Chemical Engineering Journal 139 (2008) 304–317

Chemical Engineering Journal

www.elsevier.com/locate/cej

Development and validation of mathematical model for aerobic composting process

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Received 6 November 2006; received in revised form 30 July 2007; accepted 3 August 2007

Abstract

By integrating the reaction kinetics with the mass and heat transfer between the three phases of the system, a new dynamic structured model for aerobic composting process was developed in this work. In order to evaluate kinetic parameters in mathematical model and to validate the model, experiments were performed with the reactor of volume 32 L, in controlled laboratory conditions. Different ratios of poultry manure to wheat straw were mixed and used as a substrate. Rosenbrock optimization method was used for parameter estimation. In order to solve the system of 12 non-linear differential (and corresponding algebraic) equations, Runge–Kutta–Fehlberg method was used, with approximation of fourth and fifth order and adjustment of step size. Both algorithms were implemented in FORTRAN programming language. In order to achieve as accurate description of the process dynamics as possible, the developed mathematical model was validated by the results of several experimentally measured dynamic state variables. Comparisons of experimental and simulation results for temperature of substrate, organic matter conversion, carbon dioxide concentration and oxygen concentration, in general showed good agreement during the whole duration of the process in a reactor. In the case of ammonia, an agreement was achieved for the first 4 days and for the last 3 days of the process. A sensitivity analysis was performed to determine the key parameters of the model. Analysis showed that two parameters had a great influence on the main characteristics of the process. With validated model for aerobic composting of mixture of poultry manure and wheat straw, optimal values were determined: initial moisture content (70%) and airflow (0.541 $\text{min}^{-1}\,\text{kg}_{\text{OM}}^{-1}$).

Keywords: Mathematical model; Aerobic composting; Reactor; Model parameters; Simulation; Model validation

1. Introduction

The objectives of modelling are the development of mathematical tool to allow an integration of knowledge on the considered phenomena, to orientate experimental design, to evaluate experimental results, to test hypothesis, to reveal relations among variables, to predict the evolution of a system and, finally, to design optimal process and management strategies.

Composting is a complex bioprocess that involves many coupled physical and biological mechanisms. These coupled, and often nonlinear, mechanisms yield a broad spectrum of process behaviours that are challenging to analyze both empirically and theoretically. Mathematical modelling provides one approach for understanding the dynamical interactions between these coupled mechanisms, and provides a framework for rational process design [1]. Mathematical reactor models can serve as an essential tool for faster and better process designs, system analysis, and operational guidance [2].

Increased computational power has made it feasible to use mathematical models of the composting process, which can improve understanding and reduce the need for costly experimentation. Mathematical models of the composting process have appeared in the literature since 1976 [3]. The models [1,4–29] showed more or less success in predicting the profiles of: temperature, moisture, solids, oxygen and carbon dioxide. Each of these models had some advantages and disadvantages, but there are some general lacks in these models. Firstly, the above mentioned models, partly or not at all, described mass and heat transfer between three phases of the system, and most of them did not describe dynamics of the gas phase and the dissolved gases in water at composting material. Secondly, most of these models did not use the original parameter values but they used those from existing literature. Thirdly, model validations were carried out either only with one or two experimentally

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doi:10.1016/j.cej.2007.08.017

measured dynamic state variables, or were not carried out at all.

The aims of this work were the following: (1) to develop the new dynamic and structured model for aerobic composting process by connecting the reaction kinetics with mass and heat transfer between three phases of the system, (2) to evaluate the kinetic parameters in suggested kinetics of the model by using the experimental results from laboratory reactor, (3) to validate the model with several experimentally measured dynamic state variables, (4) to show the efficiency of the validated model through the determination of the effects of the main process factors on the degradation of organic waste and evaluations of their optimum values.

2. Materials and methods

2.1. Description of model

The model describes the three-phase system and it is based on basic principles of chemical reaction engineering: kinetics, stoichiometry, mass and heat balances. At the beginning of the process, the substrate consists of organic part, inorganic part and water. Organic part of the substrate is degraded by biochemical reaction, with consumption of oxygen and generation of carbon dioxide, water and ammonia. Because of exothermic reaction, the heat is released. Considering substrate as a reactant, the model of batch reactor can be assumed. Air of constant composition is introduced into reactor, and gas phase composition is changed at reactor outlet.

The role of air is to ensure sufficient concentration of oxygen for oxidation of organic matter and to take away the excess of moisture from the substrate. The complete mixing of material is assumed and it is achieved by agitation or efficient aeration. Reactor model can be approximated by the model of continuous stirred tank reactor (CSTR) at unsteady state with respect to present gases.

One part of the reactor is filled with substrate (represented by solid and liquid phases), while the rest of the volume is occupied by gaseous mixture (oxygen, nitrogen, carbon dioxide, water vapour, ammonia) (Fig. 1). According to biochemical reaction, solid and liquid phases are responsible for the release of heat. Mass transfer of dissolved gasses and evaporated water occurs on the boundary between liquid and gas phases. The considered heat transfers are: heat transfer released from biochemical reaction, heat transfer from reactor to surroundings, convective heat transfer between phases, heat transfer of evaporated/condensed water.

2.2. Model assumptions and simplifications

The following assumptions were taken into account while developing the model:

- The part of reactor volume with gas mixture has a constant value.
- The system maintains a constant pressure.
- Gas mixture is saturated with water vapour.
- Mass flows of the air at reactor inlet and outlet are equal (air has a constant flow).
- Liquid and solid phases have uniform temperatures.
- The substrate is a homogeneous mixture of uniform composition.
- Elementary composition of organic matter in the substrate (carbon, hydrogen, oxygen, nitrogen) is known at the beginning of the process.
- The composting rate is expressed as the rate of organic matter degradation.

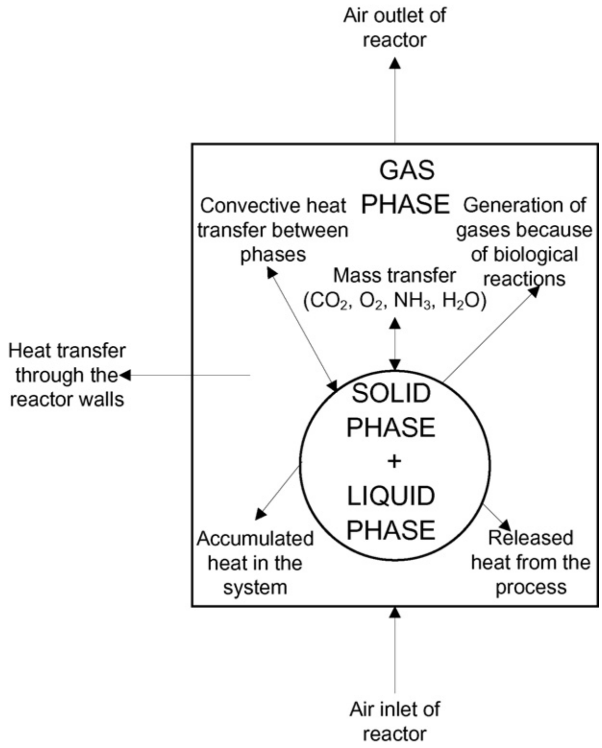

Fig. 1. Mass and heat transfer phenomena included in the model.

The assumption about constant volume of the gas phase above the composting material is based on considerations of anaerobic digestion model [30]. In reality, the volume of gas phase depends on variations in water content, degradation of organic matter and compaction of the material.

The assumption about maintenance of the constant pressure is justified because variations of total pressure of the gas phase are small comparing to pressure of the surroundings [27].

The assumption about constant air humidity is valid if the substrates with initial moisture content between 60 and 65% are used [31]. Air that leaves the compost is saturated in the case of the moisture content above 50% [17,31,32]. Typical composting process maintains the moisture content above 50%.

The assumption about constant airflow ensures that oxygen is distributed uniformly in the voids, eliminating anaerobic conditions [18].

The assumption about uniform temperature comes from the fact that there is little or no resistance to heat transfer from the compost matrix to the air in the reactor [1,8].

