

Optimization of control parameters for petroleum waste composting

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Abstract: Composting is being widely employed in the treatment of petroleum waste. The purpose of this study was to find the optimum control parameters for petroleum waste in-vessel composting. Various physical and chemical parameters were monitored to evaluate their influence on the microbial communities present in composting. The CO₂ evolution and the number of microorganisms were measured as the activity of composting. The results demonstrated that the optimum temperature, pH and moisture content were 56.5–59.5°C, 7.0–8.5 and 55%–60%, respectively. Under the optimum conditions, the removal efficiency of petroleum hydrocarbon reached 83.29% after 30 days composting.

Keywords: optimization; control parameters; petroleum waste; composting

Introduction

In recent years, petroleum industry has developed rapidly in China and produced a great deal wastewater and petroleum wastes, which contaminated natural environment severely. It is imperative to seek a new and cost-effective technology for petroleum waste treatment. Among all those waste treatment technologies, composting is becoming an increasing extrusive method and has been receiving great attentions from all over the world, since there are more and more pressure in land and energy resources and the stronger and stronger desire of human being for return to nature. As a controllable ecological system, the advantages of in-vessel composting lie in that the abiotic factors that affect activities of microorganism can be controlled artificially in the system (Davis, 1993; Hay, 1990). Hence the maximum pollutant removal efficiency may be obtained under the optimum conditions. The key control parameters that affect composting efficiency include temperature, pH, moisture content, aeration, and so on (Finstein, 1987; Cookson, 1995; Nakasaki, 1993).

Temperature is the most important factor, which is able to affect microbial activity (Finstein, 1987; Nakasaki, 1985). It is a very effective method of controlling temperature during composting to obtain the maximum degradation rate. Many researchers had investigated the optimum range of temperature during composting process (Bach, 1984; Suler, 1977; Vicky, 1984), but the results were quite different. In addition, few people studied the optimum temperature for the various composting substrates. Sular and Finstein (Sular, 1977) reported that different waste needed different optimum temperature under different treatment conditions. The pH is another important parameter that should be taken into account in composting, since it can affects not only microbial growth and cell membrane transport but also the balance of enzymatic reactions (Cookson, 1995). Generally, pH was approximately controlled at pH 7.0 and no excess of range of pH 4.0 to 10.0 (Brodkorb, 1992; Dhawale, 1992). Although microorganism can live in a relatively wide range of pH, some Japanese researchers still considered that accurate controlling of pH could accelerate the degradation process of organic matter effectively (Nakasaki, 1993). Moisture content of solid waste also has an important impact on composting. It would affect bioavailability of pollutants, gas transfer, toxic effect of pollutants, microbial movement,

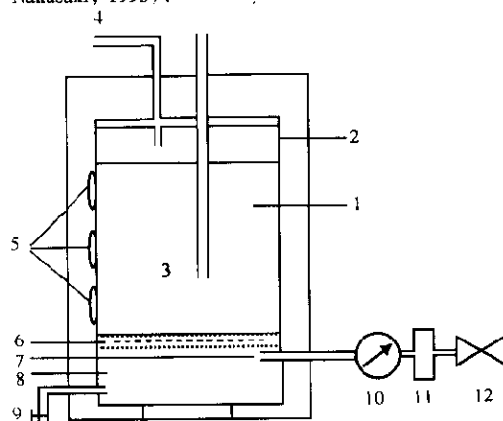


Fig.1 Schematic diagram of composter

1. compost material; 2. composter chamber; 3. thermometer hole; 4. air outlet; 5. sampling holes; 6. percolator layer; 7. air inlet; 8. water collecting zone; 9. water outlet; 10. flow meter; 11. air compressor; 12. buffer; 13. wooden box for heat preservation

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growth and distribution. Overly low moisture content can restrict cell movement and metabolic reactions, which can result in the inhibition of microorganism activities. Overly high moisture content however would block gas transfer, and seriously affect the aerobic metabolic activities (Cookson, 1995).

The present study was to investigate the influence of various parameters on composting efficiency, and find the optimum control parameters for petroleum waste in-vessel composting.

1 Materials and methods

1.1 Experimental materials

Experimental apparatus: Three composters were made of organic glass (Fig. 1; each volume was 12.5 litre, with a height/diameter ratio of 2.2:1). Temperature inner composter was kept at about 40°C by heating exteriorly.

