

# COMPARISON OF FIRST-ORDER AND NTH-ORDER KINETIC MODELS FOR COMPOSTING PROCESS OF MUNICIPAL SOLID WASTE

ORIGINAL SCIENTIFIC ARTICLE

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## ABSTRACT:

The aim of this study was to propose six first-order kinetic models and then compare with nth-order kinetic model for composting process of municipal solid waste. Kinetic parameters for kinetic models were determined using a nonlinear regression method. For the first-order kinetic models, the reaction rate constant is expressed through experimental variables (time, pH, electrical conductivity, temperature, oxygen concentration, carbon dioxide concentration and moisture content). For nth-order kinetic model, rate constant and reaction order are simultaneously determined. A comparison of simulated and experimental values was performed. Based on statistical indicators (correlation factor, adjusted correlation factor, root mean square deviation, variance and 95% confidence interval), the obtained results between kinetic models were also compared. In order to choose the kinetic model that best describes the experimental data, organic matter content for three reactors were calculated. For first-order kinetic models, maximum differences between experimental and model data based on organic matter content for the first reactor, the second reactor and the third reactor were ranged from 10.30% to 18.64%, from 4.77% to 14.51% and from 6.60% to 14.00%, respectively. Mean differences for the first reactor, the second reactor and the third reactor were ranged from 3.36% to 5.42%, from 4.77% to 14.52% and from 0.43% to 1.62%, respectively. For nth-order kinetic model, maximum differences between experimental and model based on organic matter content for the first reactor, for the second reactor and for the third reactor were 2.30%, 1.22% and 1.50%, respectively. Mean differences for the first reactor, the second reactor and the third reactor were 0.005%, 0.002% and 0.001%, respectively. The nth-order kinetic model showed better agreement with experimental data of organic matter content than first-order kinetic models proposed in this study and in the previous studies.

**KEYWORDS:** polyphenols, flavonoids, cytotoxicity, antibacterial activity, antioxidant potential

## INTRODUCTION

Composting process includes biochemical reactions in which various microorganisms decompose organic matter in the presence of oxygen. The main factors controlling the composting process include environmental parameters (temperature, moisture content, pH and oxygen) and the nature of substrate (C/N ratio, particle size and nutrient content) [1]. There are four phases of the composting process: mesophilic phase, thermophilic phase, cooling phase and maturation phase. In the mesophilic phase, readily biodegradable compounds are consumed, which leads to a slight increase in temperature. In the thermophilic phase, increasing temperature also increases the biodegradation of complex substrates, ultimately destroying most microorganisms. Then, in the cooling phase, microorganisms decompose higher polymers such as starch or cellulose, and finally, in the maturation phase, non-degradable compounds appear, and fungi predominate among microorganisms [2].

Modeling of composting kinetics is necessary for plant operation in accordance with requirements and environmental protection laws. Proper design and operation of composting reactors is essential to obtain good compost and reduce emissions to the environment [3]. Since composting is primarily a microbial process, the main function of a composting reactor is to achieve the optimal conditions. To define these optimal conditions, it is necessary to determine the kinetics of composting process. However, knowing only the optimal conditions is not enough in the most cases. The optimal composting temperature can be up to 45°C, but a higher temperature is needed to reduce pathogenic microorganisms, so here there is a conflict between temperature values. Therefore, it is necessary to choose a temperature that will lead to a reduction of pathogenic microorganisms but will not slow down the rate of the composting process [3].

Mathematical models and simulation of the composting process play an important role in understanding the process and the basic mechanisms that drive the observed process [4]. There are two main

strategies for building kinetic models for the composting process, namely the inductive and deductive strategies. The inductive model is based on a set of equations that describe the dependence of the composting rate on environmental factors (temperature, moisture content, oxygen concentration and free air space). The strategy for deriving the model structure based on theory is called the deductive strategy (classical modeling). The lack of a theoretical framework required to determine the kinetics of composting represents a major obstacle to further development of kinetics. Therefore, a deductive model is necessary to achieve further progress. Several researchers [5] have investigated the kinetics of biodegradation by microorganisms in soil, as first-order kinetics, but studies on kinetics are very limited specifically during composting process. Some researchers used first-order kinetics to investigate the degradation of organic micro-compounds during composting of sewage sludge in a thermophilic environment, although its adequacy for describing degradation has not been investigated [6]. In addition, numerous researchers ([7], [8], [9], [10], [11]) have addressed this issue, i.e. determining the composting kinetics using different types of waste materials. There is much more research on this topic, such as the study of [9] which focus is determination of the composting kinetics of municipal solid waste in three fully mechanical-biological treatments (MBT), concluding that full-scale MBT plants can be successfully modeled with the first-order kinetic model. It has been established that the decomposition of organic matter as a function of time is described by the first-order kinetic model [12].

