MODELLING THE AEROBIC DEGRADATION OF ORGANIC WASTES BASED ON SLOWLY AND RAPIDLY DEGRADABLE FRACTIONS

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Abstract

Several organic wastes of major production in the world (municipal solid wastes, wastewater sludge, manures and bulking agents) and some already treated organic wastes have been investigated to determine the partition among the several fractions that compose them and their kinetics of biodegradation. Different literature models have been explored for their suitability to predict the behaviour in respiration studies of these wastes. All the models presented limitations related to their simplicity or their excessive complexity, which makes them unsuitable for reliable and fast studies at real scale. A new model based on the rapid, the slowly and the inert organic fractions has been tested for all the wastes, showing excellent correlations with actual respiration activity. Finally, the kinetic parameters for this model in its application to all the wastes studied are presented.

Keywords: Biodegradation kinetics; Organic matter characterization; Biodegradability; Respirometry; Composting.

1. Introduction

The increasing amounts of organic solid wastes generated by municipalities, industries or agricultural activities have become a worldwide problem. Among the available technologies to treat and recycle organic wastes, composting is presented as one of the most useful options to recycle organic materials to obtain a valuable organic fertilizer or amendment known as compost.

The proper knowledge of the characteristics of the wastes to be composted is essential to carry out the process in a favourable way to obtain the desirable compost quality. The aerobic biodegradation potential can be defined as the organic carbon content that can be biodegraded and transformed into carbon dioxide, and it is a key parameter to be considered for the optimal design and performance of the composting process. Often, the total organic carbon (TOC) content is not a reliable measure for this purpose since the recalcitrant or inert carbon fraction can be sometimes higher than the biodegradable organic carbon (BOC) fraction of the sample. In addition, the knowledge of the kinetic parameters regarding the aerobic biodegradation reactions can be very helpful for the determination of the time required for a correct stabilization of the material (Lasaridi and Stentiford, 1998).

The initial C/N ratio is one of the most important factors affecting the composting process and the compost quality (Epstein, 1997; Zhu, 2007). Traditionally, the assessment of the C/N ratio in solid samples has been determined on a total organic basis through the determination of total organic carbon (TOC) and total nitrogen (N) via chemical analyses (Bisutti et al., 2004). In consequence, the C/N ratio used as an indicator of the composting process has been typically determined assuming that both nutrient sources are fully biodegradable (Eiland et al., 2001; Huang et al., 2004; Zhu, 2007). However, it seems clear that only a percentage of the carbon is really biodegradable (BOC) and only a certain BOC fraction is capable of being biodegraded during the restricted treatment time of biological processes at industrial/full scale. When an unbalanced C/N ratio based on chemical content is considered, some unwanted processes can occur such as ammonia emissions, losses of nitrogen in compost or biological source limitations. The present study is focused on the determination of BOC and its rapidly biodegradable (C_R) and slowly biodegradable (C_S) fractions under aerobic conditions. The analysis of C_R and C_S could be achieved by using a simple kinetic model. C_R and N values would be the most appropriate values for reliable determinations of the real C/N ratio. In fact, such a simple model would be of high interest for the management of composting plants in terms of process duration, plant real capacity and aeration requirements.

There are some publications related to the biodegradation potential and kinetic analysis of organic wastes, the most worthwhile recent ones being published by Adani et al. (2004), Trémier et al. (2005), Komilis (2006), Tosun et al. (2008), Bueno et al. (2008) and de Guardia et al. (2010), among others. In all these studies, except in Tosun et al. (2008), complex models are developed and tested to describe the aerobic biodegradation of wastes, obtaining the biodegradation kinetic rate constants and the different fractions in which organic matter (or organic carbon) can be classified depending on its biodegradation rate. All these models provide valuable scientific information. However, they are not easy to apply to real treatment processes, since many analyses (including physical, chemical and biological determinations) and process monitoring are required. Moreover, they are not valid for all the wastes currently composted because some kinetic parameters are only suitable for specific types of wastes such as sewage sludge (Trémier et al., 2005). On the contrast, Tosun et al.

(2008) report some simple models, which are easy to apply. However, they have not been tested with a wide range of different wastes of diverse biochemical composition.

The objectives of this study are: 1) to test some proposed models for the determination of the biodegradable organic matter content; 2) to develop a respirometric methodology and an easily applicable mathematical model that is able to characterize the waste initial organic carbon composition, defined as rapidly (C_R), slowly (C_S) and non-biodegradable or inert (C_I) fractions, and the kinetic rate constants associated with each biodegradable fraction and 3) to provide useful information in terms of material biodegradability for the management and design of composting processes.

2. Materials and Methods

2.1. Organic Wastes

Ten organic samples of different origins and at different stages of biodegradation were used in this work to include composting plants feedstocks and final products. A first group of raw wastes were composed of: mixed municipal solid waste (MSW), the source selected organic fraction of municipal solid waste (OFMSW), raw sludge (RS) and anaerobically digested sludge (DS) from wastewater treatment plants, pruning waste (PW), solid fraction of pig slurry (PM) and cow manure (CM). A second group of biologically treated wastes included: digested and further composted OFMSW (C-OFMSW), mature and refined compost from composted OFMSW (F-OFMSW) and composted wastewater sludge (CS).