The assumption about uniform substrate allows the model to neglect the statistical and spatial variations in substrate composition and density which are known to be usually present. The model predictions will be average values around which statistical variations occur [4,18].

With known mass fraction of carbon, hydrogen, oxygen and nitrogen in the substrate, the stoichiometric coefficients for oxygen, carbon dioxide, water and ammonia can be calculated from the stoichiometry of the oxidation reaction of the substrate's organic part [9]. Inorganic matter does not participate in the reaction.

The simplifications made in the model development were:

- All heat capacities are constant.
- All enthalpies are independent from the pressure.
- Gas phase consists of ideal gases.

2.3. Process kinetics

In description of kinetics for the substrate degradation, the following equation is suggested:

$$\frac{\mathrm{d}m_{\mathrm{OM}}}{\mathrm{d}t} = -k m_{\mathrm{OM}}^{n} \tag{1}$$

where m_{OT} is the mass of organic matter in the substrate (kg), t is time (h), k is reaction rate constant ($\mathrm{kg}^{1-n}\,\mathrm{h}^{-1}$) and n is reaction order (–).

Reaction rate constant is the function of temperature, oxygen, moisture and free air space [9]:

$$k = k_T k_{\mathrm{O_2}} k_{\mathrm{H_2O}} k_{\mathrm{FAS}} \tag{2}$$

For describing the effect of temperature on reaction rate constant, the equation developed in [33] was used as a basis. Using the experimental data from [34] and taking into account that 20 °C is the referent temperature and 60 °C is the optimal temperature, Haug [9] developed the equation in the following form:

$$k_{\mathrm{d}} = k_{\mathrm{d20}}[1.066^{(T-20)} - 1.21^{(T-60)}] \tag{3}$$

where k_{d20} is reaction rate constant at temperature 20 °C (h^{-1}) and T is substrate temperature (°C).

In the model, modification of the Eq. (3) is suggested as:

$$k_T = a[b^{(T-20)} - c^{(T-60)}] \tag{4}$$

where a, b and c are constants that need to be determined as well as the reaction order n in Eq. (1).

For oxygen correction function, the following equation is used [15]:

$$k_{\mathrm{O_2}} = \frac{\mathrm{O_2}}{K_{\mathrm{O_2}} + \mathrm{O_2}} \tag{5}$$

where $\mathrm{O_2}$ is oxygen concentration ($\mathrm{kg\,O_2\,m^{-3}}$) and $K_{\mathrm{O_2}}$ is oxygen saturation constant ($\mathrm{kg\,O_2\,m^{-3}}$).

For moisture correction function, the following equation is used [9]:

$$k_{\mathrm{H_2O}} = \frac{1}{\mathrm{e}^{\{-17.684[1-S_{\mathrm{m}}]+7.0622\}} + 1} \tag{6}$$

where S_{m} is solid content of the substrate (–).

For free air space correction function, the following equation is used [9]:

$$k_{\mathrm{FAS}} = \frac{1}{\mathrm{e}^{[-23.675\mathrm{FAS}+3.4945]} + 1} \tag{7}$$

Free air space (FAS) is calculated using the following equations [9]:

$$\mathrm{FAS} = 1 - \frac{\delta_{\mathrm{m}} S_{\mathrm{m}}}{G_{\mathrm{s}} \delta_{\mathrm{w}}} - \frac{\delta_{\mathrm{m}}(1 - S_{\mathrm{m}})}{\delta_{\mathrm{w}}} \tag{8}$$

$$G_{\mathrm{s}} = \frac{1}{(V_{\mathrm{s}}/G_{\mathrm{v}}) + ((1 - V_{\mathrm{s}})/G_{\mathrm{f}})} \tag{9}$$

$$\delta_{\mathrm{m}} = \frac{C}{S_{\mathrm{m}}} \tag{10}$$

where δ_{m} and δ_{w} are density of composting material and water ($\mathrm{kg\,m^{-3}}$); G_{s}, G_{v} and G_{f} are specific gravity of solids, specific gravity of volatile fraction of the solids (=1) and specific gravity of the fixed fraction of the solids (=2.5); V_{s} is volatile fraction of the solids (–); C is bulk weight coefficient for the substrate (0.15–0.4).

2.4. Stoichiometry

According to the assumption about initial elementary composition of the substrate, organic matter degradation in the substrate can be presented by the following equation:

$$\mathrm{C}_a\mathrm{H}_b\mathrm{O}_c\mathrm{N}_d + \left(\frac{4a + b - 2c - 3d}{4}\right)\mathrm{O_2} \rightarrow a\mathrm{CO_2} + \frac{b - 3d}{2}\mathrm{H_2O} + d\mathrm{NH_3} \tag{11}$$

where a, b, c and d are indexes which describe the molar fraction of carbon, hydrogen, oxygen and nitrogen in the organic part of the substrate. The stoichiometric coefficients for oxygen, carbon dioxide, water vapour and ammonia can be calculated using the defined molecular formula of organic part of the substrate and the Eq. (11).

2.5. Mass balance

2.5.1. Dissolved gases in interstitial water (O_2, CO_2, NH_3)

The general mass balance for dissolved gases in the water within the substrate is given by the following equation:

$$\frac{\mathrm{d}m_i}{\mathrm{d}t} = R_i - R_i^T \tag{12}$$

where m_i is mass of dissolved gas i in solution (kg), R_i is generation rate of gas i toward biochemical reaction in liquid phase ($\mathrm{kg\,h^{-1}}$) and R_i^T is rate of mass transfer liquid–gas for gas i ($\mathrm{kg\,h^{-1}}$).

The generation rate R_i is calculated by the following equation:

$$R_i = \pm Y_i \frac{\mathrm{d}m_{\mathrm{OM}}}{\mathrm{d}t} \tag{13}$$

where Y_i is stoichiometric coefficient of gas i. The sign (+) in Eq. (13) is valid for carbon dioxide and ammonia, and sign (−)

is valid for oxygen.The generation rate R_i^T is calculated by the following equation:

$$R_i^T = k_L a_i (\mathrm{He}_i f_i X_i - p_i) \tag{14}$$

where $k_L a_i$ is mass transfer coefficient for gas i (kg h^{-1} Pa^{-1}), He_i is Henry's constant for gas i (Pa), f_i is dissociation factor for gas i in the solution (–), X_i is molar fraction of gas i dissolved in the solution (–) and p_i is partial pressure of gas i in gas phase (Pa).

The Henry's constants for oxygen, carbon dioxide and ammonia are fitted by literature data [35]:

$$\mathrm{He}_{O_2} = 101325\mathrm{e}^{(66.7354-(8747.55/T)-24.4526\ln(T/100))} \tag{15}$$

$$\mathrm{He}_{CO_2} = -11418.84 + 43.8658T \tag{16}$$

$$\mathrm{He}_{NH_3} = 10^5\mathrm{e}^{(14.48-(4341/T))} \tag{17}$$

where T is temperature of composting material (K).

It was assumed that dissociation factors for oxygen and carbon dioxide in water solution equal to 1. The following dissociation factor for ammonia is used [36]:

$$f_{NH_3} = \frac{10^{\mathrm{pH}}}{10^{\mathrm{pH}} + \mathrm{e}^{6344/T}} \tag{18}$$

The pH value is defined as a function of the hydrogen ion as follows:

$$\mathrm{pH} = -\log_{10}[\mathrm{H}^+] \tag{19}$$

where $[\mathrm{H}^+]$ is concentration of the hydrogen ion (mol L^{-1}). It is calculated from the equlibrium relation:

$$[K] = \frac{[\mathrm{H}^+][\mathrm{NH}_3]}{[\mathrm{NH}_4^+]} \tag{20}$$

where K is the equilibrium constant (mol L^{-1}), $[\mathrm{NH}_3]$ is the concentration of free NH_3 dissolved in the water phase (mol L^{-1}), $[\mathrm{NH}_4{}^+]$ is the concentration of water-soluble NH_4–N (mol L^{-1}).