Some researchers ([3], [13], [14], [9]) have mainly been concerned with determining kinetic parameters: reaction order, decomposition rate constants of the biodegradable fraction of organic material. Due to the complex nature of the composting process, the ability to simulate the kinetics of the process in a simple and generalized manner has proven difficult due to the need to know a large number of environmental factors. Therefore, researchers [15] explored a new approach to modeling with the aim of developing simpler models that do not require many environmental factors, and provide a more accurate description of composting process than previous models. The new models achieved errors ranging from 1.13% to 6.32% and outperformed the traditional first-order model, and only two parameters are required for their determination: the decomposition rate and an estimate of the ratio between the duration of the mesophilic and thermophilic phases. The biochemical reaction processes can usually be expressed using the first-

order kinetic model, Monod model, and empirical model, among which the first-order kinetic model is most widely used ([16], [17]).

The aim of this study was to propose new first-order kinetic models for the composting process of municipal solid waste in a reactor. Also, a comparison of the first-order kinetic models with nth-order model as well as with existing kinetic models will be performed.

## METHODS

### REACTOR SYSTEM

A laboratory-scale composting system was used for this study. The experiment was lasted over the period of 22 days using three identical specially designed reactors made of stainless steel (volume 35 l, height 0.55 m, internal diameter 0.36 m). The reactors were insulated with a layer of polyethylene foam (10 mm of thickness). A vertical rotating axis with blades mixing on intermittent schedule, fixed at perforated plate made of stainless steel (with holes of 5 mm), ensures the complete mixing of compost mass. Mixing was performed once a day.

The reactors were equipped with a valve for dropping the leachate and condensate. On the reactor lid, there were two holes, for the shaft mixer and for the thermocouple. Two stainless steel tubes (tube for gas sampling with valve and tube for discharge of exhausted gases) were welded to the reactor lid. Each reactor was connected with an air compressor (Trudbenik, Bosnia and Herzegovina), which provided air into the reactors at a controlled rate ( $0.9 \text{ l air min}^{-1} \text{ kg}^{-1} \text{ OM}$ ) based on published recommendations ([1], [4]). Measurement of airflow was carried out using airflow meters (Valved Acrylic Flowmeter, Cole-Parmer, USA). Thermocouple was inserted through a drilled rubber stopper, which is then inserted through a hole in the reactor lid. In all reactors, temperature was measured through thermocouples type T (Digi-Sense, Cole-Parmer, USA), placed in the middle of substrate. Thermocouples were connected through the acquisition module Temperature Data Acquisition Card Thermocouple CardAcq (Nomadics, USA) on a laptop.

At reactor outlet, the gas mixture passed through a gas washing bottle with 1 M sodium hydroxide and a gas washing bottle with 0.65 M boric acid, in order to remove carbon dioxide and ammonia, respectively. The gas washing bottles were changed daily [18].

## EXPERIMENTAL DATA, SOFTWARE AND NUMERICAL

### METHOD

The experimental data from composting process of municipal solid waste (process time, organic matter content, process temperature, moisture content, oxygen concentration, carbon dioxide concentration, electrical conductivity, pH) required for this study were taken from the study [18]. The numerical software package Polymath was used for solving model equations, with kinetic parameters determined by the nonlinear regression method (Levenberg–Marquardt method).

### STATISTICAL INDICATORS USED TO ASSESS THE QUALITY OF KINETIC MODELS

In this study, for determination of kinetic parameters the following statistical indicators are used: correlation coefficient  $R^2$  (Eq. (2)), adjusted correlation coefficient  $R_{adj}^2$  (Eq. (3)), root mean square deviation  $R_{msd}$  (Eq. (4)) and variance  $s^2$  (Eq. (5)):

$$\bar{y} = \frac{1}{n} \left( \sum_{i=1}^n y_{i_{exp}} \right) \quad (1)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_{i_{exp}} - y_{i_{cal}})^2}{\sum_{i=1}^n (y_{i_{exp}} - \bar{y})^2} \quad (2)$$

$$R_{adj}^2 = 1 - \frac{(1 - R^2)(n - 1)}{n - p} \quad (3)$$

$$R_{msd} = \frac{1}{n} \left( \sum_{i=1}^n (y_{i_{exp}} - y_{i_{cal}})^2 \right)^{\frac{1}{2}} \quad (4)$$

$$s^2 = \frac{\sum_{i=1}^n (y_i - \bar{y})^2}{n - 1} \quad (5)$$

where:  $n$  – number of observations,  $p$  – number of kinetic parameters,  $y_i$  – specific observation,  $\bar{y}$  – mean of specific observations. The notations “*exp*” and “*cal*” relate to experimental data and calculated data, respectively.