All the municipal organic samples (MSW, OFMSW, C-OFMSW and F-OFMSW) were obtained from a mechanical-biological treatment (MBT) plant located in Barcelona (Spain). Briefly, the plant operation is divided into three successive units: i) mechanical pre-treatment (to extract non-organic materials such as plastics, glass and metals for recycling), ii) anaerobic digestion (21 days) and iii) composting (2-4 weeks). The plant processes both the OFMSW and MSW in two independent lines with a total capacity of 240,000 Mg per year. The complete and detailed information about the plant can be found in a previous study by Ponsá et al. (2008). RS and DS were directly obtained from the sludge dehydration lines of the Besòs (Barcelona, Spain) and Sabadell (Barcelona, Spain) municipal wastewater treatment plants, respectively. CS came from the Olot (Girona, Spain) composting plant, that processes municipal non-digested wastewater sludge using the invessel (tunnel) technology for rapid decomposition and static aerated piles for maturation (Cadena et al., 2009). PM and CM samples were selected as typical farm wastes around the Barcelona province and they were collected from a farm in Vic (Barcelona, Spain). No composting was carried out in these farms at the moment of collection. Finally, a sample of PW from La Selva (Girona, Spain) composting plant was studied as a waste typically used as a bulking agent in composting processes. This plant also uses the invessel (tunnel) technology for rapid decomposition and static aerated piles for maturation (Ruggieri et al., 2008).

Following Ponsá et al. (2010a), analytical methods were carried out on a representative sample (approximately 40 kg) obtained by mixing four sub-samples (10 kg each) taken from different points of the bulk material. Samples derived from MSW and the OFMSW were ground to 15-20 mm particle size to reduce the dimension of the original materials. All the samples were frozen at -18°C within 12 hours after sampling. Before each analysis the samples were thawed during 24 hours at room temperature.

2.2. Respirometric tests

Microbial respiration was measured as O_2 consumption and CO_2 production in a dynamic respirometer built and started-up by Ponsá et al. (2010a), which is based on the methodology described by Adani et al. (2006).

Briefly, a 150 g organic sample was placed in a 500 mL Erlenmeyer flask that was introduced in a water bath at 37 ºC. A constant airflow was supplied to the sample and the on-line O_2 and CO_2 contents in the exhaust gases were measured and monitored. From the curves of oxygen concentration vs. time and carbon dioxide vs. time, two Dynamic Respirometric Indices (DRI or simply DRI) related to O_2 consumption or CO_2 production were obtained from each sample. DRI represents the average oxygen uptake rate during the 24 hours of maximum biological activity observed during the respirometric assay and it reports the stability degree (Adani et al., 2004; Ponsá et al., 2010a). It is expressed in mg of O_2 consumed per g of dry matter per hour. However, to achieve the objectives of this study, the DRI is also required to be expressed in mg of CO_2 produced per g of dry matter per hour.

All measurements were carried out in duplicate. Low porosity samples were mixed with an inert bulking agent (only in the case of wastewater sludge: RS and DS and manures: CM and PM). This bulking material is formed by small pieces (20 x 10 mm) of a biologically inert material (Spontex, Iberica) and mixed with the sample in a 1:10 wet weight ratio (bulking agent:sample).

2.3. Biodegradable Organic Carbon (BOC)

The cumulative CO_2 production was calculated to know the total BOC content for each sample using a methodology presented by Ponsá et al. (2010a) to determine the cumulative oxygen consumption for a specific time.

An increase in the time of the respirometric test permitted the determination of the total cumulative CO_2 production. The time required depended on the bio-stability of each sample; in consequence, the determination was finished when the CO_2 production rate was negligible. It was assumed that the assay could be finished when the measure of oxygen uptake rate (OUR) was below 5 % of the maximum OUR achieved during the respiration experiment (Komilis, 2006; Sánchez, 2007).

As it is well known, during the aerobic degradation of organic matter the biodegradable organic carbon is transformed by oxidation to CO_2. Thus, the total CO_2 production measured by the respirometric test is an indirect BOC measure of a sample, since this fraction is all the carbon dioxide produced by means of the biological activity. From these data, and considering that one mol of CO_2 corresponds to one mol of C, BOC can be calculated as a dry weight percentage from the final cumulative CO_2 production and the molecular weight ratio between carbon and carbon dioxide (12/44), as shown in Equation 1.

$$BOC(\%, db) = \mathit{final\ cumulative\ CO_2\ production}\left[\frac{mg\ CO_2}{g\ DM}\right]\cdot\frac{12}{44}\cdot\frac{100}{1000} \qquad \text{Equation (1)}$$

where: BOC is the biodegradable organic carbon; the final cumulative CO_2 production (or carbon mineralized) is expressed in mg CO_2 g DM^{-1}; 12 and 44 are the molecular weights of C and CO_2, respectively; 1000 is the conversion factor from mg to g and 100 is used to express BOC as percentage (dry matter basis).

Finally, it is necessary to point out that the main objective of this methodology is to determine the biodegradable organic carbon under composting conditions. Consequently, neither inocula nor additional nutrients were added.

2.4. Analytical methods

Water content, dry matter (DM), organic matter (OM) content and total organic carbon content (TOC) were determined according to the standard procedures (The U.S. Department of Agriculture and The U.S. Composting Council, 2001). Three replicates were analysed for each sample.

2.5. Assessment of biodegradable organic matter fractions through biodegradation kinetics modelling

Data of cumulative CO_2 produced or mineralized was fitted to the four models described by Tosun et al. (2008) to characterize the biodegradable organic matter content of a given waste by means of quantitative measures of the easily and the slowly biodegradable organic matter fraction and the biodegradation kinetic rate constants. These models were considered as a first approach since they were simple and easy to apply, although some of them do not consider the fractionation of the biodegradable organic matter. However, it should be mentioned that these models are mainly empirical, as they do not imply a structured modelling of organic matter and its biodegradations by specific microbial communities, unlike other published models (Solé-Mauri et al., 2007).

