processes

MDPI

Article

Design of a Bioreactor for Aerobic Biodegradation of Biowaste Based on Insight into Its Composition and Estimated Process Parameters

Tomislav Domanovac [1], Dajana Kučić Grgić [2], Monika Šabić Runjavec [2] and Marija Vuković Domanovac [2,*]

[1] IPZ Uniprojekt TERRA, Voćarska cesta 68, 10000 Zagreb, Croatia; tomislav@ipz-uniprojekt.hr
[2] University of Zagreb, Faculty of Chemical Engineering and Technology, Trg Marka Marulića 19, 10000 Zagreb, Croatia; dkucic@fkit.unizg.hr (D.K.G.); msabic@fkit.unizg.hr (M.Š.R.)
* Correspondence: mvukovic@fkit.unizg.hr

Abstract: Biowaste, which often accounts for more than 50% of municipal waste, is an environmental problem if disposed of improperly in landfills but has great potential to achieve the recycling targets set out in Directive (EU) 2018/851. Despite the knowledge in theory and practice about the processing of biowaste and the benefits of recycling, there is a lack of methodological approaches in describing the process of aerobic biodegradation in a concise and suitable way for decision makers, environmental engineers, and project designers. This paper presents how basic data on the properties of biowaste can be used, using theoretical models, to determine basic indicators of the dynamics and material balance of the process. The maximum rate of CO_2 generation on the 4th day was R_m = 45.3 g/d, with the potential of available, readily biodegradable components of the biowaste sample of P = 526 g CO_2/kg VS. A substrate conversion of 51.7% was achieved in the bioreactor by the 17th day of treatment. The results of this analysis, together with future analyses of sensitivity and boundary conditions of the process, are useful for rapidly sizing a biological treatment system for municipal solid waste in a given area.

Keywords: biodegradation model; biowaste; composting; kinetic parameters

check for updates

Citation: Domanovac, T.; Kučić Grgić, D.; Šabić Runjavec, M.; Vuković Domanovac, M. Design of a Bioreactor for Aerobic Biodegradation of Biowaste Based on Insight into Its Composition and Estimated Process Parameters. *Processes* **2024**, *12*, 545. https://doi.org/10.3390/pr12030545

Academic Editor: Bipro R. Dhar

Received: 21 February 2024
Revised: 4 March 2024
Accepted: 8 March 2024
Published: 10 March 2024

1. Introduction

Waste is one of the biggest problems in environmental protection today. As the human population on planet Earth grows, the amount of waste produced also increases proportionally [1–4]. Worldwide, 2.01 billion tonnes of municipal solid waste are generated annually. Global waste generation is expected to increase to 3.40 billion tonnes by 2050, which is more than double the population growth over the same period. The composition of waste varies according to income level and reflects different consumption patterns [3].

In low- and middle-income countries, a predominant feature of municipal solid waste is the high proportion of organic, biodegradable materials (biowaste). This often accounts for more than 50% of the total waste generated and can be as high as 80% [4]. With rapid urbanization and population growth, effective biowaste management is becoming an urgent issue. While biowaste has traditionally been disposed of in landfills, the lack of landfills and the negative impact on the environment have led to the introduction of alternative methods for its recovery [1,2].

Sustainability, which is enshrined in the 17 "Sustainable Development Goals" (SDGs), has been defined as the perfect balance between the economic, environmental, and social aspects of a system, product, or process. This concept has been applied to describe the performance of different alternatives for biowaste (food waste and green waste) to obtain value-added products and energy vectors at the laboratory, pilot, bench, or industrial scale [5,6]. It is therefore very important to gain insight into the composition of biowaste as a heterogeneous mixture of different biodegradable components, its physico-chemical properties, and parameters of biodegradability such as respiration coefficient and biogas potential, but also the dynamics of biowaste generation as this stream is seasonal [7].

Globally, food loss and waste account for a significant proportion of food and green waste (around 30%). This corresponds to 1.3 billion tonnes per year [3]. Biowaste is defined as biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers, and retail establishments, and similar waste from food processing plants [8]. The characterization of biowaste is necessary for the management of this type of waste. The choice of appropriate technology for solid waste management is influenced by the composition of waste materials [1,2].

The treatment, collection, and conversion of biowaste can make a positive contribution to climate change mitigation, as biowaste is one of the main causes of greenhouse gas emissions in landfills [9,10]. Bioconversion technology is an environmentally friendly and sustainable approach that utilizes the metabolic potential of living organisms to recycle organic solid waste. Composting, anaerobic digestion, vermicomposting, insect-based biorefinery, fermentation technologies, etc. are used for the bioconversion of organic waste [2]. Each of the mentioned technologies of biodegradation of biowaste has advantages and disadvantages that can be minimized by controlled process management conditions and the properties of the input substrate (biowaste). Some of the advantages of composting compared to other technologies are less sensitivity to pretreatment or preparation of the substrate, large processing capacities, and proven technology. The absence of the mentioned advantages in other technologies can be a significant disadvantage when choosing a solution for the treatment of biowaste.

Aerobic biological treatment, composting, is a common solution for solid organic waste management due to its cost effectiveness [9] and involves the controlled aerobic decomposition of organic material, resulting in a relatively stable organic end product [2,4]. Composting of organic material is driven by a diverse population of microorganisms that break down organic material, producing carbon dioxide, water, and heat. Controlling the process means controlling, managing, and adjusting the prevailing parameters, such as organic material composition (carbon–nitrogen ratio), particle size, free air space, aeration, temperature, moisture, or pH, to achieve rapid decomposition and good compost quality. If the conditions are not optimal, the process can be slowed down or not take place at all [1,2,4,10].

Biological stabilization aims to reduce the weight of the organic fraction and inactivate all biologically active organic materials, resulting in stabilized residues [10,11]. Composting technologies are invaluable for the stabilization of biodegradable waste due to their environmental friendliness. Composting is a biochemical and heterogeneous process that mineralizes organic material and produces a stabilized end product that can be used as a potential source of organic fertilizer or for soil amendment [10,12]. A successful process involves the use of the right mixing ratio, optimization of process parameters, and the use of mathematical models to effectively simulate the composting process [12,13].

Mathematical modeling is widely used in science and engineering to improve the understanding of system behavior and to explore new theoretical concepts. Mathematical models are an effective tool for predicting how the composting process will occur and can be used to guide the design and evaluation of conditions. For this reason, they are often used to simulate and predict the physical and biological laws that govern the composting process [13–15].

The number of model parameters required influences the usefulness of mathematical models and determines to some extent whether they are used as operational or research tools. Simulations provide information on the applicability of the model to changes in operating parameters. However, their value is limited if validation against experimental data is not considered [14].

