

# Co-composting kinetics of rose processing waste with OFMSW

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## Abstract

The objective of this study was to evaluate the kinetics of co-composting of rose processing waste (RPW) and organic fraction of municipal solid waste (OFMSW). Experimental data was obtained from 65-L batch reactors. Mixtures settled up with different ratios of RPW, OFMSW, inoculation, and bulking agent. The data was consisting of CO<sub>2</sub> evolution and inner temperature changing with time in the reactors. Decomposition process was evaluated based on rapidly and slowly biodegradable fractions of organic matter. The experimental data has been analyzed by kinetic models including the first-zero-order, first-first-order, Chen and Hashimoto's and Levi-Minzi's kinetic models using non-linear regression techniques. Kinetic parameters and rate constants were evaluated based on the average relative errors and coefficient of determination. The results of study showed that the best fitting kinetic model is the first-first-order.

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## 1. Introduction

The yearly average of harvested rose flower in Isparta City, which has the majority of Turkey's rose flower production, is around 12,000 ton. In rose oil industry, one unit of rose flower milled gives about two units of processing waste on a wet weight basis. In addition to the undesirable appearance of the local environment, due to the putrescible aspects of this waste, a substantial environmental problem is caused for a short period between May and June; especially for aquatic bodies and groundwater wells (Tosun et al., 2004).

Biological treatments offer a cost-effective sustainable solution for urban organic wastes. In practice, the main biological process applied for solid wastes is composting (Tchobanoglous et al., 1993). Composting, recognized as a viable alternative and beneficial use of end-product for waste management, is the biological degradation of highly

concentrated biodegradable organic wastes in the presence of oxygen (aerobically) to carbon dioxide and water. The final product of composting is a stable humus-like material known as compost (Bari and Koenig, 2001). Compost material can be used for improving soil structure, which can act as a soil conditioner or fertilizer (Zorpas et al., 2000). Composts obtained from composting of olive mill wastewater sludge have a high level of humification and without phytotoxic effects (Paredes et al., 2001).

To find out biodegradation behavior of wastes is important for an optimized design regarding composting process parameters such as the processing time, size of reactor or pile area and the product quality. A high degradation rate usually indicates lower capital and operational costs for composting plants.

Composting kinetics has been investigated recently by many researchers to describe the decomposition of organic wastes. Bernal et al. (1998a) studied the organic C mineralization rates of different organic wastes and emphasized that C mineralization followed a combined first- and zero-order kinetic model in most of the samples. Biological degradation rates of food waste and mixed office waste

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paper were determined by Bari et al. (2000). Hamoda et al. (1998) and Huang et al. (2000) also worked on solid waste composting kinetics. Nakasaki et al. (1998) examined the degradation patterns of organic materials in dog food in batch and fed-batch. Kirchmann and Bernal (1997) used first-zero-order model for different material types such as cattle dung, pig dung, and sewage sludge-cotton waste mixture. Paredes et al. (2002) found organic matter losses followed a first-order kinetic equation for biodegradation of cotton waste and olive mill wastewater sludge. Ekinici et al. (2006) developed a decomposition rate model considering the fast and slow fractions of degradable substrate. Tosun (2003) has also studied biodegradation of rose processing waste (RPW) with organic fraction of municipal solid waste (OFMSW).

RPW contains high proportion of organic matter and plant nutrients. Unlike MSW and some other industrial wastes, it does not contain harmful components such as heavy metals and organic contaminants. The purpose of this study is to demonstrate co-compostability of RPW and OFMSW at different mixture ratios and to evaluate the kinetic models including the first-zero-order, first-first-order, Chen and Hashimoto and Levi-Minzi's kinetic model using non-linear regression technique to distinguish rapid and slow biodegradable fractions of waste mixture.

## 2. Methods

### 2.1. Reactors

The composting of RPW and OFMSW was conducted in five insulated closed batch reactors, each of which has a total volume of approximately 65 L. For insulation purpose, 8-cm-thick layers of glass wool were used by wrapping the sides of the reactor. The experimental work was conducted at room temperature. Forced aeration was provided intermittently by an air blower. The exhaust gas was cooled down to ambient temperature by passing through a condensation arrangement. The condensate from the gas coolers was collected in a gas absorption bottle. Leachate was drained by a tap at the bottom of the reactor. Turning operation was performed on day 11, 21, and 50 of composting. The temperatures in the centre of the composting material and ambient were measured using K type thermocouples twice a day.