Petroleum waste: The petroleum waste (collected from Qianjiang Refinery Plant, Jiangnan Oil Field in China) was a mixture of crude oil and slurry, appeared as a darkish-gray semisolid matter. Moisture content, pH and petroleum hydrocarbon content was 7.71%, 3.67 and 7.42 E+5 mg/kg (d.w.), respectively.

Soil: The fertile soil was picked from certain parterre at Wuhan University, and provided abundant microorganisms. It was air-dried and screened by 20-mesh sieve before used.

Wood chip: The wood chip was collected from woodshed at Wuhan University. It was also air-dried and screened by 20-mesh sieve before used.

Canteen leftover and rotted vegetable: Canteen leftover and rotted vegetable, which can offer readily biodegradable substances, served as ameliorants in composting.

1.2 Optimization of pH and temperature during composting

Three mixed substances with the optimum compost material ratio were prepared as described by Zhang *et al.* (Zhang, 1999), and each included petroleum waste (0.2 kg), soil (2.6 kg), Canteen leftover and rotted vegetable (6.0 kg), and wood chip (added by 2 times of the whole volume). After homogeneously mixed, pH was adjusted to 6.70, 8.73 and 10.14 with lime water, respectively. Then three substances were put into three different composters at the same temperature. All of them had the similar C/N ratio (approximately 30:1), moisture content (about 50%), and aeration condition (air supplied by air compressor at 0.3 Nm³/h with timer control as 18s on/42s off) at the beginning of experiments. The CO₂ yield and microbial biomass were measured as the activities of metabolism. Changes in temperature, pH and CO₂ yield were monitored daily. Microbial biomass and petroleum hydrocarbon content were analysed by taking samples at regular intervals. Water added to keep constant moisture during composting from the third day till the 27th day. The running period was 30 days.

1.3 Optimization of moisture content during composting

The experiments were designed on the basis of study results derived above. Three mixed substances were prepared as above, each of pH was adjusted to the optimum value. Moisture contents were controlled as 50%, 55% and 60%, respectively. After homogeneously mixed, each of them was put into different composter to start composting. At the first stage, aeration strength was 0.2 Nm³/h, and timer control was 18s on/42s off. Then, changed the aeration strength or timer control to keep the temperature constant after composting temperature reached the optimum range, based on Rutgers aeration mechanism (MacGregor, 1981). In addition, maintained pH in the optimum range and moisture content of each composting substance constant during composting. Volatile material (VM) and petroleum hydrocarbon content were analysed by taking samples every 5 days. Conversion of volatile material (*X_{vm}*) and degradation rate of petroleum hydrocarbon were measured to determine the suitable moisture content. The running period was 30 days.

1.4 Determination of related parameters

The mixed sample was oven-dried at 60°C to constant weight for measuring moisture content. The oven-dried sample was heated at 600–700°C for 2–3h to determine volatile material content (VM). Total carbon content of sample was determined by a wet oxidation method, using K₂Cr₂O₇, recovering mainly organic carbon. Total nitrogen was determined using a wet oxidation Kjeldahl method. The pH was determined in distilled water solution (1:9, w/v) with an electric pH meter

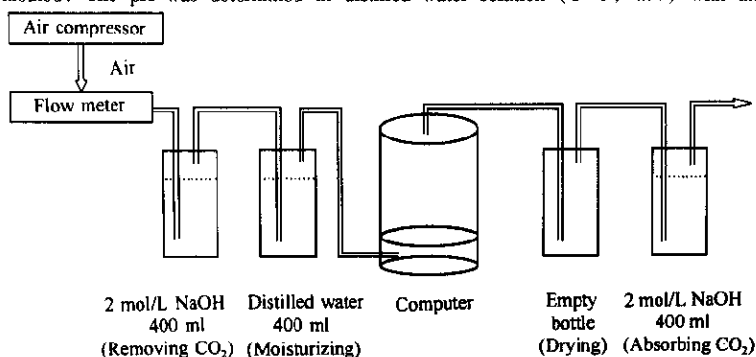


Fig. 2 Flow chart of the laboratory scale system used to determine the evolution of CO₂