Material balance is an important first step in the design of a new process or the analysis of an existing process. It provides information on the intensity of the impact on the environment, such as air pollution caused by the emission of biodegradable gases. In addition, the mass balance of the process is important information for the dimensioning of the required process spaces and equipment for biowaste treatment plants, such as input and output storage, bioreactors for intensive decomposition, areas for compost maturation, etc. [15]. It is almost always a prerequisite for all other calculations when solving process engineering problems according to the law of conservation of mass, which states that mass can neither be created nor destroyed [16,17]. The second step, which is important for the design and simulation of biodegradation, is the reaction rate in the conversion of biowaste into stable compost. Therefore, there are numerous mathematical models describing the process, so that the determination of the kinetic parameters provides useful information for the optimal selection of the type and amount of equipment to carry out the biodegradation process of biowaste [14,18,19].

In this study, insight was given into the most important input parameters of the process of aerobic stabilization of biowaste by composting, i.e., the aerobic biodegradation process of a real sample of biowaste in a bioreactor. Based on the physicochemical and kinetic parameters, the dynamics and mass balance of the aerobic biodegradation process were evaluated. The parameter values determined served as the basis for providing quick insight into the data required for designing a plant under real conditions, i.e., for dimensioning the necessary plant and process equipment. This methodological approach bridges the gap between theoretical, comprehensive, and detailed baseline analyses and the necessary data containing all important parameters for decision making and process design when analyzing options for the biological treatment of biowaste. A complicating factor in the analysis and modeling is that biowaste under real conditions is a heterogeneous mixture of different biodegradable components, with accompanying impurities and seasonal variations in appearance and properties. Therefore, it is important to consider the spatially specific composition of biowaste by taking representative samples and the temporal dimension of the representative sample, which is achieved by determining the composition and properties of biowaste in four seasons [20]. A similar approach can be applied to other biological processes of biowaste treatment.

2. Materials and Methods

2.1. Biowaste

For the experiment of aerobic stabilization by composting, a representative sample of biowaste (substrate) from the continental part of the Republic of Croatia from the Zagreb area was used, which was obtained from the company IPZ Uniprojekt TERRA, Zagreb. The preparation of a representative biowaste sample and determination of the composition of the biowaste was carried out in accordance with the provisions of the document "Methodology used in determining the composition and quantity of municipal waste and mixed municipal waste" [20] and using the standards and guidelines of HRI CEN/TR 15310-1:2008 and HRN EN 14899:2007 [21,22]. This document describes the sampling method, the preparation and reduction procedures of the biowaste sample, the analysis and data processing, as well as the spatial and temporal dimensions of the determination of the composition and quantity of biowaste.

Statistical data processing and mathematical modeling were performed with the Microsoft Excel package "Solver" using the built-in statistical functions and the GRG nonlinear optimization method.

2.2. Process of Aerobic Biodegradation of Biowaste

The composting experiment of biowaste aerobic stabilization was conducted in a closed adiabatic cylindrical stainless steel bioreactor (d = 212 mm, h = 330 mm) with a working volume of 10 L (University of Zagreb Faculty of Chemical Engineering and Technology, Croatia). The initial mass of composting substrate added from the top of the bioreactor was 4.5 kg. The bioreactor was thermally insulated with 10.5 $\pm$ 1.5 mm thick AF/Armaflex® foam (Armacell, Münster, Germany). Substrate aeration was ensured by the air inlet at the bottom of the bioreactor, where it was aerated with a constant air flow rate set to 0.78 L/min/kg VS during the 21 days of the experiment. An air compressor (DE 50/204 FIAC, Italy) was used for the air inlet. The air flow rate was controlled by an air flow meter (Cole Parmer, Vernon Hills, IL, USA). To reduce drying of the substrate in the bioreactor and ensure constant air humidity, the air was saturated with water while passing through a Dreschel bottle before entering the bioreactor. At the exit from the bioreactor, a graduated cylinder was used to collect the produced condensate throughout the process of biowaste aerobic biodegradation. For absorption of the produced CO_2 from substrate aerobic biodegradation, 1 mol/L NaOH was used. The temperature was monitored daily by temperature sensors placed in the center of the bioreactor and connected to a computer, while the temperature value was read using the Lab View program. Substrate sampling was carried out through the opening at the top of the bioreactor. Before taking the substrate samples, the substrate was mechanically mixed.

2.3. Physicochemical Analyses

During the aerobic stabilization process of the biowaste by composting, substrate samples were taken regularly and the most important physicochemical parameters (C/N ratio, pH value, moisture, dry solid (DS) and volatile solid (VS) content) were determined on duplicate samples according to the Austrian standard methods for compost analysis [23], while the pH value was determined as previously described [24]. The concentration of CO_2 was determined by titration of excess 1 mol/L NaOH with 1 mol/L HCl [25].

3. Results and Discussion

Based on the analysis of the data on the components and performance of aerobic biodegradation of a real sample of biowaste (substrate) under experimental conditions for 21 days, an overview of the results is given below. These data provide the input data for the evaluation of the initial kinetic parameters of the process and the mass balance using a simulation model for the operation of the bioreactor process on a laboratory scale.

3.1. Characterization of Biowaste

The results of analyzing the composition of a real sample of biowaste are shown in Table 1. In the biowaste sample, kitchen waste of vegetable origin was the most represented, while the rest consisted of biodegradable impurities and impurities that are biodegradable to a lesser extent (<50%). The composition of biowaste from the kitchen varies seasonally [7] and regionally [26]. It is assumed that the composition of biowaste in the Zagreb area corresponded to the composition for the continental part of the Republic of Croatia, with the largest share of residues resulting from the preparation of cabbage, potatoes, carrots, and residues of unused bread. There was also other food waste that is generated throughout the year, such as banana peels and citrus fruits. The proportion of the kitchen fraction in the biowaste amounted to 93% of the fresh sample and 79% of the dry sample. Applying the recommendations for assessing the biodegradable fractions of the individual components of the biowaste (it is assumed that 50% of the textiles, skin, and bones are biodegradable) [20], the proportion of the biodegradable fraction of the biowaste was estimated at 99.5% of the fresh sample and 98.5% of the dry sample of the biowaste. Common foods consumed around the world were recognized as components of the biowaste, which was consistent with similar studies in different parts of the world [1,10,27,28]. Such similarities are not unusual, as these are staple foods for human nutrition and consumption. Managing and recycling the growing amounts of biowaste, especially food waste (the generation of food waste is almost unavoidable), therefore brings a double benefit. The first benefit is the reduction of the global pollution problem caused by the disposal of biowaste in landfills and emissions into the environment. Another benefit is the potential of using separately collected food waste as a substrate in microbiological processes (the total sugar and protein contents of food waste are between 35.5% and 69% and between 3.9% and 21.9%, respectively) [28] for the production of bioproducts such as organic fertilizers, soil conditioners, and other bioproducts such as enzymes and biopolymers (material recovery, recycling), and for the production of clean energy sources such as methane, hydrogen, ethanol, and biodiesel (energy recovery).