The four models are described below:

1) First-zero-order kinetic model:

The first-zero-order kinetic model is expressed as:

$$C = C_R(1-\exp(-k_R t)) + C_S k_s t \qquad \text{Equation (2)}$$

where: C is the cumulative C-CO_2 mineralized (or produced) at a given time t (days) (%, on TOC basis); C_R is the rapidly biodegradable TOC fraction expressed as percentage of remaining TOC (%, on TOC basis); C_S is the slowly biodegradable TOC fraction expressed as percentage of remaining TOC (%, on TOC basis); and k_R and k_S are the rapid and slow rate constants (day^{-1}), respectively.

- First-first-order kinetic model:

The first-first-order kinetic model is expressed as:

$$C = C_R(1-\exp(-k_R t)) + C_S(1-\exp(-k_s t)) \qquad \text{Equation (3)}$$

where the parameters are the same as those of Equation (2).

- Chen and Hashimoto's kinetic model:

The model is expressed by the following equation as suggested by Tosun et al. (2008):

$$C = 100 - 100 \times (R + (1-R)K/(\mu_m t - 1 + K)) \qquad \text{Equation (4)}$$

where R is the refractory coefficient, K is the Chen and Hashimoto dimensionless kinetic constant and μ_m is maximum specific growth rate of microorganisms (day^{-1}).

- Levi-Minzi's kinetic model:

Levi-Minzi's model expresses the net mineralization of organic matter with an exponential kinetic:

$$C = kt^m \qquad \text{Equation (5)}$$

where k is a constant that characterizes the units used for the variables used to express organic matter and m is a constant that characterizes the shape of the biodegradation curve.

Matlab v2007a software package (MathWorks Inc., Massachusetts, USA) was used to fit the value of the model parameters presented in Equations 2-5.

3. Results and discussion

3.1. Physico-chemical characteristics

The main properties of the samples studied are shown in Table 1. As expected, dry matter content was higher and organic matter and TOC content were lower in final products than in raw materials. TOC content was around 45 % in most of the raw wastes. Besides, F-OFMSW presented higher organic matter and TOC contents than C-OFMSW, since inert materials and bulking agents were removed after the final product post-treatment (Ruggieri et al., 2008). In MSW and OFMSW samples, the values found for TOC and OM content are statistically similar, which again highlights the difficulties of having these values with an acceptable precision when dealing with these extremely heterogeneous wastes. This supposes a clear limitation of the models only based on TOC when they are applied to bulk municipal wastes.

3.2. Dynamic respiration index (DRI)

Table 1 shows the DRI based on the CO_2 production and O_2 consumption to know the carbon degradation rate and the stability degree, respectively. It is assumed that 1 mg O_2 g OM^{-1} h^{-1} is the maximum DRI threshold for biological stability (Adani et al., 2004; Baffi et al., 2007). Only C-OFMSW, F-OFMSW, CS and PW were below this limit and could be considered stabilized samples with low rapidly biodegradable organic matter content. On the contrary, high stability indices were found for RS, CM, OFMSW, MSW and DS. Recently, Ponsá et al. (2010a) has presented a qualitative classification of wastes into three categories, which are based on the material typology and its stability respiration indices. According to this classification, RS, PM and OFMSW are highly biodegradable wastes because they present a stability index higher than 5 mg O_2 g DM^{-1} h^{-1}; DS and CM can be classified as moderately biodegradable wastes since they present a DRI between 2 to 5 mg O_2 g DM^{-1} h^{-1} and the rest of the materials are wastes of low biodegradability, which have a DRI below 2 mg O_2 g DM^{-1} h^{-1}. The only exceptional case in this study is the abnormally low respiration value of mixed MSW, which in other studies is clearly within the range of moderately biodegradable wastes (DRI within 2 and 5 mg O_2 g DM^{-1} h^{-1}). The reason for this value must be found in the inherent variability of MSW (Ponsá et al., 2008; Ponsá et al., 2010a; Ponsá et al., 2010b).

3.3. Biodegradable Organic Carbon (BOC)

The total BOC content of the samples analysed is presented as percentage of dry matter and shown in Table 1. BOC correlated relatively well with total OM ($r=0.801$, $p<0.001$) and it was 29.4 % of OM as average. BOC was determined from a continuous respirometric test; therefore, the evolution of the BOC cumulative consumption could be monitored and it will be used in the following sections. Each sample presented a different total time of assay according to the threshold established to finish the process. Only the pruning waste assay was stopped before reaching this threshold because it behaves as a really slowly biodegradable material and it was considered that in 90 days the assay was long enough for a correct biodegradable carbon determination. Essentially, the DRI obtained for PW was 0.82 mg O_2 g DM^{-1} h^{-1}, which was the lowest value observed for the different raw wastes analysed. After 90 days, OUR was 0.18 mg O_2 g DM^{-1} h^{-1} (20% of DRI and the lowest value observed for any analysed waste).

As expected, most of the samples obtained after anaerobic digestion and/or composting treatments presented lower BOC values than raw materials since in both biological treatments most of the BOC is biodegraded. According to these data, it can be hypothesized that the total BOC could be directly related to the biological stability degree, which was measured as DRI (Table 1). However, no significant statistical correlation was found. This has been also observed in other studies, where the relationship between the respiration rate and the total oxygen consumed resulted in a deficient coefficient of linear regression (Mojaher et al., 2009). The possible reason is that two different samples can present a similar BOC and very different DRI, depending on their biochemical composition, that is, how rapidly or slowly BOC biodegrades. For instance, PW and RS presented a similar BOC (approximately 18 % on a dry basis), while the DRI of PW was much lower, according to the lower rate of decomposition of fibres. Accordingly, the characterization of BOC and its fractionation into rapidly and slowly degradable fractions would be of interest (Trémier et al., 2005).

