DOI 10.7251/JEPM1709036K
UDC 631.879:66.011

Journal of
Engineering & Processing
Management

ORIGINAL SCIENTIFIC PAPER

Composting kinetics for mixture of poultry manure and wheat straw based on volatile solids content

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Keywords:
Composting kinetics, poultry manure, wheat straw, volatile solids content.

Abstract
The aim of this study was to determine the composting kinetics for mixture of poultry manure and wheat straw based on the volatile solids content. Experimental data was fitted with the first-order and the nth-order kinetic model. The nth-order kinetic model showed better prediction performance than the first-order kinetic model. For the first-order kinetic model, maximum and mean differences between experimental and simulation results for the content of volatile solids were 5.43% and 3.00%, for the first reactor, and 4.68% and 2.12% for the second reactor, respectively, for the nth-order kinetic model, maximum and mean differences were 4.92% and 1.68%, for the first reactor, and 4.09% and 1.42% for the second reactor, respectively.

1. INTRODUCTION

Composting has gained an important role in municipal solid waste management. The main factors in the control of a composting process include environmental parameters (temperature, moisture content, pH and aeration) and substrate nature parameters (C/N ratio, particle size, and nutrient content) [1]. One of the byproduct of livestock industry is a biodegradable waste. This byproduct must be removed with a suitable method to avoid negative impacts on the environment (odor, emissions, pollution of land and water, etc., [2]).

Numerous mathematical models [3, 4, 5, 6, 7] have been developed where emphasis has been made on the thermodynamic and kinetic changes taking place during the composting process and the effect of temperature and moisture (or other factors) on the rate of microbial activity. Kinetic modeling is a useful tool to investigate the composting process for its optimization at the industrial scale. The waste degradation rate might be estimated by using the kinetic patterns of process displays such as heat, organic matter content, moisture content, O2/CO2 concentration, pH, C/N ratio, and particle size [8]. Composting of organic substrates has been studied by numerous researchers in different types of reactors and the self-heating reactor has been widely employed for modeling the heat transfer phenomenon of this process [9]. The self-heating reactor is a reactor relying solely on microbial heat production to reach and maintain process temperatures and having no temperature control besides some external insulation within the apparatus [10].

Production of poultry manure and wheat straw are two important agricultural branches in Bosnia and Herzegovina, which produces large amounts of manure and straw. Co-composting is very good method from an engineering point of view, because poultry manure has high moisture content and a small carbon/nitrogen ratio, while wheat straw has the opposite characteristics. Mixing the poultry manure and wheat straw provides improved moisture control and more balanced nutrients for the microorganisms during the composting process.

The main aim of this study is to determine the composting kinetics for mixture of poultry manure and wheat straw based on the volatile solids content.

2. MATERIAL AND METHODS

2.1. Kinetic model

The composting reaction rate is described by the *VS* (volatile solids) degradation rate through the first-order kinetic model:

$$VS_{\mathrm{c,model}} = \left[BVS_0\right]\cdot\left(1-e^{-k\cdot F(T)\cdot F(MC)\cdot F(O_2)\cdot F(FAS)\cdot t}\right) \quad (1)$$

where: $VS_{\mathrm{c,model}}$ – the amount of VS consumed at time t (%), BVS_0 – initial content of biodegradable volatile solids (%), k – first-order reaction rate constant (day^{-1}). $F(T)$, $F(MC)$, $F(O_2)$ and $F(FAS)$ are corrections factors for temperature, moisture content, oxygen concentration and free air space, respectively.

The correction factor for temperature is described by the equation [10]:

$$F(T)=\frac{\left(T-T_{\max}\right)\cdot\left(T-T_{\min}\right)^2}{\left(T_{opt}-T_{\min}\right)\cdot\left[\left(T_{opt}-T_{\min}\right)\cdot\left(T-T_{opt}\right)-\left(T_{opt}-T_{\max}\right)\left(T_{opt}+T_{\min}-2\cdot T\right)\right]} \quad (2)$$

where: T – temperature (°C), T_{min} – minimum temperature for the biodegradation (°C), T_{max} – maximum temperature for the biodegradation (°C).

