Mechanism and kinetics of organic matter degradation based on particle structure variation during pig manure aerobic composting

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HIGHLIGHTS

• The median diameter of manure particles decreased exponentially during composting.
• Pig manure particles were degraded uniformly along different radial directions.
• Particle porosity increased linearly mainly because of hemicellulose degradation.
• Effects of particle structure on organic matter degradation kinetics was quantified.

ABSTRACT

Characterization of the dynamic structure of composting particles may facilitate our understanding of the mechanisms of organic matter degradation during pig manure–wheat straw aerobic composting. In this study, changes in the size, shape, pores, chemical compositions, and crystal structures of pig manure particles during composting were investigated. The results showed that the median diameter ($D_{50}$) decreased exponentially, while the particle aspect ratio and sphericity were unchanged, suggesting that particles were degraded uniformly along different radial directions. Pores had a mean diameter of 15–30 µm and were elliptical. The particle porosity increased linearly mainly because of hemicellulose degradation. Furthermore, the influence of particle structure variation on the first order rate constant ($k$) of organic matter degradation was corrected, which may facilitate the optimization of operation conditions. The $k$ value was proportional to the reciprocal of $D_{50}$ according to the specific surface area of particles, and it decreased with increased porosity due to the stabilized chemical compositions and crystal structures of particles. However, the applicability of these data to other composting materials should be verified.

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1. Introduction

The global production rate of animal manure is projected to increase to approximately 0.23 billion tons nitrogen equivalents per year in 2030 because of the fast-growing livestock population [1]. Aerobic composting is attracting increasing attention for its effectiveness in biodegrading animal manure into humified
end-products that are free of pathogens, and the mechanism of organic matter degradation during aerobic composting is being explored [2]. Some researchers have regarded composting particles as a basic unit of the composting pile, the main characteristics of which are particle size, particle shape, and pore structure [3–8]. Sieving is the principal method used to determine particle size distribution (PSD). Pig manure particle size has been shown to decrease during aerobic composting [9,10], and similar results have been obtained for olive mill waste composting and tomato crop residue–almond shell composting [5,11]. Given the limitations of measurement methods, particles have been roughly characterized as having a discrete PSD, and the mean particle size needs to be quantified [7]. Previous studies have often assumed substrate particles to be spherical [3–5]; however, few reports have described the shape parameters of composting particles. Pores are thought to be distributed primarily on the surfaces of composting particles because of the intensive microbial activities occurring on particle surfaces [12,13], but additional studies are required to determine the validity of this assumption and to quantitatively characterize the changes in the pore structure.

Digital and thin-section image analyses are effective methods for characterizing the microscopic features of particles and pores, respectively. These methods have been used to measure the PSD and particle shape for various biomass materials, such as straw pellets, bagasse, and soy hulls [14,15], and have allowed the quantification of soil pore size [16,17].

In this study, we used pig manure as the main reactant and quantified the structural changes of pig manure particles (particle size, particle shape, and pore structure) during aerobic composting. Additionally, we explored the relationship between these changes and the kinetics of organic matter degradation. The results provided theoretical support for the improvement of composting models to simulate organic matter degradation, which may facilitate the optimization of operation conditions.

2. Materials and methods

2.1. Aerobic composting experiments

Pig manure was collected from the livestock and poultry test site of the Chinese Academy of Agricultural Sciences (Changping, Beijing, China). Wheat straw, which was collected from suburban areas of Beijing, was chopped into 3–5-cm lengths and used as a bulking agent. The mass ratio of pig manure to wheat straw was 7:1 to control the moisture content (MC) at around 65%, and the carbon to nitrogen (C/N) ratio ranged from 15 to 20; these conditions are considered appropriate for aerobic composting [2,18]. The materials were mixed thoroughly by hand for about 10 min. A total of 5.6 kg of the mixture was loaded into a 15-L cylindrical composting reactor (0.40 m height × 0.25 m internal diameter; Fig. 1) [19]. Given the variation in pig manure, two independent aerobic composting experiments (Experiments I and II) were performed to reduce errors. The duration of both composting trials was 35 days. The reactor was intermittently injected with an air supply of 0.17 L min−1 kg VS−1 at 1-h intervals to maintain sufficient aeration. The composting temperature was monitored and documented at 20-min intervals using a Pt100 temperature sensor and a programmed data acquisition system (DT85, DataTaker Pty Co. Ltd., Australia) to calculate the mean daily temperature. The volume fraction of oxygen in the upper part of the reactor was recorded when the air was supplied, which was performed five times per day at 07:30, 11:30, 15:30, 19:30, and 23:30 using an oxygen sensor (O2S-FR-T2-18X; Apollo Electronics Co. Ltd., Zhuhai, China) to calculate the mean daily oxygen concentration. On days 0, 7, 14, 21, 28, and 35, 300- g samples were collected after mixing. Samples were frozen at −4 °C until analysis.