Correlation coefficients are often used to assess whether the investigated model describes the experimental data well. If the values of the correlation coefficients are close to 1, it means that the examined model better describes the experimental data. The correlation coefficients are not sufficient for evaluating the model, because in some situations its

values can be close to 1, but the model is still not appropriate for the given experimental data, and it is necessary to take into account other statistical indicators. As correlation coefficients, root mean square standard deviation and variance are used to describe the performance of a model in describing of experimental data. If the values of these indicators are very close to zero, it means that a model excellent describes experimental data.

### APPLIED KINETIC MODELS

The following kinetic models were proposed (Eqs. (6)-(13)):

The first-order kinetic models:

$$-\frac{d(OM)}{dt} = k_T \cdot OM \quad (6)$$

$$k_T = pH^a \cdot \exp\left(\frac{Mc}{T}\right)^b \cdot c^{(T-23)} \cdot \frac{EC}{T^d} \quad (7)$$

$$k_T = \exp\left(\frac{CO_2}{O_2}\right) \cdot pH^a \cdot \exp\left(\frac{Mc}{T}\right)^b \cdot c^{(T-23)} \cdot \frac{EC}{T^d} \quad (8)$$

$$k_T = \exp(CO_2 + O_2)^a \cdot T^b \cdot pH^c \cdot \exp\left(\frac{Mc}{T}\right)^d \cdot EC \quad (9)$$

$$k_T = \exp(CO_2 + O_2)^a \cdot b^{(T-23)} \cdot pH^c \cdot \left(\frac{EC}{T}\right)^d \cdot \left[\left(\frac{Mc}{T}\right)^d\right]^{0.5} \quad (10)$$

$$k_T = \frac{O_2}{O_2^a} \cdot b^{(T-23)} \cdot pH^c \cdot \left(\frac{Mc}{T}\right)^d \cdot EC \quad (11)$$

The nth-order kinetic model:

$$-\frac{dOM}{dt} = k_T \cdot OM^n \quad (12)$$

where:  $k_T$  – reaction rate constant (unit depends on reaction order);  $t$  – time (days),  $OM$  – organic matter content (%);  $T$  – process temperature (°C);  $Mc$  – moisture content (%);  $O_2$  – oxygen concentration (%),  $CO_2$  – carbon dioxide concentration (%);  $EC$  – electrical conductivity (dS m<sup>-1</sup>);  $pH$  – pH value (-);  $n$  – reaction order (-);  $a, b, c, d$  – constants/kinetic parameters.

In first-order kinetic models, a reaction rate constant is first determined based on measured experimental data, then organic matter content is calculated by model and compared with experimental data. In the nth-order model, reaction rate constant and reaction order are determined simultaneously using the Levenberg–Marquardt method.

## RESULTS AND DISCUSSION

### FIRST-ORDER KINETIC MODELS

Six kinetic models are used for three reactors, and corresponding kinetic parameters with statistical analysis are presented in Tables 1, 2, and 3.