The values for the parameters in the equation (2) can be found in the reference [10] and the resulting correction factor for temperature is presented in the equation (3):

$$F(T)=\frac{(T-71.6)\cdot(T-5)^2}{(58.6-5)\cdot[(58.6-5)\cdot(T-58.6)-(58.6-71.6)(58.6+5-2\cdot T)]} \quad (3)$$

The correction factor for oxygen is described by the equation [11]:

$$F(O_2)=\frac{[O_2]}{F_{O_2}(20.95\%)\cdot(0.83+[O_2])} \quad (4)$$

where: O_2 – oxygen concentration (%).

The correction factor for moisture content is described by the equation [5]:

$$F(MC)=\frac{1}{e^{(-17.684(1-[DM]))+7.0622)}+1} \quad (5)$$

where: *DM* – fractional dry matter of the composting material (1-*MC*).

The correction factor for free air space content is described by the equation [5]:

$$F(FAS)=\frac{1}{e^{(-23.675FAS+3.4945)}+1} \quad (6)$$

The free air space was calculated using the following equations [5]:

$$FAS=1-\frac{\delta_m\cdot S_m}{G_s\cdot\delta_w}-\frac{\delta_m\cdot(1-S_m)}{\delta_w} \quad (7)$$

$$G_s=\frac{1}{(V_s/G_v)+((1-V_s)/G_f)} \quad (8)$$

$$\delta_m=\frac{C}{S_m} \quad (9)$$

where: *δm* and *δw* – densities of composting material and water (kg/m^3); *Gs*, *Gv* and *Gf* – specific gravities of solids, volatile fraction of the solids (= 1) and fixed fraction of the solids (= 2.5), *VS* – volatile fraction of the solids (-); *C* – bulk weight coefficient for the substrate (0.25).

The following equation was proposed as the *nth*-order kinetic model:

$$-\frac{dVS}{dt}=k'\cdot VS^n \quad (10)$$

where: *n* – reaction order (-), *k'* is defined as the product of *k* (corrected first-order reaction rate constant) multiplied by given environmental correction factors [5]:

$$k'=k\cdot F(T)\cdot F(MC)\cdot F(O_2)\cdot F(FAS)=K\cdot F(TOT) \quad (11)$$

Combining the equation (10) with the equation (11) the following equation was obtained:

$$-\frac{dVS}{dt}=k\cdot F(T)\cdot F(MC)\cdot F(O_2)\cdot F(FAS)\cdot VS^n \quad (12)$$

From the equation (12) the following equation is obtained:

$$VS=\left(\frac{-\frac{dVS}{dt}}{k\cdot F(T)\cdot F(MC)\cdot F(O_2)\cdot F(FAS)}\right)^{\left(\frac{1}{n}\right)} \quad (13)$$

Normalized root mean square error *NRSME* (%) is calculated as [10]:

$$NRSME=\frac{RMSE}{BVS_0}\cdot 100\% \quad (14)$$

where: *RSME* – root mean square error (-), BVS_0 – initial biodegradable volatile solids content (-).

The *VS* (volatile solids) content data was used to calculate the profiles of *VS* consumption against time for each reactor, using the following equation [5]:

$$VS_{c,\exp}=\frac{VS_i-VS_t}{(100-VS_t)\cdot VS_i}\cdot 10^4 \quad (15)$$

where $VS_{c,exp}$ – *VS* consumed in the process time *t* (%), VS_i – initial concentration of *VS* (%), VS_t – concentration of *VS* at process time *t* (%).

2.2 Applied numerical method and software

Nonlinear regression method (Levenberg-Marquardt algorithm) was used for a numerical solution of system of nonlinear algebraic equations. For determining the values of reaction rate constants and for prediction of volatile solid contents, the numerical software package Polymath 6.0 [11] was used.