Table 1. Composition of biowaste.

Primary Components	Secondary Components	Fraction of Fresh Waste, %	Fraction of Dry Waste, %
Kitchen waste *	banana peel	10.4	4.5
	celery rind	3.3	2.1
	beet peel	2.2	0.9
	apple peel	3.0	2.1
	potato skins	29.7	17.1
	lemon peel	4.4	3.8
	onion peel	3.3	11.1
	carrot peel	9.9	4.3
	orange peel	3.0	4.1
	tomato peel	4.4	1.1
	squash peel	2.2	1.1
	bread	11.2	37.5
	cabbage	12.1	6.3
	egg shells	1.1	4.1
	subtotal	100.0	100.0
Contaminants **	paper	84.2	84.5
	textiles	11.1	10.8
	skin and bones	2.7	2.7
	wood	2.0	2.0
	subtotal	100.0	100.0

* The proportion in the biowaste was 93% in the fresh sample and 79% in the dry sample. ** The proportion in the biowaste was 7% in the fresh sample and 21% in the dry sample.

Table 2 shows the results of the basic physicochemical properties of a real sample of biowaste. The values obtained correspond to the published results for biowaste [1,12] and kitchen waste [10,27].

Table 2. Physicochemical properties of biowaste.

Substrate	C/N	pH	Dry Solids (DS), %	Volatile Solids (VS), %
Biowaste	19.8	5.8	37.4	85.1

3.2. Aerobic Bioreactor Degradation of Biowaste

A real sample of kitchen waste was subjected to a biostimulated aerobic biodegradation process in an aerated adiabatic bioreactor. The results of the experiment are shown in Table 3.

The time column shows the cumulative time lapse with a step corresponding to the time lapse between sampling for analysis (Table 1). On the basis of the value determined for the volatile components (VS), an indicator of compost stability was calculated, namely the rate of microbial respiration, which was expressed as g CO_2/kg VS per day. The degree of stability as a measure of the completion of the maturation process of the compost depends on the end use of the compost and is not unambiguously determined. Thus, the rating "very stable" describes a compost with a respiration rate of <1 [29] or <2 [30]. The determined value of the compost stability indicator of 4.4 indicated the need for additional compost stabilization, i.e., maturation. In practice, additional stabilization is carried out outside the bioreactor in heaps ("windrows") if a very stable compost is to be achieved.

Table 3. Results of the process of aerobic biodegradation of biowaste.

t, d	*T*, °C *	*m* (CO_2), g **	*m* (VS), kg	*m* (CO_2)corr., g/d ***	*m* (CO_2), g/kgVS_0/d ****
0	11.6	0.0	1.43	0.0	0.0
1	35.2	11.4	1.35	13.0	9.1
2	43.8	32.9	1.31	41.6	29.0
3	45.2	42.1	1.25	40.4	28.2
4	46.6	42.8	1.18	41.1	28.7
6	50.9	42.5	1.06	22.2	15.5
7	48.4	42.3	0.99	42.3	29.5
8	42.4	41.0	0.94	41.0	28.6
9	39.8	40.9	0.89	40.9	28.6
10	31.8	37.8	0.85	37.8	26.4
13	25.8	31.1	0.75	10.4	7.2
15	28.7	25.8	0.72	12.9	9.0
17	24.4	19.1	0.69	9.6	6.7
20	25.0	18.8	0.67	6.3	4.4
21	24.4	6.3	0.67	6.3	4.4

* Temperature values at the time of sampling to determine the amount of CO_2 produced and the proportion of VS. ** The mass of CO_2 produced since the previous measurement. *** The mass of CO_2 formed in one day. **** Specific mass of CO_2 per initial amount of VS (t = 0) formed in one day.

The data from the temperature measurements of the aerobic biodegradation process (Table 3, Figure 1) showed that the duration of the thermophilic phase was 5 days (temperatures ranged between 45.2 °C and 50.9 °C). The temperature above 50 °C was maintained for almost 2 days, which enabled hygienization of the biowaste mixture, i.e., the elimination of pathogenic microorganisms and weed seeds [31].

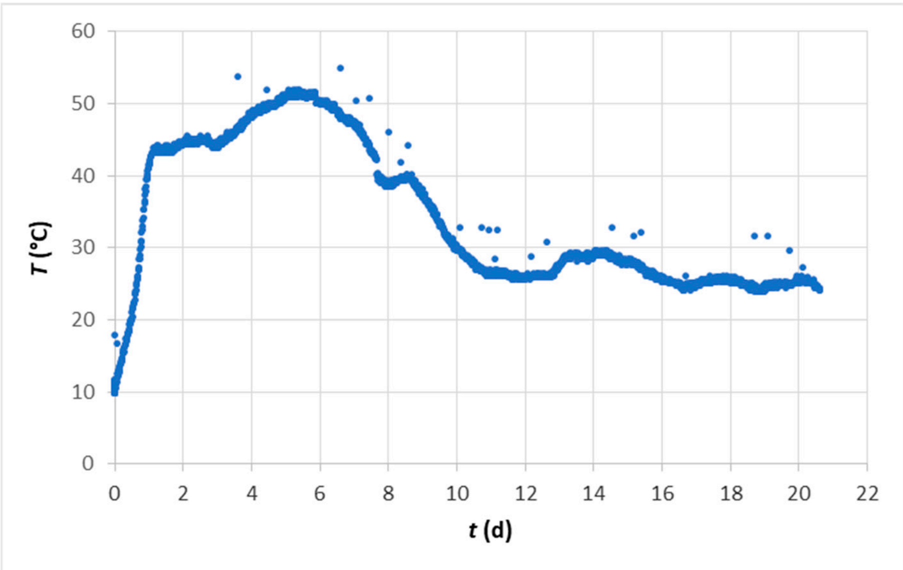

Figure 1. Temperatures measured during the experiment on the aerobic stabilization of biowaste in the reactor.

The duration of biological treatment at temperatures above 50 °C depends on the type of microorganisms in the mixture and the type of biowaste and can last from a few hours to several days [32,33]. For the substrate used, i.e., the biowaste sample, according to the European and Mediterranean Plant Protection Organization—EPPO (2008) and German "Ordinance on the Utilisation of Biowastes on Land used for Agricultural, Silvicultural and Horticultural Purposes—BioAbfV (1998) [34], it was necessary to prolong the thermophilic phase in a closed biowaste mixture and keep it at 55 °C for 14 days (consecutively) or at 60 °C for 7 days (consecutively) and at a moisture content of 40% and more to ensure hygienization. An increase in temperature can also be achieved by optimal aeration with occasional mixing of the substrate [35]. This depends on the technical performance of the aerobic biodegradation process to prevent the channeling of air currents through the mixture. It also depends on the composting mixture being composed of a structural material that maintains looseness, i.e., an optimal free air space (FAS) of about 30% for the exchange of substrates and metabolites of biodegradation under aerobic conditions [15,36] and with high nitrogen content of structural material for microbial growth in order to prevent the slowing down of the biodegradation process [12]. In addition, a deviation from the trend was observed in the measured value of CO_2 mass in the thermophilic phase of the process (Table 3), which could be interpreted as insufficient capacity of the system to absorb CO_2 from the output stream of gaseous degradation products, resulting in non-registration of emissions from the reactor.