(Nakasaki, 1992). Microbial biomass was determined using spread plate counting method (Germida, 1993), and the incubation temperature was the same as that of the composting temperature when sampled. The CO_2 evolution was determined following Fig. 2, which using 2 mol/L NaOH solution to absorb CO_2 produced by composting. The CO_2 yield was calculated after each 24 h, by titration method using 1 mol/L HCl solution, and 1% phenolphthalein alcohol solution served as indicator (Yusuf, 1990; Michel, 1995). Petroleum hydrocarbon was measured using 752 ultraviolet spectrophotometer (λ : 254 nm). Smashed sample (dried at 60°C) screened by 80-mesh sieve to remove wood chips, and a certain mass of sample was weighed and extracted using chloroform (analytical grade with further redistillation) at 75°C for 6h. Then chloroform was concentrated and the residue was dissolved in petroleum ether (analytical grade with further redistillation, boiling range: $60-90^\circ\text{C}$, $T\% > 95\%$) for petroleum hydrocarbon measurement (Xie, 1990).

2 Results and discussion

2.1 Variation of pH with composting days

At the beginning, initial pH of composting in composters A, B and C were adjusted at 6.71, 8.73 and 10.14, respectively. While each of them declined rapidly to 4.31, 5.45 and 6.41 on the second day, and then followed by an increase at different rate, but none of them recovered their initial pH after the end of experiments (Fig.3). The pH was in the range of 4.0–5.0 from 2–30 days, and took on an evident acidic condition in composter A. In composter B, pH was mostly in the range of 5.0–6.0 from 2–19 days, and up to 6.0–7.0 from 20–30 days with an acidulous condition. While in composter C, pH exceeded 7.0 since the 5th days of composting and was mostly in excess of 9.0 from 13–30 days. A great deal of documents reported that variation of pH took on an increasing trend during composting (Atchley, 1979; MacGregor, 1981). But our experimental results were quite different. The pH variation followed a trend of increase after an initial drop in our experiment, which coincided with the conclusion drawn by Poincelot (Poincelot, 1974) and Minnas (Minnas, 1997). Chen and Zhang (Chen, 1990) summarized that composting matter was hydrolyzed to organic acid at the early stage of composting, hence pH declined to 4.5–5.0 and then increased gradually. Vicky and Vestal (Vicky, 1985) reported that microorganism metabolized organic acid to CO_2 and H_2O , then sent out NH_3 by using nitrogen source to increase pH value. Consequently, variation of pH could be regarded as an indirect indicator of microorganism activities. The microbial activity in each composter in our study could be reasonably estimated as $\text{C} > \text{B} > \text{A}$.

2.2 Combined analysis related to CO_2 evolution, microbial biomass and variations of temperature and pH

Composting is a complex biochemical process, in which microbial biomass and activity were the biological basis of organic matter degradation. The biochemical reactions would impel composting temperature increase and pH change. Moreover, variations of temperature and pH can conversely affect variation of microbial biomass and activity. Controlling composting temperature and pH can therefore affect the process of biochemical reaction during composting. The CO_2 evolution is influenced by various factors, and it is a reflection of composting efficiency. The optimum temperature and pH for petroleum waste composting were studied by analyzing CO_2 yield, microbial biomass and variations of temperature and pH integratively, since it's easily and credibly to determine CO_2 yield and temperature during composting (Fig.4–6). Fig. 4 indicated that