### 2.2. Materials

The essential components in the reactors were RPW and OFMSW as organic materials, hornbeam pieces sized 2 cm × 2 cm × 1.5 cm as bulking agent, and rose compost as inoculums. The RPW was supplied by the Gürkan Rose Oil Factory in Isparta, and the OFMSW was supplied by Odayeri Municipal Landfill in Istanbul. The seed material comprising of composted RPW was supplied from previous laboratory trials. Chemical characterization of the composting materials is given in Table 1. Mixtures of RPW and

Table 1

Chemical characterization of RPW, OFMSW and seeding material (dry basis)

	RPW	OFMSW	Seed (RPW compost)
Water content, %	90.5	80.3	5.2
Volatile solids, VS, %	84.2	84.1	26.7
Total organic carbon, TOC, %	50.6	37.8	21.2
TOC/VS	60.1	45	79.4
TKN, %	3.7	1.89	1.5
C/N	13.6	20	13.9
pH	5.8	5.4	6.4

Table 2

Mixing ratios of materials packed in the reactors (dry weight basis)

Mixtures	RPW	OFMSW	Seed (RPW compost)	Bulking agent	Turning operation
K1	4	1	1	2	+
K2	2	1	0.6	1.2	+
K3	1	1	0.4	0.8	+
K4	3	–	1	2	–
K5	2	1	0.6	1.2	–

OFMSW prepared at five different ratios are given in Table 2. But mixture K4 is designed to evaluate decomposition of rose waste only. K4 and K5 reactors without turning operation were to determine the effect of turning operations. Before the experiments, the moisture contents of the mixtures were adjusted by 60% by addition of water.

The particle size distribution of each mixture was determined, before and after composting process, by dry sieving through 30, 10, and 4.75 mm screens. Fifty percent for raw RPW was higher than 4.75 mm.

Biological stability degree of compost was determined with Dewar flask by self-heating procedure how the rising temperature of moist compost added to the flask is monitored over a 2–5 day period and recorded.

### 2.3. Analytical methods

The samples from the reactors were dried at 105 °C for 24 h, ground in a stainless steel mill with 0.3 mm sieve, and analyzed for the total organic carbon, organic matter (Nelson and Sommers, 1996), Kjeldahl-N and PO<sub>4</sub>-P (APHA, AWWA and WEF, 1995). The exhaust gas from the reactor was collected and was analyzed by an Orsat-type gas analyzer to determine instantaneous CO<sub>2</sub> concentration. Cumulative CO<sub>2</sub>-C was calculated by integration of instantaneous CO<sub>2</sub>-C concentration over time.

### 2.4. Statistical analysis of data

For the kinetic analysis, first-zero-order, first-first-order, Chen and Hashimoto's and Levi-Minzi's kinetic models were applied to CO<sub>2</sub>-C evolved as a function of time. Kinetic parameters for these models were calculated by using non-linear regression analysis. A minimization proce-

ture using the solver add-in function of the Microsoft Excel has been adopted to solve kinetic equations by minimizing the HYBRID error function (Porter et al., 1999) between the predicted values and the experimental data. In order to quantitatively compare the applicability of kinetic models in fitting to data, non-linear coefficient of determination and average relative error ( $\Delta C$ , %) (Kapoor and Yang, 1989) were calculated.

### 3. Results and discussion

#### 3.1. Temperature histories

The temperature patterns developed at the centre of the packed material in each reactor are illustrated in Fig. 1. In all trials, temperature reached up to 70 °C within 2–3 days. The rapid rise in temperature was due to the breakdown of the easily decomposable fractions of the mixtures as stated by Yamada and Kawase (2006) for waste activated sludge. In all trials, thermophilic conditions above 55 °C were observed for at least a week. This case, as stated by Epstein (1997), satisfies the requirements for pathogen decay. Following previous rapid increment, it declined gradually within a few days.

To see the effect of a possible turning while this gradually decrement, as stated by Paredes et al. (2001) and Garcia-Gomes et al. (2003), the reactors are turned in order to improve both the homogeneity of the material and the fermentation process. After each turning, temperature started to increase again. Material temperatures lowering to the ambient temperature showed that bio oxidative phase lasted for about 50 days.

#### 3.2. CO<sub>2</sub> evolution

CO<sub>2</sub> evolution rates for the reactors showed a similar behavior with temperature variation. During the process, the maximum CO<sub>2</sub>-C evolution rate occurred within a few days of incubation, probably due to easily biodegradable substrate (Fig. 2). CO<sub>2</sub> evolution rate gradually decreased in all reactors and it became fairly constant after almost 20 days.

