pulp sludge and ashes from the Kraft mill recovery boiler was found as a satisfactory land conditioner [6]. Actually, variation in composting process pH evolution due to grits addition should inhibit the metabolic activity of the composting process. Comparatively, not much knowledge about the biological and biochemical activities as indicators to evaluate the rate of the process is available, even when the utility of the biological activities as indicators of microbial activity has been proved [26–28]. For instance, Ryckeboer et al. [29] proved the applicability of enzyme assay based on the hydrolysis of the FDA to make a prediction of microbial activity during the composting process.

On the premise that untreated or deficiently treated compost directly applied on the land to amend degraded soils may have potentially negative effects on the environment, this paper is aimed at evaluating the best composting condition to achieve a correct composting design for pulp waste revalorization. In this paper, the best composting condition is defined from an experimental combination of grit additions and composting process time, whereas the correct composting design is defined from a threshold for certain physicochemical and biochemical parameters.

2. Materials and Methods

2.1. Solid Waste

The solid waste was acquired from a kraft pulp mill industry located close to Collipulli city in Araucanía Region (IX) in southern Chile, where there are other pulp factories. Figure 1 shows the location of the selected kraft pulp industry. The plant makes an elemental chlorine-free bleached and complies with the standards related to the emission of organochlorine substances [30]. The sludges were obtained from the sedimentation pond, the bark (1–10 mm) was obtained from the wood debarking, and the grits were obtained from the lime slacker clarifier (re-causticizing process). After, the sludge was stored at 4 °C in a cold room. The sludge has a high moisture content (87.8%) and a low C:N ratio (8.9). Includes macronutrients, such as K (0.24%), P (0.39%), Mg (0.44%), Ca (1.7%), and micronutrients, such as Zn (0.12%) and Fe (0.47%), which are necessary for plant growth. Grits were air-dried and sieved to 0.2 mm before mixing with the sludge [13]. Its alkalinity (pH 12.7) is probably due to the unslaked lime encapsulated in the particles ‘grits’ slowly reacting and releasing hydroxide ions [31].

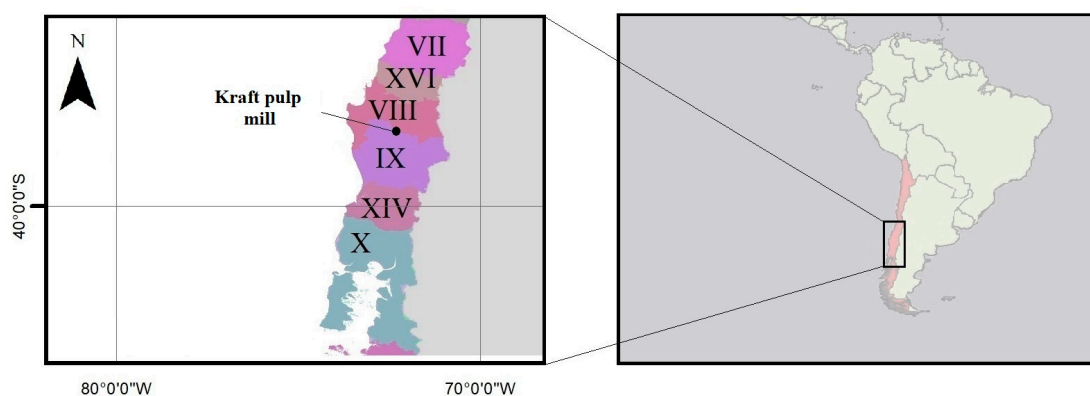


Figure 1. Location of the kraft pulp mill.

2.2. Bulking Agent

As a bulking agent, a mixture of Pine bark (1–10 mm)—12.8% moisture, 4.0 pH and 265 C:N ratio of 265—and wood chips of 25–50 mm diameter was used [31].

2.3. Bio-Amendment

In order to achieve thermophilic conditions, in the laboratory reactor, 1 kg glucose (dry weight) per 55 dm³ was used as a supplemental source of C. The temperature of an optimized composting process was simulated (Aislapol S.A., Santiago, Chile), considering a large-scale process with the addition of cheap sources of bioavailable C [31,32].

2.4. Mixtures

According to the experimental design, grits were added to the pulp mill sludge in five dissimilar portions; bark addition was always 45%. The mixture (*v/v* proportion) was meticulously mixed before adding wood chips. They were collected from the rejected wood handling area and added at a volume-weighted ratio of 1:0.8 (pulp mill sludge: wood chips ratio) [31].

For a better statistical significance of findings, the composting process time and grit addition were considered independent variables.

The composting process time was selected mainly for its relevance in the final volume of the design of the composting reactor. Grits addition was selected to obtain an appropriate composting process due to its importance in the mixing. Using the response surface methodology (RSM) based on an experimental design, it was possible to relate dependent (pH, released CO₂ evolution, MBC and FDA hydrolysis) and independent variables with the minimum number of experiments, a face-centered central composite for two factors was used [31].

The use of RSM allows the determination of second-order polynomials and the identification of the statistical significance of the variables. The number of observations required for the two independent variables (composting process time and grits) was 11. For this, three levels (−1, 0, +1) and the central point replicated three times were considered. Thus, grits addition and composting process time used in the experimental design were 6%, 8% and 10%, and 20, 30 and 60 days, respectively. Experimental data were fitted to the following polynomial [31]:

$$Y = b_0 + b_1 \cdot t + b_2 \cdot G + b_{11} \cdot t^2 + b_{22} \cdot G^2 + b_{12} \cdot t \cdot G + \varepsilon \quad (1)$$

where *Y* represents the predictive response, *b* is the regression coefficients, *t* is the composting process time, and *G* is the added grits. This is a square regression model in terms of actual values. For regression analysis of the experimental data, the Design Expert software version 6.06 (State-Ease, Inc., Minneapolis, MN, USA) was used to fit the experimental equations and evaluate their statistical significance. The F-test (ANOVA) was used to check the statistical significance of a polynomial model [31,33].