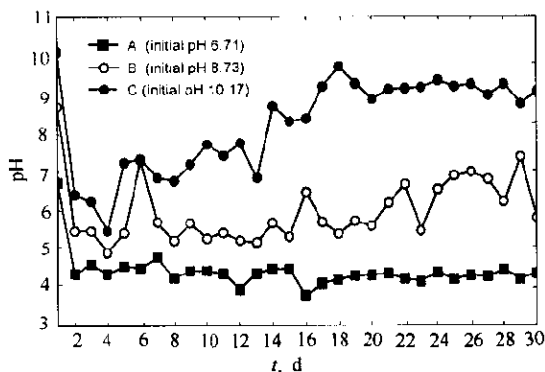


Fig.3 Variation of pH with composting days

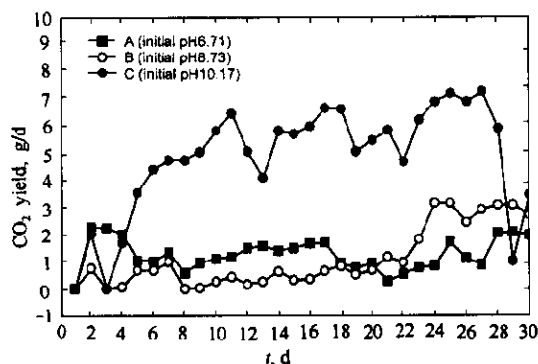


Fig.4 Effect of pH on CO_2 yield during composting

CO_2 was produced right after the beginning of composting. The CO_2 yield increased in several days and kept high value during the whole composting period. The CO_2 yield in composter C was far greater than that in composter A and B, which implied microbial activity in composter C was much higher than that in others.

Variation of microbial biomass can reflect the conversion degree of organic matter and environmental conditions in composting, which is shown in Fig. 5. Comparing it with Fig.3, we concluded that pH can affect variation of microbial biomass. When pH was under alkaline conditions, microbial biomass was up to the maximum (e.g. microbial biomass in composter C within 16 days with approximate pH of 8.40). Then microbial biomass decreased significantly when pH kept up to 9.0 (e.g. microbial biomass in composter C after 16 days),

which was even lower than microbial biomass in composte B with acidic condition. In brief, the results demonstrated that the farther pH was away from neutral, the more restrained microbe growth would be. It showed that pH also affected microbial activity dramatically from Fig. 3 and Fig. 4. The CO_2 yield in composte A was higher than that in composte B from 1–19 days, which showed that there were lots of microorganisms can utilize organic acid at pH 4.0–5.0. While CO_2 yield in composte B was much higher than that in composte A from 20–30 days, which showed that microbial activity at pH 6.0–7.0 was much higher than that at pH 4.0–5.0. Moreover, the curve of CO_2 yield in composte C showed that CO_2 yield was up to the maximum when pH was higher than 7.0. Thus it can be concluded that the order of microbial activity at different pH conditions should be: pH higher than 7.0 > pH 6.0–7.0 > pH 4.0–5.0 > pH 5.0–6.0. Of course, pH can not exceed 7.0 too much in case that it would restrain the growth of most microorganisms.

The composting temperature in composte A increased most rapidly and was up to the maximum among three composters during the first 7 days. While the composting temperature in composte C was up to the maximum from 8–14 days, and the composting temperature in composte B was up to the maximum from 15–20 days. It should be noticed that temperature in composte C reoccupied the highest value dramatically after 21 days of composting. It showed that there existed a certain correlation between variations of temperature and microbial biomass, comparing with Fig. 5. In the first 6 days, microbial biomass in composte A was the largest on the whole, therefore heat output by metabolism activity was consequently high and the composting temperature also increased most rapidly in composte A. At the stage of 8–15 days, microbial biomass in composte C was up to the maximum and the composting temperature increased to the highest. During the composting period of 5–19 days, microbial biomass in composte A increased by 100 times from 10^6 to 10^8 , while it increased steadily in composte B around 10^7 , and decreased by 10 times from 10^8 to 10^7 in composte C. The composting temperature in composte B was the highest during this period, which indicated that heat output by metabolism activity corresponded not only with the variation of microbial biomass, but also with the stability of this variation.

Suler *et al.* (Suler, 1977) considered that there might have been a delay period between the attainment of temperature unfavorable for microbe growth and the expression of adverse effect caused by such condition, during which microbial enzymes formed previously continued to function. This viewpoint just coincided with our experimental result on the variation of microbial biomass. Whilst, the variation of microbial biomass was not sure to correspond exactly with suitability of temperature while sampled each time, although it is very important that microbial biomass was larger at the optimal temperature. The variation of microbial biomass in three composters displayed a process of increase, decrease and increase, decrease again in turn. A common explanation was that microorganisms reproduced themselves magnificently through using readily biodegradable organic matter at the first stage of composting, then microbial biomass began to decrease after the readily biodegradable organic matter exhausted. In addition, microorganisms can use resistant-to-biodegrade matter and reproduce themselves after adapted to such conditions, and this phenomenon was called secondary growth of microorganisms (Minna, 1997). Hence, the curve of microbial biomass should have 2 peaks. But as shown in our experimental curves (Fig.5), there were 3–4 peaks instead. This result also confirmed that the variation of microbial biomass was related not only to the secondary growth but also to the variation of pH. With the changing of pH during composting, microbial biomass variation curve with more peaks might occur. Microbial activity was judged mainly by CO_2 evolved. Generally, the higher CO_2 yield, the more powerful metabolic activity of microorganism would be. Temperature was a most notable factor judging the metabolic activity of microorganism, which can affect CO_2 yield directly. Microbial activity was most powerful at the optimal temperature, therefore CO_2 yield was up to the maximum value by then. So we can determine the optimal composting temperature by correlatively analyzing of CO_2 yield and temperature.