2.2. Chemical analysis of raw materials

The MC and organic matter content (OM) of raw materials and initial mixed samples of two experiments were measured according to standard procedures [20]. The C/N ratio was calculated from the total carbon content (Ct) and total carbon content (Nt), which were determined by dry combustion using a Vario EL III elemental analyzer (Elementar, Hanau, Germany). Chemical properties were determined using three replicates for each sample.

Table 1

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Pig manure</th>
<th>Wheat straw</th>
<th>Initial mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment I</td>
<td>Experiment II</td>
<td>p</td>
</tr>
<tr>
<td>MC (%)</td>
<td>71.17 ± 0.78</td>
<td>75.00 ± 0.98</td>
<td>0.006</td>
</tr>
<tr>
<td>OM (%)</td>
<td>84.96 ± 0.04</td>
<td>82.53 ± 2.73</td>
<td>0.199</td>
</tr>
<tr>
<td>Ct (%)</td>
<td>42.30 ± 0.15</td>
<td>43.42 ± 0.84</td>
<td>0.086</td>
</tr>
<tr>
<td>Nt (%)</td>
<td>4.23 ± 0.02</td>
<td>4.37 ± 0.02</td>
<td>0.000</td>
</tr>
<tr>
<td>C/N</td>
<td>9.99 ± 0.01</td>
<td>9.93 ± 0.16</td>
<td>0.532</td>
</tr>
</tbody>
</table>

MC – moisture content; OM – organic matter content; Ct – total carbon content; Nt – total nitrogen content; C/N – ratio of total carbon to total nitrogen; p – significance level. Differences with p values of less than 0.05 were considered statistically significant.

a Based on wet weight.
b Based on dry weight.
2.3. Sample dispersion

Given the inferior biodegradability of straw over a limited time [21,22], pig manure was considered the major reactant, and thus, the structural changes in manure particles and pores were investigated. To minimize the effects of MC and aggregates, the sample was dispersed by freeze-drying mechanical vibration as follows [23]. Mixed samples were frozen at -80 °C for 8 h, dehydrated using an ALPHA 1–2 LD plus freeze dryer (Christ, Osterode, Germany) at -42 °C and 10 Pa for 24 h, and gently dispersed with rubber and glass beads. A 3.0-mm mesh was selected for sieving to obtain pig manure particle samples.

2.4. Characterization of the size and shape of pig manure particles

The size and shape of manure particles were analyzed in three replicates (10 g each) for each sample using a CAMSIZER digital image processing system (Retsch Technology GmbH, Haan, Germany) according to the guidelines of the International Organization for Standardization (13,322-2) [24]. Outputs included the median diameter of the volume (D50) and shape parameters. The value of D50 – considered as the mean particle size – was defined as the cutoff size larger than 50% of manure particles according to volume [25]. Shape parameters included particle aspect ratio (AR) and sphericity (SPHE), which were defined as:

\[
AR = \frac{1}{n} \sum_{i=1}^{n} \frac{W_i}{L_i}
\]

\[
SPHE = \frac{1}{n} \sum_{i=1}^{n} \frac{4\pi A_i}{P_i^2}
\]

where \(n\) is the particle number, \(W_i\) is the width of the \(i\)th particle (\(\mu m\)), \(L_i\) is the length of the \(i\)th particle (\(\mu m\)), \(A_i\) is the area of the \(i\)th particle (\(\mu m^2\)), and \(P_i\) is the perimeter of the \(i\)th particle (\(\mu m\)). The AR value represents overall particle elongation, with a value of 1.0 indicating a perfectly spherical particle, whereas SPHE describes surface irregularity, with a value of 1.0 indicating a perfectly smooth surface [26,27].

2.5. Characterization of the pore structure of pig manure particles

Over 20 particles from each sample were sputter-coated with gold and imaged with an S-3400 N scanning electron microscope (Hitachi, Tokyo, Japan) to observe changes in the surface of pig manure particles.