2.5. Batch Composting Assays

First, Kraft mill sludge, pine bark, grits, glucose and wood chips were mixed using hand and fed to the reactors. Primary samples were obtained, and the filled reactors were connected to the control process equipment. There were 6 Islapol reactors (Aislapol S.A., Santiago, Chile) with a capacity of 55 dm³; these were connected to Siemens S7-200 Programmable Logic Controller (PLC) [31]. The outputs of this controller were connected with 4 on/off valves; these supplied an air flow using a 100 dm³ capacity compressor. The composting process considered the control of the temperature, which should not be higher than 55 °C. The temperature sensors were connected to the PLC for its supervision (Figure 2).

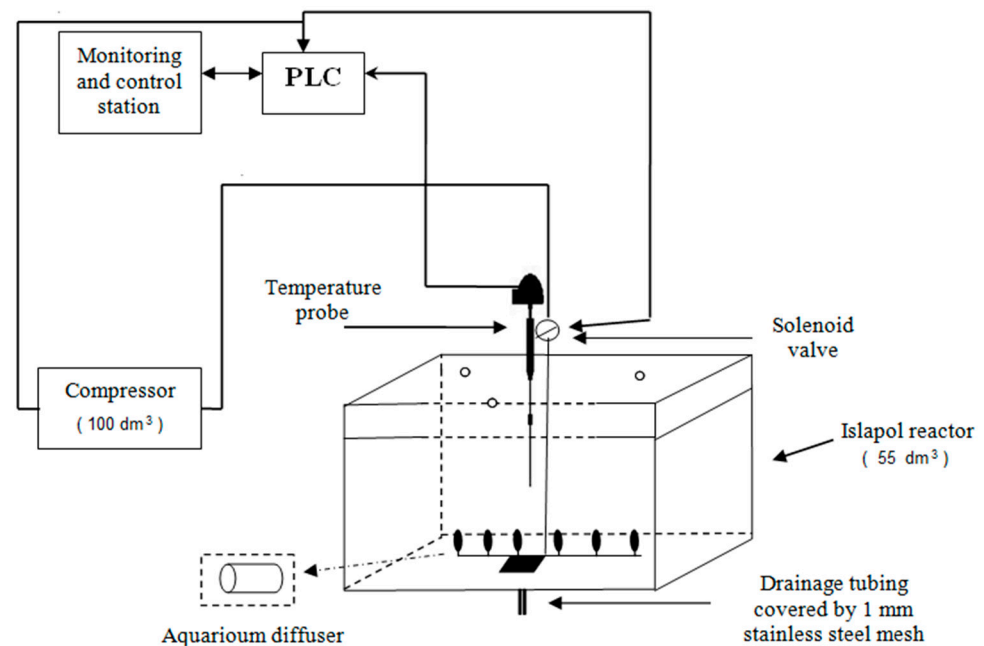


Figure 2. Diagram of the composting reactor.

For temperature control, the airflow injected into the lower part of each reactor was regulated. For this, solenoid valves were used considering an average airflow of $1 \text{ dm}^3 \cdot \text{min}^{-1}$, while an airflow of $3 \text{ dm}^3 \cdot \text{min}^{-1}$ was considered if the temperature was higher than $55 \text{ }^\circ\text{C}$. Data recording was carried out using System Control and Acquisition Data (SCADA) (Scadata, Inc., Mobile, AL, USA) [31].

Two 0.01-m holes were drilled in the upper part of the reactors. In addition, Master flex precision tubes with aquarium diffusers were placed at the bottom of each reactor to improve homogeneous aeration. Additionally, a leachate outlet was installed at the bottom of each reactor. The initial percentage of moisture for the mixtures fluctuated between 55% and 65% (moist basis), close to the 50–70% threshold reported in the literature [34]. Considering that the substrates have 70% initial humidity, it is not necessary to add water during the process. This condition differed from the 55–60% moisture content maintenance reported by some authors [35–37], whereas Sundberg and Jönsson [38] reported that water addition is a non-dependent variable.

2.6. Sampling

Sampling was carried out every 10 days after disconnecting the air injection. The compost sample of 1 kg was mixed prior to performing the analyses. The composting process was monitored for 60 days [31].

2.7. Analytical Methods

Different physical and chemical parameters of the grits were analyzed. Total N content was carried out using a Fison Instrument 1108 CHNS-O elemental analyzer on a dry substrate ($105 \text{ }^\circ\text{C}$) previously ground. Total organic carbon (TOC) was carried out using a carbonaceous analyzer on a sample of ground material previously treated with diluted HCl (1:1), dried (at $80 \text{ }^\circ\text{C}$) under a protective laboratory hood and dried for a further 2-h exposition at $105 \text{ }^\circ\text{C}$ [39]. Moisture content was obtained using a thermogravimetric moisture analyzer (OHAUS GmbH, Nänikon, Switzerland), a way to directly measure the moisture content of a sample by using the loss on drying [40]. Volatile solids were measured after the loss of weight on ignition ($550 \text{ }^\circ\text{C}$) for 4-h [38,41]. An elemental analyzer (Fison Instrument 1108) was used for the elemental analysis of the sample (P, Ca, Mg, K, Na, Al, Cd, Cu, Ni, Pb, S, Zn, Fe and Cr), using an inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. Compost pH was measured on compost extract

diluted 1:5 (g H₂O:g wet compost), according to Lei and VanderGheynst [26]. Microbial biomass carbon (MBC) was determined according to the chloroform fumigation extraction method [42]. The measurement of released CO₂ evolution was conducted by placing 100 g of compost into a 500-cm³ air-tight plastic vessel. Afterward, plastic vessels were left for incubation (25° for 10 days). Every seven-day, the bottle was taken for measurement and replaced with another bottle containing 10 cm³ of KOH. Next, the excess of KOH was titrated with 0.1 M HCl after BaCl₂ was added to the bottle. Lastly, CO₂ measurement was performed eight times during incubation on 7, 14, 21, 28, 35, 42, 49 and 56 days of incubation [43,44]. The N-NO₃⁻ and N-NH₄⁺ contents were measured by the MgODevarda alloy method using 2 N KCl extracts (sample/solution = 1:20) [45].

The microbial activity of compost was obtained using Spectrophotometric determination of the hydrolysis of fluorescein diacetate (FDA) [29,31]. This measurement considered 5 g of compost suspended in a phosphate solution 0.1 M to pH 7.6, which was subsequently stirred for 15 min, and FDA was added. Subsequently, this mixture was incubated at 25 °C for one hour. The stop of the reaction considered the addition of acetone in a final concentration of 50% *v/v*; later, it was filtered. The Optical density of the filtrate was measured at 490 nm (752 UV-visible spectrophotometers, Yoke Instrument, Shanghai, China), and the product formed was determined using a regression equation generated from standards of known concentrations. Blanks, without FDA addition, were also included to correct for background absorbance. The enzyme activity values are reported on a dry compost basis, while analysis was performed in triplicate [31].