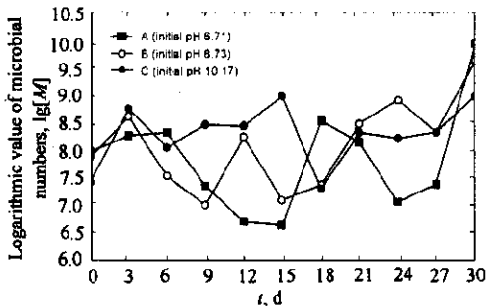


Fig.5 Effect of pH on microbial biomass during composting

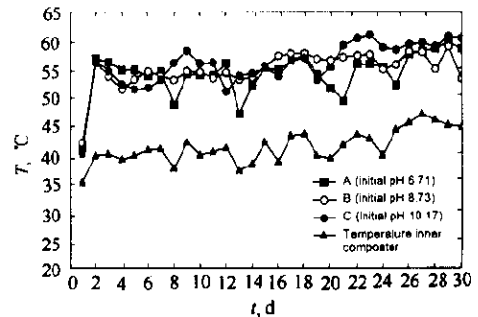


Fig.6 Profile of temperature during composting at different pH conditions

As Fig.7 shown, temperature referred to eight peaks of CO_2 evolution were 59.50, 58.33, 59.25, 58.67, 56.83, 56.50 and 56.83°C in turn relating to CO_2 yield. Yet temperature referred to the five lowest points were 60.67, 60.33, 53.00, 53.83 and 54.83°C in turn relating to CO_2 yield from low to high. The CO_2 yield decreased dramatically at 56.8–55.5°C and 59.5–60.67°C. All these phenomena implied that the optimal range for temperature in composte C was 56.5–59.5°C. Followed the above analysis, the optimal temperature for composte A and B were 55.0–58.5°C and 54.0–58.0°C, respectively (Fig.8–9). It needed 2–3 days to reach the optimal temperature for composte A, 5 days and 7 days for

composter B and C, which showed that higher pH value at the beginning would prolong the required time for reaching the optimal temperature. However, the pH during composting process seems to be much more important than initial pH influencing the composting efficiency.

As above analysis, based on CO₂ yield and microbial biomass, the optimal process pH for composting should be alkalinescent condition and no excess of 8.5 (pH 7.0 – 8.5) avoiding the restraint of microbe growth, and the optimal temperature range was 56.5 – 59.5℃.

2.3 Degradation rate of petroleum waste

Degradation rates of total petroleum hydrocarbon for three composters were 40.89%, 50.09% and 69.44%, respectively (Fig.10). This result coincided with above analysis, and it showed that the order of microbial activity in three composters was C > B > A. Besides, it also showed that pH was a very important control parameter during composting, and degradation rates increased significantly when pH was at 7.0 – 8.5.