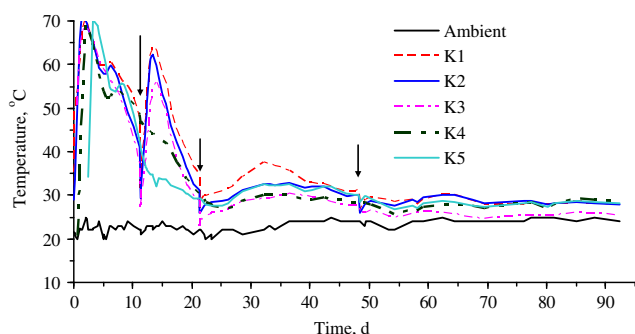


Fig. 1. Temperature development during the composting process. The arrows indicate turning operations.

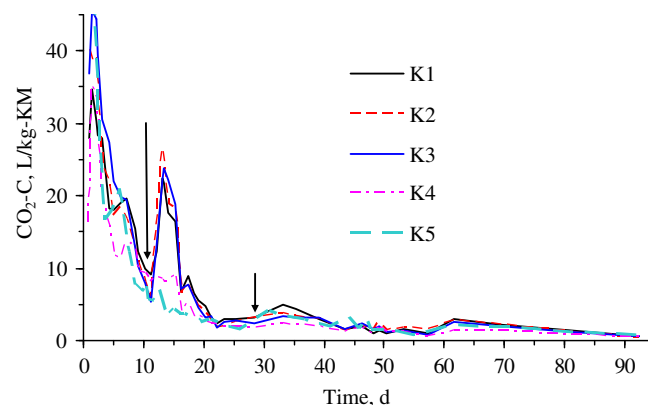


Fig. 2. The variation of CO<sub>2</sub> evolution rate.

Cumulative CO<sub>2</sub> evolution values in all reactors were 460, 465, 478, 315 and 391 L/kg dry solids after 92 days of composting, respectively. Accordingly the results, K1, K2, K3 reactors with turning operation yielded higher CO<sub>2</sub>-C than other two reactors (K4, K5) without turning operation. By comparison, 16% cumulative evolution difference was determined between K2 (turned) and K5 (unturbed) having the same mixture ratio. This difference is due to the stabilization effect of turning operation. Shi et al. (1999) explained watering and turning accelerate the decomposition rate of dairy wastes during the composting process. Different mixture rates of OFMSW (K1–K3) did not exhibited a significant difference in cumulative CO<sub>2</sub> evolution that changes between 460 and 478 L/kg dry solids.

#### 3.3. Particle size of RPW

Particle size distribution of raw RPW and end products obtained from K1–K5 reactors is shown in Fig. 3. After completion of the composting process, 60–80% of RPW compost was smaller than 4.75 mm. The critical particle size for OFMSW was about 40 mm and small particles prevent to the oxygen entrance inside of particles (Hamoda

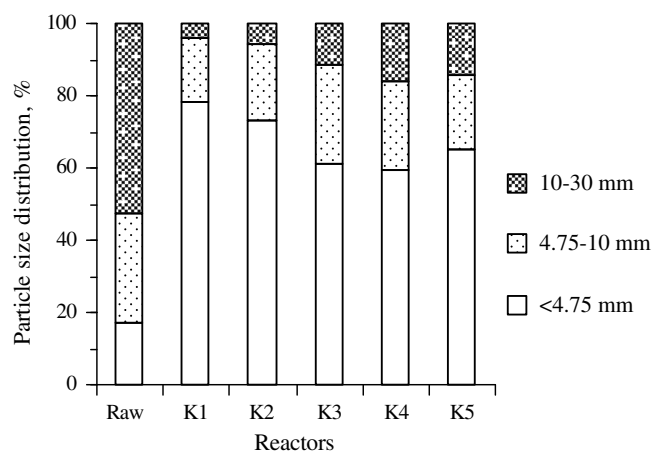


Fig. 3. Particle size of RPW before and after composting.

et al., 1998). If the voids between the particles are big, then the oxygen has better access to the particles and biodegradation proceeds faster. Accordingly, oxygen limitation was not observed for RPW compost due to its homogenous size distribution. These results are in agreement with a study on the effect of particle size on the decomposition of grass (Klass et al., 1976).