3. Results and Discussion

3.1. Experimental Results

Chemical characterization showed the alkaline properties of the grits, which originated from the carbonate hydrolysis to calcium oxide [31]. The reactivity to water is the property that helped to slow down the pH diminution at the beginning of the process caused by the presence of organic acids (Table 1).

Table 1. The chemical and physical characterization of the grits.

Parameter	Units	Grits ¹
Humidity (%)	(%w/w ±RSD)	7.60 ± 0.1
N-total	(%w/w ±RSD)	<0.2
Phosphorus	(%w/w ±RSD)	0.74 ± 0.4
Potassium	(%w/w ±RSD)	0.14 ± 0.1
Calcium	(%w/w ±RSD)	37.50 ± 2.3
Magnesium	(%w/w ±RSD)	0.34 ± 0.3
Sodium	(%w/w ±RSD)	1.42 ± 0.1
Sulfur	(%w/w ±RSD)	1.20 ± 1.3
Aluminum	(%w/w ±RSD)	0.14 ± 0.9
Zinc	(%w/w ±RSD)	0.0019 ± 0.1
Copper	(%w/w ±RSD)	0.0021 ± 0.3
Iron	(%w/w ±RSD)	0.018 ± 1.9
Manganese	(%w/w ±RSD)	0.0029 ± 0.8
Boron	(%w/w ±RSD)	0.00053 ± 0.9
Organic matter	(%w/w ±RSD)	0.12 ± 3.3
pH		12.7

¹ Results were obtained using Fison's Elemental Analyzer.

Another important feature is referred to the potential fertilizing capability of the waste since its composition includes essential nutrients for the plants, such as phosphorus (0.74%), potassium (0.14%), magnesium (0.34%) and calcium (38%). Regarding the bark, its C:N ratio was 265, with 12.8% humidity content and 4.0 pH. The experiments were performed in concordance with the face-centered central composite design experimental plan (Table 2).

Table 2. Matrix of the face-centered composite design used to fit a second-order model.

Batch Experiment	Days	Grits Added G, %	pH	CO ₂ -C ¹	MBC ²	FDA ³
1	0	6	6.7	1860	15	137
2	60	6	8.9	195	2	145
3	0	10	7.3	1386	14	108
4	60	10	9.3	364	4	141
5	0	8	7.1	1699	12	131
6	60	8	9.4	265	3	145
7	30	6	8.9	265	3	185
8	30	10	9.3	384	4	156
9	30	8	9.1	264	3	171
10	30	8	9.1	362	3	170
11	30	8	9.0	364	3	175

¹ CO₂-C in µg·g⁻¹·d⁻¹. ² MBC—Microbial biomass carbon in mg C·g⁻¹. ³ FDA—Fluorescein diacetate in µgF·g⁻¹·h⁻¹.

3.2. Experimental Dependent Variables Functions

The experimental plan was used to analyze the effects of grits addition and composting process time on pH, released CO₂ evolution, MBC and FDA hydrolysis. The value obtained of the variable means the average of three samples. The deviations of these parameters were all less than 5% of the probability level relative to their respective means. The following polynomial function represents the effects of grit addition and operating time on pH.

$$\text{pH} = 4.84 + 0.11t + 0.41G - 0.00165t^2 - 0.016G^2 - 0.00013tG \quad (2)$$

The ANOVA of the quadratic regression function shows the suitable statistical significance of the model. In fact, the F-value of 174 (p -value ≤ 0.05) did demonstrate that this regression was statically significant at a 95% confidence level. Further, the model goodness-of-fit was checked by a 99% determination coefficient (R^2). Thus, the model fails to explain the 1% of variations in the response only.

The response surface shows the variation of pH regarding the number of grits added and the composting process time. As observed in Figure 3, the composting process time presents a greater influence on the pH in comparison with the added grits. The same was observed with dregs addition [32]. Initially, the pH ranged from 6.7 to 7.3 for all the mixtures. Between 6 and 10 days, the pH reached a maximum (8.0) during the thermophilic phase. In the response surface, a maximum pH (8.2) is observed during the 50–60-day maturation phase for grits addition. Then, the pH slightly decreased to reach final stable values in the 8.8–9.1 range for all the mixtures. These pH values satisfy the 5.0–8.5 established by the Chilean Standards for Composting 'Norma Chilena 2.880—Compost: Clasificación y requisitos', which is applicable to all types of compost [46].

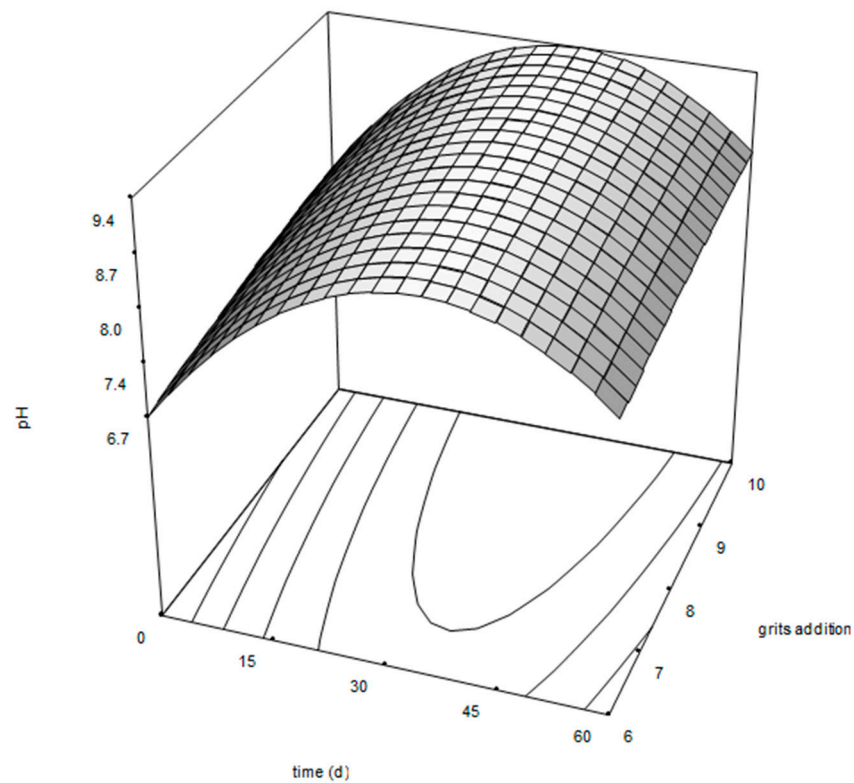


Figure 3. Variation of pH during the composting process for the mixtures is described in Table 2.