3.4. Assessment of biodegradable organic matter fractions through biodegradation kinetics modelling

To provide a quantitative measure of the different fractions of biodegradable organic matter that is contained in organic wastes, the data of CO_2 produced or mineralized were fitted to different models. The objective was to assess the different biodegradable organic fractions by means of a simple, rapid and easily applicable model. Therefore, the percentage of carbon mineralized was calculated as the amount of cumulative C-CO_2 produced at a given time on the basis of the initial total organic carbon (constant value and characterization parameter), which is the BOC/TOC ratio for any given time, as thus a time-variable parameter. The following discussion and evaluation of the biodegradable organic matter fractions will be carried out on the basis of BOC.

The four models described by Tosun et al. (2008) were fitted to the obtained experimental data for the ten different wastes studied. Figure 1 shows the percentage of carbon mineralized with time and the fitting of the four models considered for one of the MSW replicates. A similar behaviour was observed for all the organic wastes except for CS. In this case, any of the tested models provided a good fitting.

The kinetic parameters obtained when fitting the experimental data to the models are shown in Table 2. Levi-Minzi's model did not correctly fit the experimental data. Chen and Hashimoto's model fit to the data was mathematically acceptable, but the resulting parameters did not offer reliable information; with K values ranging from 1 to 10^{16} and μ_{max} ranging from 1.7 to 10^{13} depending on the waste considered. Consequently, both models were not considered in further discussion.

First-zero-order and first-first-order models fitted well to the experimental data, but the best fit was observed for the first-first-order kinetic model, with correlation coefficients that were always near to 0.99.

Higher values of C_R were obtained for F-OFMSW (16.19%) than for C-OFMSW (6.06%). As previously commented, this can be explained by the organic matter concentration occurring in the MBT post-treatment where the material, after being composted, is subjected to bulking agent separation and inorganic material removal before commercialization. Another possible explanation could be the presence of intensive anaerobic digestion in the case C-OFMSW.

As expected from the DRI data, the lowest content of rapidly mineralizable fraction (C_R) was obtained for C-OFMSW and PW. In general, it was observed that wastes with high DRI also presented high values of C_R. However, no significant correlation was found between C_R or k_R and DRI.

The data presented in Table 2 confirmed a low content of rapidly biodegradable organic carbon content (or equivalently biodegradable organic matter content) in treated samples and in pruning waste. On the contrary, raw samples presented a rapidly biodegradable content of organic matter higher than 24%. In the case of pig manure, although the first-first-order model fitting showed a relatively small fraction of rapidly biodegradable carbon (9.67%), the high kinetic constant k_R observed (0.547 day^{-1}) is in agreement with the high DRI observed (Table 1).

When analysing and discussing these results, it is important to consider the limitations that this methodology presents. The first-zero-order and first-first-order models permit the classification of the carbon content into two different categories: easily and slowly biodegradable fractions. However, this does not necessarily mean that, for example, the characteristics of the easily organic matter contained in a sample of the OFMSW may be comparable to the same fraction in a sample of pig manure. The unique equivalent meaning for all samples is the next: the easily biodegradable fraction of a given waste has a biodegradation rate constant much higher than the slowly biodegradable fraction. In this sense, it is very important to simultaneously consider both parameters: the percentage of easily biodegradable carbon and the corresponding biodegradation rate constant. The higher the rate constant is, the faster the biodegradation takes place on the rapidly biodegradable waste fraction. In conclusion, a general classification for a sample with different organic fractions can be established from the first-first-order model fit. It can be considered that a sample or a fraction is easily biodegradable if the biodegradation constant rate ranges from 0.096 to 0.6 day^{-1} and slowly biodegradable if it ranges from 0.001 to 0.011 day^{-1}. When biodegradation constant rates are equal to 0 or lower than 0.001 day^{-1}, the corresponding organic or carbon fraction of the entire sample could be considered as inert organic matter. Similar conclusions can be obtained from the data presented by Tosun et al. (2008). Also, according to results reported in Komilis' kinetic study (Komilis, 2006), the threshold estimation between both fractions is obtained for biodegradation constant rates of approximately 0.05 day^{-1}.

However, the most important limitation when using the first-zero-order and the first-first-order models is the consideration of the non-biodegradable (inert) organic matter or organic carbon as a slowly biodegradable fraction. This leads to non-completely reliable results as there is a wide group of organic wastes in which this fraction can be significant or even predominant, as discussed later.

Two additional models that permit the characterization of easily and slowly biodegradable organic matter fractions were considered in this study. The model suggested by Komilis (2006) was more complete than those described by Tosun et al. (2008), but it requires additional chemical analysis (final TOC and initial dissolved organic carbon) and it was discarded according to the aims of this work. The model suggested by Trémier et al. (2005) was also fitted to experimental data. This model had been optimized for sludge:bulking agent mixtures and provided good results for the sludge experimental data of this work (data not shown). However, the model did not properly fit the respirometric profile of the rest of wastes. Trémier's model requires five kinetic parameters and two stoichiometric parameters to estimate the three active compounds present in the substrate: biomass, rapidly and slowly biodegradable fractions. The determination of these seven parameters of the model requires performing experiments with substrates of different biochemical composition. In consequence, model optimization is necessary for each waste prior to its use. For this reason, Trémier's model was also discarded in this study, although it is evident that it can be of use if the specific characteristics of a waste are well known.

To overcome the limitations of the first-zero-order and first-first-order models described by Tosun, the first-first-order model was modified to include the three different fractions in which organic matter or carbon can be divided: C_R, C_S and inert fraction (C_I).