**Table 1.** Kinetic parameters and statistical indicators for the first-order kinetic models for reactor 1

No.	Kinetic model	Kinetic parameters	95% confidence	$R^2$	$R_{adj}^2$	$R_{msd}$	$s^2$
1	$k_T = \left(\frac{O_2}{O_2^a}\right) \cdot b^{(T-23)} \cdot pH^{c \left(\frac{Mc}{T}\right)^d}$	$a = -2.6455$ $b = 0.5555$ $c = -3.4124$ $d = 0.6104$	1.5121 0.1248 1.5389 0.4229	0.9980	0.9977	0.0021	0.0001
2	$k_T = pH^a \cdot \exp\left(\frac{Mc}{T}\right)^b \cdot c^{(T-23)} \cdot \frac{EC}{T^d}$	$a = -10.5760$ $b = -2.8448$ $c = 0.5482$ $d = -8.1637$	2.3763 1.9390 0.1229 2.9797	0.9992	0.9990	0.0014	$5.3 \cdot 10^{-5}$
3	$k_T = \exp\left(\frac{CO_2}{O_2}\right) \cdot pH^a \cdot \exp\left(\frac{Mc}{T}\right)^b \cdot c^{(T-23)} \cdot \frac{EC}{T^d}$	$a = -10.5361$ $b = -2.1720$ $c = 0.5762$ $d = -7.4994$	2.4836 2.0224 0.1343 3.1156	0.9991	0.9990	0.0014	$5.7 \cdot 10^{-5}$
4	$k_T = \exp(CO_2 + O_2)^a \cdot T^b \cdot pH^c \cdot \exp\left(\frac{Mc}{T}\right)^d \cdot EC$	$a = -0.7795$ $b = 2.5334$ $c = -0.7415$ $d = 2.9502$	0.0173 0.1119 0.2053 0.0983	0.9992	0.9991	0.0013	$5.1 \cdot 10^{-5}$
5	$k_T = \exp(CO_2 + O_2)^a \cdot b^{(T-23)} \cdot pH^c \cdot \left(\frac{EC}{T}\right)^d \cdot \left[\left(\frac{Mc}{T}\right)^d\right]^{0.5}$	$a = -0.7611$ $b = 1.4219$ $c = 1.1642$ $d = 31.2627$	$3 \cdot 10^{-7}$ $1.6 \cdot 10^{-5}$ $2.3 \cdot 10^{-6}$ $1.1 \cdot 10^{-5}$	0.9982	0.9979	0.0020	0.0001
6	$k_T = \frac{O_2}{O_2^a} \cdot b^{(T-23)} \cdot pH^c \cdot \left(\frac{Mc}{T}\right)^d \cdot EC$	$a = -1.2468$ $b = 0.9079$ $c = -5.8239$ $d = 2.2784$	0.0433 0.0354 0.0787 0.1188	0.9988	0.9986	0.0016	$7.6 \cdot 10^{-5}$

**Table 2.** Kinetic parameters and statistical indicators for the first-order kinetic models for reactor 2

No.	Kinetic model	Kinetic parameters	95% confidence	$R^2$	$R_{adj}^2$	$R_{msd}$	$s^2$
1	$k_T = \left(\frac{O_2}{O_2^a}\right) \cdot b^{(T-23)} \cdot pH^{c \left(\frac{Mc}{T}\right)^d}$	$a = -6.6165$ $b = 1.2551$ $c = -15.769$ $d = -0.2102$	0.0246 0.0096 0.0508 0.0031	0.9996	0.9995	0.0010	$2.6 \cdot 10^{-5}$
2	$k_T = pH^a \cdot \exp\left(\frac{Mc}{T}\right)^b \cdot c^{(T-23)} \cdot \frac{EC}{T^d}$	$a = -10.576$ $b = -2.8448$ $c = 0.5482$ $d = -8.1637$	2.3763 1.9390 0.1229 2.9797	0.9992	0.9990	0.0014	$5.3 \cdot 10^{-5}$
3	$k_T = \exp\left(\frac{CO_2}{O_2}\right) \cdot pH^a \cdot \exp\left(\frac{Mc}{T}\right)^b \cdot c^{(T-23)} \cdot \frac{EC}{T^d}$	$a = -11.941$ $b = 3.0572$ $c = 0.9698$ $d = -4.0256$	0.0119 0.0079 0.0060 0.0069	0.9997	0.9996	0.0009	$2.2 \cdot 10^{-5}$
4	$k_T = \exp(CO_2 + O_2)^a \cdot T^b \cdot pH^c \cdot \exp\left(\frac{Mc}{T}\right)^d \cdot EC$	$a = 0.1530$ $b = 3.4775$ $c = -12.4632$ $d = 2.8616$	0.2053 0.4568 1.2763 0.2927	0.9998	0.9998	0.0007	$1.2 \cdot 10^{-5}$

No.	Kinetic model	Kinetic parameters	95% confidence	$R^2$	$R_{adj}^2$	$Rmsd$	$s^2$
5	$k_T = \exp(CO_2 + O_2)^a \cdot b^{(T-23)} \cdot pH \cdot \left(\frac{EC}{T}\right)^c \cdot \left[\left(\frac{Mc}{T}\right)^d\right]^{0.5}$	$a = -1.8570$ $b = 2.0599$ $c = -0.8158$ $d = 67.0533$	0.1868 0.1372 1.3642 4.6788	0.9986	0.9984	0.0018	$9.4 \cdot 10^{-5}$
6	$k_T = \frac{O_2}{O_2^a} \cdot b^{(T-23)} \cdot pH^c \cdot \left(\frac{Mc}{T}\right)^d \cdot EC$	$a = -4.2114$ $b = 1.1770$ $c = -11.9571$ $d = 5.1288$	$8.1 \cdot 10^{-7}$ $1.4 \cdot 10^{-6}$ $1.3 \cdot 10^{-6}$ $2.4 \cdot 10^{-6}$	0.9997	0.9997	0.0008	$1.9 \cdot 10^{-5}$

