



The impact of silver nanoparticles on the co-composting of sewage sludge and agricultural waste: Evolutions of organic matter and nitrogen



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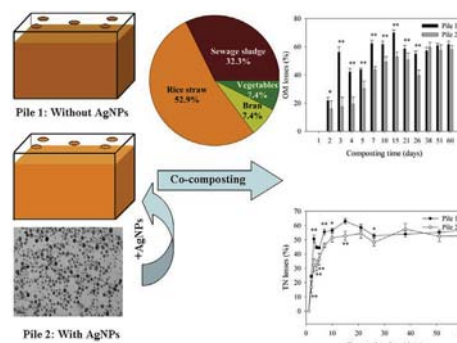
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HIGHLIGHTS

- Conduct co-composting of sewage sludge, straw, vegetables and bran.
- Synthesis PVP-AgNPs successfully.
- Evaluate the impact of PVP-AgNPs on evolutions of organic matter and nitrogen during co-composting process.
- Less organic matter losses in co-composting pile treated with PVP-AgNPs.
- AgNPs can reduce the losses of total N but increase losses of mineral N.

GRAPHICAL ABSTRACT



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ABSTRACT

This study evaluated the influence of silver nanoparticles (AgNPs) on evolutions of organic matter and nitrogen during co-composting of sewage sludge and agricultural waste. Two co-composting piles were conducted, one was treated without AgNPs (pile 1) and the other with AgNPs (pile 2). Results showed that the AgNPs affected the quality of final composts. Less organic matter (OM) losses were determined in pile 2 (57.96%) than pile 1 (61.66%). 27.22% and 30.1% of the initial total organic matter (TOC) was decomposed in pile 1 and pile 2, respectively. The final water soluble carbon (WSC) concentration in pile 2 was 23559.27 mg/kg DW compost which was significantly lower than pile 1 (25642.75 mg/kg DW compost). Changes of different forms of nitrogen in the two piles showed that AgNPs could reduce the losses of TN but increase the losses of mineral N.

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1. Introduction

Composting has been widely applied to dispose many kinds of wastes, such as agricultural wastes, sewage sludge (SS), feces, bio-waste, etc. (Wang et al., 2013; Zhang et al., 2015). It can con-

vert the biodegradable components into nuisance-free, sanitary and humus-like materials, which allows the reuse of the wastes as soil conditioners, fertilizers and soil remediation (Chen et al., 2015; Su et al., 2015). SS is an unavoidable by-product of wastewater treatment plants and it is rich of organic substances and nutrients. Since the technology and capacity of wastewater treatment were improved, SS production increased by more than 50% in EU-15 during 13 years from 1992 to 2005. And by 2020, the production of dry solids from Urban Waste Water Treatment in EU-

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12 countries will exceed 13 million tons annually (EC, 2006; Léonard, 2011). In China, the SS production of wastewater treatment plants (WWTPS) was about 30 million tons and increased yearly by exceeding 13% during 2007–2015 (Cai et al., 2016). However, approximately 80% SS was disposed improperly (Yang et al., 2015). Since SS usually contains varieties of contaminants (including toxic heavy metal, pathogenic microbes and organic micro-pollutants, etc.), it is thus crucially important to dispose the SS safely before its application to agriculture. Composting has been the most common approach to dispose SS in many countries like Finland, Italy, Spain, etc. (Kelessidis and Stasinakis, 2012) and it has caused more and more attentions (Li et al., 2013; Zhang et al., 2016a).

SS compost is widely applied to agriculture due to the high contents of nutrient elements in it, such as nitrogen and phosphorus. While the high moisture content and low carbon to nitrogen ratio (C/N) provide a favorable environment for ammonia release which leads to losses of nitrogen (Fukumoto et al., 2003), even some times the losses of nitrogen can be up to 80% during composting process (Nakhshiniev et al., 2014). Too many nitrogen losses will reduce the compost fertility and cause air pollution. Hence, it is wise to conduct SS composting with bulking agents or carbon amendments (Ammari et al., 2012). There have been many attempts to conduct co-composting of SS with different bulking agents such as grass waste, sawdust, textures, straw, etc. (Ammari et al., 2012; Su et al., 2015) and these bulking agents can improve the aeration by absorbing the moisture and the final compost quality (Tremier et al., 2005). Lots of studies about SS composting have introduced bulking agents to improve composting conditions. However, the lignocelluloses contained in the bulking agents are difficult to be biodegraded (Yu et al., 2009). To solve this problem, researchers integrated some easily degradable organic wastes (e.g. vegetables) to enhance the composting process and the final compost quality (Ammari et al., 2012).