Internal pores of manure particles were examined in thin sections. Over five particles from each dispersed sample were embedded in optimal cutting temperature compound (Sakura Finetek, Torrance, CA, USA) and sectioned at a thickness of 20 μm on a CM3050-S cryostat (Leica Microsystems GmbH, Wetzlar, Germany). Sections were imaged using a DM 2500 optical microscope (Leica Microsystems GmbH). Image segmentation and analysis were performed with Image Pro Plus 6.0 software (Media Cybernetics, Rockville, MD, USA). Outputs included mean pore diameter (\(d\)), pore aspect ratio (\(ar\)), and porosity [28], calculated as follows:

\[
d = \frac{1}{m} \sum_{i=1}^{m} d_i
\]

\[
ar = \frac{1}{m} \sum_{i=1}^{m} \frac{W_i}{L_i}
\]

\[
\text{porosity} = \frac{1}{A} \sum_{i=1}^{m} a_i \times 100\%
\]
Fig. 4. Representative images of pig manure particles during aerobic composting acquired using (a) SEM at 100× magnification and (b) light microscopy.

Fig. 5. Changes in (a) mean pore diameter ($d$) and pore aspect ratio ($ar$), and (b) porosity of pig manure particles during aerobic composting.
Fig. 6. Changes in organic matter content of pig manure particles during aerobic composting.

where \( m \) is the number of pores, \( d_i \) is the diameter of the \( i \)th pore (\( \mu m \)), \( w_i \) is the width of the \( i \)th pore (\( \mu m \)), \( l_i \) is the length of the \( i \)th pore (\( \mu m \)), \( a_i \) is the area of the \( i \)th pore (\( \mu m^2 \)), and \( A \) is the area of the measured particle (\( \mu m^2 \)).

2.6. Characterization of organic matter of pig manure particles

Changes in OM value of pig manure particles during aerobic composting were measured according to standard procedures [20]. Each sample was determined in three replicates.

Changes in chemical compositions of pig manure particles were characterized by Fourier transform infrared spectroscopy (FTIR). Freeze-dried pig manure particles were mixed and ground with KBr powder to produce a transparent KBr disc. Spectral analysis was performed using a Fourier transform infrared microscope (PerkinElmer Spotlight 400, Waltham, MA, USA). The spectral range, spectral resolution, and scan number were 4000–650 cm\(^{-1}\), 8 cm\(^{-1}\), and 32 times, respectively. For comparison, each spectrum was baseline-corrected at 4000, 2000, and 840 cm\(^{-1}\) using the manufacturer’s software installed on the device (Spectrum, PerkinElmer Inc., USA) [29].

Changes in the crystal structures of pig manure particles were recorded using an X-ray diffraction (XRD) diffractometer (XRD 6000, Shimadzu, Japan) equipped with Ni-filtered Cu Ka radiation operating at 40 kV and 40 mA. Pig manure particles were scanned from 2\( \theta \) = 5–50\( ^\circ \) at a scanning speed of 4\( ^\circ \) min\(^{-1}\) with a step interval of 0.02\( ^\circ \). XRD data analysis software (Jade, Materials Data Inc., Livermore, CA, USA) was used for background correction. The crystallinity index (CI) was calculated as \((I_{22} - I_{16})/I_{22}\), where \( I_{22} \) is the intensity of the crystalline area at 2\( \theta \) = 22\( ^\circ \), and \( I_{16} \) is the intensity of the amorphous region at 2\( \theta \) = 16\( ^\circ \) [30,31].

2.7. Statistics and analysis

One-way analysis of variance and the least significant difference tests were performed, with the significance level set at \( p < 0.05 \), using SPSS v.15.0 software (SPSS Inc., Chicago, IL, USA) to determine the significant differences in (1) initial chemical properties between two aerobic composting experiments and (2) particle shape parameters of different composting stages.

Matlab software (The Mathworks, Natick, MA, USA) was used to perform regression analysis for each parameter and to calculate the coefficient of determination (\( R^2 \)) and standard error of the estimate (SEE).

3. Results and discussion

3.1. Initial chemical properties and composting processes

Chemical properties of raw materials and initial mixtures are listed in Table 1. For the two independent experiments, each value

Fig. 7. FTIR spectral changes of pig manure particles at (a) 2925 cm\(^{-1}\), (b) 1320 cm\(^{-1}\), and (c) 875 cm\(^{-1}\) during Experiment I. FTIR spectral changes at (e) 2925 cm\(^{-1}\), (d) 1320 cm\(^{-1}\), and (f) 875 cm\(^{-1}\) during Experiment II.
was within or near the optimal range for aerobic composting of manure [2]. Statistical analyses showed that there were no significant differences (p > 0.05) between the two initial mixtures, while significant differences were observed in the MC and N\textsubscript{T} of pig manure. However, the freeze-drying process before PSD measurements, thin-section image analyses, FTIR analysis, and XRD analysis can minimize the influence of the MC of pig manure. For the N\textsubscript{T} of pig manure, its effect on the particle structure can be neglected, while the influence on the results of FTIR and XRD analyses could be reduced by employing two independent experiments.