Table 3. Kinetic parameters and statistical indicators for the first-order kinetic models for reactor 3

No.	Kinetic model	Kinetic parameters	95% confidence	$R^2$	$R_{adj}^2$	$Rmsd$	$s^2$
1	$k_T = \left(\frac{O_2}{O_2^a}\right) \cdot b^{(T-23)} \cdot pH^{c \left(\frac{Mc}{T}\right)^d}$	$a = -6.9296$ $b = 1.5663$ $c = -22.1121$ $d = -0.5787$	1.1609 0.3153 3.5452 0.2205	0.9981	0.9978	0.0022	0.0001
2	$k_T = pH^a \cdot \exp\left(\frac{Mc}{T}\right)^b \cdot c^{(T-23)} \cdot \frac{EC}{T^d}$	$a = -17.547$ $b = 0.6596$ $c = 0.7982$ $d = -9.5305$	2.6001 1.3165 0.0809 2.5209	0.9996	0.9995	0.0010	$2.9 \cdot 10^{-5}$
3	$k_T = \exp\left(\frac{CO_2}{O_2}\right) \cdot pH^a \cdot \exp\left(\frac{Mc}{T}\right)^b \cdot c^{(T-23)} \cdot \frac{EC}{T^d}$	$a = -18.966$ $b = -0.0618$ $c = 0.7249$ $d = -10.961$	1.0909 0.6368 0.0304 0.9246	0.9993	0.9992	0.0013	$4.8 \cdot 10^{-5}$
4	$k_T = \exp(CO_2 + O_2)^a \cdot T^b \cdot pH^c \cdot \exp\left(\frac{Mc}{T}\right)^d \cdot EC$	$a = -0.0661$ $b = 4.3394$ $c = -12.2652$ $d = 3.7352$	0.1113 0.4595 1.2427 0.2155	0.9993	0.9992	0.0013	$4.6 \cdot 10^{-5}$
5	$k_T = \exp(CO_2 + O_2)^a \cdot b^{(T-23)} \cdot pH \cdot \left(\frac{EC}{T}\right)^c \cdot \left[\left(\frac{Mc}{T}\right)^d\right]^{0.5}$	$a = -0.7466$ $b = 1.6715$ $c = 3.1398$ $d = 42.2303$	0.4354 0.1254 3.1729 5.7123	0.9988	0.9986	0.0017	$8.4 \cdot 10^{-5}$
6	$k_T = \frac{O_2}{O_2^a} \cdot b^{(T-23)} \cdot pH^c \cdot \left(\frac{Mc}{T}\right)^d \cdot EC$	$a = 0.6343$ $b = 1.4517$ $c = -10.049$ $d = 17.6361$	0.8996 0.0726 1.2660 2.3379	0.9991	0.9989	0.0015	$6.4 \cdot 10^{-5}$

Figures 1, 2, and 3 show experimental values and calculated functions of time for three reactors for six first-order kinetic models.

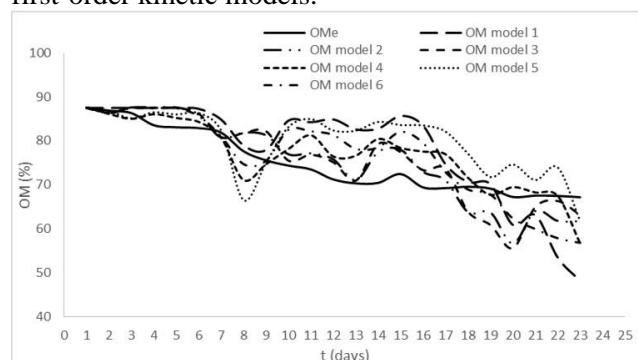


Figure 1. Comparison of experimental data and first-order kinetic models for organic matter content for reactor 1