Nanoparticles, as known, possess comparatively high surface area to volume ratio which leads to higher toxicity than the bulk material (Vance et al., 2015; Xu et al., 2012). Nowadays, silver nanoparticles (AgNPs) have attracted much attention and been applied as antifungal or antibacterial agents to a wide range of consumer products. For instance, AgNPs are frequently discovered in personal-care products, cosmetics, liquid fabric softeners and detergents, coating materials, food storage containers, fabrics and clothing, medical appliances, dietary supplements, and sporting goods (Kim et al., 2010). Studies about the characterization of silver released from textiles showed that approximately 34% to 80% of Ag were released in the form of AgNPs (Lorenz et al., 2012). Other modeling analysis found that Ag⁺ or AgNPs released from textiles and biocidal plastics accounted for about 15% (Geranio et al., 2009). The manufactured AgNPs in consumer products may be released into the environment during or after their lifetime. At the end of the service life, parts of products are commonly disposed as municipal solid wastes and then AgNPs are released into the solid wastes (Gitipour et al., 2013). Additionally, there were also some AgCl nanoparticles in the waste solution of a laundry (Hassellöv and Kaegi, 2009) and it was found that AgNPs and Ag⁺ were released into water from socks when washing them (Benn and Westerhoff, 2008). During processes of wastewater treatments, AgNPs may be doped into the sewage sludge by sorption or aggregation and may be enriched with time (Benn and Westerhoff, 2008). With the application of composted sewage sludge to agriculture, AgNPs may also enter into the agricultural wastes. According to Gitipour et al. (2013), 2 mg/kg solid wastes AgNPs was a relatively low concentration that might exist in a real environment. Given the antimicrobial activity of AgNPs, it is important to pay attention to the possible impacts of AgNPs on the composting process of sewage sludge or agricultural wastes.

The aim of this study is to evaluate the impact of AgNPs on co-composting of sewage sludge and agricultural wastes in terms of the evolution of organic matter and nitrogen. The composting materials were composed of sewage sludge, rice straw, vegetables and bran. Two composting piles, one was treated with AgNPs and another was set as blank control, were conducted in laboratory for two months. This research represented the minority studies integrating vegetables as the easily degradable component and bran to adjust the initial C/N. Meanwhile, this study concerned the existence of AgNPs during co-composting of sewage sludge with agricultural wastes.

2. Methods

2.1. Synthesis and characterization of AgNPs

In previous researches, it was reported that polyvinylpyrrolidone (PVP) was one of the most common capping agents for AgNPs. The PVP coated AgNPs (PVP-AgNPs) could still maintain stability under high valence background electrolytes condition of high ionic strength solution which was the general environment of a composting system (Gitipour et al., 2013). Therefore, PVP-AgNPs were introduced into this study for evaluating the impacts of AgNPs on co-composting sewage sludge with agricultural waste. The PVP-AgNPs were synthesized referring to the instruction described by El-Badawy et al. (2011) with slight modifications. Briefly, 2.5×10^{-3} M NaBH₄ was dissolved in 300 mL 1% PVP solution. And then, 100 mL 5×10^{-3} M AgNO₃ was dripped into the above mixed solutions and stirred for an additional hour after AgNO₃ was completely added. All the steps were conducted in the condition of ice bath. Purification of AgNPs was performed using 1 kDa dialysis membrane. To verify the formation of nanosilver, certain volumes of suspensions were subjected to a Shimadzu UV-2550 (Japan) from 300 to 800 nm to obtain the UV adsorption spectrum. Zetasizer Nanoseries (Malvern Instruments, UK) was used for measurement of Zeta potential and hydrodynamic diameter (HDD). Samples for transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) analysis were prepared by putting a drop of AgNPs suspension onto a carbon coated copper grid and dried at room temperature. Measurement of total Ag concentrations was conducted using a flame atomic absorption spectrometry (AAS700, PerkinElmer, USA) after HNO₃ digestion.

2.2. Preparation of composting materials

Dewatered sewage sludge was collected from Yuelu wastewater treatment plant in Changsha, China, and was sieved through the 100-mesh screen after being air-dried. Rice straw, as the representative agricultural waste which is difficult to be degraded, was obtained from suburb of Changsha, China, and also air-dried before being cut into 10–20 mm lengths. Some kinds of air-dried vegetable wastes were cut into 10–20 mm lengths and added into the mixtures as the easy-degradable materials. Air-dried bran was added to adjust the initial C/N ratio of the composting systems. The characteristics of the raw co-composting materials are shown in Table 1.

2.3. Co-composting set-up and sampling

Indoor experimental co-composting systems with wet weight of about 15 kg were set up in 65 L boxes with dimension of 0.54 m × 0.39 m × 0.31 m (length × width × height). On the lids of boxes, there were some holes for a good ventilation environment. The raw co-composting materials sewage sludge, rice straw, vegetables and bran were blended evenly at a weight ratio of

Table 1
The physico-chemical characteristics of the raw co-composting materials (dry weight).

Materials	Moisture content (%)	TOC (g/kg)	TN (g/kg)	C/N ratio	pH
Sewage sludge	9.48	178.9	24.2	7.4	6.74
Rice straw	10.35	488.9	10.3	47.5	– ^a
Vegetables	94.84	446.4	19.6	22.8	– ^a
Bran	14.62	528.2	25.1	21.0	– ^a

^a Samples not determined. TOC, total organic carbon; TN, total nitrogen; C/N, TOC/TN.