Figure 4 shows the temperature evolution during the process. Our experience shows a comparable pattern to that found in many other composting systems [47]. All reactors kept temperatures between 45 °C and 56 °C for about 10 days, with a subsequent decrease in environmental conditions.

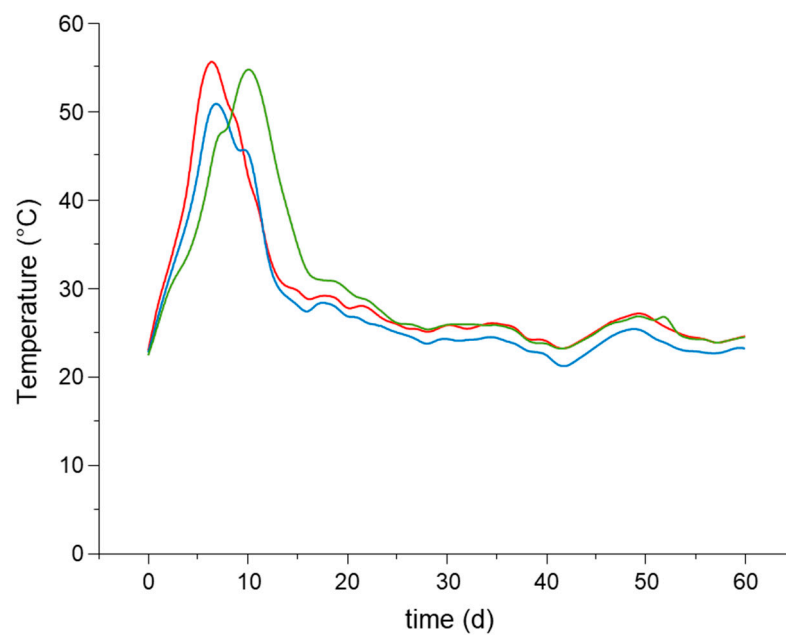


Figure 4. Temperature evolution for 6% (red line), 8% (blue line) and 10% (green line) addition of grits along the composting process.

Otherwise, the released CO₂ evolution was analyzed as a function of the actual values of grit addition and composting process time, with the following empirical relationship:

$$\text{CO}_2 = 2127.23 - 86.91t - 20.72G - 0.71t^2 - 4.70G^2 - 2.68tG \quad (3)$$

The significance of this function was demonstrated with an F-value of 117.9 more than the tabulated F-value of 5.05. The lack of fitting is not significant (p -value ≤ 0.05), with a high determination coefficient (R^2) of 99%.

Figure 5 shows how the released CO₂ evolution was more influenced by the composting process time than the grits added, which is a similar finding to that reported by Zambrano et al. [32]. Maximum released CO₂ evolution occurred close to the temperature peak, and a declining evolution was observed as temperature decreased. This result agrees with the conclusions from Ekinci et al. [48], who described that a maximum CO₂ progress rate occurred at 56 °C.

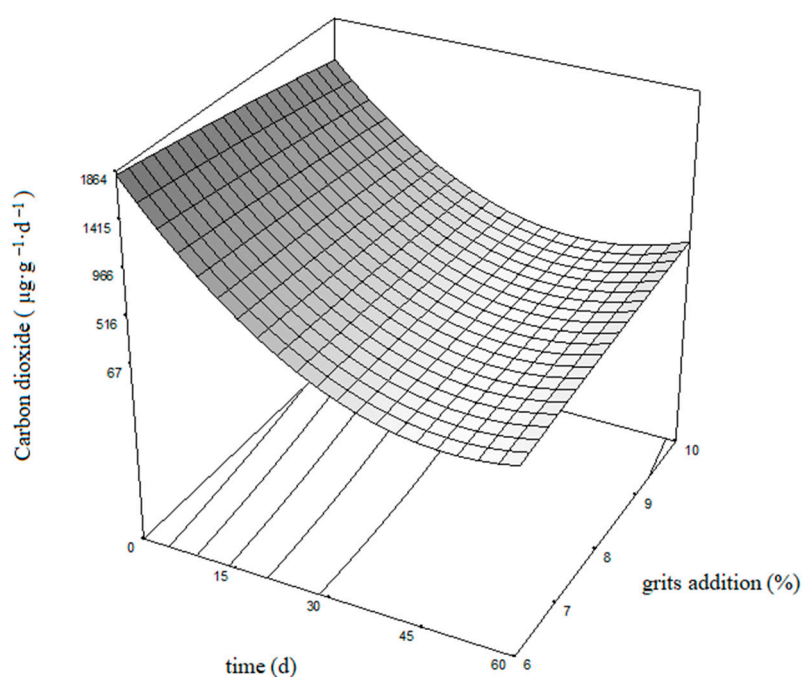


Figure 5. Released CO₂ evolution as a function of the composting process time and grits addition.

Initial basal respiration was about 2000 μg·g⁻¹·d⁻¹ and decreased at the end of the process to stable values in the 300–430 range for all the grit addition ranges. Similar values in the 300–600 μg·g⁻¹·d⁻¹ range were informed by Gattinger et al. [49] and Zambrano et al. [32], as long as Brewer and Sullivan [50] described values of 700 μg·g⁻¹·d⁻¹ at the end of a 70-day forced aeration composting process.