The exact concept of the Tosun model and its mathematical expression is unable to predict the inert fraction. However, instead of monitoring the evolution of the carbon emitted in form of CO_2, the remaining carbon that still has not been degraded can be monitored, by assuming that the initial TOC corresponds to the 100% of the carbon in the sample and subtracting the carbon emitted from this initial value. The remaining carbon of the sample can be expressed as a percentage of the initial TOC and some profiles based on this procedure can be observed in Figure 2.

The mathematical modelling of these data corresponds to the following expression:

$$C_W = C_R \exp(-k_R t) + C_S \exp(-k_S t) + C_I \qquad \text{Equation (6)}$$

where: C_W is the remaining carbon of the sample (%) at time t (days), C_R and C_S are the percentages of rapidly and slowly biodegradable fractions, respectively, C_I is the inert fraction and k_R and k_S are rapid and slow rate constants (day^{-1}), respectively. This expression consists of two exponential decay terms (first-order kinetics) and an independent and constant term.

Although it is not always necessary, when fitting the model is recommendable to add the restriction of the equivalency of the total biodegradable carbon fractions (C_R plus C_S) to the total BOC degraded. Otherwise, the model could lead to wrong results since all the organic matter in the sample could be considered as potentially biodegradable. This implies a previous chemical analysis of TOC as well as the biological analysis of BOC for all the samples studied.

All data from the wastes analysed were fitted to this model and the results obtained are shown in Table 3. The model fittings and the evolution of C_R, C_S and the evolution of organic matter degradation when no distinction between C_R and C_S can be distinguish (C_{BIO}) is provided by the model and are plotted in Figure 2 for all the wastes analysed (time scales are different for each waste to clearly observe the model fitting).

After fitting the experimental data to the model, it can be concluded that this model permits the determination of the three carbon or organic matter fractions (C_R, C_S and C_I) and the two biodegradation rate constants (k_R and k_S). This method is more reliable than those proposed by Tosun, since the consideration of non-biodegradable carbon as a part of the total organic carbon is clearly necessary for a complete waste characterization. In this regard, values of C_R and C_S and the new C_I fraction are different from those obtained in Tosun models. In addition, this model is validated by the wellness of the model fitted to the experimental data ($p<0.001$ in all cases) and by the correlation coefficients ($r>0.97$ in all cases).

Although it is not presented in Table 3 for C-OFMSW, F-OFMSW, PW and CS, the proposed model gives values for both C_R and C_S. However, the kinetic constants k_R and k_S present the same numeric value and consequently the organic matter included in C_R and C_S fractions is mathematically equivalent. Therefore, when considering the values of the kinetic rate constants, it can be observed that biologically treated wastes and wastes in which low biodegradation potential is expected (such as PW) only present one type of organic matter, which can be classified as slowly biodegradable. In this case, the kinetic rate constants are always lower than 0.12 day^{-1}.

On the contrast, two different fractions of organic matter with different biodegradation rate constants are obtained for all the raw waste samples with a low standard deviation among the replicates analysed. The difference between the biodegradation rate constants is always higher than 61%, which means that C_R and C_S have clearly different biodegradation characteristics. From these results, the threshold between rapidly and slowly biodegradable carbon rate constants would be approximately between 0.12 and 0.24 day^{-1}, although this difference is not absolute and only an estimation. Additional experiments with other waste typologies would help in establishing this limit with more accuracy.

All the samples have a percentage of organic matter that is not biodegradable (C_I) and this value is directly estimated by the model fitting. As expected, the biologically treated wastes are those that present the highest percentage of non-biodegradable carbon, ranging from 94% (for CS) to 82% (for C-OFMSW). On the contrary, feedstock samples always present a percentage of C_I lower than 73%, except for the case of DS when C_I values are close to 80%. DS is a special case, since it presents a C_R value around 10% when the total biodegradable organic carbon is similar to those wastes with a low biodegradation potential. Probably, this is due to the presence of hydrolysed organic matter that have not been biodegraded by the methanogenic bacteria during the process of anaerobic digestion and that it is easily biodegradable organic matter under aerobic conditions.

The wastes with the highest biodegradable organic matter percentages were the OFMSW (54%) and CM (49%). The wastes with the highest C_R fraction were the OFMSW and RS with values around 13%. The highest k_R (1.5 day^{-1}) was obtained for PM waste. The lowest k_S value was obtained for PW, which indicated that this waste was the most slowly biodegradable but not the least biodegradable, since C_I only represented 50% of the initial TOC.

When comparing the values obtained from the proposed model with the values obtained from Tosun models, it is evident that the values significantly differ, since initial considerations are also different. In this new adapted model, k_R is never lower than 0.24 day^{-1}, whereas in Tosun models carbon was considered as rapidly biodegradable when k_R was higher than 0.096 day^{-1}. Probably the existence of the inert carbon fraction that is not considered in Tosun models causes a reduction effect in the resulting kinetic constants for C_R and C_I. Further studies are necessary to clarify this point.

Finally, it can be considered that an entire sample or fraction is rapidly biodegradable when the biodegradation constant rate is over 0.25 day^{-1} and it can be considered as slowly biodegradable when biodegradation constant rate ranges approximately from 0.001 to 0.12 day^{-1}. When biodegradation constant rates are equal to 0 or lower than 0.001 day^{-1}, the corresponding organic or carbon fraction or the entire sample could be considered as inert organic matter. These results are not in agreement to those obtained by Komilis (2006) and establish a new classification and methodology to discern among the biodegradation potentials of different wastes that can be used to consistently characterize the waste organic matter fractions in terms of biodegradability.