The equilibrium constant K is calculated from the following equation [37]:

$$\ln\left(\frac{K}{K_{298}}\right) = -\frac{\Delta H_0}{R}\left(\frac{1}{T} - \frac{1}{298}\right) \tag{21}$$

where K_{298} is the equilibrium constant at temperature 298 K ($K_{298} = 10^{-9.24}$ mol L^{-1}), ΔH_0 is the change of reaction enthalpy ($\Delta H_0 = 86400$ J mol^{-1}), R—universal gas constant ($R = 8.314$ J mol^{-1} K^{-1}).

The concentration of NH_3 in the gas phase is assumed to be in equilibrium with free NH_3 dissolved in the water phase of compost.

The partial pressure of gas in the gas phase p_i can be described by equation of ideal gas state:

$$p_i = \frac{n_i R\psi}{V_g} \tag{22}$$

where n_i is number of mole of gas i (kmol), R is universal gas constant (J kmol^{-1} K^{-1}), ψ is temperature of gas phase (K), V_g is volume of gas phase (m^3) (it is calculated as a difference between reactor volume and volume occupied by composting material).

2.5.2. *Water in composting material*

The general mass balance for water in composting material is given by the following equation:

$$\frac{\mathrm{d}m_w}{\mathrm{d}t} = R_w - R_w^T \tag{23}$$

where m_w is mass of water in composting material (kg), R_w is generation rate of water toward biochemical reaction (kg h^{-1}) and R_w^T is rate of mass transfer liquid–gas for water (kg h^{-1}).

The generation rate R_w is calculated by the following equation:

$$R_w = -Y_w \frac{\mathrm{d}m_{OM}}{\mathrm{d}t} \tag{24}$$

where Y_w is stoichiometric coefficient of water.

The generation rate R_w^T is calculated by the following equation:

$$R_w^T = k_L a_w (P_s - P_v) \tag{25}$$

where $k_L a_w$ is mass transfer coefficient liquid–gas for water (kg h^{-1} Pa^{-1}), P_v is pressure of water vapour in gas phase (Eq. (19)) (Pa) and P_s is pressure of water vapour saturated at temperature of gas phase (Pa).

The pressure P_s is fitted by the literature data [35]:

$$P_s = 10^{(22{,}443-(2795/\psi)-1{,}6798\ln\psi)} \tag{26}$$

2.5.3. *Gases in gas phase (O_2, CO_2, NH_3, N_2, H_2O)*

In general, the mass balance equation for the components in the gas phase can be described by the following equation:

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = F_{i,0} + \bar{R}_i^T - F_{i,f} \tag{27}$$

where $F_{i,0}$ and $F_{i,f}$ are molar flows at inlet and outlet for component i (kmol h^{-1}) and $\bar{R}_i^T$ is generation rate for component i at outlet from liquid phase (kmol h^{-1}).

It was assumed that there was no carbon dioxide in inlet air. The molar flows of oxygen, nitrogen and water vapour are calculated by the following equations:

$$F_{O_2,0} = 0.21\frac{(P_T - P_s)Q}{R\psi_0} \tag{28}$$

$$F_{N_2,0} = 0.79\frac{(P_T - P_s)Q}{R\psi_0} \tag{29}$$

$$F_{H_2O,0} = \frac{P_s Q}{R\psi_0} \tag{30}$$

where P_T is total pressure (Pa) and Q is volumetric airflow (m^3 h^{-1}).

The pressure of water vapour P_s is calculated by the Eq. (23), but at initial temperature of gas phase ψ_0.

The outflows are calculated by the following equation:

$$F_{i,\mathrm{f}} = n_i \frac{R\psi}{PV_\mathrm{g}} \left(F_{T,0} + \sum_i \bar{R}_i^T \right) + \frac{n_i}{\psi} \frac{\mathrm{d}\psi}{\mathrm{d}t} \tag{31}$$

2.6. Heat balance

2.6.1. Gas phase

The temperature of the gas phase is calculated as:

$$\frac{\mathrm{d}\psi}{\mathrm{d}t} = \frac{Q_\mathrm{c}^T + (\psi_0 - \psi)\left(\sum_i c_{\mathrm{p}i} F_{i,0}\right) + (T - \psi)\sum_i c_{\mathrm{p}i} \max\{0, \bar{R}_i^T\}}{\sum_i n_i c_{\mathrm{p}i}} \tag{32}$$

where $c_{\mathrm{p}i}$ is specific heat capacity of gas i (J kmol^{-1} K^{-1}).

The convective heat transfer from solid–liquid phase to gas phase can be described by Newton's equation:

$$Q_\mathrm{c}^T = h_\mathrm{c}(T - \psi) \tag{33}$$

where h_c is convective heat transfer coefficient between two phases (J h^{-1} K^{-1}).

The third term of the numerator in Eq. (32) takes into account the heat transfer liquid–gas in the following way (*max* is elemental intrinsic function which returns the maximum value in an argument list): (1) if $\bar{R}_i^T > 0$ then follows that the difference between temperature at phase border and gas phase are equal to $(T - \psi)$, (2) if $\bar{R}_i^T < 0$ then follows that the difference between temperature at phase border and gas phase are equal to 0.

2.6.2. Solid–liquid phase

The temperature of the solid–liquid phase is calculated as:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{Q_\mathrm{cw} + Q_\mathrm{G} - Q_\mathrm{c}^T - \sum_i(\max\{0, \bar{R}_i^T\}\bar{h}_i(T) + \min\{0, \bar{R}_i^T\}\bar{h}_i(\psi)) - (T - 273.15)(c_\mathrm{pw}(\mathrm{d}m_\mathrm{w}/\mathrm{d}t) + c_\mathrm{pOM}(\mathrm{d}m_\mathrm{OM}/\mathrm{d}t))}{c_\mathrm{pw}m_\mathrm{w} + c_\mathrm{pOM}m_\mathrm{OM} + c_\mathrm{pIM}m_\mathrm{IM}} \tag{34}$$

where c_pw, c_pOM and c_pIM are specific heat capacities of water, organic matter and inorganic matter, respectively; $\bar{h}_i(T)$ and $\bar{h}_i(\psi)$ are molar enthalpies of gas at temperature of solid–liquid and gas phase, respectively.

The specific heat capacities are calculated by the following equation [9,38]:

$$c_\mathrm{p} = 1.48 - 0.64 ash + 4.18 w_\mathrm{c} \tag{35}$$

where *ash* is the ash or mineral content of the material (−) and w_c is the dry-basis moisture content (−).

The heat transfer through the reactor walls Q_cw is calculated as:

$$Q_\mathrm{cw} = UA(T_\mathrm{a} - T) \tag{36}$$

where U is overall heat transfer coefficient (J h^{-1} m^{-2} K^{-1}), A is area of heat exchange (m^2) and T_a is ambient temperature (K).

The overall heat transfer coefficient U is calculated by the following equation [31]:

$$U = \frac{\lambda_\mathrm{f} A_\mathrm{lm}}{LA} \tag{37}$$

where λ_f is thermal conductivity of insulator (J h^{-1} m^{-1} K^{-1}), A_lm is logarithmic mean of surface area of insulator surrounding the reactor (m^2) and L is mean thickness of insulator (m).

Table 1
Dynamic state variables in the mathematical model

No.	Dynamic state variable	Symbol	Unit	Equation
1	Mass of organic matter	m_OT	kg	(1)
2	Mass of dissolved O_2	m_{O_2}	kg	(12)
3	Mass of dissolved CO_2	m_{CO_2}	kg	(12)
4	Mass of dissolved NH_3	m_{NH_3}	kg	(12)
5	Mass of water in the substrate	m_w	kg	(23)
6	Molar amount of O_2 (gas phase)	n_{O_2}	kmol	(27)
7	Molar amount of CO_2 (gas phase)	n_{CO_2}	kmol	(27)
8	Molar amount of NH_3 (gas phase)	n_{NH_3}	kmol	(27)
9	Molar amount of H_2O vapor (gas phase)	n_{H_2Ov}	kmol	(27)
10	Molar amount of N_2 (gas phase)	n_{N_2}	kmol	(27)
11	Temperature of gas phase	ψ	K	(32)
12	Temperature of solid–liquid phase	T	K	(34)

The biochemical heat generation Q_G is calculated as:

$$Q_\mathrm{G} = -\Delta h \frac{\mathrm{d}m_\mathrm{OM}}{\mathrm{d}t} \tag{38}$$

where Δh is the reaction enthalpy (J kg$_\mathrm{OM}^{-1}$).