Table 4 shows the results at the beginning and end of the experiment on the aerobic stabilization of biowaste by composting. The results showed that, after 21 days in the reactor, about 50% of the volatile solids were degraded, which corresponded to the values determined in similar experiments and in practice under real conditions [37,38].

Table 4. Results of the biowaste analysis at the beginning and end of aerobic biodegradation.

t, d	*m* (Substrate), kg	Moisture, %	*m* (DS), kg	*m* (VS), kg	Conversion (VS), %
0	4.50	62.62	1.67	1.42	–
21	3.29	72.35	0.92	0.72	50.57

The specific aeration during the entire duration of the experiment was 0.55 L/min/kg VS, which corresponded with the usual initial flows in bioreactors and was between 0.39 and 0.52 and between 0.07 and 0.20 L/min/kg VS [39], and between 0.03 and 0.28 L/min/kg DS [40], i.e., between 0.3 and 0.7 L/min/kg organic matter [41]. Low specific air flow rates of less than 0.1 L/min/kg DS resulted in a low oxygen concentration in the biowaste mixture (less than about 5%), which slowed down the aerobic biological process of biowaste decomposition. Therefore, the process must be maintained under conditions with an oxygen concentration between 10% and 15% or more [4,42,43].

At the end of the experiment, the moisture content of the mixture increased by 15.5%, with a specific aeration of 0.55 L/min/kg VS. In order to be able to influence the process parameters during the process, the possibility of variable aeration is one of the most important process control parameters. Controlling the process, especially the temperature and moisture, is important to avoid drying out or lowering the oxygen concentration below 10% vol. (the oxygen concentration in the air is 21%) and to prevent the transition from aerobic to anaerobic conditions and the development of volatile organic compounds and ammonia as carriers of unpleasant odors [44].

3.3. Mass Balance of the Process of Aerobic Biodegradation of Biowaste

The mass balance of the composting process is based on the stoichiometric equation of the aerobic decomposition of the substrate (1), as shown by the gross chemical formula [45]:

$$C_aH_bO_cN_d + [(4a + b - 2c - 3d)/4]O_2 = aCO_2 + [(b - 3d)/2]H_2O + dNH_3 \quad (1)$$

The gross chemical formula of the biowaste sample, which depended on the final analysis of the biowaste components and their proportion in the biowaste [45] with which the experiment was performed, was $C_{22}H_{38}O_{13}N$, which was consistent with the expected values of the composition of a similar type of biowaste [1]. Equation (2) can be represented as follows:

$$C_{22}H_{38}O_{13}N + 25O_2 = 22CO_2 + 17H_2O + NH_3 \quad (2)$$

The mass balance of the aerobic biodegradation process of a biowaste sample with a conversion of biodegradable volatile solids of 50.57% is shown in Figure 2 [15]. The mass balance was presented using the help of the Microsoft Excel 2019 program package using stoichiometric parameters and process input parameters.

The input parameters for the evaluation of the mass balance of the mentioned process during 21 days were: the average operating temperature of the process was 33 °C, the relative humidity of the inlet air was 75%, the inlet temperature was 20 °C, and the conversion of volatile solids from biowaste was 50.57%. No additional water was introduced into the process and the amount of leachate produced was not taken into account.

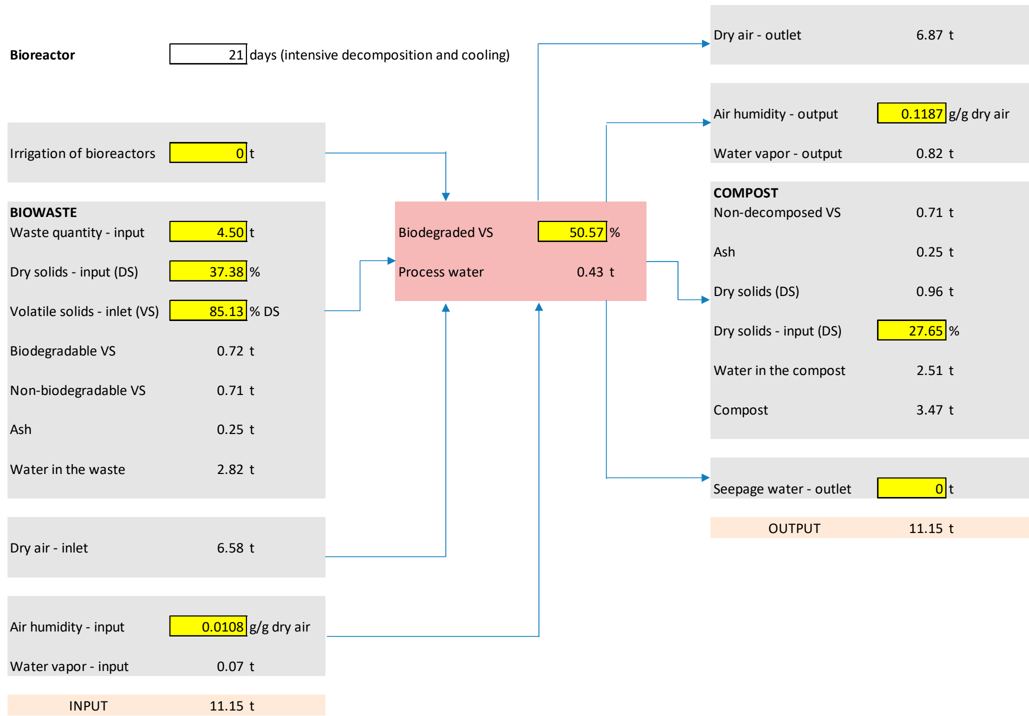

Figure 2. Mass balance of the aerobic biodegradation process of a biowaste sample (Excel worksheet screenshot).

A comparison of the experimental data with the theoretical model of the mass balance of the process at the end of the experiment showed a high degree of agreement (Microsoft Excel function "correl", i.e., correlation coefficient = 0.9995) (Table 5).

Table 5. Mass balance of the process—comparison of experiments and theoretical model.

Matter	*m* (Experiment), kg	*m* (Model), kg
Volatile solids	0.71	0.71
Water	2.38	2.51
Inert solids	0.20	0.25
Total	3.29	3.47

In the experiment, the mass loss of the total substrate during aerobic biodegradation of the biowaste sample over 21 days amounted to 23.0%, with an increase in moisture of 15.5%. It can be assumed that the mass of compost produced from the amount of biowaste added was most dependent on the moisture of the mixture and the duration of the process, with the process theoretically tending toward 100% conversion.