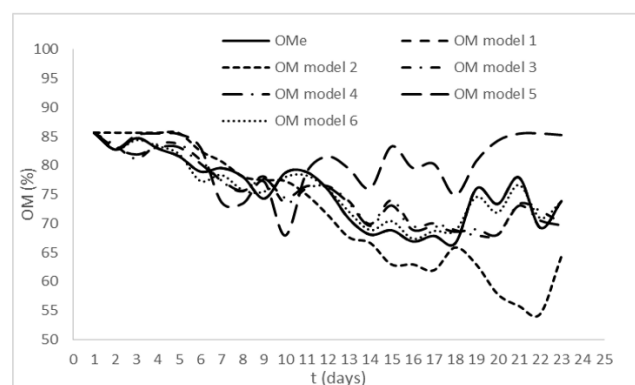
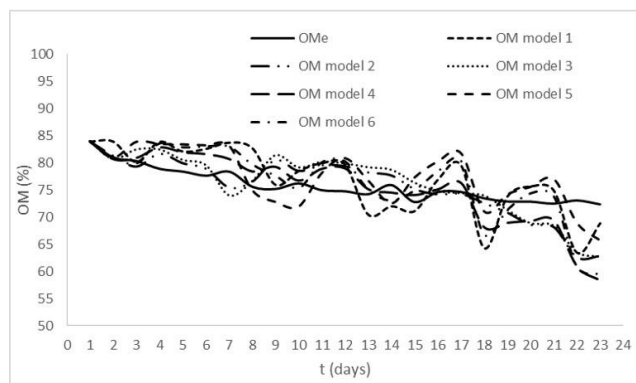


Figure 2. Comparison of experimental data and first-order kinetic models for organic matter content for reactor 2



**Figure 3.** Comparison of experimental data and first-order kinetic models for organic matter content for reactor 3

The maximum and mean differences of experimental data for organic matter content for first-order kinetic models are shown in Tables 4, 5, and 6 for three reactors.

**Table 4.** Maximum and mean differences between experimental data and first-order kinetic models for organic matter content for reactor 1

Model	Maximum difference				Mean difference			
	0-5 days	6-14 days	15-22 days	0-22 days	0-5 days	6-14 days	15-22 days	0-22 days
1	-0.0009	-1.3853	18.9991	18.9995	-2.4559	-8.8268	2.7461	-3.1395
2	0.4066	1.2253	10.6432	10.6433	-2.0282	-3.5695	3.9628	-0.5475
3	0.4114	1.0184	11.6363	11.6368	-2.0859	-3.6315	3.1154	-0.8815
4	1.2945	6.5188	10.4802	10.4801	-0.6604	-3.3831	-1.1446	-1.8942
5	-1.3340	-6.3339	-6.1358	11.0848	-1.3341	-6.3339	-6.1358	-4.9607
6	0.5097	2.8621	10.3042	10.3047	-1.9616	-5.4603	2.5206	-1.7716

**Table 5.** Maximum and mean differences between experimental data and first-order kinetic models for organic matter content for reactor 2

Model	Maximum difference				Mean difference			
	0-5 days	6-14 days	15-22 days	0-22 days	0-5 days	6-14 days	15-22 days	0-22 days
1	0.3075	6.5658	5.1973	6.5658	-0.6489	-0.0863	-0.7245	-0.4551
2	-0.0007	9.2216	14.5096	14.5096	-2.9762	1.6864	14.5097	3.3582
3	1.6081	4.7653	3.3458	4.7653	-0.9715	-0.2528	0.7331	-0.0974
4	0.8759	5.0678	3.4912	5.0678	-0.7396	-0.1895	1.0839	0.1099
5	0.0844	8.1269	-3.0903	8.1269	-2.5653	-2.1300	-11.2738	-5.4240
6	1.4935	5.7897	4.2915	5.7897	-0.4384	-0.0880	-0.8312	-0.4378

**Table 6.** Maximum and mean differences between experimental data and first-order kinetic models for organic matter content for reactor 3

Model	Maximum difference				Mean difference			
	0-5 days	6-14 days	15-22 days	0-22 days	0-5 days	6-14 days	15-22 days	0-22 days
1	0.1682	3.8928	9.5882	9.5882	-2.7203	-1.7795	1.1230	-1.0154
2	1.0352	2.9411	10.4432	10.4435	-0.7903	-2.5281	4.0372	0.2088
3	0.2797	4.4183	9.6891	9.6891	-1.5587	-3.0090	3.5914	-0.3348
4	0.3209	1.3916	14.0051	14.0051	-1.9296	-2.0534	4.9988	0.4319
5	0.0394	4.2286	6.6031	6.6031	-3.0974	-1.1616	-1.0203	-1.6174
6	0.4487	2.8707	12.8509	12.8509	-2.3466	-2.3242	2.6209	-0.6100