The fourth term of the numerator in Eq. (34) takes into account the heat transfer liquid–gas in the following way (*max* and *min* are elemental intrinsic functions which return maximum and minimum value in an argument list): (1) if $\bar{R}_i^T > 0$ then follows that molar enthalpy of gas $\bar{h}_i$ is at temperature of solid–liquid phase T, (2) if $\bar{R}_i^T < 0$ then follows that molar enthalpy of gas $\bar{h}_i$ is at temperature of solid–liquid phase ψ.

2.7. Structure of mathematical model

Mathematical model consists of 12 nonlinear differential equations (Eqs. (1), (12) for O_2, CO_2, NH_3, (23), (27) for O_2, CO_2, NH_3, N_2, H_2O, (32), (34)) with corresponding algebraic equations (Eqs. (2), (4)–(10), (13)–(22), (24)–(26), (28)–(31), (33), (35)–(38)). Therefore, the system of equations is described by 12 dynamic state variables (Table 1).

2.8. Model inputs

Four different categories of data are required in the model: initial values of the dynamic state variables, constants (physical, thermodynamic and stoichiometric), kinetic parameters and operational conditions.

Calculation of initial mass values for dissolved oxygen, carbon dioxide and ammonia in interstitial water was based on solubility data from literature [35].

Initial mole values of gases in gas phases were calculated using the initial values of molar flows of gases, airflow rate and volume of gas phase.

Table 2
Physical, thermodynamic and stoichiometric constants used in the model.

Description of the constant	Symbol	Value	Unit	References
Specific heat capacity for N_2	c_{pN_2}	29.132	$\mathrm{J\,kmol^{-1}\,K^{-1}}$	[35]
Specific heat capacity for O_2	c_{pO_2}	29.500	$\mathrm{J\,kmol^{-1}\,K^{-1}}$	[35]
Specific heat capacity for CO_2	c_{pCO_2}	38.154	$\mathrm{J\,kmol^{-1}\,K^{-1}}$	[35]
Specific heat capacity for H_2Ov	c_{pH_2Ov}	32.130	$\mathrm{J\,kmol^{-1}\,K^{-1}}$	[35]
Specific heat capacity for NH_3	c_{pNH_3}	36.501	$\mathrm{J\,kmol^{-1}\,K^{-1}}$	[35]
Specific heat capacity for H_2O in substrate	c_{pw}	4200	$\mathrm{J\,kmol^{-1}\,K^{-1}}$	[35]
Specific heat capacity for organic matter	c_{pHOT}	1320	$\mathrm{J\,kmol^{-1}\,K^{-1}}$	Eq. (32), [38]
Specific heat capacity for inorganic matter	c_{pNT}	848	$\mathrm{J\,kmol^{-1}\,K^{-1}}$	Eq. (32), [38]
Mass transfer coefficient for O_2	$k_La_{O_2}$	10^{-4}	$\mathrm{kg\,h^{-1}\,Pa^{-1}}$	According to [30]
Mass transfer coefficient for CO_2	$k_La_{CO_2}$	10^{-4}	$\mathrm{kg\,h^{-1}\,Pa^{-1}}$	According to [30]
Mass transfer coefficient for H_2O	$k_La_{H_2O}$	10^{-4}	$\mathrm{kg\,h^{-1}\,Pa^{-1}}$	According to [30]
Mass transfer coefficient for ammonia	$k_La_{NH_3}$	10^{-4}	$\mathrm{kg\,h^{-1}\,Pa^{-1}}$	According [30]
Convective heat transfer coefficient	h_c	100000	$\mathrm{J\,h^{-1}\,K^{-1}}$	Assumed
Reaction enthalpy	Δh	1.54×10^7	$\mathrm{J\,kg_{OM}^{-1}}$	[39]
Overall heat transfer coefficient multiplied by area of heat exchange	UA	1900	$\mathrm{J\,h^{-1}\,K^{-1}}$	Eq. (34), Bach et al. [31]
Oxygen saturation constant	K_{O_2}	0.07	$\mathrm{kg\,O_2\,m^{-3}}$	[15]
Stoichiometric coefficient for O_2 oxygen	Y_{O_2}	0.705	$\mathrm{kg_{O_2}\,kg_{OM}^{-1}}$	Using the formula $C_8H_{19}O_5N$ [10]
Stoichiometric coefficient for CO_2	Y_{CO_2}	1.276	$\mathrm{kg_{CO_2}\,kg_{OM}^{-1}}$	Using the formula $C_8H_{19}O_5N$ [10]
Stoichiometric coefficient for H_2O	Y_{H_2O}	0.360	$\mathrm{kg_{H_2O}\,kg_{OM}^{-1}}$	Using the formula $C_8H_{19}O_5N$ [10]
Stoichiometric coefficient for NH_3	Y_{NH_3}	0.069	$\mathrm{kg_{NH_3}\,kg_{OM}^{-1}}$	Using the formula $C_8H_{19}O_5N$ [10]

Table 2 shows the constants for application of the proposed model while the operational conditions were given in the experimental procedure.

2.9. Numerical methods

Direct nonlinear regression analysis based on the Rosenbrock optimization method [40] was performed to determine a, b, c (Eq. (4)) and n (Eq. (1)) in process kinetics. The model (Table 1) was fitted taking into account the following experimental data from experiment 1: temperature, generated carbon dioxide and ammonia, conversion of organic matter, consumed oxygen. All 12 differential equations of mass and heat balance are mutually connected and nonlinear and therefore, they have to be solved simultaneously not separately. As criterion of agreement between values obtained by model and experimental data, the following target function F was taken as:

$$F = \sum_{j=1}^{m}\sum_{i=1}^{n} W_j \| Y_{ij,\mathrm{model}} - Y_{ij,\mathrm{eksp}} \|^2 \tag{39}$$

where W_j is the weighting coefficient, $Y_{ij,\mathrm{model}}$ is the value of dynamic state variable obtained by model, and $Y_{ij,\mathrm{eksp}}$ is the value of dynamic state variable obtained by experiment (i is the ordinal number of time step, j is the ordinal number of dynamic state variable included in optimization procedure).

The relative importance of variables was expressed using the corresponding weighting coefficients:

$$W_j = \frac{1}{\sum_{i=1}^{n} \| Y_{ij,\mathrm{eksp}} - \overline{Y}_{j\,\mathrm{eksp}} \|^2} \tag{40}$$

where $\overline{Y}_{j,\mathrm{eksp}}$ is mean value of dynamic state variable obtained by experiment.

After determining the optimal values of the kinetic parameters, the set of 12 differential equations describing the system was numerically solved using Runge–Kutta–Fehlberg method, with approximation of fourth and fifth order and adjustment of step size [41]. Both algorithms, for parameter estimation and simulation, were implemented in FORTRAN programming language. The stability and convergence of algorithms were checked by comparison of solutions obtained with different time steps. Simulations were performed on Pentium III and IV computers. FORTRAN program created two output files containing the results of numerical simulations in the form suitable for graphical presentation.

2.10. Experimental materials

Poultry manure and wheat straw were used as materials for testing the model. The main characteristics of raw materials are shown in Table 3. Poultry manure is a significant source of nitrogen, but small amount of carbon in the form of straw needs to be

Table 3
Characterization of poultry manure and straw before mixing (three measurements, mean value ± standard deviation)

Material for composting	Dry matter (%ww)	Organic matter (%dw)	pH	EC ($\mathrm{dS\,m^{-1}}$)
Manure	27.41 ± 0.97	78.07 ± 1.83	8.17 ± 0.06	3.34 ± 0.10
Straw	89.13 ± 0.95	87.91 ± 1.11	7.18 ± 0.05	1.91 ± 0.03

ww, wet weight; dw, dry weight.