In order to estimate the time required to achieve the intended conversion of biodegradable volatile solids, i.e., the prescribed amount of organic matter in the compost depending on the final purpose of the compost, after the mass balance of the process, the dynamics of the process was determined by determining the initial kinetic parameters of the process.

3.4. Evaluation of the Kinetic Parameters of the Aerobic Biodegradation Process of Biowaste

Modeling the process of aerobic biodegradation of biowaste is a tool that improves the prediction of process dynamics but also the control of the process itself by monitoring parameters such as temperature and moisture of the biowaste during biological treatment. Furthermore, process modeling provides quick insight into the necessary indicators used in the organization of the biological treatment system for biowaste in an area [46] and later in the design of the plant, and it improves the quality of input data for decision makers in the early stages of the project [47].

Common approaches to determine the rate of the aerobic biodegradation process are to monitor the change in the concentration of the biowaste, i.e., the substrate, by determining the constant rate of the first-order reaction or by monitoring the amount of reactions of gaseous products such as CO_2 [14,15,48,49].

Among the various mathematical models that describe the physical picture of the aerobic biodegradation process is the modified Gompertz model, which describes the formation of CO_2 in the process of aerobic biowaste treatment [14]:

$$H(t) = P \exp(-\exp(R_m e/P(\lambda - t) + 1)) \quad (3)$$

where $H(t)$ (g) is the cumulative amount of CO_2 produced in time t (d); P (g) is the potential amount of CO_2 that can be produced; R_m (g/d) is the maximum specific CO_2 production rate; e is Euler's number, which is approximately 2.718282; and λ (d) is the lag phase.

The specific amount of CO_2 produced in time t is described by Equation (4):

$$dH(t)/dt = R_m \exp(2 + R_m e/P(\lambda - t) - \exp(R_m e/P(\lambda - t) + 1)) \quad (4)$$

where P, R_m, and λ are the biokinetic parameters in time t described above.

The maximum rate of the CO_2 formation reaction is reached in the time t_{max}, calculated according to the equation:

$$t_{max} = \lambda + P/(R_m e) \quad (5)$$

where R_m is calculated according to the equation:

$$R_m = P k \quad (6)$$

and where k (1/d) is the reaction rate coefficient.

If the expression $P/(R_m e)$ is marked as σ, which is an indicator of the duration of the biodegradation process and whose value is 4.3 d (Table 6), then the characteristic values of time are $t_1 = \lambda + 2\sigma = 8.6$ and $t_2 = \lambda + 4\sigma = 17.1$ [48]. These two times provide useful information for a quick estimation of the duration of the aerobic biodegradation process of biowaste for the purpose of dimensioning the biological treatment plant, because it is estimated that in the process of aerobic biodegradation, about 70% of the total amount of CO_2 is formed in time t_1 and about 95% of the total amount of CO_2 is formed in time t_2. In other words, these times show the percentage of the total conversion of biodegradable volatiles that is achieved in the bioreactor under certain process conditions and biowaste composition.

The parameter λ was estimated at 0.036 days based on the temperature data (Figure 1), which means that the duration of the lag phase of the process in this experiment was negligible. The reason for this is that a realistic sample of biowaste was used in which the biodegradation processes had already started at the collection point. The values of the biokinetic parameters P and R_m were estimated using the Microsoft Excel 2019 package "Solver" with the GRG nonlinear optimization method. The maximum values of the correlation coefficients and the f-test were used as criteria for the agreement between the obtained experimental and calculated values $H(t)$ according to the Gompertz model (Equation (5)) in time t.

A graphical representation of the biokinetic parameters of the modified mathematical Gompertz model described in Equations (4) and (5) and the simulation of CO_2 formation as a product of the biological aerobic degradation of the biowaste sample are shown in Figure 3.

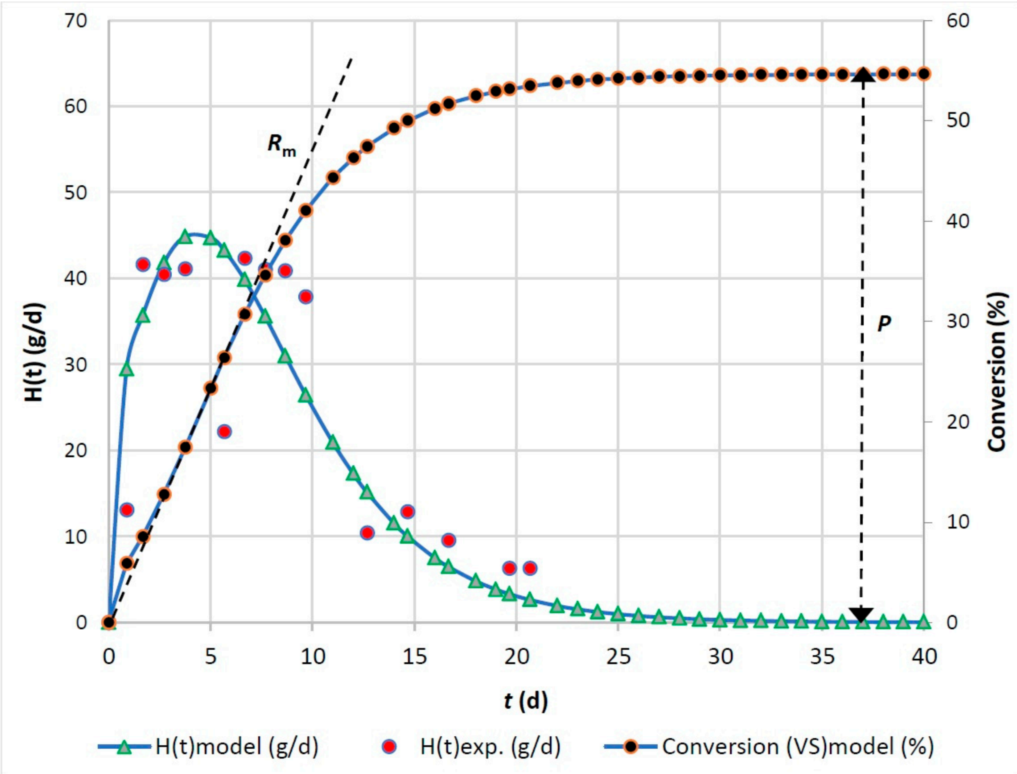

Figure 3. Simulation of CO_2 formation and conversion of biodegradable VS in the process of aerobic biodegradation of a biowaste sample.

The values of the biokinetic parameters obtained by optimizing the model and the data from the experiments, which describe the specified process of aerobic biodegradation of biowaste, are shown in Table 6.