22:36:5:5. The initial C/N ratio and moisture content were adjusted to about 25:1 and 65%, respectively. Two co-composting piles were conducted in the study, pile 1 was used as the blank control (without PVP-AgNPs) and pile 2 was treated with PVP-AgNPs at a concentration of 2 mg kg⁻¹ compost. To provide a favorable aerobic environment for the processes lasting for 60 days, the co-composting piles were turned once a day during the first two weeks and once a week afterwards. Three subsamples from different positions of the co-composting piles were taken at 9 am on day 1, 2, 3, 4, 5, 7, 10, 15, 21, 26, 38, 51, and 60, respectively. Samples of the same day were homogenized and stored at 4 °C before analyzed.

2.4. Analytical methods

The temperatures in five different locations of the co-composting piles were determined using a thermometer. Analyses of ammonium (NH₄⁺-N), nitrate (NO₃⁻-N) and nitrite (NO₂⁻-N) concentrations were conducted using spectrophotometric methods after shaking the samples with 2 M of KCl solution at a ratio of 1:50 (w/v, sample: water) for 1 h. The NO₂⁻-N concentration was ignored in this study since the values of it were too low. Samples were dried at 105 °C for 24 h and ground for total nitrogen (TN) determinations by methods of Kjeldahl digestion. Organic matter (OM) and ash concentrations were determined by dry combustion at 550 °C for 6 h. Organic N was obtained from the difference value between TN and mineral N which was the sum of NH₄⁺-N and NO₃⁻-N. The OM and TN losses were calculated according to the following equations (Fornes et al., 2012), respectively,

$$\text{OM loss (\%)} = 100 - 100[X_1(100 - X_n)]/[X_n(100 - X_1)] \quad (1)$$

$$\text{TN loss (\%)} = 100 - 100[(X_1N_n)/(X_nN_1)] \quad (2)$$

where X_1 and X_n were the initial ash content and the ash content on each corresponding day, N_1 and N_n were the initial total nitrogen concentration and the total nitrogen concentration on each corresponding day, respectively.

The total organic carbon (TOC) concentration was obtained from the ash content referring to the following formula (Zeng et al., 2010):

$$\% \text{TOC} = (100 - \% \text{ash})/1.8 \quad (3)$$

For the water soluble carbon (WSC) determination by Total Organic Carbon Analyzer (TOC-5000A, Shimadzu, Japan), fresh samples were shaken in ultrapure water (fresh sample to water ratio of 1:10, w/v) at 200 rpm for 40 min. And then the suspensions were centrifuged at 12,000 rpm for 10 min and filtered through a 0.45 μm membrane filter.

2.5. Statistical analysis

All the determinations, apart from pile temperature which was determined in five locations, were conducted in triplicate and the mean values were shown in the present study. One-way analysis of variance (ANOVA) was performed using SPSS 19.0 to test the significant differences of means between composts from different

sampling time and the average values of different treatments at 95% confidence level.

3. Results and discussion

3.1. Characterizations of AgNPs

Fig. S1A presents the UV–vis absorbance spectra of the prepared PVP-AgNPs suspensions. The result that the spectra peak appeared at 400 nm indicated the successful synthesis of PVP-AgNPs (Yang et al., 2014). The HDD and zeta potential (ζ) of the suspension were 8.5 nm and -0.7 mV (Fig. S1B) which was similar to other studies (El-Badawy et al., 2010). Though ζ potential may be not enough for electrostatic stabilization, PVP can assist AgNPs in resisting aggregation under complex environmental conditions through steric stabilization (El-Badawy et al., 2013). The TEM and EDX analysis images were shown in Figs. S2 and S1C, respectively. Different from HDD, AgNPs average diameter obtained by TEM was about 6 nm. This might be due to the possible slight increase in size during the period of placing before HDD determination. The spectrum of EDX analysis for TEM image further illustrated the formation of AgNPs.

3.2. Changes of temperature and pH during the co-composting processes

Temperature is an important parameter for assessing the performance of the composting process, including decomposition rates and microbial activity, etc. (Zhang et al., 2015). In this study, temperatures were measured from five different locations in the core and four corners of the co-composting piles. Fig. 1A shows the average temperatures changes during co-composting of the two treatments and reflects the typical temperatures patterns which were similar to most of composting processes. At the beginning of both the co-composting processes, the temperatures increased immediately and rose to thermophilic phase (exceeding 50 °C) within 3 days, indicating the generation of heat by the rapid consumption of easily degradable organic matters which were used as the necessary nutrients for microbial activity and growth (Chan et al., 2016). The temperatures between the two piles during day 1 to day 5 were significant different which indicated that AgNPs might inhibit the microbial activities during the early stage of the co-composting process. The thermophilic phase in both of the two composting piles lasted for about 10 days. While the days in which temperatures exceeded 55 °C were lasted for 6 days and 3 days for pile 1 and pile 2, respectively, and pathogens from the compost could be destroyed under this condition (Yu et al., 2007). In pile 1, the temperature increased to the highest level of 59.6 °C on the 5th day, while in pile 2, highest temperature of 55.8 °C was achieved on the 7th day. The slower and lower increase of temperature in pile 2 might be due to the antimicrobial properties of AgNPs (Levard et al., 2012). Two path ways for the toxicity of AgNPs to microbes have been demonstrated by some previous studies: (1) release and transport of Ag⁺ across membranes affect cellular respiration and cause cell death by the effects on enzymes