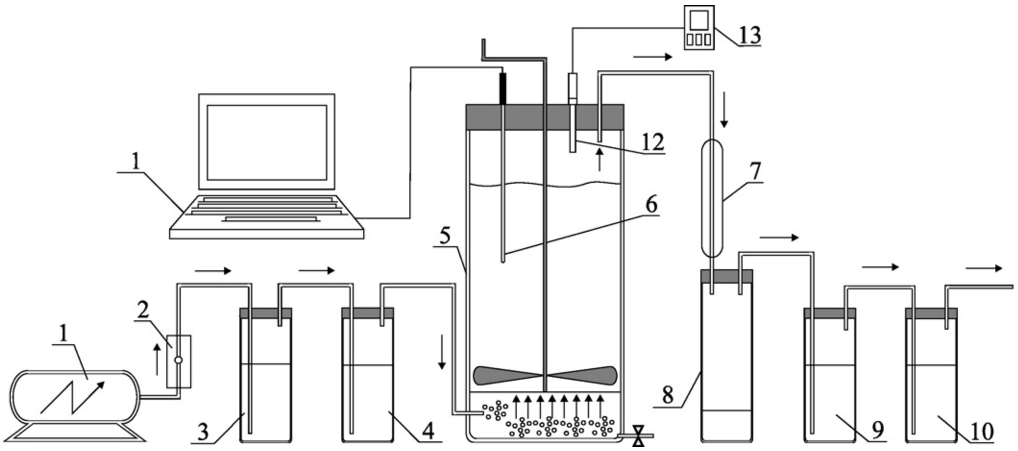

Fig. 2. Schematic diagram of the reactor system. (1) Air compressor, (2) airflow meter, (3) gas washing bottle with solution of sodium hydroxide, (4) gas washing bottle with distilled water, (5) reactor, (6) thermocouples, (7) condenser, (8) graduated cylinder, (9) gas washing bottle with solution of sodium hydroxide, (10) gas washing bottle with solution of boric acid, (11) laptop, (12) sensor for carbon dioxide, (13) datalogging carbon dioxide meter.

added for faster degradation of organic matter in aerobic composting process. Before mixing with manure, the straw was cut on pieces 2.5 cm long. Poultry and straw were manually mixed in plastic boxes for 30 min, by hands, in order to achieve better homogenization of material.

2.11. Composting apparatus

Fig. 2 shows the schematic diagram of the reactor system.

Laboratory 32-L cylindrical reactor (0.48 height × 0.30 internal diameter m) made of high-density polyethylene was used for composting experiments. The reactor was insulated with a layer of polyurethane foam (1 cm of thickness). A vertical rotating axis with blades mixing on intermittent schedule, fixed at perforated plate made of chrome, ensures the complete mixing of the composting mass. The reactor is equipped with a valve for dropping the leachate and condensate.

An air compressor EURO 8/24 (Einhell, Germany) was used for constant aeration ($0.9\,\mathrm{L\,min^{-1}\,kg^{-1}}$ OM) of the reactor. Measurement of airflow was carried out using airflow meter (Valved Acrylic Flowmeter, Cole-Parmer, USA).

Before inlet to the reactor, the air had been introduced into solution of sodium hydroxide in order to remove traces of carbon dioxide. Then, air passed through the gas washing bottle with distilled water in order to maintain the humidity at reactor inlet.

At outlet, the gas mixture passed through a condenser, a gas washing bottle with 1 M sodium hydroxide and a gas washing bottle with 0.65 M boric acid, in order to remove the condensate, carbon dioxide and ammonia, respectively.

2.12. Experimental design and analysis

Two 14-day experiments with two different mixture ratios (73% and 84% poultry manure on dry weight, respectively) were performed (Table 4), in order to obtain the parameter values and to validate the model. For the first and second experiment, the reactor was filled with 6.5 kg and 12.5 kg of the compost mass, respectively.

Temperature was measured at the intervals of 15 min through thermocouples type T (Digi-Sense, Cole-Parmer, USA), placed in the middle of the substrate. This is their optimal location considering the maximum dry matter loss corresponding to energy use per initial mass of the compost dry matter [42]. Thermocouples were connected through the acquisition module Temperature Data Acquisition Card Thermocouple CardAcq (Nomadics, USA) on a laptop. Automatic registration of data for temperature was performed over the whole period of the experiment, using special software (Nomadics, USA). The temperature in the laboratory was also measured.

The oxygen in the exit gas mixture was measured by an Orsat O_2 analyzer (W. Feddeler, Germany) in the reactor. Determination of oxygen was performed daily. The exception was the first day when four values (0 h, 4.5 h, 10.5 h, 24 h) were recorded in order to obtain as precise profile of oxygen as possible.

A sensor for carbon dioxide, connected to datalogging meter GM70 (Vaisala Oyj, Finland), was set above the composting material in the reactor. During the process, the measurements of carbon dioxide concentrations were performed at intervals of 15 min.

Table 4
Characterization of poultry manure and straw after mixing (three measurements, mean value ± standard deviation)

Experiment	Dry matter (%ww)	Organic matter (%dw)	pH	EC ($\mathrm{dS\,m^{-1}}$)
1	40.78 ± 1.67	77.66 ± 2.25	7.95 ± 0.08	2.84 ± 0.10
2	30.89 ± 0.43	80.22 ± 0.66	7.40 ± 0.04	3.10 ± 0.02

ww, wet weight; dw, dry weight.

For determination of ammonia content, an aliquot volume of boric acid solution (used as a "trap"), with the indicator of bromcresol green-methyl, was titrated by standard solution of 1 M hydrochloric acid. The difference in titration between sampled and blank probes was used for calculation of mass of the "trapped" ammonia.

Moisture content in the substrate was calculated from the difference between the masses before and after drying of samples in a dry oven at 105 °C for 24 h [43]. After cooling in a desiccator (30 min), the samples were incinerated at 550 °C for 6 h, and then cooled again in a desiccator. The difference in the masses between dried and incinerated samples represents the mass of organic matter [43].

The loss of organic matter is calculated from the initial and final organic matter contents, according to the Eq. (38) [9,44]:

$$k = \frac{\lfloor \mathrm{OM_m}\,(\%) - \mathrm{OM_p}\,(\%) \rfloor\, 100}{\mathrm{OM_m}\,(\%)[100 - \mathrm{OM_p}\,(\%)]} \tag{41}$$

where $\mathrm{OM_m}$ is the organic matter content at the beginning of the process; and $\mathrm{OM_p}$ is the organic matter content at the end of the process.

pH and electrical conductivity were measured by using a PC 510 Bench pH/Conductivity meter (Oakton, Singapore) in aqueous extract, which was obtained by shaking the samples mechanically for 30 min with distilled water at a compost to water ratio of 1:10. Suspension (10 g of sample and 100 mL of distilled water) was filtrated through the filter paper Whatman 42 Ashless Circles 125 mm Dia (Whatman, Great Britain) for 3 h.

The composting material was mixed several times per day (for 15 min each time). After mixing, samples (about 50 g) were taken every day at the same time, from different places in the substrate (top, middle, bottom). The analysis of the fresh samples was performed immediately after taking them out of the reactor. The additional water was not added to composting material during the process.

Each analysis was done in triplicate with calculation of the mean value.

3. Results and discussion

3.1. Model evaluation

In the review of mathematical modelling of the composting process, Mason [3] concluded that models incorporating either empirical kinetic expressions or first-order kinetics (with empirical corrections for temperature and moisture) were generally more successful in predicting the evolution of dynamic state variables (temperature, solids, moisture, oxygen and carbon dioxide concentration) than models incorporating Monod-type kinetic expressions. The Monod approach may be difficult to adopt on a broader basis for mixed and variable microbial composting populations, due to difficulties in parameter estimation. In most of the cases [2,11,15,21,23,29], Monod-type models are not calibrated and they usually use the values of kinetic parameters from available literature. Furthermore, Monod-type models require an estimate of initial microbial mass [14,15,21]. On the other hand, the applicability of first-order kinetics to simulate substrate degradation also has some limitations. For instance, in the case of chicken manure the data of Keener et al. [45] show that this model is applicable over a short time period (approximately 3 days), after such a period the rate constant had to be updated, to reflect the changes in waste composition. In the case of yard waste the model is applicable over a much longer period once the peak activity has been reached [46]. Mathematical models [24,25] use calculated values of reaction orders that are not common for composting process (2.236 and 1.9). However, relatively good agreement between model and experimental data was achieved with these reaction orders for a whole period of the composting process. Findings from these works [24,25] showed that models with reaction order greater than 1 give better simulation results for composting process. It should be emphasized that preliminary simulations with first-order model applied on experimental data in this work showed great differences, especially during the mesophilic phase and while reaching the thermophilic phase. It was obvious that the exponential decrease of organic matter described by the first-order model should be replaced by different mathematical description, which would take into account fast degradation of organic matter, great evolution of carbon dioxide and consumption of oxygen in the first 24 h. Therefore, one of the motives for this work was to propose a reaction order greater than 1 for the mathematical model which is not too much complex to solve (as Monod-type models), which enables the calculation of kinetic parameters with a corresponding optimization method, and finally which is applicable over a whole period of composting process. Calculated values of kinetic parameters in the proposed model based on the Rosenbrock optimization procedure are presented in Table 5.