Table 6. Values of estimated biokinetic parameters and indicators of the simulation model.

P_{total}, g/kg VS	P, g/kg VS *	k, 1/d	R_m, g/d	λ, d	σ, d	$\lambda + 4\sigma$, d	Conversion (VS), % **
1.881	526	0.086	45.3	0.04	4.3	17.1	51.7

* sum of CO_2 g/d produced by the biodegradation of biowaste. ** conversion (VS) model on day 17 ($t = \lambda + 4\sigma$) of the readily biodegradable components of the biowaste sample.

The theoretical potential amount of CO_2 that can be produced stoichiometrically from the biodegradable fraction of the biowaste according to Equations (1) and (2) was 1.881 g/kg VS. The amount of CO_2 determined in the experiment was 526 g/kg VS, which indicated the presence of slowly degradable lignocellulosic components at lower temperatures in the thermophilic phase (45–70 °C) [49] and the limited availability of biodegradable volatiles for intensive aerobic biodegradation processes due to the possible inhomogeneous distribution of the air flow through the mixture in the bioreactor. This indicated the need to add a larger proportion of structural material to the composting mixture. Structural material with a high nitrogen content, such as woody waste from gardens and parks, plays a dual role, as it allows good aeration of the mixture and would increase the initial value of the C/N ratio of the biowaste sample studied from 19.8, which was in line with the values found for the Mediterranean region (C/N = 20) [10], to an optimal value of about 30 [4,10,50], which is necessary to supply the microorganisms with energy (carbon) and substances for cell building (nitrogen) [12].

The determined value of the reaction rate coefficient k of 0.086 1/d agreed with the values determined in experiments with similar substrates in biological treatment plants, which ranged between 0.021 and 0.830, with an average value of 0.061 1/day [51], indicating that the simulation of the aerobic biodegradation process of the biowaste sample with the indicated biokinetic parameters had a high degree of agreement (Microsoft Excel functions "correl" = 0.856 and "f-test" = 0.983) with the data from the experiment performed.

In addition, the data obtained from the simulation model of the biodegradation of a sample of biowaste can provide data for the further design of real plants for the biological treatment of biowaste, as these plants represent a very important segment for achieving the waste recycling targets of 65% of municipal waste by 2035 prescribed in Directive (EU) 2018/851 of the European Parliament and of the Council of May 30, 2018 amending Directive 2008/98/EC on waste [9].

Thus, it can be seen from the parameter σ that the maximum degradation rate was reached on day 4 ($t = \lambda + \sigma = 4.3$) and that, under optimal conditions of biodegradation in the bioreactor, the biowaste could be held for up to 17 days ($t = \lambda + 4\sigma = 17.1$), whereby according to the simulation model, about 94.6% of the total conversion of the biodegradable volatile components of the biowaste was achieved, which corresponded to 51.7%. These data also agreed with the empirical expression, which took into account the proportion of kitchen waste in the biowaste and the time required to reach 60 °C in the reactor, which would be 17.7 days [52] or 18–20 days [10] in the case of biodegradation of the biowaste sample. It could be seen from the data that the minimum retention time of the biowaste in the bioreactor under optimal, controlled conditions was 18 days or more. Since the total amount of readily biodegradable volatiles in the biowaste sample was 51.7%, which was converted in 17 days, based on an estimated total conversion of 54.6% [48], an increase in conversion would be achieved if the waste was removed from the bioreactor, homogenized, and returned to the bioreactor in the period between $t = \lambda + \sigma$ and $t = 3\ \sigma$ until the total biodegradation time in the bioreactor was about 17 days. The reduced conversion also indicated that the composting process must be carried out at temperatures between 55 °C and 60 °C and up to 70 °C to increase the biodegradation of the lignocellulosic components of the biowaste and to ensure the required hygienization [4,34,49].

In order to rationally utilize the capacity of the bioreactor for biodegradation, the process of biodegradation of biowaste is continued on maturing surfaces. In this decomposition phase, the biowaste, also known as immature compost, is transferred in the "windrows" from thermophilic to mesophilic conditions, wherein the slow process of biodegradation of the less biodegradable components with high lignin content continues. The completion of compost maturation, i.e., reaching maturity of the biowaste sample at <1 g CO_2/kg VS [29], was estimated to take about 4 weeks under optimal bioreactor conditions. Under real conditions, however, experience has shown that maturation in the windrows takes 2 to 8 weeks, depending on the conversion of the substrate in the previous treatment stage in the bioreactors, i.e., depending on the type of substrate or the use of compost. The total time for the bioreactor process of biowaste composting can therefore take up to 14 weeks [45]. A comparison of the results of this study (values of the process parameters and process dynamics) with the results of similar studies and empirical data showed agreement. In this way, it has been shown that by using basic data on the characteristics of biowaste and mathematical modeling of the aerobic biodegradation process, useful data can be obtained for decision making and further planning of processes and plants for biological treatment, since the size of the plant and construction facilities, as well as the amount of equipment installed and infrastructure required, significantly influence the choice of technology and the justification of the project in the end.

4. Conclusions

The data used to simulate the dynamics of the process of aerobic biodegradation of a real sample of biowaste from the wider Zagreb area were obtained by conducting a biological treatment experiment under laboratory conditions, in which the proportion of fresh kitchen waste was 93.1%, the gross chemical composition was $C_{22}H_{38}O_{13}N$, the proportion of dry matter was 37.4%, the share of the biodegradable organic component was 85.1%, and the C/N ratio was 19.8. The output streams were estimated from the material balance of the composting process, whereby a mass reduction of the mixture of 23% and a conversion of the biodegradable portion of the biowaste sample of 50.57% was achieved after 21 test days.

The biokinetic parameters of the Gompertz model were estimated using the nonlinear process optimization method, namely the maximum rate of CO_2 generation R_m = 49.8 g/d and P = 526 g CO_2/kg VS, with conversion of the biodegradable component of the biowaste sample achieved by the 17th day. From the results of the experiment and the simulation of the process of the biodegradation of biowaste, which corresponded in its characteristics to the biowaste sample studied, it can be concluded that the basic initial conditions of the process must be ensured for the optimal course of the process. The basic parameters that must be determined in order to be monitored during the process are the C/N ratio, the temperature, and the moisture of the biowaste. In this way, the maintenance of thermophilic degradation conditions for hygienization of the biowaste is ensured, as well as the dynamics of the process, which follows an intensive biodegradation over 2 to 4 weeks under controlled bioreactor conditions and a maturation of the resulting compost of up to 8 weeks, depending on its final use.