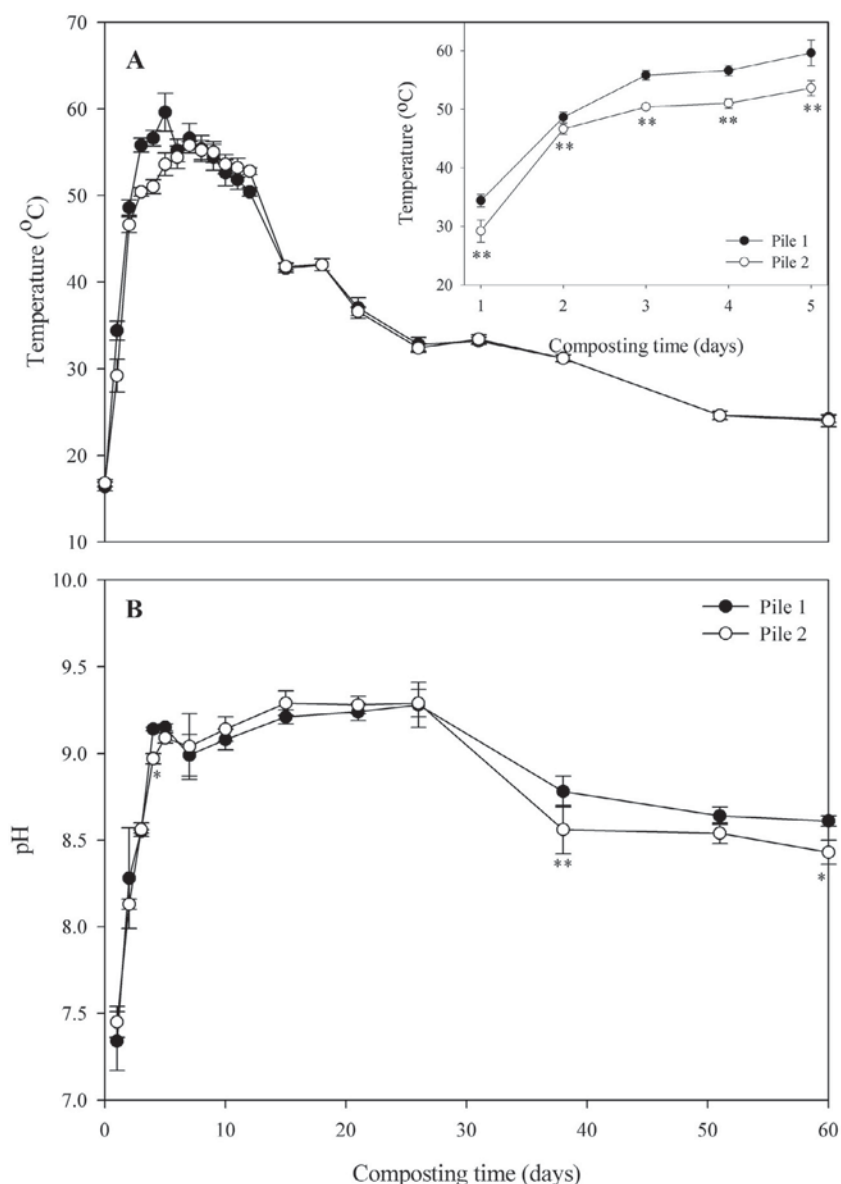


Fig. 1. Changes of pile temperature (A) and pH (B) during co-composting processes. Mean values and standard deviations (the bars, $n = 3$) are shown. Asterisks under the curves indicate significant differences between the two treatments at $^*P < 0.05$, $^{**}P < 0.01$ according to the least significant difference test.

and proteins (Bottero et al., 2011), and (2) the production of reactive oxygen species (ROS) at the surface of AgNPs brings oxidative stress (Choi and Hu, 2008). pH is an important parameter to assess the performance of composting in that it can influence the activities and communities of microbes (Chan et al., 2016). As shown in Fig. 1B, the pH in both the two treatments increased rapidly during the early stage of co-composting processes, and then decreased until the end of co-composting processes. During the decreasing process, pH in pile 2 was significantly lower than pile 1, and this may be caused by the lower concentration of $\text{NH}_4\text{-N}$ in pile 2 (Fig. 3B) during this stage. Previous studies suggested that the acidic pH during composting could inhibit the microbial activities and cause acidic odour emission (Wang et al., 2016). The alkaline pH in the present study indicated good composting processes.