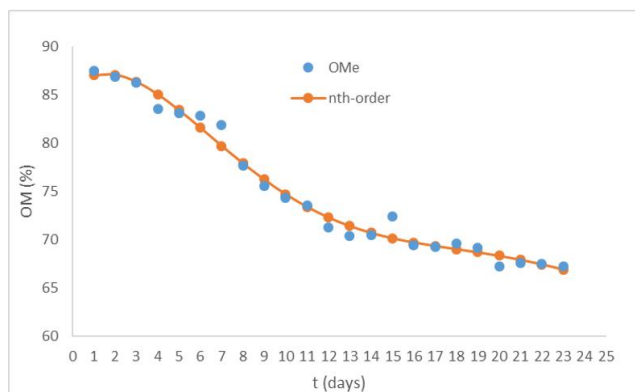
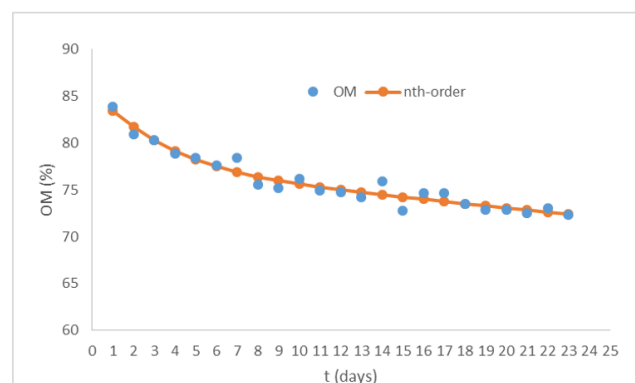
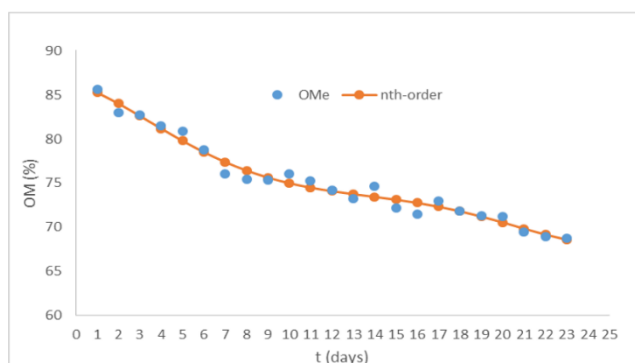
## NTH-ORDER KINETIC MODEL

In order to more accurately determine the reaction order that best describes the experimental data, the nth-order model was used. Using a nonlinear regression method, the values for  $k_T$  and  $n$  were

simultaneously determined for three reactors, as shown in Table 7. Based on the kinetic parameters, organic matter content was calculated and compared with experimental data, which are shown in Figures 4, 5 and 6.

**Table 7.** Kinetic parameters and statistical indicators for the nth-order kinetic model for reactor 1

Reactor	$k_T$	$n$	95% confidence	$R^2$	$R_{adj}^2$	$R_{msd}$	$s^2$
1	1.0484	0.9891	$k_T \pm 0.2106$ $n \pm 0.0464$	0.9891	0.9885	0.1514	0.5778
2	1.0695	0.9844	$k_T \pm 0.2670$ $n \pm 0.0577$	0.9830	0.9822	0.1279	0.4118
3	1.0283	0.9935	$k_T \pm 0.1655$ $n \pm 0.0372$	0.9929	0.9926	0.0525	0.0694

**Figure 4.** Comparison of experimental data and nth-order kinetic model for organic matter content for reactor 1**Figure 6.** Comparison of experimental data and nth-order kinetic model for organic matter content for reactor 3**Figure 5.** Comparison of experimental data and nth-order kinetic model for organic matter content for reactor 2

The calculated maximum and mean differences for experimental values and calculated values of organic matter are shown in Table 8.

**Table 8.** Maximum and mean differences between experimental data and nth-order kinetic model for organic matter content

Reactor	Maximum difference				Mean difference			
	0-5 days	6-14 days	15-22 days	0-22 days	0-5 days	6-14 days	15-22 days	0-22 days
1	1.2876	2.2966	0.5391	2.2966	-0.0705	0.0949	-0.0682	-0.0049
2	1.0891	1.2187	0.7047	1.2187	0.2156	-0.1116	-0.0318	0.0015
3	0.4800	1.5013	0.8881	1.5013	-0.0356	-0.0753	0.1079	-0.0012

## COMPARISONS OF KINETIC MODELS

Statistical analysis showed that the highest values of the correlation factor and adjusted correlation factor, and the lowest values of the mean and standard deviation and variance, were found in the first-order

kinetic models 2, 3, and 4. On the other hand, the 95% confidence interval for almost each kinetic parameters in the first-order and nth-order kinetic models were less than the values of kinetic parameters. Higher values of 95% confidence interval indicated possible

measurement errors or poor estimation of the initial values of the model parameters.