Based on the experience gained from the experiment and the simulation of the process, further research is recommended to determine the boundary conditions for the composition and the physicochemical properties as well as the biodegradability of the biowaste samples in order to evaluate the biokinetic parameters of the process. The analysis of the sensitivity of the input data on the composition of the biowaste to changes in the parameters of the process of aerobic stabilization by composting also contributes significantly to the understanding of the dynamics of the process. In this way, high quality input data can be obtained for the design and assessment of plant capacity and area as well as for the evaluation of operational investment costs for the aerobic biological treatment of biowaste as a key stream of municipal waste to achieve the recycling targets according to Directive (EU) 2018/851.

Author Contributions: Conceptualization, T.D. and M.V.D.; methodology, T.D. and M.V.D.; validation, T.D. and M.V.D.; formal analysis, T.D.; investigation, T.D., D.K.G. and M.Š.R.; resources, T.D. and M.V.D.; writing—original draft preparation, T.D., M.Š.R. and M.V.D.; writing—review and editing, T.D., M.V.D. and D.K.G.; visualization, T.D.; supervision, D.K.G. and M.V.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Dataset available upon request from the authors.

Conflicts of Interest: Author Tomislav Domanovac was employed by the company IPZ Uniprojekt TERRA, Zagreb, Croatia. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as potential conflicts of interest.

References

1. Kim, M.; Chowdhury, M.M.I.; Nakhla, G.; Keleman, M. Characterization of typical household food wastes from disposers: Fractionation of constituents and implications for resource recovery at wastewater treatment. *Bioresour. Technol.* **2015**, *183*, 61–69. [CrossRef]
2. Adetunji, A.I.; Oberholster, P.J.; Erasmus, M. From garbage to treasure: A review on biorefinery of organic solid wastes into valuable biobased products. *Bioresour. Technol. Rep.* **2023**, *24*, 101610. [CrossRef]

3. Kaza, S.; Yao, L.C.; Bhada-Tata, P.; Van Woerden, F. *What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050*, 1st ed.; World Bank: Washington, DC, USA, 2018; pp. 17–38. [CrossRef]
4. Lohri, C.R.; Diener, S.; Zabaleta, I.; Mertenat, A.; Zurbrügg, C. Treatment technologies for urban solid biowaste to create value products: A review with focus on low- and middle-income settings. *Rev. Environ. Sci. Biotechnol.* **2017**, *16*, 81–130. [CrossRef]
5. Solarte-Toro, J.C.; Cardona Alzate, C.A. Biorefineries as the base for accomplishing the sustainable development goals (SDGs) and the transition to bioeconomy: Technical aspects, challenges and perspectives. *Bioresour. Technol.* **2021**, *340*, 125626. [CrossRef] [PubMed]
6. Solarte-Toro, J.C.; Cardona Alzate, C.A. Sustainability of biorefineries: Challenges and perspectives. *Energies* **2023**, *16*, 3786. [CrossRef]
7. Li, Z.; Zhou, H.; Zheng, L.; Wang, H.; Chen, T.; Liu, Y. Seasonal changes in bulk density-based waste identification and its dominant controlling subcomponents in food waste. *Resour. Conserv. Recycl.* **2021**, *168*, 105244. [CrossRef]
8. Waste Management Act (OG 84/2021, 143/23). Available online: https://mingor.gov.hr/o-ministarstvu-1065/djelokrug/uprava-za-procjenu-utjecaja-na-okolis-i-odrzivo-gospodarenje-otpadom-1271/zakoni-i-propisi-7637/zakoni-i-propisi-iz-podrucja-gospodarenja-otpadom/7593 (accessed on 15 January 2024).
9. Siegfried, K.; Günther, S.; Mengato, S.; Riedel, F.; Thrän, D. Boosting biowaste valorisation—Do we need an accelerated regional implementation of the European law for end-of-waste? *Sustainability* **2023**, *15*, 13147. [CrossRef]
10. Margaritis, M.; Dimos, V.; Malamis, D.; Loizidou, M. An experimental investigation of the composting process in an innovative home composting system: The influence of additives. *Clean. Mater.* **2023**, *8*, 100185. [CrossRef]
11. Bernat, K.; Wojnowska-Baryła, I.; Zaborowska, M.; Samul, I. Insight into the Composition of the stabilized residual from a full-scale mechanical-biological treatment (MBT) plant in terms of the potential recycling and recovery of its contaminants. *Sustainability* **2021**, *13*, 5432. [CrossRef]
12. Onwosi, C.O.; Igbokwe, V.C.; Odimba, J.N.; Eke, I.E.; Nwankwoala, M.O.; Iroh, I.N.; Ezeogu, L.I. Composting technology in waste stabilization: On the methods, challenges and future prospects. *J. Environ. Manag.* **2017**, *190*, 140–157. [CrossRef]
13. Vasiliadou, I.A.; Chowdhury, A.K.M.B.; Akratos, C.S.; Tekerlekopoulou, A.G.; Pavlou, S.; Vayenas, D.V. Mathematical modeling of olive mill waste composting process. *Waste Manag.* **2015**, *43*, 61–71. [CrossRef] [PubMed]
14. Mason, I.G. Mathematical modelling of the composting process: A review. *Waste Manag.* **2006**, *26*, 3–21. [CrossRef] [PubMed]
15. Haug, R.T. *The Practical Handbook of Compost Engineering*, 2nd ed.; Lewis Publishers: Boca Raton, FL, USA, 1993.
16. Yonemura, S.; Gurjar, B.R. *Environmental Science and Engineering (Instrumentation, Modelling and Analysis)*; Studium Press LLC: Houston, TX, USA, 2017.
17. Zhang, H.; Matsuto, T. Comparison of mass balance, energy consumption and cost of composting facilities for different types of organic waste. *Waste Manag.* **2011**, *31*, 416–422. [CrossRef] [PubMed]
18. Hamoda, M.F.; Abu Qdais, H.A.; Newham, J. Evaluation of municipal solid waste composting kinetics. *Resour. Conserv. Recycl.* **1998**, *23*, 209–223. [CrossRef]
19. Sladarriaga, J.F.; Gallego, J.L.; López, J.E. Determination of kinetics parameters for composting process of the organic fraction of municipal solid waste separated at source. *Chem. Eng. Trans.* **2018**, *70*, 217–222. [CrossRef]
20. Croatian Agency for the Environment and Nature. *Methodology Used in Determining the Composition and Volume of Municipal Waste and Mixed Municipal Waste*; Croatian Environment Agency: Zagreb, Croatia, 2015.
21. *HRI CEN/TR 15310-1:2008*; Croatian Standard: Characterization of Waste—Sampling of Waste Materials—Part 1: Guidance on Selection and Application of Criteria for Sampling under Various Conditions. Croatian Standards Institute: Zagreb, Croatia, 2008.
22. *HRN EN 14899:2007*; Croatian Standard: Characterization of Waste—Sampling of Waste Materials—Framework for the Preparation and Application of a Sampling Plan. Croatian Standards Institute: Zagreb, Croatia, 2007.
23. *ÖNORM S 2023*; Austrian Standard: Analytical Methods and Quality Control for Waste Compost. Austrian Standards Institute: Vienna, Austria, 1986.
24. Kopčić, N.; Vuković Domanovac, M.; Kučić, D.; Briški, F. Evaluation of laboratory-scale in-vessel co-composting of tobacco and apple waste. *Waste Manag.* **2014**, *34*, 323–328. [CrossRef] [PubMed]
25. Kučić, D.; Kopčić, N.; Briški, F. Biodegradation of agro-industrial waste. *Chem. Biochem. Eng. Q.* **2017**, *31*, 369–374. [CrossRef]
26. Domanovac, T.; Orašanin, R. Municipal solid waste composition for continental and coastal part of Croatia. In Proceedings of the VII International Symposium Waste Management, Zagreb, Croatia, 13–15 November 2002.
27. Adhikari, B.K.; Barrington, S.; Martinez, J.; King, S. Characterization of food waste and bulking agents for composting. *Waste Manag.* **2008**, *28*, 795–804. [CrossRef]
28. Kiran, E.U.; Trzcinski, A.P.; Ng, W.J.; Liu, Y. Bioconversion of food waste to energy: A review. *Fuel* **2014**, *134*, 389–399. [CrossRef]
29. Switzenbaum, M.S.; Pincince, A.B.; Donovan, J.F. *Developing Protocols for Measuring Biosolids Stability: Werf Report Collection and Treatment Project 99-pum-3*, 1st ed.; Water Environment Federation: Alexandria, VA, USA, 2002.
30. Brinton, W.F. *Compost Quality Standards and Guidelines: Final Report*; Woods End Research Laboratories for the New York State Association of Recyclers: Mount Vernon, ME, USA, 2000.
31. Vandaele, E. *Hygienisation Requirements for Composting*; EU Soilcom, Interreg: Workpackage 5. Report 2; European Environment Agency: Kopenhagen, Denmark, 2019.
32. Tontti, T.; Heinonen-Tanski, H.; Karinen, P.; Reinikainen, O.; Halinen, A. Maturity and hygiene quality of composts and hygiene indicators in agricultural soil fertilised with municipal waste or manure compost. *Waste Manag Res.* **2011**, *29*, 197–207. [CrossRef]