According to Haug [51], a lower microbial activity associated with mature compost produces a lower respiration level. The diminution of the released CO₂ evolution at a different compost maturation pace was accompanied by a diminution of the total microbial biomass, not even for maximum pH values of 8.5–9.2 obtained during the composting process. The experimental results were evaluated through the following Microbial Biomass Carbon (MBC) polynomial function:

$$\text{MBC} = 26.45 - 0.59t - 3.17G + 0.005t^2 + 0.18G^2 + 0.01tG \quad (4)$$

The ANOVA of the quadratic regression function demonstrates the suitable statistical significance of the model. The F-value of 85.6 (p -value ≤ 0.05) demonstrates that this regression was statically significant at a 95% confidence level. The model goodness-of-fit was checked by a 99% R^2 . Thus, the model fails to explain the 1% of variations in the

response only. Figure 6 shows how the MBC is more affected by the composting process time than the grits addition in its linear and quadratic form. During 40 days, the MBC changes fluctuated between 9 to 15 $\text{mg}\cdot\text{g}^{-1}$, which is similar to the 5–12 $\text{mg}\cdot\text{g}^{-1}$ range informed by Charest et al. [52] for the first half of the composting period. MBC stabilized at values close to 4 $\text{mg}\cdot\text{g}^{-1}$, which is equivalent to the 3 $\text{mg}\cdot\text{g}^{-1}$ and 5 $\text{mg}\cdot\text{g}^{-1}$ described by Gattinger et al. [49] and Hellmann et al. [53], accordingly.

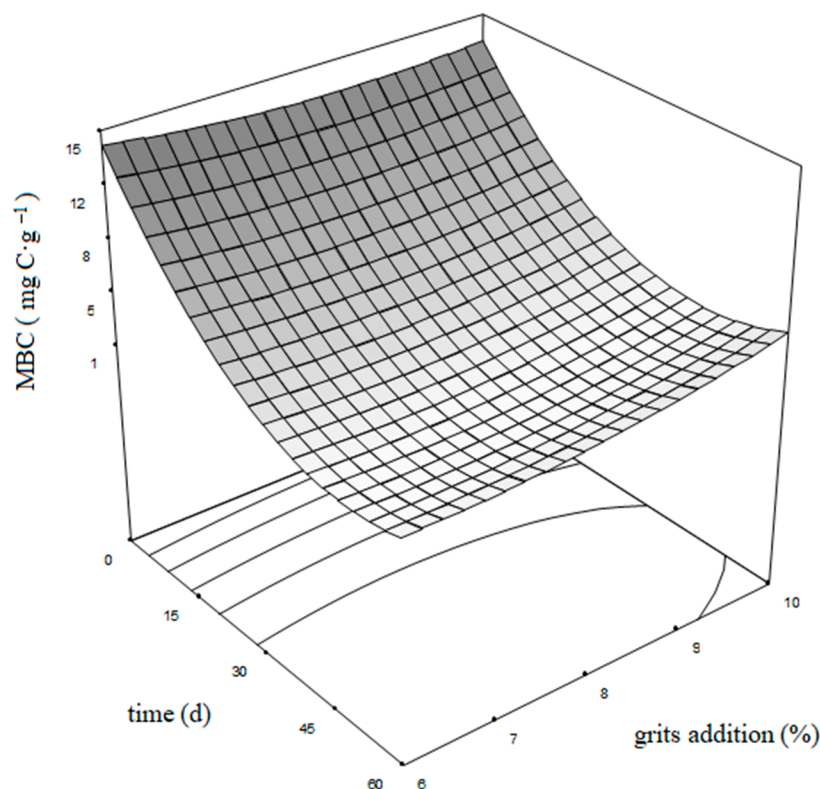


Figure 6. MBC evolution as a function of the composting process time and grits addition.

The effect of grits addition and composting process time on FDA hydrolytic activity is represented for the following second-order polynomial function:

$$\text{FDA} = 138.40 + 1.87t + 5.60G - 0.040t^2 - 0.870G^2 + 0.10tG \quad (5)$$

As shown, the linear and quadratic forms of the composting process time explain 74% of the response, while the linear form of grits addition explains 13% of the response. No interaction or high-order terms associated with the quadratic form of grits addition was observed. A high model goodness-of-fit was demonstrated with R^2 of 98% (p -value ≤ 0.05). This indicates the good predictive capacity of the polynomial function with low noise. The F-values were 56.66.

The response surface shows higher activity over 30 days, with doses of grits ranging from 6% to 8% (Figure 7). At the first stage of the composting process, the FDA hydrolytic activity varied in the 131–137 $\mu\text{gF}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ range for a 6–8% range of grits addition. These values were high during the thermophilic stage, with fluorescein production rates in samples taken from the diverse compost combinations close to 185 $\mu\text{gF}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$.

Later, MBC and FDA hydrolysis decreased toward the composting process end, probably due to a lack of nutrients, thus indicating stability. Final ammonium concentrations of 8–10 $\text{mg}\cdot\text{kg}^{-1}$ are inferior to the maximum recommended for a mature compost of 400 $\text{mg}\cdot\text{kg}^{-1}$ proposed by Zucconi et al. [54] and the 500 $\text{mg}\cdot\text{kg}^{-1}$ indicated by the Chilean regulation for composting [46]. Doses of grits of 6–10% had final nitrate concentrations ranging from 200 to 300 $\text{mg}\cdot\text{kg}^{-1}$, which are indicative of mature compost.

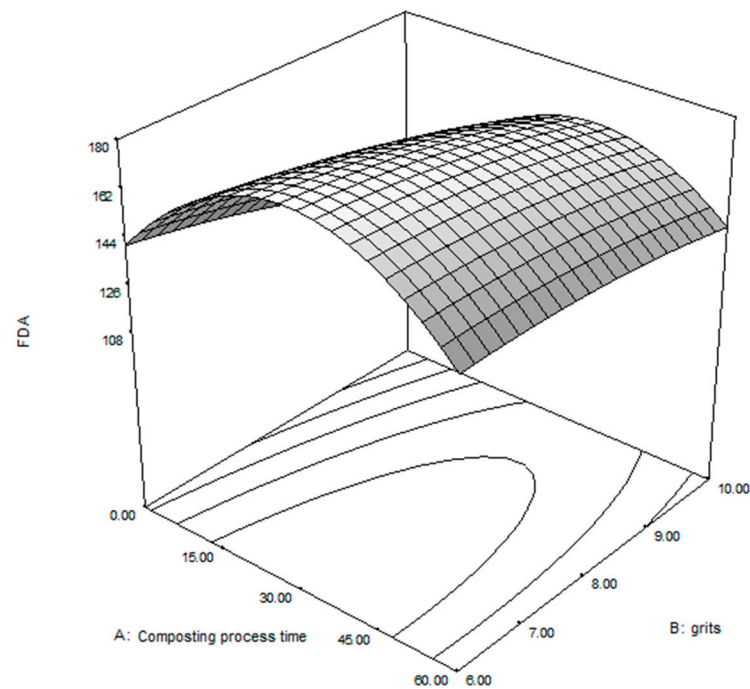


Figure 7. Fluorescein diacetate hydrolysis during the composting process for the mixtures is described in Table 2.