3.3. Organic matter degradations during the co-composting processes

As a valuable indication for a successful composting process (Wang et al., 2016), the degradation of OM was calculated through the contents of ash (Table 2) to evaluate the co-composting perfor-

mance (Fig. 2). The OM concentrations (Fig. 2A) from both of the two treatments presented reducing trends on the whole during co-composting processes. Sharp drops were observed during the mesophilic and thermophilic phases, indicating that OM was rapidly broken down by microorganisms. During cooling and maturation phases, slower degradations of OM were observed due to the depletions of easily degradable OM and lignocelluloses in rice straw were difficult to degrade. During the mesophilic stage and maturation stage, OM concentrations in pile 2 were significantly lower than that in pile 1. To quantify the OM mineralization, losses of organic matter with the time course during co-composting were calculated (Fig. 2B). Contrary to the time courses of OM concentrations, the losses of OM were increased rapidly with time during mesophilic and thermophilic phases and then increased slowly during cooling and maturation stages. This trend was similar between the two treatments. From day 2 to day 26, the OM losses in pile 2 were significantly lower than that in pile 1. Less OM losses were detected at the end of composting process (57.96%) in the pile 2, while 61.66% in pile 1. This phenomenon might be ascribed to the presence of AgNPs, which could stimulate humins formation,

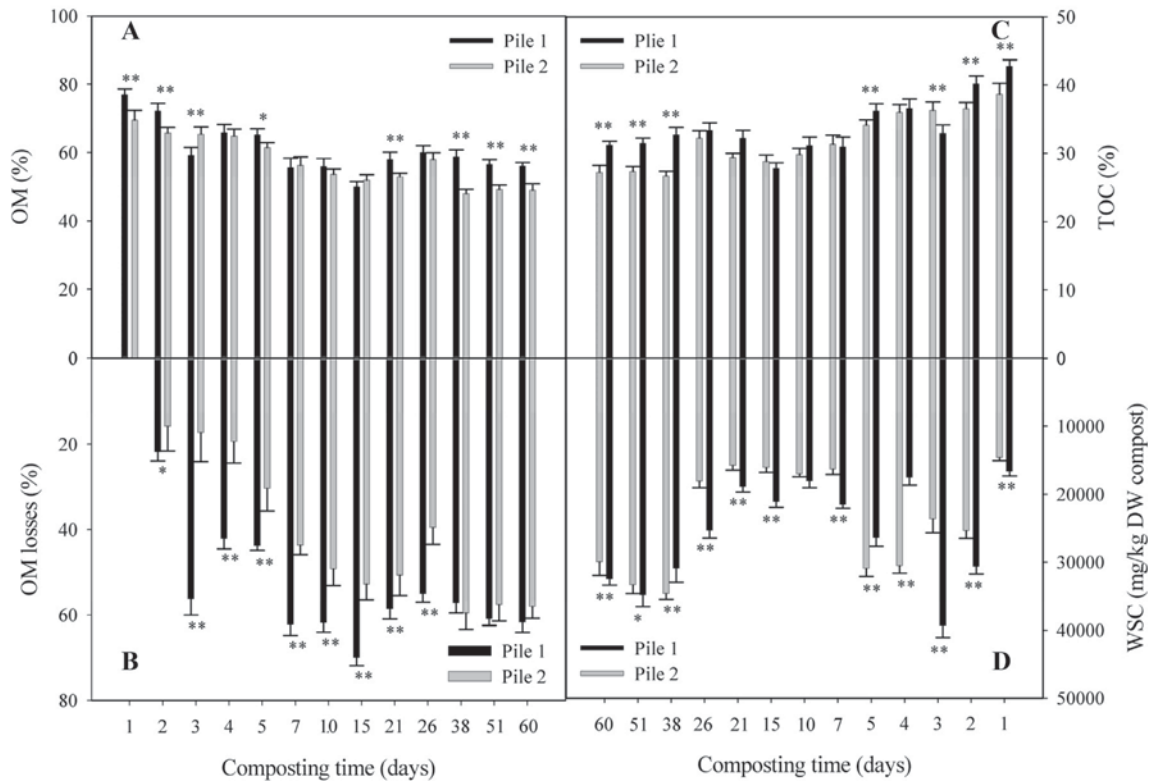


Fig. 2. Evolutions of (A) OM, organic matter; (B) OM losses, organic matter losses; (C) TOC, total organic carbon; (D) WSC, water soluble carbon, during co-composting processes. Mean values and standard deviations (the bars, $n = 3$) are shown. Data are presented on a dry-weight compost basis. Asterisks above or under the bars indicate significant differences between the two treatments at $^*P < 0.05$, $^{**}P < 0.01$ according to the least significant difference test.