33. Vinneras, B.; Agostini, F.; Jönsson, H. Sanitation by composting. In *Microbes at Work*; Insam, H., Franke-Whittle, I., Goberna, M., Eds.; Springer: Berlin/Heidelberg, Germany, 2010; pp. 171–191. [CrossRef]
34. Wichuk, K.M.; Tewarim, J.P.; McCartney, D. Plant pathogen eradication during composting: A literature review. *Compost Sci. Util.* **2011**, *19*, 244–266. [CrossRef]
35. Alkoaik, F.N. Integrating aeration and rotation processes to accelerate composting of agricultural residues. *PLoS ONE* **2019**, *14*, e0220343. [CrossRef] [PubMed]
36. Chang, J.I.; Chen, Y.J. Effects of bulking agents on food waste composting. *Bioresour. Technol.* **2010**, *101*, 5917–5924. [CrossRef] [PubMed]
37. Atauzzaman, M.; Bari, Q.H. Effect of passive and forced aeration on composting of market solid waste. In *Organic Fertilizers—New Advances and Applications*; Hakeem, K.R., Ed.; IntechOpen: London, UK, 2023. [CrossRef]
38. Kučić, D.; Briški, F. Emission of gases during composting of solid waste. *Kem. Ind.* **2017**, *66*, 467–474. [CrossRef]
39. Ahn, H.K.; Richard, T.L.; Choi, H.L. Mass and thermal balance during composting of a poultry manure—Wood shavings mixture at different aeration rates. *Process Biochem.* **2007**, *42*, 215–223. [CrossRef]
40. Guardia, A.; Petiot, C.; Rogeau, D. Influence of aeration rate and biodegradability fractionation on composting kinetics. *Waste Manag.* **2008**, *28*, 73–84. [CrossRef]
41. Gao, M.; Li, B.; Yu, A.; Liang, F.; Yang, L.; Sun, Y. The effect of aeration rate on forced-aeration composting of chicken manure and sawdust. *Bioresour. Technol.* **2010**, *101*, 1899–1903. [CrossRef]
42. Lai, J.C.; Then, Y.L.; Hwang, S.S.; Lee, C.S. Optimal aeration management strategy for a small-scale food waste composting. *Carbon Resour. Convers.* **2024**, *7*, 100190. [CrossRef]
43. Zhang, H.; Li, G.; Gu, J.; Wang, G.; Li, Y.; Zhang, D. Influence of aeration on volatile sulfur compounds (VSCs) and NH_3 emissions during aerobic composting of kitchen waste. *Waste Manag.* **2016**, *58*, 369–375. [CrossRef]
44. Sundberg, C.; Jönsson, H. Higher pH and faster decomposition in biowaste composting by increased aeration. *Waste Manag.* **2008**, *28*, 518–526. [CrossRef]
45. Tchonabogolous, G.; Theisen, H.; Vigil, S.A. *Integrated Solid Waste Management, international ed.*; McGraw-Hill: New York, NY, USA, 1993.
46. Walling, E.; Vaneeckhaute, C. Novel simple approaches to modeling composting kinetics. *J. Environ. Chem. Eng.* **2021**, *9*, 105243. [CrossRef]
47. Daskal, S.; Asi, O.; Sabbah, I.; Ayalon, O.; Baransi-Karkaby, K. Decentralized composting analysis model—Benefit/cost decision-making methodology. *Sustainability* **2022**, *14*, 16397. [CrossRef]
48. Chang, J.I.; Tsai, J.J.; Wu, K.H. Composting of vegetable waste. *Waste Manag. Res.* **2006**, *24*, 354–362. [CrossRef] [PubMed]
49. Liu, Q.; He, X.; Luo, G.; Wang, K.; Li, D. Deciphering the dominant components and functions of bacterial communities for lignocellulose degradation at the composting thermophilic phase. *Bioresour. Technol.* **2022**, *348*, 126808. [CrossRef] [PubMed]
50. Puyuelo, B.; Ponsá, S.; Gea, T.; Sánchez, A. Determining C/N ratios for typical organic wastes using biodegradable fractions. *Chemosphere* **2011**, *85*, 653–659. [CrossRef] [PubMed]
51. Baptista, M.; Silveira, A.; Antunes, F. Theoretical analysis of the kinetic performance of laboratory- and full-scale composting systems. *Waste Manag. Res.* **2012**, *30*, 700–707. [CrossRef]
52. Fowles, M.; Mohabuth, N.; Stamawska, A.; Webb, A.; Whiteley, J.; Border, D. *Defra New Technologies Demonstrator Programme: Demonstration of a Double-Ended In-Vessel Composting System*; Envar Ltd.: Huntingdon, UK, 2010.