2.3 Experimental materials

Poultry manure and wheat straw were used as experimental material. Characteristic of poultry manure and wheat straw before and after mixing are given in Table 1 and Table 2, respectively. Poultry manure and wheat straw were mixed in two different ratios (Table 3). The straw was cut into 2.5 cm long pieces. Poultry and straw were mixed manually for 30 min, in order to achieve better homogenization of material.

Table 1. Characteristics of poultry manure and wheat straw before mixing (three measurements, mean ± standard deviation)

Reactor	Composting material	Moisture (% w.b.)	Volatile solids (% d.b.)	pH (-)	EC (dS m^{-1})
1	Manure	65.31±1.97	71.37±1.35	8.27±0.09	3.94±0.05
	Straw	10.42±0.83	87.38±1.78	7.87±0.03	1.94±0.04
2	Manure	74.93±1.27	73.20±1.92	8.49±0.06	4.17±0.24
	Straw	12.55±0.21	90.38±0.74	7.13±0.03	1.24±0.09

w.b. – wet basis; d.b. – dry basis

Table 2. Characteristics of poultry manure and wheat straw after mixing (three measurements, mean ± standard deviation)

Reactor	Moisture (% w.b.)	Volatile solids (% d.b.)	pH (-)	EC (dS m^{-1})
1	59.22±1.67	77.66±2.25	7.95±0.08	2.84±0.20
2	67.17±0.64	73.75±0.20	78.17±0.08	3.55±0.13

w.b. – wet basis; d.b. – dry basis

Table 3. Percentages of poultry manure and wheat straw, masses of mixtures and air flow rates for reactors

Reactor	Manure (% d.b.)	Straw (% d.b.)	Mass of mixture (kg)	Air flow rate (l min^{-1})
1	73.45	26.55	6.509	1.80
2	78.00	22.00	9.924	2.00

d.b. – dry basis

2.4. Experimental reactors

Two specially designed reactors with volume of 32 L (0.48 height x 0.30 internal diameter m), made of high density polyethylene, were used for experiments. The reactors were insulated with a layer of polyurethane foam (1 cm of thickness). Schematic representation of the reactor system is given in Figure 1 (1. air compressor, 2. air flow metre, 3. gas washing bottle with solution of sodium hydroxide, 4. gas washing bottle with distilled water, 5. reactor, 6. thermocouple, 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 metre).

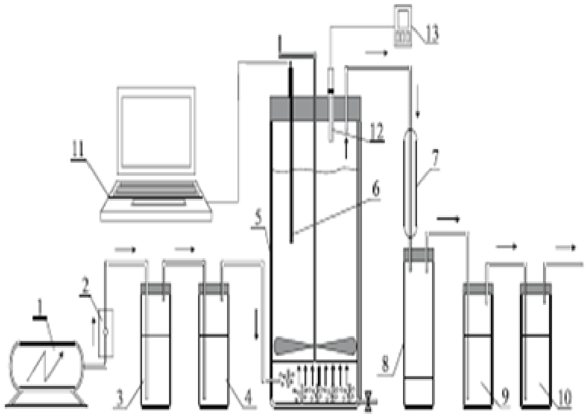

Figure 1. Schematic diagram of the large reactor with experimental apparatus

Before inlet to reactors, 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.

2.5. Measurements and analysis

The air compressor was used for constant aeration (0.6 L min-1 kg-1 OM). The measurement of airflow was carried out using air flow meter (Valved Acrylic Flowmeter, Cole-Parmer, USA). In the reactors, the temperature was measured in the intervals of 15 min through thermocouple type T (Digi-Sense, ColeParmer, USA), placed in the middle of the substrate. Thermocouple was connected through the acquisition module on a laptop. The oxygen in the exit gas mixture was measured by an Orsat O2 analyzer (W. Feddeler, Germany) in each reactor. Moisture content and volatile solids were determined according to APHA [12]. The composting material was mixed several times per day. After mixing, the samples were taken every day at the same time, from different places in the reactor (top, middle, and bottom). Each analysis was done in triplicate with calculation of the mean value. The experiments were performed in duplicate.