### 3.4. Dewar self-heating test

The self-heating test is applied to determine the degree of biological stability of the compost according to stability index (SI) (Reinhardt, 1999, Bari and Koenig, 2001). The SI of waste is classified in degrees from I to V, and ranges from raw, unstabilized waste to completely stabilized waste. Temperature rise in turned reactors were measured ranging from 2 to 3 °C, indicating completely stable mature compost. On the other hand, temperature rise in unturned reactors, K4 and K5, were 22 and 15 °C, respectively. Higher rises in temperature indicate less mature compost and it is an indirect indicator of respiration rate.

### 3.5. Kinetic analysis

The fitting of kinetic equations to cumulative CO<sub>2</sub>-C evolution makes it possible to analyze the rapid and slow fractions of potentially biodegradable C and biodegradation rates (Bernal et al., 1998a,b). Experimental data obtained in the study have been analyzed by the following kinetic models to describe the decomposition of RPW-OFMSW mixtures and compared graphically in Fig. 4.

#### 3.5.1. First-zero-order kinetic model

The carbon mineralization of organic wastes follows a combined two-step kinetic: one first order, rapid phase, and the other, zero order, slow phase (Bernal et al., 1998a). The first-zero-order kinetic model is expressed as:

$$C = C_R(1 - \exp(-k_R t)) + C_S k_S t \quad (1)$$

where,  $C$  is cumulative CO<sub>2</sub>-C mineralized (%) at time  $t$ ,  $C_R$ ,  $C_S$  are percentage of rapidly and slowly mineralizable fraction, respectively, and  $k_R$  and  $k_S$  are rapid and slow rate constants (day<sup>-1</sup>), respectively. It should be noted that

the sum of  $C_R$  and  $C_S$  has the same physical meaning as total organic carbon.

The first-zero-order parameters, coefficient of determination and the average relative errors are presented in Table 3 for all reactors. Average rapidly degradable organic matter content was about 43% and 30% and the remaining slowly degradable fraction was 57% and 70% for turned and unturned reactors, respectively. The reason for low  $C_R$  value for unturned reactors, K4 and K5, was due to oxygen limitation. The rate constants were almost the same for all

Table 3  
Rate constants and statistical comparison values obtained by application of the kinetic models

	K1	K2	K3	K4	K5
CumCO <sub>2</sub> -C <sub>exp.</sub> , %	60.3	60.5	60.6	44.3	50.8
t <sub>CO<sub>2</sub>-C,40%</sub> , d	18	16	15	62	36
<i>First-zero-order (1 + 0)</i>					
C <sub>R</sub> , %	44.73	41.50	43.57	31.76	28.56
C <sub>S</sub> , %	55.27	58.50	56.43	68.24	71.44
k <sub>R</sub> , d <sup>-1</sup>	0.087	0.113	0.117	0.109	0.236
k <sub>S</sub> , d <sup>-1</sup>	0.0033	0.0038	0.0035	0.0021	0.0039
HYBRID	0.048	0.135	0.092	0.063	0.068
ΔC, %	1.94	3.51	2.74	3.00	2.66
r <sup>2</sup> (non-linear)	0.998	0.994	0.995	0.998	0.991
<i>First-first-order (1 + 1)</i>					
C <sub>R</sub> , %	43.13	39.37	41.97	31.22	27.11
C <sub>S</sub> , %	56.87	60.63	58.03	68.78	72.89
k <sub>R</sub> , d <sup>-1</sup>	0.090	0.119	0.121	0.111	0.254
k <sub>S</sub> , d <sup>-1</sup>	0.0041	0.0050	0.0045	0.0023	0.0049
HYBRID	0.048	0.130	0.089	0.063	0.044
ΔC, %	1.95	3.40	2.68	2.98	2.03
r <sup>2</sup> (non-linear)	0.998	0.994	0.995	0.998	0.995
<i>Chen and Hoshimoto</i>					
R	0.30	0.36	0.34	0.53	0.51
K	90.08	79.26	89.93	26.31	41.05
μ <sub>m</sub> , d <sup>-1</sup>	6.057	7.205	8.409	2.514	5.881
HYBRID	0.061	0.144	0.079	0.040	0.296
ΔC, %	2.14	3.60	2.72	2.45	5.78
r <sup>2</sup> (non-linear)	0.997	0.992	0.995	0.997	0.961
<i>Levi-Minzi</i>					
k, mg/kg day	8.40	10.05	10.53	6.82	11.46
m	0.472	0.431	0.424	0.453	0.348
HYBRID	1.837	1.300	1.769	1.645	0.474
ΔC, %	15.37	11.95	14.29	17.18	7.43
r <sup>2</sup> (non-linear)	0.927	0.931	0.914	0.912	0.969