An addition of glucose was needed for the composting of grits and Kraft mill secondary sludge. Sugar is a carbon source that promotes the growth of degrading microbes and hastens composting process [55,56]. Moreover, Keeling et al. [57] and Mondini et al. [58] exhibited that application of glucose at low concentrations lets survive dormant populations, whereas Ezelin et al. [59] confirmed how glucose influences the asymbiotic nitrogen fixation during lignocellulosic waste composting.

Regarding the evolution of MBC and CO_2 , it was highest at the initial composting (Table 2) and, after that, declined rapidly. These variations were less marked for FDA hydrolytic activity as opposed to what Ryckeboer et al. [29] found.

4. Conclusions

This paper demonstrates the feasibility of using the compost produced from grits and secondary sludge from Kraft mill facilities to improve the properties of agricultural soils, making possible its application in agriculture. This action has two positive benefices for the environmental conditions. The first is minimizing the current sanitary landfill usage and the environmental problems associated with a necessary increase in land occupation near urbanized areas. The second is the cost reduction in agriculture, which will always be a primary need for food production. The management alternative described in this paper presents great potential since it produces a liquated compost that is easy to transport and rich in inorganic micronutrients and degradable organic matter, both contributing to enhancing the soil's nutritional content without reporting negative impacts on the environment, especially on soils and water bodies, as has been reported in some controlled applications performed to date [60,61]. These arguments make the described methodology a feasible and sustainable way of recycling these wastes. As for other agrochemicals, the produced composts will be subjected to periodical controls and monitoring on the field to determine the proper doses of application to avoid unwanted damage.

Regarding the specific results, this paper shows how (I) a moderate amount of grits (6%) would be the best compromise to optimize the composting process in order to obtain a high-quality product at 60 days of composting process time, due to Figure 3 it is observed that the pH variation fluctuated between 6.7 to 8.5 for the addition of 6% grits at the end of

the composting process (60 days), which improve enzymatic activity and (II) the incubation experiment at 60 days provides a compost with acceptable chemical and biological properties for direct usage. In addition, no additional treatments are needed since the obtained compost met the Chilean quality standards of mature compost in relation to the released CO₂ evolution, final ammonium concentrations, and pH. The introduced methodology is easy to reproduce and can be used in other countries with similar regulatory requirements for compost production.

Author Contributions: Conceptualization, M.Z.R., M.A. and G.V.; investigation, M.Z.R., M.A. and G.V.; methodology, M.Z.R., M.A., G.V. and D.R.-L.; writing original draft, M.Z.R., O.R. and D.R.-L.; supervision, G.V. and M.A.; reviewing and editing, F.J.A., M.A. and F.E.-M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by DIUFRO grant EP-DI14-0079.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data used are already reflected in the article.

Acknowledgments: Authors wish to thank the Laboratory of Renewable Resources of the University of Concepción for the chemical and physical characterization of the feedstocks.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Valois, M. Paper, paperboard and wood pulp market. In *UNECE/FAO Forest Products Annual Market Review, 2011–2012*; UN: Geneva, Switzerland, 2011.
2. Honnold, V. Developments in the Sourcing of Raw Materials for the Production of Paper. *J. Int. Commer. Econ.* **2009**, *2*, 195–219.
3. Barbosa, M. The South American Pulp and Paper Industry: The Cases Brazil, Chile, and Uruguay. *World For.* **2012**, *17*, 243–283. [[CrossRef](#)]
4. Seyyedali-pour, S.; Kebria, D.; Malidarreh, N.; Norouznejad, G. Study of Utilization of Pulp and Paper Industry Wastes in Production of Concrete. *J. Eng. Res. Appl.* **2014**, *4*, 115–122.
5. Gavrilesco, D. Solid waste generation in kraft pulp mills. *Environ. Eng. Manag. J.* **2004**, *3*, 399–404. [[CrossRef](#)]
6. Hackett, G.; Easton, C.; Duff, S. Composting of pulp and paper mill fly ash with wastewater treatment sludge. *Bioresour. Technol.* **1999**, *70*, 217–224. [[CrossRef](#)]
7. Gea, T.; Artola, A.; Sánchez, A. Composting of de-inking sludge from the recycled paper manufacturing industry. *Bioresour. Technol.* **2005**, *96*, 1161–1167. [[CrossRef](#)]
8. Monte, M.; Fuente, E.; Blanco, A.; Negro, C. Waste management from pulp and paper production in the European Union. *Waste Manag.* **2009**, *29*, 293–308. [[CrossRef](#)]
9. Gopinathan, M.; Thirumurthy, M. Evaluation of Phytotoxicity for Compost from Organic Fraction of Municipal Solid Waste and Paper & Pulp Mill Sludge. *Environ. Res. Eng. Manag.* **2012**, *1*, 47–51. [[CrossRef](#)]
10. Cherian, C.; Siddiqua, S. Pulp and Paper Mill Fly Ash: A Review. *Sustainability* **2019**, *11*, 4394. [[CrossRef](#)]
11. Zawadzińska, A.; Salachna, P.; Nowak, J.S.; Kowalczyk, W.; Piechocki, R.; Łopusiewicz, Ł.; Pietrak, A. Compost Based on Pulp and Paper Mill Sludge, Fruit-Vegetable Waste, Mushroom Spent Substrate and Rye Straw Improves Yield and Nutritional Value of Tomato. *Agronomy* **2022**, *12*, 13. [[CrossRef](#)]
12. Zambrano, M.; Parodi, V.; Gallardo, F.; Vidal, G. Characterization of dregs and grits from pulp Kraft mill: Study for its application to acid soils. *Afinidad* **2003**, *60*, 16–25.
13. Zambrano, M.; Parodi, V.; Baeza, J.; Vidal, G. Acids soils' pH and nutrient improvement when amended with inorganic solid wastes from kraft mill. *J. Chil. Chem. Soc.* **2007**, *52*, 1088–1091. [[CrossRef](#)]
14. Żołnowski, A.C.; Sądej, W.; Suski, M.S.; Wyrwas, A.; Skrocki, D. Impact of paper mill waste on physicochemical properties of soil, crop yield, and chemical composition of plants. *CLEAN Soil Air Water* **2019**, *47*, 1900080. [[CrossRef](#)]
15. Bajpai, P. *Management of Pulp and Paper Mill Waste*; Springer: Patiala, India, 2015. [[CrossRef](#)]
16. Rodríguez-Luna, D.; Vela, N.; Alcalá, F.J.; Encina-Montoya, F. The environmental impact assessment in Chile: Overview, improvements, and comparisons. *Environ. Impact Assess. Rev.* **2021**, *86*, 106502. [[CrossRef](#)]
17. Campbell, A.; Folk, R.; Tritopi, R. Wood ash as an amendment in municipal sludge and yard waste composting process. *Compost Sci. Util.* **1997**, *5*, 62–73. [[CrossRef](#)]
18. Saeli, M.; Senff, L.; Tobaldi, D.M.; La Scalia, G.; Seabra, M.P.; Labrincha, J.A. Innovative Recycling of Lime Slaker Grits from Paper-Pulp Industry Reused as Aggregate in Ambient Cured Biomass Fly Ash-Based Geopolymers for Sustainable Construction Material. *Sustainability* **2019**, *11*, 3481. [[CrossRef](#)]