3. RESULTS AND DISCUSSION

The time changes of volatile solid content, temperature, moisture content and oxygen concentration in both reactors are shown in Figures 2-5. These data were used for parameter estimation and for prediction of volatile solid contents.

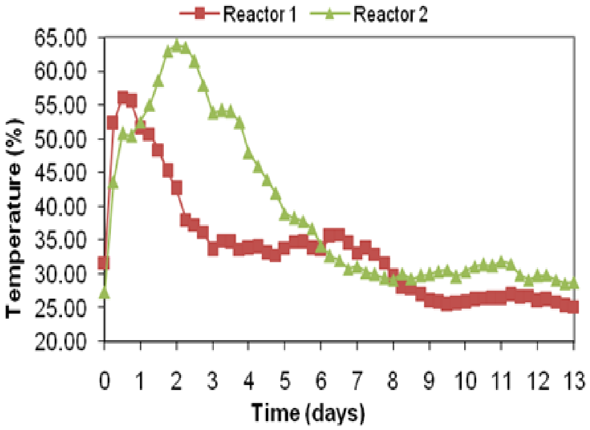

Figure 2. Changes of mixture temperature during the composting process

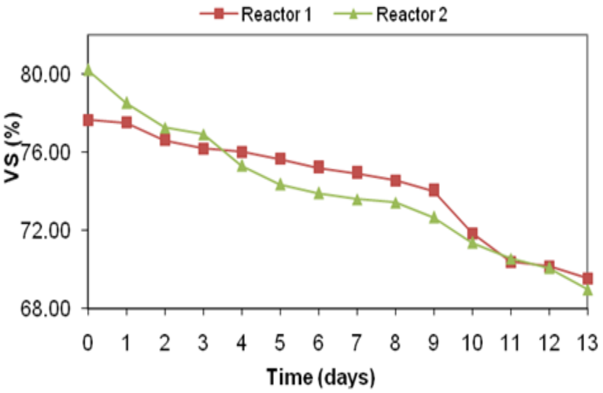

Figure 3. Changes of volatile solids content during the composting process

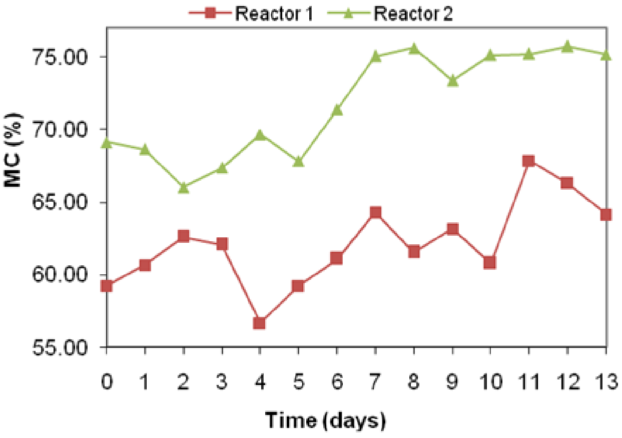

Figure 4. Changes of moisture content during the composting process

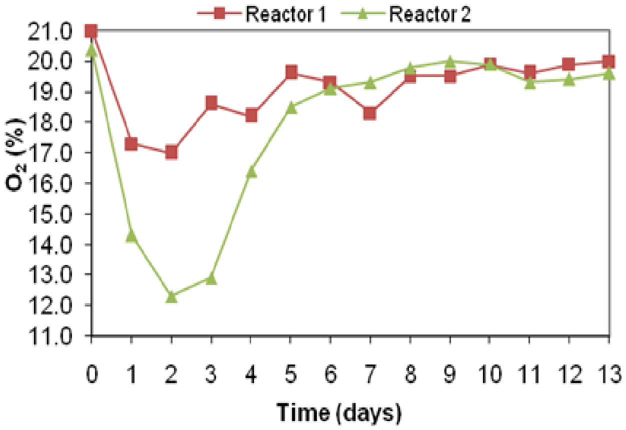

Figure 5. Changes of oxygen concentration during the composting process

A key issue for the development of the kinetic model is the quality of the experimental data. There is a few deficiency with data for volatile solids that appears mostly at sampling, but with increasing the number of samples this deficiency are reduced. Comparison of experimental and simulation results for the first-order kinetic model for both reactors are given in Figures 6 and 7.