Although the statistical analysis showed very good results with first-order models, when compare the graphs comparing the experimental data and the calculated values for organic matter content for used models, it can be seen that the maximum and mean differences are greater for first-order models than for nth-order model. These deviations can also be seen in Tables 4, 5 and 6, where the maximum difference ranges from 10.30 to 18.64% for the first reactor, from 4.76 to 14.51% for the second reactor, and from 6.60 to 14.00% for the third reactor, and mean difference from -4.96 to -0.55% for the first reactor, -5.42 to 3.36% for the second reactor and from -1.62 to 0.43% for the third reactor for days 0-22. The highest value for the maximum difference was for 15-22 days for the first reactor, 6-14 days for the second reactor, and 15-22 days for the third reactor, and the highest value for the mean difference was for 6-14 days for the first reactor, 15-22 days for the second and third reactor. Large deviations from experimental data can be explained by the fact that the mixture that was composted was very heterogeneous, and therefore it was difficult to take samples that would contain all composted components [7]. Also, it should be taken into account that not all components degrade at the same rate, some slower and some faster, which can lead to errors in experimental data [12].

The nth-order kinetic model showed the best results for three reactors, as it can be seen in the Figures 4, 5 and 6. The maximum difference between the experimental data and the calculated values is 2.30% for the first reactor, 1.22% for the second reactor, and 1.50% for the third reactor, and the mean difference is -0.005% for the first reactor, 0.002% for the second reactor, and 0.001% for the third reactor for days 0-22. In the study [18], the maximum difference was 3.91% for the first reactor, 4.07% for the second reactor, and 3.93% for the third reactor, and the mean difference is 1.30% for the first reactor, 1.60% for the second reactor, and 1.76% for the third reactor for days 0-22, in which first-order kinetics was used. By comparing the statistical analysis and the values for the maximum and mean difference for the experimental data and the calculated values for organic matter content obtained with nth-order model in this study and for the first order models used in the study [18], it can be concluded that the nth-order kinetic model gave the best results.

An n-th order model for composting is often preferred over first-order kinetics because it offers more flexibility in modeling the non-linear nature of the composting process. The composting rate typically

decreases over time as substrates are consumed, and the n-th order model can better represent this dynamic process. It allows for the incorporation of various factors, including microbial activity, substrate concentration, and environmental conditions, making it a more realistic choice for describing composting kinetics.

Although the nth-order kinetic model gives better results than the first-order, the n-th order kinetic model offers a simplified approach to understanding the composting process, but it has several limitations when it comes to capturing the complexities and variability inherent in composting. It's often more useful for understanding general trends in decomposition rather than predicting the exact dynamics of the process under varying conditions. For more accurate predictions, more complex models or experimental data might be required to account for factors like temperature, moisture content, microbial communities, and the heterogeneity of the organic material, which are present in the first-order kinetic model.

## CONCLUSION

In this study, six new first-order kinetic models nth-order kinetic model for composting process of municipal solid waste were applied to experimental data. Nonlinear regression method was used for evaluation of kinetic parameters. Six kinetic first-order models were proposed based on the following experimental data: organic matter content, pH, electrical conductivity, oxygen concentration, carbon dioxide concentration, temperature and moisture content.

Among six first-order kinetic models, kinetic models 2, 3 and 4 showed better statistical analysis compared to other models. For six first-order kinetic models, maximum differences between experimental and model data based on organic matter content for the first reactor, the second reactor and the third reactor were ranged from 10.30 to 18.64%, from 4.77 to 14.51% and from 6.60 to 14.00%, respectively. Mean differences for the first reactor, the second reactor and the third reactor were ranged from 3.36 to 5.42%, from 4.77 to 14.52% and from 0.43 to 1.62%, respectively. For nth-order kinetic model, maximum differences between experimental and model based on organic matter content for the first reactor, the second reactor and the third reactor were 2.30%, 1.22% and 1.50%, respectively. Mean differences for the first reactor, the second reactor and the third reactor were 0.005%, 0.002% and 0.001%, respectively. The nth-order kinetic model showed better agreement with experimental data of organic matter content than first-



order kinetic models proposed in this study and in the previous studies.

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