Table 5
Results of estimated parameters

Parameter	Value	Unit
a	0.0000883	$\mathrm{kg}^{1-n}\,\mathrm{h}^{-1}$
b	1.0533	–
c	1.2247	–
n	2.8944	–

Mean square deviation, S.D. = 0.0441

Using the second set of experimental data (experiment 2), comparisons of experimental and simulation results for temperature of substrate, organic matter conversion, carbon dioxide concentration and oxygen concentration (Figs. 3–6), in general showed a good agreement during the whole duration of composting process in the reactor.

In order to compare model's predictive capacity to that of others, reference [3] was used. For comparisons, two composting models were chosen, the first one [14] as a representative of Monod-type models and the second one [18] as a representative of first-order models. In both models researchers used column type of reactor with the similar duration of study, and this has been done in this work as well. Comparisons of this model's predictive capacity with other two models are shown in Table 6. Maximum difference between modelled and experi-

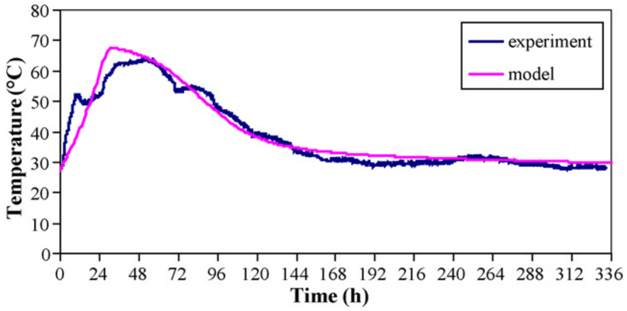

Fig. 3. Comparison of experimental data and model predictions for temperature. (The experimental data are from the experiment 2. The following parameter settings were used for the simulation: airflow 0.18 m^3 h^{-1}, moisture 69.11%, organic matter 80.22% dw.)

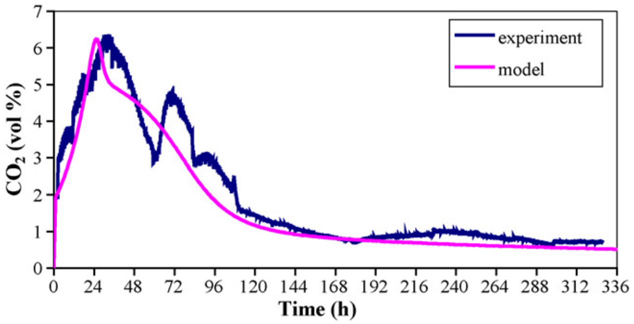

Fig. 5. Comparison of experimental data and model predictions for carbon dioxide concentration. (The experimental data are from the experiment 2. The following parameter settings were used for the simulation: airflow 0.18 m^3 h^{-1}, moisture 69.11%, organic matter 80.22% dw.)

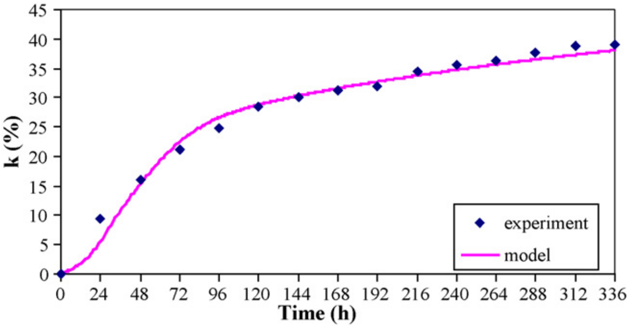

Fig. 4. Comparison of experimental data and model predictions for organic matter conversion. (The experimental data are from the experiment 2. The following parameter settings were used for the simulation: airflow 0.18 m^3 h^{-1}, moisture 69.11%, organic matter 80.22% dw.)

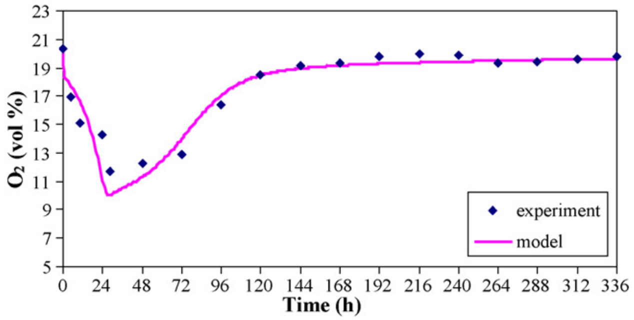

Fig. 6. Comparison of experimental data and model predictions for oxygen concentration. (The experimental data are from the experiment 2. The following parameter settings were used for the simulation: airflow 0.18 m^3 h^{-1}, moisture 69.11%, organic matter 80.22% dw.)

mental temperature–time profiles in this work is slightly greater than in the reference [14] but smaller than in the reference [18]. It should be pointed out that this difference occurred during the initial period of rapid temperature rise (Fig. 3), because of standstill in transition between mesophilic and thermophilic phase. This standstill can be explained by the process inhibition when pH value is combined with temperature above mesophilic optimum [47–51]. These references concern a composting of acidic waste with a low initial pH, with minimum pH bellow 6 during the mesophilic phase. However, in this work the initial pH of the mixture in experiment 2 was 7.40, which was well above neutral. During the initial 24 h, two values of pH were measured, 6.91 on the 0.5th day and 7.29 on the 1st day. A decrease in pH was probably caused by increased production of organic acids or increased nitrification. After the initial 24 h, pH values increased to maximum value 8.86 on the 8th day, then decreased to 8.58 on the 10th day, and again increased to 8.85 on the 14th day. Thus, there are strong connections between decrease of pH and changes in temperature during the initial phase related to the transition from mesophilic to thermophilic phase. This observation was confirmed by results of previous studies with similar and even higher initial pH values, from 7.44 to 8.20 [52,53]. Mesophilic microorganisms were inactivated by high temperature, while thermophilic microorganisms were

Table 6
Temperature, oxygen, carbon dioxide and solids vs. time validation performance of composting models

References	Temperature difference between model and data (°C)			Time to peak (d)		A_{40}[a] ratio	O_2 or CO_2 concentration difference between model and data (%)		Solids difference between model and data	
	Max.	Mean	Peak	Model	Data		Max.	Mean	Max.	Mean
[14]	13.3	4.1	3.3	3.9	1.7	0.83	8.86[b]	1.77[b]	–	–
[18]	16.5	4.2	0.5	9.4	8.9	1.66	11.00[c]	2.00[c]	0.14 kg[d]	0.05 kg[d]
This model	14.3	2.3	3.4	2.1	1.4	0.93	1.40[b]	0.38[b]	3.84%[e]	1.01%[e]
							3.26[c]	0.57[c]		

[a] A_{40} is the area bounded by the curve and a baseline of 40 °C; ratio is A_{40} (model)/A_{40} (data) [3].

[b] CO_2.

[c] O_2.

[d] Dry matter.