19. Zambrano, M.; Freer, J.; Villarroel, M.; Vidal, G.; Baeza, J. Using a second order polynomial model to determined the optimum dregs/bark ratio for industrial-biosolid composting: The inicial conditioning stage. *Waste Manag. Res.* **2007**, *25*, 319–326. [[CrossRef](#)]
20. Jordan, M.; Sánchez, M.; Padilla, L.; Céspedes, R.; Osses, M.; González, B. Kraft mill residues effects on Monterrey pine growth and soil microbial activity. *J. Environ. Qual.* **2002**, *31*, 1004–1009. [[CrossRef](#)]
21. Jordan, M.; Rodríguez, E. Effect of solid residues from the cellulose industry on plant growth. *J. Plant Nutr. Soil Sci.* **2004**, *167*, 351–356. [[CrossRef](#)]
22. Davis, C.; Donkin, C.; Hinch, S.; Germishuizen, P. Changes in microbial population numbers during the composting of pine bark. *Bioresour. Technol.* **1992**, *39*, 85–92. [[CrossRef](#)]
23. Liang, C.; Das, K.; McClendon, R. The influence of temperature and moisture contents regimes on the aerobic microbial of a biosolid composting blend. *Bioresour. Technol.* **2003**, *86*, 131–137. [[CrossRef](#)] [[PubMed](#)]
24. Lynch, D.; Voroney, R.; Warman, P. Use of ¹³C and ¹⁵N natural abundance techniques to characterize carbon and nitrogen dynamics in composting and in compost-amended soils. *Soil Biol. Biochem.* **2006**, *38*, 103–114. [[CrossRef](#)]
25. Levy, S.; Taylor, B. Effects of pulp mill solids and three compost on early growth tomatoes. *Bioresour. Technol.* **2003**, *89*, 279–305. [[CrossRef](#)] [[PubMed](#)]
26. Lei, F.; VanderGheyns, J. The effect of microbial inoculation and pH on microbial community structure changes during composting. *Process Biochem.* **2000**, *35*, 923–929. [[CrossRef](#)]
27. Mondini, C.; Fornasier, F.; Sinicco, T. Enzymatic activity as a parameter for the characterization of the composting process. *Soil Biol. Biochem.* **2004**, *36*, 1587–1594. [[CrossRef](#)]
28. Vuorinen, A. Effect of the bulking agent on acid and alkaline phosphomonoesterase and β-D-glucosidase activities during manure composting. *Bioresour. Technol.* **2000**, *75*, 139–148. [[CrossRef](#)]
29. Ryckeboer, J.; Mergaert, J.; Coosemans, J.; Deprins, K.; Swings, J. Microbiological aspects of biowaste during composting in monitored compost bin. *J. Appl. Microbiol.* **2003**, *94*, 127–137. [[CrossRef](#)] [[PubMed](#)]
30. Nakamata, K.; Ohi, H. Examination of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in process water of kraft pulp bleaching mill using chlorine dioxide from the aspect of environmental water quality. *J. Wood Sci.* **2003**, *49*, 525–530. [[CrossRef](#)]
31. Hough, G. *Chemical Recovery in the Alkaline Pulping Process*; Tappi Press: New York, NY, USA, 1985; p. 330.
32. Zambrano, M.; Pichún, C.; Alvear, M.; Villarroel, M.; Velásquez, I.; Baeza, J.; Vidal, G. Dreg effect on secondary sludge composting from Kraft pulp mill wastewater treatment plant. *Bioresour. Technol.* **2010**, *101*, 1028–1035. [[CrossRef](#)]
33. Zar, J. *Biostatistical Analysis*, 4th ed.; Prentice Hall: Hillsdale, NJ, USA, 1999; pp. 180–195.
34. Guo, R.; Li, G.; Jiang, G.; Schuchardt, F.; Chen, T.; Zhao, Y.; Shen, Y. Effect of aeration rate, C/N ratio and moisture content on the stability and maturity of compost. *Bioresour. Technol.* **2012**, *112*, 171–178. [[CrossRef](#)]
35. Díaz, M.; Eugenio, M.; Jiménez, L.; Madejón, E.; Cabrera, F. Modelling vinasse/cotton waste ratio incubation for optimum composting. *Chem. Eng. J.* **2003**, *93*, 233–240. [[CrossRef](#)]
36. Chang, J.; Tsai, J.; Wu, K. Thermophilic composting of food waste. *Bioresour. Technol.* **2006**, *97*, 116–122. [[CrossRef](#)]
37. Komilis, D.; Ham, R. Carbon dioxide and ammonia emissions during composting of mixed paper, yard waste and food waste. *Waste Manag.* **2006**, *26*, 62–70. [[CrossRef](#)]
38. Sundberg, C.; Jönsson, H. Process inhibition to organic acids in fed-batch composting of food waste—Influence of starting culture. *Biodegradation* **2005**, *16*, 205–213. [[CrossRef](#)]
39. Jackson, M.; Line, M. Composting pulp and paper mill sludge—Effect of temperature and nutrient addition method. *Compost Sci. Util.* **1997**, *5*, 74–81. [[CrossRef](#)]
40. Ferraz, A.; Parra, C.; Freer, J.; Rodríguez, J.; Baeza, J. Occurrence of iron-reducing compounds in biodelignified “palo podrido” wood samples. *Int. Biodeterior. Biodegrad.* **2001**, *47*, 203–208. [[CrossRef](#)]
41. Wang, P.; Changa, C.; Watson, M.; Dick, W.; Chen, Y.; Hoitink, H. Maturity indices for composted dairy and pig manures. *Soil Biol. Biochem.* **2004**, *36*, 767–776. [[CrossRef](#)]
42. Nannipieri, P.; Alef, K. *Methods in Applied Soil Microbiology and Biochemistry*; Harcourt Brace Company Publishers: San Diego, CA, USA, 1998; pp. 376–387.
43. Saviozzi, A.; Cardelli, R.; N’kou, P.; Levi-Minzi, R.; Riffaldi, R. Soil biological activity as influenced by green waste compost and cattle manure. *Compost Sci. Util.* **2006**, *14*, 54–58. [[CrossRef](#)]
44. Syamsiyah, J.; Sunarminto, B.H.; Hanudin, E.; Widada, J.; Mujiyo. Carbon dioxide emission and carbon sequestration potential in Alfi sol. *Bulg. J. Agric. Sci.* **2019**, *25*, 42–48.
45. Saviozzi, A.; Cardelli, R.; Levi-Minzi, R.; Riffaldi, R. Evolution of Biochemical Parameters during Composting of Urban Wastes. *Compost. Sci. Util.* **2004**, *12*, 153–160. [[CrossRef](#)]
46. Instituto Nacional de Normalización. *Norma Chilena N°2880. Compost—Clasificación y Requisitos*; Gobierno de Chile: Santiago, Chile, 2004.
47. Kulku, R.; Yaldiz, O. Determination of aeration rate and kinetics of composting some agricultural wastes. *Bioresour. Technol.* **2004**, *93*, 49–57. [[CrossRef](#)] [[PubMed](#)]
48. Ekinci, K.; Keener, H.; Akbolat, D. Effects of feedstock, airflow rate and recirculation ratio on performance of composting systems with air recirculation. *Bioresour. Technol.* **2006**, *97*, 922–932. [[CrossRef](#)]
49. Gattinger, A.; Bausenwein, U.; Bruns, C. Microbial biomass and activity in compost of different composition and age. *J. Plant Nutr. Soil Sci.* **2004**, *167*, 556–561. [[CrossRef](#)]