DRI results can not be directly related to a single parameter of the model. High values of DRI are a consequence of high C_R values with a moderate k_R or moderate values of C_R with high values of k_R. This is in accordance to Ponsá et al. (2010a), who concluded that DRI can not be used as a single parameter to determine a waste aerobic biodegradability potential and, in consequence, longer and cumulative aerobic respirometric indices need to be used. Alternatively, the correlations between DRI and the product $C_R k_R$ for the six feedstocks used in the study were checked. The results were: for OFMSW, RS, CM and PM: $r = 0.991$; adding MSW: $r = 0.951$ and adding DS: $r = 0.861$; all of them with $p < 0.05$. This can be of high interest because it establishes a new relationship between a very fast parameter to characterize a waste (DRI) and parameters that are inherent to the model proposed for the biodegradation of a given waste. In fact, it means that DRI is reflecting the rapidly biodegradable organic matter of a waste, as it can be statistically correlated with the product C_Rk_R for different organic wastes of different biochemical composition. The research of the possible relationships between DRI and other kinetic parameters can be the objective of further investigations.

4. Conclusions

The present work establishes a new respirometric methodology that permits a complete organic matter characterization by fitting the experimental respiration data to a simple and an easy-to-apply mathematical model based on the monitoring of the organic carbon depletion. This new model approach overcomes the limitations, complexity and considerable physico-chemical analysis required in the existing methodologies and models.

Different raw and biologically treated wastes have been completely characterized in terms of C_R, C_S, C_I, k_R and k_S, which presents a new classification based on their biodegradation rates.

The results from the model cannot be directly correlated to DRI, which indicates, as suggested in Ponsá et al. (2010a), that the organic matter in real wastes can not be characterized by a unique parameter. Therefore, the different organic matter fractions and biodegradation rates must be considered together for a reliable characterization.

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Tables

Table 1. Characterizations of the different wastes used for the assessment of biodegradable organic matter fractions.

	DM (%, wb)	OM (%, db)	TOC (%, db)	BOC (%, db)	$DRI-O_2$ (mg O_2· g DM^{-1}· h^{-1})	$DRI-CO_2$ (mg CO_2· g DM^{-1}· h^{-1})
MSW	62 ± 6	38 ± 6	34 ± 3	12.6 ± 0.1	1.50 ± 0.09	1.70 ± 0.01
OFMSW	29 ± 3	77 ± 3	44 ± 3	23.4 ± 0.2	4.10 ± 0.06	5.5 ± 0.6
C-OFMSW	65 ± 2	28 ± 3	16 ± 1	1.8 ± 0.2	0.22 ± 0.06	0.26 ± 0.01
F-OFMSW	50.2 ± 0.8	33.3 ± 0.9	38 ± 3	3.7 ± 0.4	0.55 ± 0.07	0.70 ± 0.08
Raw Sludge	29.4 ± 0.8	77.1 ± 0.9	45 ± 3	17.7 ± 0.2	6.1 ± 0.9	6.57 ± 0.03
Digested Sludge	19.6 ± 0.1	54.8 ± 0.1	29 ± 2	11 ± 3	3.2 ± 0.2	2.9 ± 0.3
Composted Sludge	57.4 ± 0.4	65 ± 2	38 ± 4	2.19 ± 0.04	0.14 ± 0.02	0.20 ± 0.01
Cow Manure	23.5 ± 0.2	84.9 ± 0.9	47 ± 3	23.1 ± 0.4	2.69 ± 0.02	3.03 ± 0.08
Pig Manure	12.7 ± 0.3	85.1 ± 0.4	67 ± 4	22 ± 3	5.3 ± 0.2	6.4 ± 0.6
Pruning Waste	60.4 ± 1.1	92 ± 1	42 ± 1	19 ± 4	0.82 ± 0.09	1.1 ± 0.2

wb: wet basis. db: dry basis. OFMSW: Organic Fraction of Municipal Solid Waste. C-OFMSW: Digested and Composted OFMSW. F-OFMSW: Mature and refined compost from composted OFMSW. OM: Organic Matter. DM: Dry Matter. TOC: Total Organic Carbon. BOC: Biodegradable Organic Carbon. DRI: Dynamic Respiration Index (referred to O_2 consumption or CO_2 production).

Table 2. Kinetic parameters for the different models analyzed fitted to experimental BOC respiration evolution determined in this study.

Kinetic model	Model parameter	MSW	OFMSW	C-OFMSW	F-OFMSW	RS	DS	CM	PM	PW	CS
First-zero-order	C_R (%)	33.70	33.96	6.06	16.19	25.06	16.01	50.66	9.62	13.41	0.097
	C_S (%)	66.30	66.04	93.94	83.81	74.94	83.99	49.34	90.39	86.59	99.90
	k_R (day^{-1})	0.10	0.193	0.161	0.127	0.229	0.415	0.095	0.69	0.062	2.786
	k_S (day^{-1})	0.001	0.009	0.002	0.000	0.007	0.001	0.000	0.01	0.004	0.002
First-first-order	C_R (%)	33.57	31.66	5.92	16.18	24.24	16.00	50.58	9.67	7.90	0.068
	C_S (%)	66.43	68.34	94.08	83.82	75.76	84.00	49.42	90.33	92.10	99.93
	k_R (day^{-1})	0.10	0.202	0.165	0.127	0.234	0.416	0.096	0.547	0.182	4.51
	k_S (day^{-1})	0.001	0.011	0.002	0.000	0.008	0.001	0.000	0.006	0.005	0.002
Chen and Hashimoto	R	0.551	0.125	0.822	0.783	0.537	-0.086	0.410	0.006	0.164	-0.256
	K	17.72	1773.7	$2.61\ 10^{11}$	29.43	12.06	$8.17\ 10^{15}$	14.19	1.006	$6.11\ 10^{14}$	$1.14\ 10^{4}$
	μ_{max} (day^{-1})	850.5	63.07	$1.20\ 10^{10}$	3.66	1.96	$5.14\ 10^{13}$	1.736	2.006	$5.64\ 10^{12}$	23.02
Levi-Minzi	k	48942	11.85	1.672	4.135	9.141	8.843	13.59	3.006	2.221	0.262
	m	0.394	0.439	0.564	0.431	0.453	0.225	0.348	4.006	0.657	0.975