[e] Organic matter conversion.

stopped by lower pH value and organic acids. As pH increased, thermophilic microorganisms were no longer inhibited. Therefore, microbiological activity and substrate temperature also increased. The mean difference between experimental and simulation temperature showed that this model adequately predicts the composting process during the whole period. Peak temperature in this model is predicted as in the model [14], but the time to reach peak temperature is shorter. The shortest time to reach peak temperature was achieved in the model [18]. Predicted and experimental A_{40} values in this model are in closer agreement than in other two models. In terms of shape characteristics, this model simulates the typical profile very closely (except for the initial phase, 0–24 h).

Over the whole period of composting process, this model showed a very good fit to selected data of organic matter conversion (Fig. 4). Some discrepancies were noticed, but they were not very significant.

Predicted percentages of carbon dioxide (Fig. 5) and oxygen (Fig. 6) in the exhaust gas mixture follow qualitatively experimental results. The deviations found could be explained by opening of the reactor during sampling periods, and they could also be attributed to the variation of the liquid–gas transfer rate as the material is dried. Comparison of validation results for carbon dioxide and oxygen with other two models (Table 6) shows that this modelling approach is very useful.

Comparison of experimental and simulation results for ammonia showed an agreement for the first 4 and the last 3 days of the process (Fig. 7). The volatilization of ammonia started when the process moved from mesophilic to thermophilic phase. The largest emission was noticed during the most intensive period of thermophilic phase. The aerobic and anaerobic processes occur simultaneously [54]. Emission of ammonia started to increase rapidly after the first day when pH was shifted. After microorganisms reached their maximum activity, ammonia emission decreased with time of immobilization of NH_4^+–N.

For better description of the process, the effect of carbon to nitrogen ratio should be included in the model kinetics. Corrective function can be developed on the basis of clearly designed experiments, or an existing expression from literature can be used (e.g. [55]).

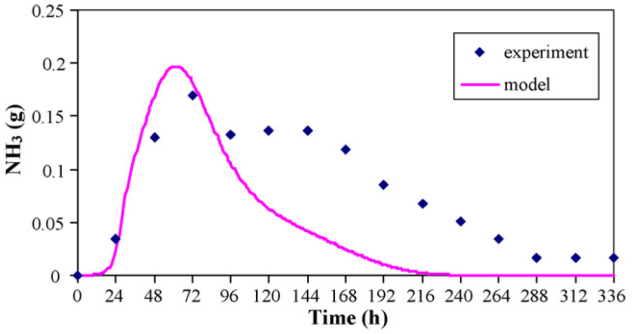

Fig. 7. Comparison of experimental data and model predictions for ammonia mass. (The experimental data are from the experiment 2. The following parameter settings were used for the simulation: airflow 0.18 $m^3\,h^{-1}$, moisture 69.11%, organic matter 80.22% dw.)

Evolved ammonia can stay in the solution in the form of NH_4^+, it can be transformed in nitrites and nitrates by nitrification, it can be used for synthesis of new cells, or it can be released in the gas phase. Therefore, modelling of all possible ways is a very complicated task. For better prediction of ammonia, the following processes should be modelled in the future investigations: immobilization of NH_4^+–N to microbiological mass, intensive mineralization of nitrogen during the thermophilic phase, nitrification of NH_4^+ and precipitation of carbonates with pH above 8.5. A possible solution would be development of pH model based on the reference [28]. Also, for better prediction of temperature in the initial phase it might be helpful to combine the kinetics developed in this work and microbiological sub-kinetics for description of the transition from mesophilic to thermophilic phase. Anyway, a decision has to be made between the extremes of treating the substrate as a single material and the whole of the biomass as a homogeneous culture or splitting the substrate into different components according to ease of degradability and the microbial culture into many different species. The former approach carries the attendant risk of failing to model the process sufficiently accurately, and the latter approach carries the risk of creating a model that is too complex with too many unknowns. Therefore, parameter estimation would be a very challenging task. The modified deductive approach in modelling of composting kinetics was suggested in reference [56], which stated that main parameters in the model should be combined with smaller number of so called combined parameters which have the unique values. Therefore, these parameters are identifiable and have a clear relationship with the basic parameters. The advantage of this approach is that it enables to use information from existing knowledge (as represented by the basic parameters) with the information retained in the data (as represented by the identifiable combined parameters).

Different simulations were performed with the model in order to study the effects of initial moisture content and airflow rates on the substrate temperature and organic matter conversion (Figs. 8–11). Five moisture values (45%, 60%, 69.11%, 70%, 75%) and six airflow rates (0.09 $m^3\,h^{-1}$, 0.10 $m^3\,h^{-1}$, 0.14 $m^3\,h^{-1}$, 0.18 $m^3\,h^{-1}$, 0.22 $m^3\,h^{-1}$, 0.26 $m^3\,h^{-1}$,) were tested.

Simulations showed that initial moisture contents of 45% and 75% were limiting for the microbial activity, especially the first one. Higher values of temperature and organic matter conver-

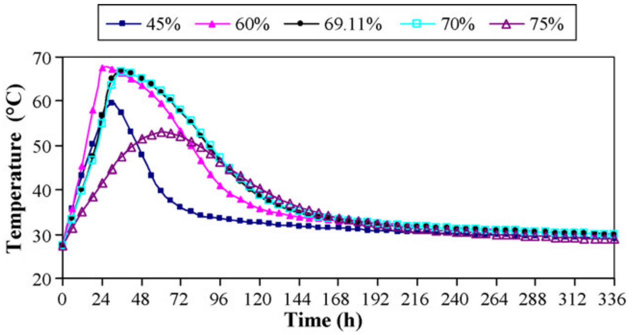

Fig. 8. Profiles of substrate temperature with different initial moisture content.

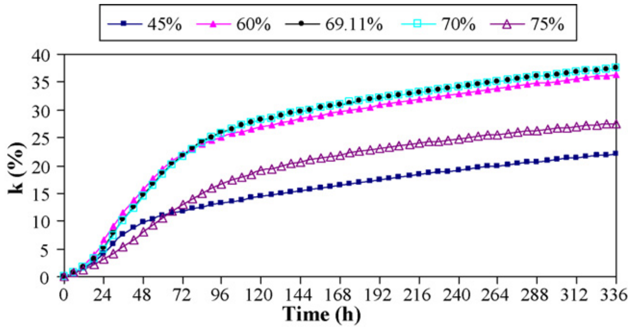

Fig. 9. Profiles of organic matter conversion with different initial moisture content.

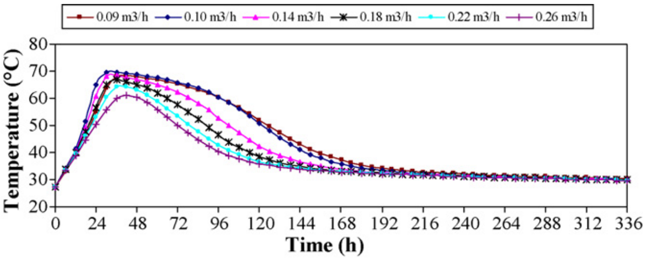

Fig. 10. Profiles of substrate temperature with different airflows rate.

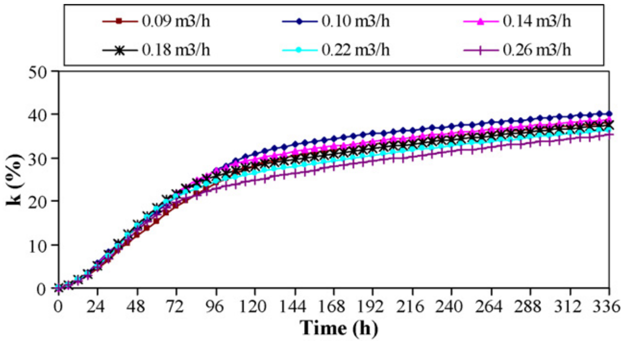

Fig. 11. Profiles of organic matter conversion with different airflows rate.

sion were achieved with the moisture contents 60%, 69.11% and 70%. The calculated optimum value of moisture content was 70%, which means that moisture of composting material was good adjusted (69.11%) in the second experiment. Obtained value corresponds to the literature data for the same and different substrates [57–60]. Simulations (which are not shown in Figs. 8 and 9) showed that composting process was impossible when moisture content was above 78% or below 31%.