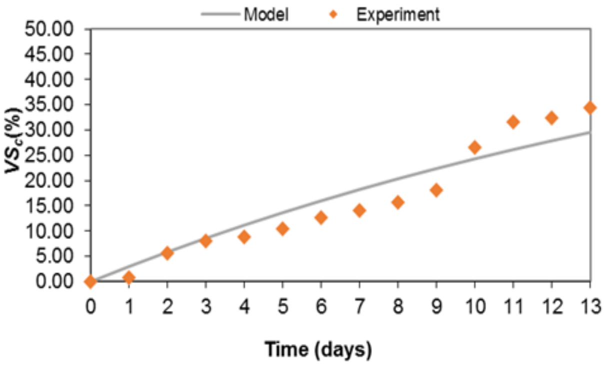

Figure 6. Comparison of experimental and simulation results for the first-order kinetic model for reactor 1

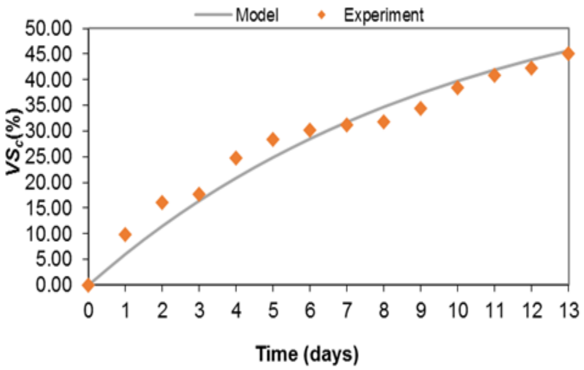

Figure 7. Comparison of experimental and simulation results for the first-order kinetic model for reactor 2

Comparison of experimental and simulation results for the *nth*-order kinetic model for both reactors are given in Figures 8 and 9.

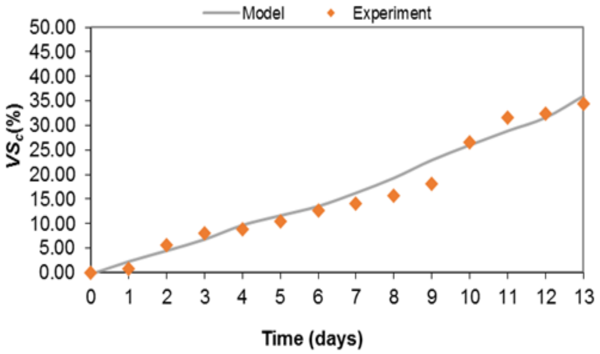

Figure 8. Comparison of experimental and simulation results for the nth-order kinetic model for reactor 1

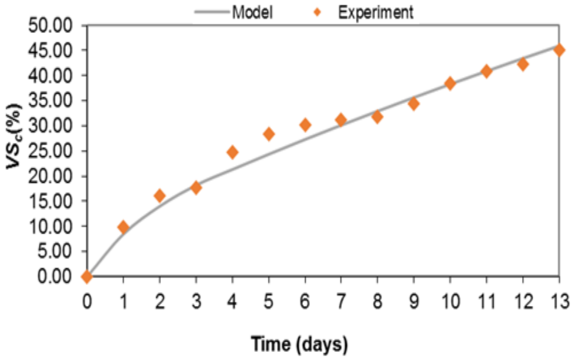

Figure 9. Comparison of experimental and simulation results for the nth-order kinetic model for reactor 2

Comparisons of the experimental and simulation results in general showed very good agreement during the whole duration of the process. In the first stage of the composting process, easily degradable components of the substrate are degraded. After ten days of the process, easily degradable components of the substrate have been degraded, so only hardly degradable components remain in the mixture. This fact can explain the deviations between the model and experimental values of the volatile solids content. Maximum and mean difference between the experimental and simulation results for volatile solids content using the first-order kinetic model and the *nth*-order kinetic model are given in Table 4 and 5, respectively.