As shown in Fig. 2, oxygen concentrations in two experiments had obvious differences, but both were maintained at more than 5% to ensure an aerobic environment. Additionally, the composting temperature followed the classic three-phase pattern with mesophilic, thermophilic, and cooling phases, and high temperatures (≥50 °C) lasted approximately 5 days, ensuring that pathogens were killed [32]. After composting, the mixture was dark brown and loosely structured, with characteristics similar to those of soil. Moreover, wheat straw was nearly intact, and the length of straws showed almost no change after 35 days of composting. Because microorganisms preferentially used easily degradable carbon sources [21,22], pig manure was considered as the major reactant during the limited composting period. In this study, wheat straw mainly acted as a bulking agent.

3.2. Changes in the structure of pig manure particles

3.2.1. Particle size and shape

As shown in Fig. 3, the D\textsubscript{50} value of pig manure particles at the start of composting was 506 ± 5 μm, which was consistent with the results obtained by the sieving method [33]. The tendency of the particle size to become smaller was consistent with earlier investigations [5,9], and the evolution of D\textsubscript{50} exhibited an exponential decrease:

\[
D_{50} = 428.222e^{77.163e^{-0.144t}} \tag{6}
\]

where t is the composting time (d). The values of R\textsuperscript{2} and SEE were 0.97 and 4.40, respectively. Statistical analyses showed that shape parameters of pig manure particles (AR and SPHE) were constant (Table 2), indicating that the particles were degraded uniformly along different radial directions.

3.2.2. Pore structure of pig manure particles

Scanning electron microscopic (SEM) images and optical micrographs on day 0 showed that initial particles were large, with a relatively smooth external surface and a nearly intact internal structure (Fig. 4). During the mesophilic–thermophilic phase (day 7), there was a dramatic decrease in particle size, cracks had appeared on the particle surface, and an increased number of internal pores was observed, which can be attributed to the high microbial activity [34]. Thus, the substrate was degraded not only from the outer layer of particles, but also from within. The cracks had deepened by day 14, and more fragments were attached to the particle surface on day 21. Between days 28 and 35, the number of internal pores, which showed an elongated shape, multiplied. In general, the structure of pig manure particles changed during the degradation of organic matter; these changes included a decrease in particle size, an increase in surface roughness, and the formation of fragments and pores, consistent with the composting process of other materials, such as oil palm biomass, polyurethane foam, and mixtures of cow manure, animal flesh, and leaf litter [34–36].

Quantification of these changes is illustrated in Fig. 5. The d values fluctuated between 15 and 30 μm (Fig. 5a). According to the classification of pore sizes for soil particles, the pores of pig manure particles were determined to be macropores [37], and pig manure particles exhibited a cellular structure [38]. The ar value remained within 0.6–0.8, except during the last week, with pores maintaining an elliptical shape [39]. The decrease in ar during the last week (days 28–35) indicated that more irregular pores were generated during this period, which was consistent with observations from optical micrographs (Fig. 4b). As shown in Fig. 5b, the porosity of pig manure particles increased linearly throughout the composting process:

\[
\text{Porosity} = (0.002t + 0.010) \times 100\% \tag{7}
\]

The values of R\textsuperscript{2} and SEE were 0.98 and 0.41, respectively. This trend was consistent with the results observed from the degradation of poly-(l-lactide)-based nanocomposites [38].

3.3. Changes in organic matter of manure particles and the related mechanism analysis

3.3.1. Organic matter content

The OM value of both aerobic composting experiments showed a decreased-stable pattern (Fig. 6). The slope of the curve was increased on days 14–28, indicating an increased degradation rate; however, the OM value was not changed after 28 days, during which the materials were converted into mature compost. The evolution of OM is usually thought to follow first order kinetics [7,40]:

\[
\text{OM} = \text{OM}_0 \times e^{-kt} \tag{8}
\]

where OM\textsubscript{0} is the initial organic matter content (%) and k is the first order rate constant (day\textsuperscript{−1}). As shown in Fig. 6, the changes in OM did not exactly correspond with first order kinetics, probably because the k value was influenced by the particle structure [41,42].