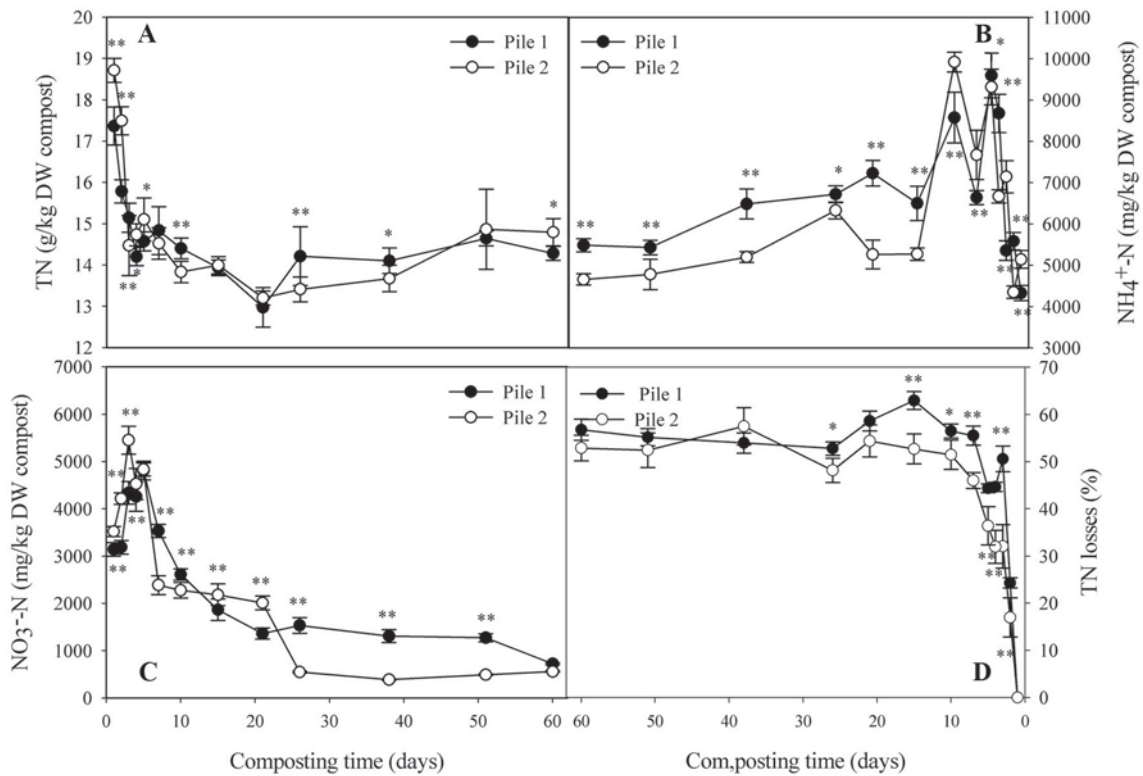


Fig. 3. Time courses of different forms of N during co-composting processes. (A) TN, total nitrogen; (B) $\text{NH}_4^+\text{-N}$, ammonium nitrogen; (C) $\text{NO}_3^-\text{-N}$, nitrate nitrogen; (D) TN losses, total nitrogen losses. Mean values and standard deviations (the bars, $n = 3$) are shown. Data are presented on a dry-weight compost basis. Asterisks above or under the curves indicate significant differences between the two treatments at $^*P < 0.05$, $^{**}P < 0.01$ according to the least significant difference test.

Table 2
Ash content in composts during co-composting processes (dry weight).

Time (days)	1**	2**	3**	4	5 [~]	7	10	15	21**	26	38**	51**	60**	
Ash content (%)	Pile 1	23.08	27.73	40.74	34.13	34.79	44.33	44.00	50.00	42.00	40.00	41.18	43.40	43.90
	Pile 2	30.44	34.20	34.63	35.17	38.57	43.68	46.30	48.08	47.06	42.00	52.00	50.80	51.00

Asterisks in the cells indicate significant differences between the two treatments at [~] $P < 0.05$ and ** $P < 0.01$ according to the least significant difference test.

while the accumulation of humins would impede the degradation of OM (Rice, 2001; Stamou and Antizar-Ladislao, 2016). Besides, it might also be due to that the activities of microorganisms were inhibited by AgNPs.

The TOC is usually used as the energy sources for microorganisms during composting process (Chan et al., 2016) and the degradation of TOC could be used to illustrate the level of compost maturity (Vargas-Gracia et al., 2010). Meanwhile, the degradation of TOC may cause the OM concentration reduced. As shown in (Fig. 2C), with the developments of co-composting processes, the TOC concentrations in all treatments decreased. Similar to OM, the significant difference of TOC concentrations between the two treatments was also found during mesophilic and maturation stages. At the end of composting, 27.05% and 29.55% of the initial TOC were degraded in pile 1 and pile 2, respectively. The reason might be that AgNPs promoted the degradation of carbon which included carbon mineralization. Stamou and Antizar-Ladislao (2016) also found that the carbon mineralization was higher in composting pile AT 50 (50 mg Ag/2250 mg Ag/Ti per kg OM (d. w.)) than other piles in which the concentration of NPs was lower and this study also suggested that NPs could had an impact on formation of humins and hence affected the carbon mineralization.

WSC, which can be easily directly absorbed by microorganisms, is an unstable component of organic matter and is always used as a biologically active parameter to evaluate the degree of compost stability. In this study, WSC concentrations of the two treatments increased rapidly at the beginning of co-composting processes (Fig. 2D) and reached peak values on day 3 and day 5 for pile 1 and pile 2, respectively. This might be due to the fact that the syntheses of WSC by microorganisms and microbial growth, or by the solubilization of some simple organic compounds were greater than the degradation and utilization of WSC (Castaldi et al., 2008). The changes of WSC concentrations included two rises and two decreases. This trend was similar to the study by Zhang et al. (2016b) during chicken manure composting added with different surfactants. The maximum WSC concentration in pile 1 was 39280.92 mg/kg dry weight (DW) compost which was significantly higher than that in pile 2 (34594.90 mg/kg DW compost). The average concentrations of WSC in pile 1 and pile 2 were 25642.76 and 23559.27 mg/kg DW compost, respectively. These results suggested that AgNPs could inhibit the reproduction and ability of microorganisms to degrade the organic waste, thus resulting in increase of WSC concentrations.