50. Brewer, L.; Sullivan, D. Maturity and stability evaluation of composted yard trimmings. *Compost Sci. Util.* **2003**, *2*, 96–112. [[CrossRef](#)]
51. Haug, R. *The Practical Handbook of Compost Engineering*; Lewis Publishers: New York, NY, USA, 1993; pp. 35–65, ISBN 0-87371-373-7.
52. Charest, M.; Antoun, H.; Beauchamp, C. Dynamics of water-soluble carbon substances and microbial populations during the composting of de-inking paper sludge. *Bioresour. Technol.* **2004**, *91*, 53–67. [[CrossRef](#)]
53. Hellmann, B.; Zelles, L.; Palojarvi, A.; Bai, Q. Emission of Climate-Relevant Trace Gases and Succession of Microbial Communities during Open-Windrow Composting. *Appl. Environ. Microbiol.* **1997**, *63*, 1011–1018. [[CrossRef](#)] [[PubMed](#)]
54. Zucconi, F.; Pera, A.; Forte, M.; De Bertoldi, M. Evaluating toxicity of immature compost. *Biocycle* **1981**, *22*, 54–57.
55. Gabhane, J.; Prince William, S.; Bidyadar, R.; Bhilawe, P.; Annand, D. Additives aided composting of green waste: Effects on organic matter degradation, compost maturity, and quality of the finished compost. *Bioresour. Technol.* **2012**, *114*, 382–388. [[CrossRef](#)]
56. Raut, M.; Prince, S.; Bhattacharyya, J.; Chakrabarti, T.; Devotta, S. Microbial dynamics and enzyme activities during rapid composting of municipal solid waste—A compost maturity analysis perspective. *Bioresour. Technol.* **2008**, *99*, 6512–6519. [[CrossRef](#)] [[PubMed](#)]
57. Keeling, A.; Cater, G.; Cook, J.; Wilcox, A. Application of glucose at low concentrations to grass swards in waste-derived compost can significantly increase long-term yields. *Plant Soil* **1996**, *184*, 117–121. [[CrossRef](#)]
58. Mondini, C.; Cayuela, M.; Sánchez-Monedero, M.; Roig, A.; Brookes, P. Soil microbial biomass activation by trace amounts of readily available substrate. *Biol. Fertil. Soils* **2006**, *42*, 542–549. [[CrossRef](#)]
59. Ezelin, K.; Brun, G.; Kaemmerer, M.; Revel, J. Glucose influence on the asymbiotic nitrogen fixation during lignocellulosic waste composting. In *The Science of Composting*; de Bertoldi, M., Sequi, P., Lemmes, B., Papi, T., Eds.; Springer: Dordrecht, The Netherlands, 1996; pp. 137–148.
60. Turner, T.; Wheeler, R.; Oliver, I.W. Evaluating land application of pulp and paper mill sludge: A review. *J. Environ. Manag.* **2022**, *317*, 115439. [[CrossRef](#)] [[PubMed](#)]
61. Pinto-Morales, F.; Retamal-Salgado, J.; Lopéz, M.D.; Zapata, N.; Vergara-Retamales, R.; Pinto-Poblete, A. The Use of Compost Increases Bioactive Compounds and Fruit Yield in Calafate Grown in the Central South of Chile. *Agriculture* **2022**, *12*, 98. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.