3.3.2. Chemical compositions characterized by FTIR

For FTIR spectra, peaks at 2925 cm\textsuperscript{−1} and 875 cm\textsuperscript{−1} were assigned to the C–H stretch of aliphatics and the C–O stretch of polysaccharides, respectively, and the peak at 1320 cm\textsuperscript{−1} was
assigned to the N–H stretch of aromatics [43]. As shown in Fig. 7a, c, d, and f, the peaks at 2925 cm⁻¹ and 875 cm⁻¹ were continuously decreased, demonstrating that the degradation of aliphatics and polysaccharides in organic matter of pig manure particles was maintained during composting. The band at 1320 cm⁻¹ (Fig. 7b and e) showed a typical behavior of an increase followed by a decrease, indicating the generation of resistant molecules and the reduction of microbial activities, respectively [43,44].

3.3.3. Crystal structure characterized by XRD

For XRD spectra, peaks at both 16° and 22° were decreased during composting (Fig. 8a and b), suggesting that both cellulose and amorphous components (hemicellulose and lignin) were degraded [31]. The CI value was logarithmically increased (Fig. 8c):

\[ CI = 0.363 + 0.087 \ln (t + 3.14) \]  

(9)

The values of \( R^2 \) and SEE were 0.94 and 0.02, respectively. This trend agreed with the composting process of Sam et al. [45] and can be explained by the fact that the degree of degradation of amorphous components was higher than that of cellulose, resulting in an increase in the relative content of cellulose and a stabilization in the crystal structures of pig manure particles [45,46]. Because the biodegradability of hemicellulose was higher than that of lignin, the degree of degradation of hemicellulose was the highest of these three substances. This finding was consistent with the results obtained from chemical analyses [47,48]. This high degree of hemicellulose degradation was likely because of the polysaccharide nature and amorphous structure of hemicellulose, which would facilitate its degradation by microorganisms [48]. Therefore, changes in the crystal structures of pig manure particles can be mainly attributed to the continuous degradation of hemicellulose, which is in agreement with observations of the hydrolysis of rice straw [49].

3.4. Organic matter degradation kinetics based on the particle structure

With the increased specific surface area, the greater number of microorganisms attached to pig manure particles may lead to a higher degree of degradation [41,42]. Therefore, the \( k \) value was proportional to the reciprocal of \( D_{50} \). This was consistent with the assumptions of the composting model described by Vlyssides et al. [5] and the composting processes of manure [6] and food waste [7].

The results of imaging, FTIR, and XRD analyses showed that the removal of amorphous phases and the generation of aromatics led to a stabilized particle structure, which could dramatically impair the degradation rate [50,51]. Moreover, the changes in amorphous phases resulted in the formation of pores in the manure particles [38,49,52]. Therefore, porosity can be used to quantify the influence of the crystal structure variation on the organic matter degradation process. Based on the above characteristic parameters of pig manure particles, the evolution of OM can be expressed as:

\[ OM = OM_0 \times e^{-k \frac{t}{D_{50}} (−3.982 \times \text{porosity} + 1.341)} \]  

(10)

The values of \( R^2 \) and SEE were 0.95 and 0.61, respectively. Subsequently, \( k \) can be described as follows:

\[ k = \frac{1}{D_{50}} \times (−3.982 \times \text{porosity} + 1.341) \]  

(11)

Note that shape parameters were not included here because they were nearly unchanged.

The high \( R^2 \) value demonstrated that changes in the particle structure directly affected the organic matter degradation process. The strong negative correlation between \( k \) and porosity confirmed that stable crystalline compounds could impede the decomposition. This equation, which considers the influence of the particle structure, can be used to develop improved methods for organic matter degradation in aerobic composting models, such as achieving a maximum value of \( k \) by reducing crystallinity and decreasing particle size. However, its applicability to other composting materials needs to be verified.

4. Conclusions

In conclusion, during the composting of pig manure, \( D_{50} \) decreased exponentially, while particle shape was unchanged, suggesting that particles were degraded uniformly along different radial directions. Moreover, the substrate was degraded not only from the outer layer of particles, but also from within, and the pores in particles had a mean diameter of 15–30 µm, with an elliptical shape. Particle porosity increased logarithmically mainly because of hemicellulose degradation. The \( k \) value was proportional to the reciprocal of \( D_{50} \) according to the specific surface area of particles. Finally, with increasing porosity, the chemical compositions and crystal structures of particles were more stable, thus reducing \( k \) values.

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Analysis of non-hazardous structure under Italian kinetics.