3.4. Nitrogen changes during the co-composting processes

Fig. 3 presents the dynamics of concentrations of TN, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and TN losses in the two treatments, respectively. In this study, large amounts of nitrogen in the two piles were lost during the first 21 days of co-composting processes. During the initial 21 days of co-composting, the TN concentrations decreased from 17.36 to 12.97 g/kg DW compost in pile 1, and from 18.71 to 13.20 g/kg DW compost in pile 2 (Fig. 3A). This might be attributed to the emissions of NH_3 (Ren et al., 2010; Jiang et al., 2015). After 21 days, the TN concentrations began to increase to 14.64 and 14.86 g/kg DW until day 51 for pile 1 and 2, respectively. The increases in TN might be due to the concentration effect resulted

from the intense decomposition of organic matter (Kalamdhad and Kazmi, 2009). Interestingly, slight reduces of TN during days 51–60 were detected from 14.64 to 14.28 g/kg DW compost and 14.86 to 14.79 g/kg DW compost for pile 1 and pile 2, respectively. During this stage, the previous intense degradations of organic matters have caused particle size or the porosity of the piles decreasing which could induce the anaerobic environment in the piles, and hence the responsive inhibition of nitrification and promotion of denitrification happened. Therefore, it was essential to take measures, such as pile turning and proper ventilation to reduce the nitrogen losses. At the end of co-composting, the TN concentration in pile 2 was significantly higher than that in pile 1, indicating that AgNPs were conducive to conservation of TN.

The changes of $\text{NH}_4^+\text{-N}$ are a vital hint of NH_3 emission and nitrogen changes. As shown in Fig. 3B, the $\text{NH}_4^+\text{-N}$ concentrations in pile 1 increased rapidly from 4324.32 to 9593.73 mg/kg DW compost on day 5. And in pile 2, it increased from 5140.41 to 9918.28 mg/kg DW compost on day 10. Compared to the initial value of $\text{NH}_4^+\text{-N}$, it increased by 121.86% in pile 1, which was higher than pile 2 (92.95%). The increases in $\text{NH}_4^+\text{-N}$ could be attributed to the mineralization of organic nitrogen to $\text{NH}_4^+\text{-N}$ by the ammonification process. Then, $\text{NH}_4^+\text{-N}$ concentrations began to decrease because of the assimilation as proteins, nucleic acids and amino acids by microorganisms, and losses as NH_3 at high pH and high temperature (Guo et al., 2012). It has been suggested that decrease of $\text{NH}_4^+\text{-N}$ could be used as a key parameter in terms of a good composting and maturation process (Riffaldi et al., 1986). At the end of co-composting processes, $\text{NH}_4^+\text{-N}$ concentration in pile 1 was 5482.44 mg/kg DW compost, which was significant higher than that in pile 2 (4655.25 mg/kg DW compost).

In this present study, $\text{NO}_3^-\text{-N}$ concentrations in both piles increased in the first 5 days (Fig. 3C) due to the enough $\text{NH}_4^+\text{-N}$ concentrations which were the substrates for nitrifying bacteria to carry out the nitrification. During the thermophilic stage, $\text{NO}_3^-\text{-N}$ concentrations began to decrease since the growth and activity of nitrite bacteria and nitrobacteria were blocked under condition of high temperature ($>40^\circ\text{C}$) and excessive NH_3 release (Sánchez-Montero et al., 2001). Consequently, the conversions of $\text{NH}_4^+\text{-N}$ to $\text{NO}_3^-\text{-N}$ were inhibited while organic nitrogen contents increased (Fig. 4A). At the end of co-composting processes, the $\text{NO}_3^-\text{-N}$ concentrations in two piles were relatively low and this was similar to the previous study Li et al. (2012).

Losses of TN with time during co-composting processes were obtained according to the changes of TN concentrations. During the first 15 days, TN losses were accumulated dramatically (Fig. 3D) due to the high $\text{NH}_4^+\text{-N}$ concentrations which could be conducive to NH_3 emission thus leading to losses of TN. Afterward, there were a little decreases of TN losses in the two piles and this phenomenon might be caused by the decompositions of organic carbon compounds resulting in organic nitrogen increases (Ogunwande et al., 2008). During the first 21 days, TN losses in pile 2 were significantly lower than that in pile 1, which could be due to the fact that the organic N in pile 2 was higher than pile 1. The maximum loss of TN in pile 1 was 62.96% and in pile 2 was 57.23%. However, the mineral N (Fig. 4B) in pile 1 was higher than that in pile 2 indicating the higher direct N availability of pile 1.