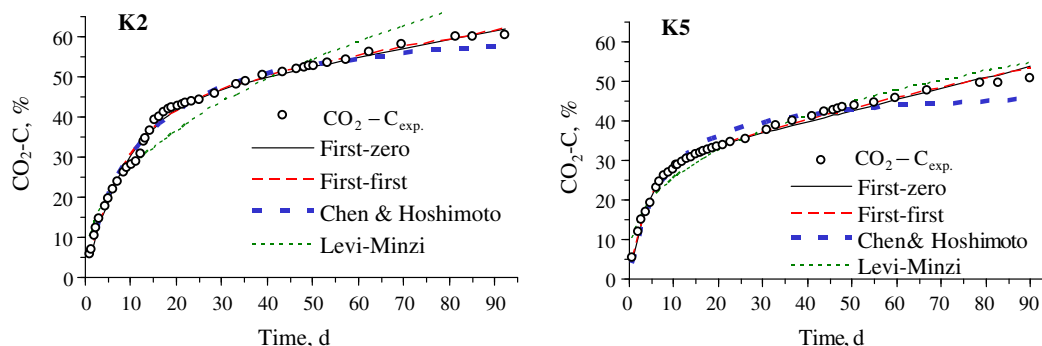


Fig. 4. Comparison of kinetic models for turned and unturned reactors. The mixture ratios RPW:OFMSW; 2:1 for K2 and K5.

reactors except for K5. Kinetic constants are in the range of 0.087–0.236 d<sup>-1</sup> and 0.0021–0.0039 d<sup>-1</sup> for rapidly and slowly mineralizable fractions, respectively. Bernal et al. (1998a) calculated similar results for first-zero-order kinetic constants as 0.085–0.128 d<sup>-1</sup> and 0.0020–0.0055 d<sup>-1</sup> for K<sub>R</sub> and K<sub>S</sub> values, respectively, for 46.5% sewage sludge and 53.5% cotton waste.

3.5.2. The first-first-order kinetic model

First-first-order reaction model is the sum of double first-order exponential equation with two components: one that decomposes faster during a few weeks of incubation and the other one that decomposes more slowly during the process.

The first-first-order kinetic model is expressed as

$$C = C_R(1 - \exp(-k_R t)) + C_S(1 - \exp(-k_S t)) \quad (2)$$

The results of fitting the first-first-order kinetic model to the CO<sub>2</sub>-C as a function of time revealed that rapid and slow biodegradable fraction of organic matter were about 42% and 58% for turned reactors, with corresponding rate constants of 0.09–0.12 d<sup>-1</sup> and 0.041–0.0050 d<sup>-1</sup>, respectively. For unturned reactors rapid biodegradable fraction of 29% and slow fraction of 71% were calculated, with corresponding rate constants of 0.111–0.254 and 0.0023–0.0049 d<sup>-1</sup>, respectively (Table 3).

3.5.3. Chen and Hosshimoto's kinetic model

The model is expressed by the following equation (Chen and Hashimoto, 1980):

$$S/S_0 = (S_b + S_r)/S_0 = R + (1 - R)K/(\mu_m t - 1 + K) \quad (3)$$

where, S<sub>0</sub> is initial (total) organic matter content, S is organic matter content at time t (S = S<sub>r</sub> + S<sub>b</sub>), S<sub>r</sub> is the refractory component of the substrate, S<sub>b</sub> is biodegradable component of the substrate, R is the refractory coefficient, K is Chen and Hashimoto dimensionless kinetic constant, and μ<sub>m</sub> is maximum specific growth rate of microorganisms, day<sup>-1</sup>.

Biodegradable organic matter content is measured by means of CO<sub>2</sub>-C emission in aerobic compost processes in common. Remaining organic matter content is an indicator of CO<sub>2</sub>-C emission.

Eq. (3) could be expressed in terms of percent CO<sub>2</sub>-C evolution as follows:

$$CO_2 - C = 100 - 100 \times (R + (1 - R)K/(\mu_m t - 1 + K)) \quad (4)$$

The kinetic constants (μ<sub>m</sub>, K) and refractory coefficient (R) of the model were estimated by non-linear regression technique. The results presented in Table 3 show that kinetic constants for turned reactors were higher than unturned reactor, while R value was high for turned reactors. The values of R averaged 0.33 and 0.52 for turned and unturned reactors, respectively. The biodegradation of mixtures that contain higher percentage of OFMSW leads to increase in K values for K1–K3 reactors. μ<sub>m</sub> increases with the increase

in OFMSW in the reactor for both turned and unturned reactors due to higher easily biodegradable nature of OFMSW than RPW. For the small K values, degradation occurs more rapidly than for large K values.