OFMSW: Organic Fraction of Municipal Solid Waste. C-OFMSW: Digested and Composted OFMSW. F-OFMSW: Mature and refined compost from composted OFMSW. RS: Raw Sludge. DS: Digested Sludge. PW: Pruning Waste. PM: Solid Fraction of Pig Manure. CM: Cow Manure. PW: Pruning Waste. CS: Composted Sludge. C_R: rapidly biodegradable carbon fraction based on initial TOC. C_S: slowly biodegradable carbon fraction based on initial TOC. k_R: rapid rate constant. k_S: slow rate constant. R: refractory coefficient. K: Chen and Hashimoto dimensionless kinetic constant. μ_m: maximum specific growth rate of microorganisms. k: model constant. m: model constant.

Table 3. Kinetic parameters for new model developed in this study.

Model parameter	C_R(%)	C_S(%)	C_I (%)	k_R (day^{-1})	k_S (day^{-1})
MSW	4.2 ± 0.4	32.34 ± 0.06	63.0 ± 0.9	0.25 ± 0.01	0.08 ± 0.01
OFMSW	13 ± 3	40 ± 2	46.0 ± 0.7	0.30 ± 0.03	0.08 ± 0.01
C-OFMSW	---	12 ± 1	87 ± 1	---	0.08 ± 0.01
F-OFMSW	---	16 ± 2	82 ± 1	---	0.120 ± 0.002
Raw Sludge	12.5 ± 0.9	26.6 ± 0.7	60.9 ± 0.2	0.77 ± 0.07	0.100 ± 0.003
Digested Sludge	10 ± 1	7 ± 1	81 ± 2	0.65 ± 0.01	0.12 ± 0.04
Cow Manure	3.2 ± 0.2	45 ± 1	51 ± 1	0.24 ± 0.05	0.094 ± 0.004
Pig Manure	4.3 ± 0.4	23 ± 1	73 ± 1	1.5 ± 0.2	0.05 ± 0.01
Pruning Waste	---	49 ± 2	50 ± 2	---	0.024 ± 0.003
Compost Sludge	---	5.8 ± 0.1	94.2 ± 0.1	---	0.068 ± 0.001

OFMSW: Organic Fraction of Municipal Solid Waste. C-OFMSW: Digested and Composted OFMSW. F-OFMSW: Mature and refined compost from composted OFMSW. C_R: rapidly biodegradable carbon fraction based on initial TOC. C_S: slowly biodegradable carbon fraction based on initial TOC. k_R: rapid rate constant. k_S: slow rate constant.

Legends to Figures

Figure 1. Evolution of the carbon biodegraded during time and fittings of kinetic models tested for one of the replicate samples of Municipal Solid Waste.

Figure 2. Evolution of carbon remaining in the sample expressed as total organic carbon (TOC), fitting of kinetic model, evolution of C_R and C_S degradation and evolution of organic matter degradation when no distinction between C_R and C_S is provided by the model (C_{BIO}) for one of the replicates of each waste sample analysed in this study. Please note the different time scales. OFMSW: Organic Fraction of Municipal Solid Waste. C-OFMSW: Digested and Composted OFMSW. F-OFMSW: Mature and refined compost from composted OFMSW. RS: Raw Sludge. DS: Digested Sludge. PW: Pruning Waste. PM: Solid Fraction of Pig Manure. CM: Cow Manure. PW: Pruning Waste. CS: Composted Sludge. C_R: rapidly biodegradable carbon fraction based on initial TOC. C_S: slowly biodegradable carbon fraction based on initial TOC.

Fig. 1.