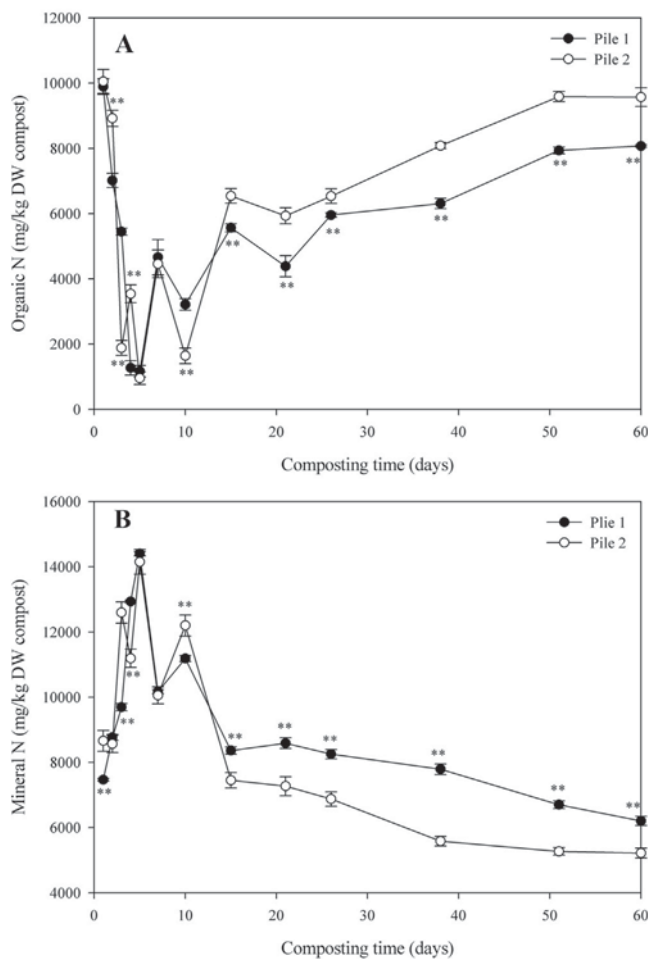


Fig. 4. Changes of organic N and mineral N during co-composting processes. (A) Organic N; (B) Mineral N. Mean values and standard deviations (the bars, $n = 3$) are shown. Data are presented on a dry-weight compost basis. Asterisks above or under the curves indicate significant differences between the two treatments at $P < 0.05$, $^{**}P < 0.01$ according to the least significant difference test.

Therefore, the existence of AgNPs could reduce the losses of TN but increase the losses of mineral N.

3.5. Evolutions of C/N ratio during the co-composting processes

The decrease of C/N ratio resulted from decomposition of OM is usually used as a parameter indicating compost maturity (Mathur et al., 1993). It was once demonstrated by Mathur et al. (1993) that the decomposition of OM could reduce C/N value and lead to CO_2 emission. Whilst because of OM degradation, mass losses might conduce to the increase of nitrogen which caused the decrease of C/N (Wang et al., 2016). In this study, C/N ratios increased during the first 4 days in pile 1 and 3 days in pile 2, and then decreased along with the co-composting processes (Fig. 5). The proportion of C/N ratio decline in pile 1 was higher than that in pile 2 due to the stronger decomposition of organic matter (Jiang et al., 2015). At the end of co-composting, the C/N ratio in pile 1 was 21.83 significantly higher than that in pile 2 of 18.41, respectively, since that AgNPs promoted the carbon mineralization and reduced the TN losses in pile 2. The final C/N ratios in both the two treatments conformed to the standard value for a successful composting (< 25) (Chan et al., 2016). The increases of C/N in the first few days of co-composting were due to the rapid declines in TN via NH_3 emissions. However, the C/N ratios decreased afterwards,

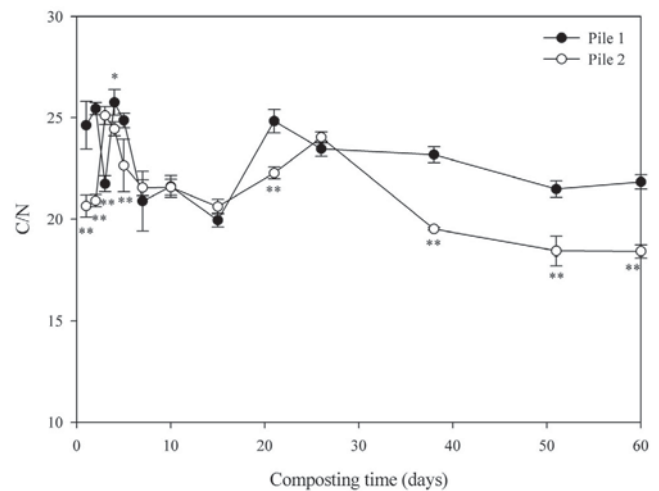


Fig. 5. Variations of C/N ratio during co-composting processes. Mean values and standard deviations (the bars, $n = 3$) are shown. Data are presented on a dry-weight compost basis. Asterisks above or under the curves indicate significant differences between the two treatments at $P < 0.05$, $^{**}P < 0.01$ according to the least significant difference test.

which was attributed to the decompositions of organic matter and the transformations of mineral nitrogen to organic nitrogen.

4. Conclusions

The OM contents in two piles dropped rapidly during mesophilic and thermophilic phases, and decreased slowly to 56.1% and 49% for pile 1 and pile 2 at the end of co-composting processing, respectively. Less OM losses was determined in pile 2 indicating that AgNPs could impede the OM decompositions. During the whole co-composting processing, existence of AgNPs could reduce the losses of TN but increase the losses of mineral N which reduced the fertilities of the final composts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2017.01.032>.

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