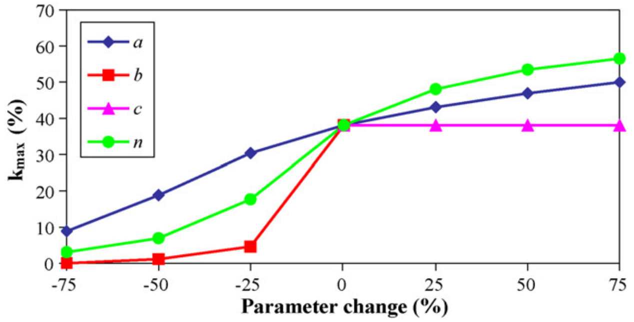

Fig. 12. Sensitivity analysis with the effect of parameter variations on the maximum organic matter conversion.

As it could have been expected, an increase in airflow rate in the composting process led to lower temperature, because of cooling of the substrate, and to slower degradation of substrate. Optimum value of airflow rate was 0.10 $m^3\,h^{-1}$, because the highest value of temperature and organic matter conversion were achieved. At the same time, oxygen concentration in the exit gas mixture from reactor did not fall bellow 5%, which is the boundary for anaerobic conditions [9]. The airflow rate of 0.10 $m^3\,h^{-1}$ expressed per mass of organic matter (3.103 kg) was 0.54 $L\,min^{-1}\,kg_{OM}^{-1}$, which corresponds to literature data for various composting materials [61–63]. In order to achieve the optimum degradation in the reactor, the corresponding temperature of the substrate needs to be maintained. An increase of degradation rate simultaneously demands an increase of airflow rate that may cool the reactor. It is not still clear where the optimum in this compromised situation is [64].

3.2. Sensitivity analysis

A sensitivity analysis was performed to evaluate the relative importance of selected model parameters (a, b, c and n). The parameters were run in the simulation program and all other parameters were set at their default values. Then each parameter was decreased by 25%, 50% and 75% of its default value and then increased by 25%, 50% and 75% of its default value over a 14-day simulation period. As one parameter was varied, all other parameters were maintained at their default values. All parameter values used are shown in Table 7. The output values examined were the maximum organic matter conversion, the maximum carbon dioxide concentration and the maximum substrate temperature during the 14-day simulation. Results from this analysis are shown graphically in Figs. 12–14.

Table 7
Parameter values used in sensitivity analysis

Parameter	Unit	Percentage change in parameter analysis (%)						
		−75	−50	−25	Default	+25	+50	+75
a	$kg^{1-n}\,h^{-1}$	0.0000221	0.0000442	0.0000662	0.0000883	0.0001104	0.0001325	0.0001545
b	–	0.2633	0.5267	0.7900	1.0533	1.3166	1.5800	1.8433
c	–	0.3062	0.6124	0.9185	1.2247	1.5309	1.8371	2.1432
n	–	0.7236	1.4472	2.1708	2.8944	3.6180	4.3416	5.0652

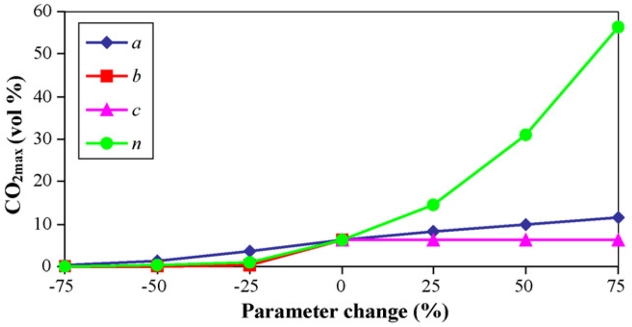

Fig. 13. Sensitivity analysis with the effect of parameter variations on the maximum carbon dioxide concentration.

The most sensitive objective function was the maximum carbon dioxide concentration, while the maximum substrate temperature showed the smallest sensitivity. The sensitivity analysis showed that parameter *b* exhibited the most pronounced effect due to its strongest influence on all three sensitivity functions. Parameter *n* had less significant effect on the objective functions than parameter *b*. Parameter *c* had the smallest effect on all three objective functions. Parameter *a* showed relatively small effect with positive variations, while its value was more pronounced for negative variations. These results are similar to those found by [25], where the authors found that two of four parameters had a very significant effect, while the other two parameters had less significant effect on the objective functions. It should be noted from Figs. 12–14 that changes of objective functions with parameter *b* are only shown for negative values, and parameter *c* only for positive values on the *x*-axis. The explanation lies in the fact that the calculated values of objective functions with variations of parameters (*b* for variations +25%, +50% and +75%; *c* for variations −75%, −50% and −25%) were non-real and without a physical sense for composting process, so the calculated procedure was stopped. Therefore, an additional sensitivity analysis was performed in order to calculate differences between mean square deviations with small variations of all parameters by −3% and +3% of their default values, and optimal mean square deviation (Table 8). This analysis confirmed that parameter *b* has the greatest influence on the model and is followed by parameter *n*. Parameters *a* and *c* have a very small influence on the model. The results from presented sensitivity analysis are the basis for the future modification of the kinetic model and new experimental design.

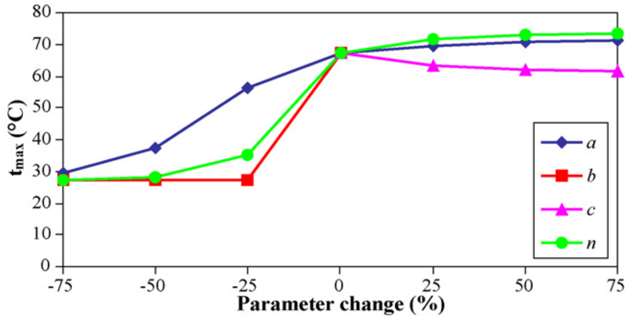

Fig. 14. Sensitivity analysis with the effect of parameter variations on the maximum substrate temperature.

Table 8
Comparison of mean square deviation (with parameter variations) and optimal mean square deviation

Parameter	$S.D._{\cdot p}$	$S.D._{\cdot p} - S.D._{\cdot opt}$
$a-3\%$	0.0516	0.0075
$a+3\%$	0.0514	0.0073
$b-3\%$	1.4229	1.3788
$b+3\%$	2.2012	2.1571
$c-3\%$	0.0517	0.0076
$c+3\%$	0.0446	0.0005
$n-3\%$	0.1085	0.0644
$n+3\%$	0.1002	0.0561

Optimal mean square deviation, S.D. = 0.0441.

4. Conclusions

By integrating the reaction kinetics with the mass and heat transfer between the three phases of the system, a new dynamic structured model for aerobic composting process was developed in this work. The model was described by a differential equation set with 12 dynamic state variables—10 describing mass balances and 2 describing heat balances. In order to evaluate kinetic parameters in mathematical model and to validate the model, experiments were performed with the reactor of volume 32 L, in controlled laboratory conditions. Different ratios of poultry manure to wheat straw were mixed and used as a substrate.

Comparisons of experimental and simulation results for temperature of substrate, organic matter conversion, carbon dioxide concentration and oxygen concentration, showed good agreement during the whole duration of the process in reactor. In the case of ammonia, an agreement was achieved only for the first 4 days and for the last 3 days of the process.

With validated model for aerobic composting of poultry manure and wheat straw mixture, optimal values were determined: initial moisture content (70%) and airflow ($0.54\,\mathrm{L\,min^{-1}\,kg_{OM}^{-1}}$).

A sensitivity analysis was performed to determine the key parameters of the model. Analysis showed that two parameters had a great influence on the main characteristics of the process.

The developed model can adequately simulate the aerobic composting process. There is a need for additional experiments with different kinds of organic waste in order to achieve a rigorous validation of the model. Future work is also directed to improvement of the structure of the model (especially for describing the ammonia dynamics and temperature evolution in the initial phase) in order to obtain a more sophisticated tool for full optimization of the composting process.

Acknowledgements

This research was financially supported by the Federal Ministry of Education and Science of Bosnia and Herzegovina (Contract No.: 04-39-4358/03).

The authors thank Pejo Pejić, Almir Šestan and Indira Alibašić for their excellent technical assistance throughout the project.

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