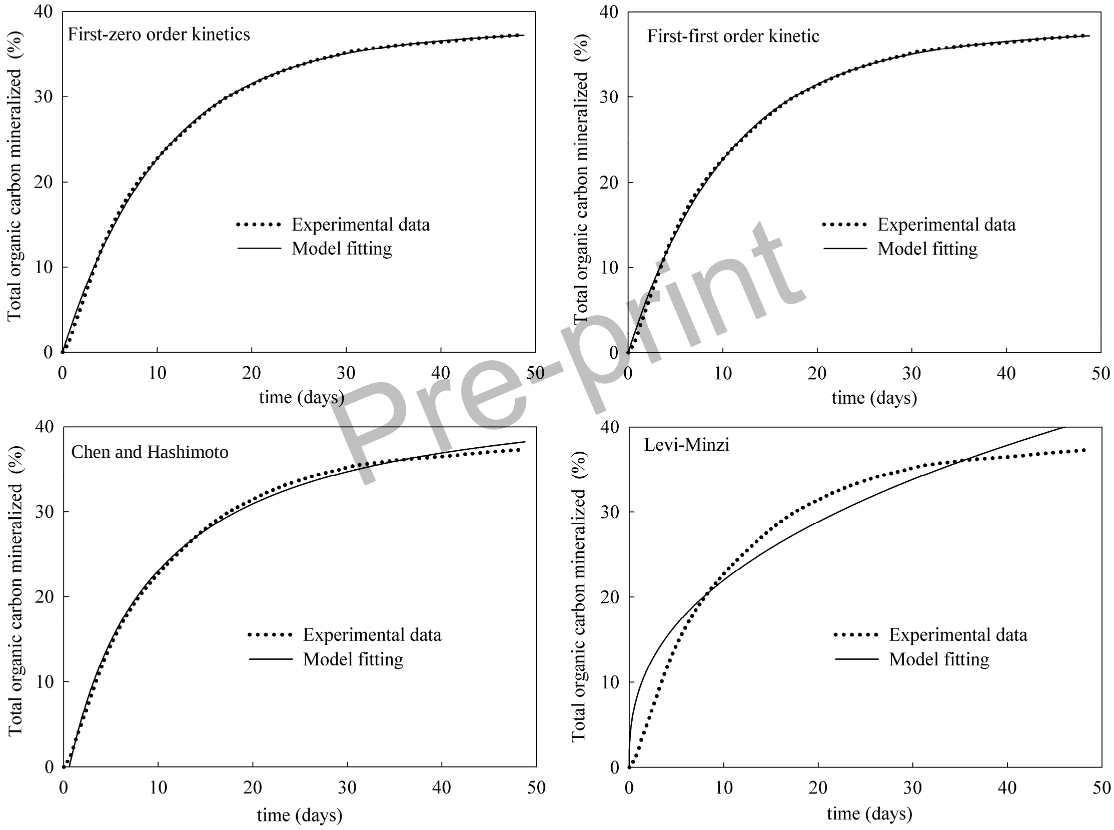
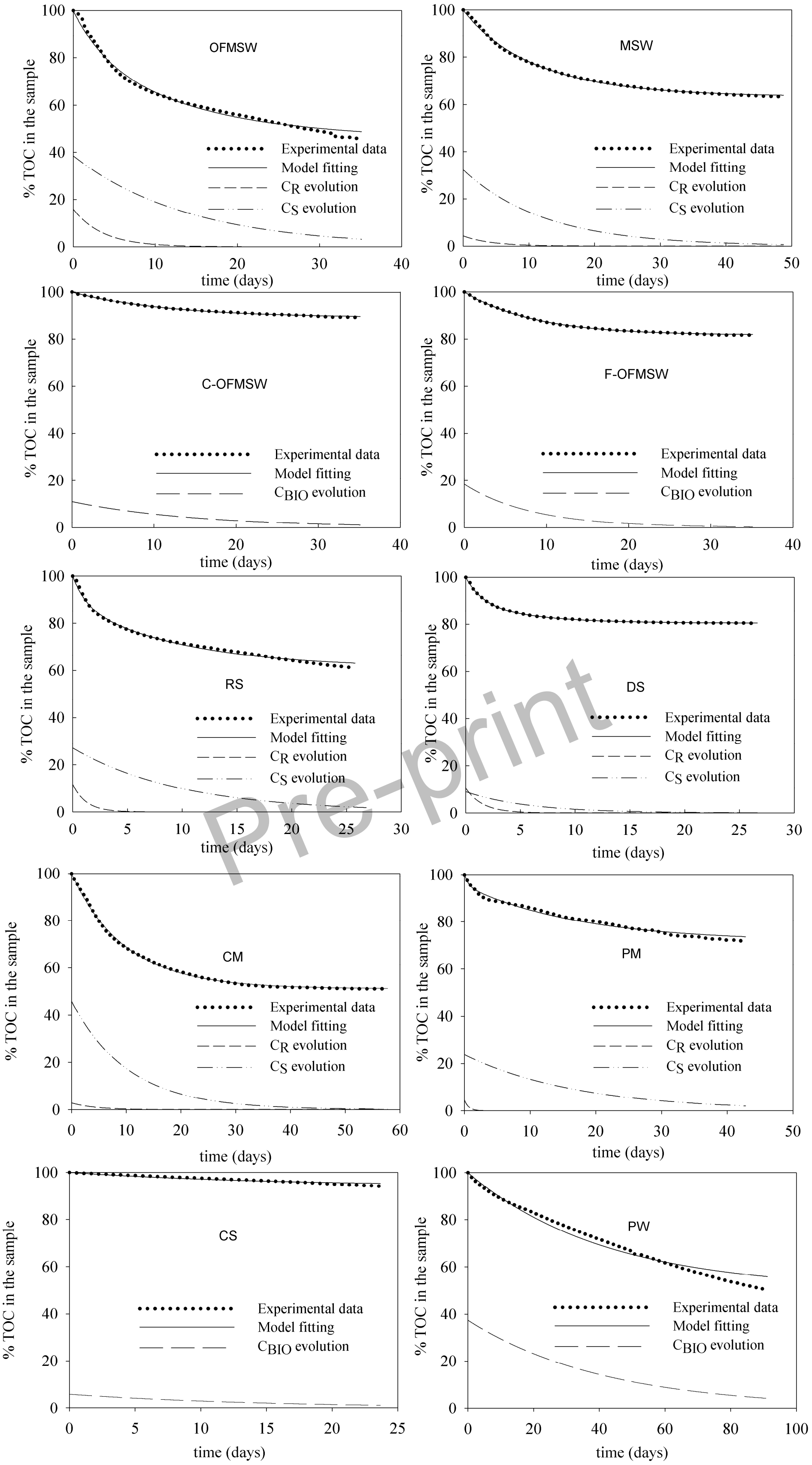

First-zero order kinetics
First-first order kinetic
Chen and Hashimoto
Levi-Minzi
Experimental data
Model fitting
Total organic carbon mineralized (%)
time (days)
0
10
20
30
40
50

Fig.2



OFMSW
MSW
C-OFMSW
F-OFMSW
RS
DS
CM
PM
CS
PW
Experimental data
Model fitting
CR evolution
CS evolution
CBIO evolution
% TOC in the sample
time (days)