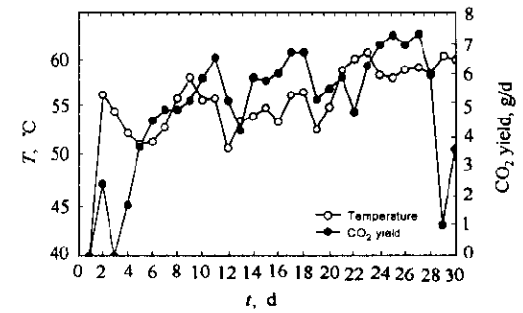


Fig.7 Time courses of temperature and CO₂ yield in composter C

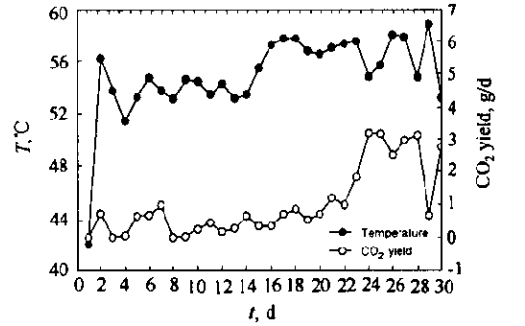


Fig.8 Time courses of temperature and CO₂ yield in composter B

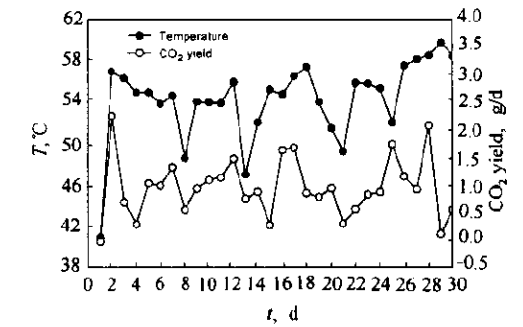


Fig.9 Time courses of temperature and CO₂ yield in composter A

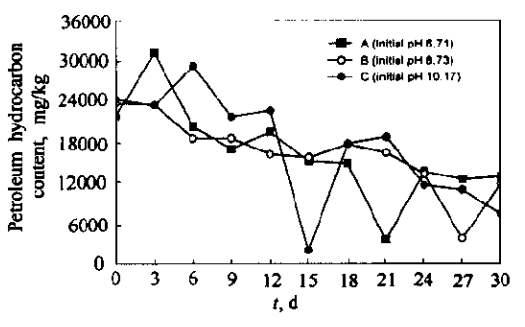


Fig.10 Effect of pH on petroleum hydrocarbon removal during composting

2.4 Optimum moisture content

Moisture content is a convenient control parameter during composting. Many researchers found that moisture content of 50% – 60% was suitable for solid waste composting, whereas 70% was too high (Cookson, 1995; Chen, 1990). The present experimental results were shown in Fig.11 – 12. The peak values for conversion of volatile material (X_{vm}) and petroleum hydrocarbon degradation were 30.32% and 83.39%, respectively, when moisture content was controlled as 60%. Similarly, X_{vm} and petroleum hydrocarbon degradation were 29.71% and 82.69% when at moisture content of 55%, while they all declined to 25.51% and 80.87% when at moisture content of 50%. It showed that the moisture content of 55% – 60% was useful to improve the petroleum hydrocarbon degradation rate during composting. Under the optimal conditions of temperature, pH, compost material ratio and moisture content, the petroleum removal efficiency reached 83.29% after 30 days composting.

3 Conclusions

Temperature and pH were two key process control parameters in composting, and they affected composting efficiency directly through influencing microbial biomass and activity. Moisture content was another convenient and useful parameter controlling composting. The present results showed that the optimum temperature, pH and moisture content for petroleum waste composting were 56.5 – 59.5℃, 7.0 – 8.5 and 55% – 60%, respectively.

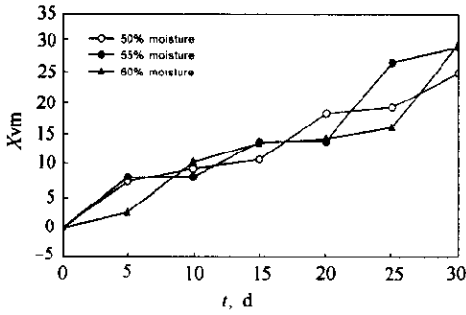


Fig.11 Effect of moisture content on the conversion of volatile material (X_{vm}) during composting

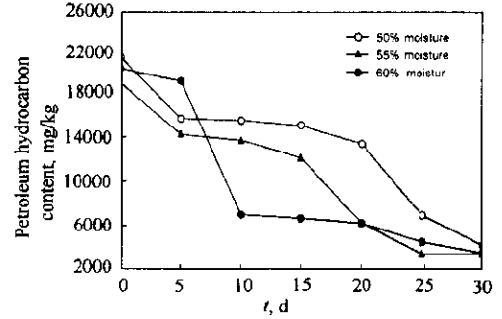


Fig.12 Effect of moisture content on petroleum hydrocarbon removal during composting

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