Table 4. Differences between the experimental and simulation results for volatile solids content using the first-order kinetic model

Reactor	Differences (%)	
	Maximum	**Mean**
1	5.43	3.00
2	4.68	2.12

Table 5. Differences between the experimental and simulation results for volatile solids content using the nth-order kinetic model

Reactor	Differences (%)	
	Maximum	**Mean**
1	4.92	1.68
2	4.09	1.42

The nth-order kinetic model showed better prediction performance than the first-order kinetic model. For the nth-order kinetic model, the values of *NRSME* were ranged from 0.34 to 0.44%. For the first-order kinetic model, the values of *NRSME* are ranged from 1.15 to 1.49%. This range can be compared with values in the literature. In the reference [13], the values for *NRSME* were 0.9 to 5.73%, while in the reference [14], the values for the *NRSME* were 0.53 to 4.43%. In the reference [15] the values for *NRSME* were 0.6 to 7.6%. As expected, the values of corrected reaction rate constant were larger than uncorrected reaction rate constant. These differences are caused by the difference between the operational environmental conditions and optimal conditions. The greater difference between operational environmental and optimal conditions, the greater difference is between corrected and uncorrected reaction rate constant. In the reference [14], the first-order kinetic model was used and obtain values for the reaction rate constant were in the range 0.03-0.63 day^{-1}. The values of corrected reaction rate constant *k* for the first-order reaction were 0.0509 day^{-1} for the first reactor and 0.1037 day^{-1} for the second reactor. For the first-order kinetic model, the values of corrected reaction rate constants k were 0.0509 day^{-1} for and 0.1037 day^{-1}, while the values of uncorrected reaction rate *k'* constants were 0,0498 day^{-1} and 0.1026 day^{-1}. For the nth-order kinetic model, the values of corrected reaction rate constants *k* were 6.330e-10%$^{-2.89}$ day^{-1} and 6.205e-08%$^{-3.08}$ day^{-1}, while the values of uncorrected reaction rate constants *k'* were 6.023e-10%$^{-2.89}$ day^{-1} and 1.817e-08%$^{-3.08}$ day^{-1}. The values of uncorrected reaction rate constant *k'* for the first-order kinetic model were 0.0498 day^{-1} for the first reactor and 0.1026 day^{-1} for the second reactor. However, the values of corrected reaction rate constant *k* for the nth-order kinetic model were 0.0509 day^{-1} for the first reactor and 0.1037 day^{-1} for the second reactor. The values of uncorrected reaction rate constant *k'* for the first-order kinetic model were 0.0498 day^{-1} for the first reactor and 0.1026 day^{-1} for the second reactor. In the reference [9] the values of uncorrected reaction rate constant were 0.0181 to 0.0749 day^{-1}. In the reference [12] the values of uncorrected reaction rate constant *k* were 0.043±0.002 day^{-1} to 0.082±0.011 dan^{-1}. In the reference [13] the values of uncorrected reaction rate constant *k* were 0.09-0.48 day^{-1}, while in the reference [14] the values of uncorrected reaction rate constant *k* were 0.03 to 0.63 day^{-1} for the first-order kinetic model.

4. CONCLUSIONS

1. Comparisons of experimental and simulation results in general showed good agreement during the whole duration of the process in the reactors.
2. The nth-order kinetic model showed better prediction performance than the first-order kinetic model.
3. For the first-order kinetic model, maximum and mean differences between the experimental and simulation results for the content of volatile solids were 5.43% and 3.00%, for the first reactor, and 4.68% and 2.12% for the second reactor, respectively.

4. For the nth-order kinetic model, maximum and mean differences between the experimental and simulation results for the content of volatile solids were 4.92% and 1.68%, for the first reactor, and 4.09% and 1.42% for the second reactor, respectively.
5. A key issue for the development of the kinetic model is the quality of the experimental data.
6.Future research will be focused on the process optimization.

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