Chen and Hosshimoto's kinetic model is consistent in its estimation of kinetic parameters and estimated values of CO<sub>2</sub>-C emission are very close to the experimental value. Average relative errors for Chen and Hosshimoto's kinetic model were about 2.14–3.60% except for K5 reactor.

3.5.4. Levi-Minzi kinetic model

Levi-Minzi model was used by Levi-Minzi et al. (1990) to express net mineralization with an exponential kinetic

$$C_t = kt^m \quad (5)$$

where k and m are constants, k characterizes the units used for the variables (mg/kg day) and m the shape of the curve.

Levi-Minzi coefficients are presented in Table 3 for all reactors. The values of k were found to be in the ranges of 8.40–10.53 and 6.82–11.46 mg/kg day for turned and unturned reactors, respectively. In comparison, Fernández et al. (2006) found k and m values as 4.28 mg/kg day and 0.54 for soils amended composted sewage sludge.

3.6. Evaluation of kinetic models

Total organic matter comprises of nonbiodegradable fraction referred to as refractory compounds and biodegradable fraction. First-zero-order and first-first-order models describe a two-step mechanism that is interpreted as rapidly and slowly controlled processes, both of them occur simultaneously. Thus, the subject of the composting kinetics is complex and there is often no sharp distinction among rapid, slow, and nonbiodegradable fractions, particularly in composting systems where long retention times are sometimes required for complete stabilization (Haug, 1993).

First-zero-order and first-first-order models were compared to determine their performance to follow experimental data for K1 (Fig. 5). Almost all reactors exhibit same

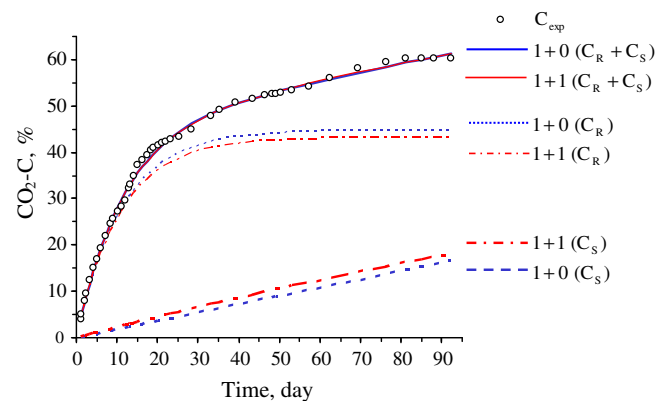


Fig. 5. Comparison of rapid and slow biodegradable fractions of RPW according to 1+0 and 1+1 kinetic models for K1 (The mixture ratios RPW:OFMSW; 4:1).

kinetic behavior during the process occurring in two phases, rapid and slow biodegradation. Average relative errors are almost the same for first-zero-order, first-first and Chen and Hoshimo's models, indicating that these models best describe the RPW composting process. On the other hand, Levi-Minzi model shows lower representation of the data than all other kinetic models.

The applicability of all the models to the composting of RPW implies that heterogeneous oxidation conditions exist under the experimental conditions. The biodegradation of RPW is thus complex, involving more than one reaction mechanism.

Time to reach 40% CO<sub>2</sub>-C evolutions ( $t_{\text{CO}_2\text{-C},40\%}$ ) for turned reactors (K1, K2, K3) and unturned reactors (K4 and K5) were 18, 16, 15 and 62, 36 days, respectively (Table 3).

#### 4. Conclusions

The following conclusions can be drawn from this study:

- The biodegradation of the OFMSW is affected in the different ratio of RPW additive. In other words, the CO<sub>2</sub> evolution decreases slightly with increasing of the RPW amount in the RPW–OFMSW mixture.
- The turning operation provides a homogeneous microbial activity in the mixtures and consequently enhances the CO<sub>2</sub> evolution. The stabilization process was completed after nearly 3 weeks as depending on the mixture composition and turning procedure.
- The kinetic behavior of the process consists of two phases as the rapid and slow degradation. The best fitting kinetic model is the first-first-order. First-zero-order fitting was also quite close to the best. The others, Chen and Hashimoto's and Levi-Minzi's models were not good.
- Time to required reaching to 40% CO<sub>2</sub>-C emission for an unturned reactor is roughly 2–3 times higher than a turned reactor.

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