



Evaluation of carbon degradation during co-composting of exhausted grape marc with different biowastes

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ABSTRACT

In this work the carbon biodegradation of exhausted grape marc (EGM) combined with other organic wastes using the turned pile composting system was studied. Four different piles were made of EGM in Pile 1, EGM mixed with cow manure and straw (CMS) in Pile 2, EGM mixed with municipal solid waste (MSW) in Pile 3 and EGM mixed with grape stalks (GS) in Pile 4. The results obtained were modelled to determine the main kinetic and stoichiometric parameters. Regarding to the rate constants of the composting processes they were increased from 0.033 d^{-1} , the value obtained when EGM was composted alone, to 0.040 and 0.044 d^{-1} when MSW and GS were added, respectively as co-substrates. However, the addition of CMS reduced the rate constant. About the biodegradable carbon fractions, it was observed that the co-composting reduced significantly the remanent carbon concentration after composting in all the piles whilst increased the readily biodegradable carbon fractions from 35, the value obtained when EGM was composted alone, to 50 and 60%, respectively when MSW or GS were added. As regards the temperature profiles, only Piles 1 and 4 achieved thermal hygienization values and about the nitrogen losses, the lowest percentage of nitrogen loss took place when GS were added, because of its optimum pH and C/N initial ratio. Thus, though any of these wastes could be used for co-composting with EGM, the use of GS as co-substrate and bulking agent for the co-composting process of EGM was recommended.

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1. Introduction

Spain is one of the world's main wine producers and a leader in development and innovation in the wine industry. Castilla-La Mancha is a region in the centre of Spain which represents the greatest wine cultivation area in Europe (60000 ha). The main wastes generated in the wineries are: Grape stalk, (GS), grape marc (GM) and wine lees (WL). According to the Council Regulation (EC) 1493/1999, GM and WL must be sent to alcohol distilleries where exhausted grape marc (EGM) and vinasse are the final solid and liquid waste, respectively. The EGM is obtained after the GM and WL alcohol and tartaric acid extraction (by means of lime addition) and centrifugation (Bustamante et al., 2008a). The main problem of the EGM is its disposal and treatment due to its seasonal character and high content of phytotoxic and antibacterial phenolic compounds. An interesting management option could be to use it as soil fertiliser because of its richness of nutrients (N, P, K) or amendment because of its organic matter content (Bustamante et al., 2008b). Moreover, this interest has grown in recent years because of the gradual soil degradation, lack of humification and consequent vulnerability to erosion (Bertran et al., 2004; Arvanitoyannis et al., 2006). However, the direct dose of winery or distillery wastes

without any pre-treatment into soils may cause several adverse effects derived from the release of degradation products which could inhibit root growth (Inbar et al., 1991) or results into phytotoxicity and detrimental effects for plant growing (Bustamante et al., 2004; Flavel et al., 2005). For that reason, a suitable option to return the organic matter and nutrients into the soil is by means of a controlled aerobic composting process which would stabilize the organic matter contained in the EGM, reducing the presence of undesirable compounds (Butler et al., 2001). Moreover, when thermophilic conditions are reached during several days an adequate disinfection of the final compost is obtained. In the case of composting windrows it is recommended to maintain temperature values of about 55°C for at least 15 d (EU, 2001) in order to ensure pathogen elimination.

With the aim to enhance the composting process, increasing the degradation rate and the quality of the final compost, several modifications have been made in the process; such as the addition of biodegradable wastes to reach the optimum C/N ratio of about 30 (Haug, 1993), that is co-composting. Co-utilization of waste-derived materials has the potential to increase the range of uses of recycled products, and to reduce odorous emissions related to pH or C/N ratio (Brown et al., 1998; Huang et al., 2004; Sánchez-Arias et al., 2008). Up to now, a few authors have reported distillery wastes co-composting using different organic wastes as co-substrates (Díaz et al., 2002; Bustamante et al., 2008a, b). However,

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not enough information is currently available on the carbon degradation of distillery wastes co-composting systems.

In this context, the aim of this work was to study the carbon degradation during the co-composting processes of EGM with several agro-food or animal biowastes produced in large amounts in Castilla-La Mancha, such as cow manure with straw (CMS), organic fraction of municipal solid wastes (MSW) or fresh grape stalks (GS). In order to obtain a better understanding of the carbon degradation during the co-composting processes, a mathematical model was developed and fitted to the experimental results so as to determine the carbon degradation kinetic constants and the biodegradable carbon fractions. Finally, the qualities of the final composts obtained in all the piles were compared.

2. Materials and methods

2.1. Composting system

Four batch pilot scale composting experiments were set using the mechanically turned pile composting system with a volume of 6 m³ each, at the experimental farm “Dehesa de Galiana” of the University of Castilla-La Mancha, near Ciudad Real (Spain). The waste materials studied in the experiments were EGM from a distillery, CMS from the “Dehesa de Galiana” farm, organic fraction of MSW from a Waste Treatment Plant, and GS from a winery. The main characteristics of these raw wastes are presented in Table 1.

The percentages of the wastes used to settle the composting piles on a wet weight basis (dry weight basis in brackets) were as follows: Pile 1: EGM; Pile 2: 50% EGM + 50% CMS (50% EGM + 50% CMS); Pile 3: 50% EGM + 50% MSW (38% EGM + 62% MSW); Pile 4: 25% EGM + 75% GS (16% EGM + 84% GS).

In the Pile 1, only EGM was composted, in Piles 2 and 3 the mixing ratio (w/w) was 50–50% (wet basis). In the fourth Pile, the EGM were mixed with GS in a 25–75% (wet basis) ratio. We decided to use this ratio because this is the ratio in which these wastes are generated in the wine industry (Gea et al., 2005) and yielded a C/N ratio within the optimum range recommended in the literature (Haug, 1993).

All the mixtures (ranging from 3000 to 4800 kg each) were composted in pilot scale trapezoidal piles (1.5 m high with a 3.5 × 3.5 m base). Aerobic conditions were maintained by turning the piles weekly for the first 6 wk and twice a month afterwards to keep oxygen levels over 10%, as several authors have reported the limit to avoid anaerobic conditions in the range 5–10% of oxygen in the air inside the pile (Leton and Stentiford, 1990; Bertran et al., 2004). A field gas analyzer provided with a 1.5 m probe (Q-RAE Plus) was used to measure oxygen concentration in the air inside the pile. The probe was introduced into the pile to a depth of approx 1 m and it was connected to the gas analyzer. The air inside the pile was pumped through the probe to the analyzer and after 5 min, a stable punctual measurement was recorded. Tempera-

tures were measured daily at the beginning of the process and periodically afterwards at three different depths ranging from 0.5 to 1 m inside the piles. The piles were periodically rewetted to maintain moisture content over 40% to allow microbial development, as recommended by most authors (Poincelot, 1975; Tiquia et al., 1996). However, it was not possible for the MSW because of the high porosity of this waste and the high environmental temperatures reached. Leaching of percolation water to the underlying soil was prevented by using non-permeable plastic material at the bottom of the piles which, due to the slight slope of the land where the piles were disposed and canalization around, allowed to collect the leachate released during the process into a 50 L plastic container. To water the pile the leachate released together with tap water were pumped into the pile when necessary.

2.2. Solid sample analyses

Solid samples were taken throughout the process at different depths inside the pile in order to obtain a representative sample. About 1 kg sample was taken from three different points, one from the surface, other from about 0.5 m from the surface and another one from 1 m from the surface. These samples, 3 kg in total, were mixed and a 2 kg aliquot was used for analysis while the rest of the sample was discarded and returned to the pile. The 2 kg aliquot was homogenized before analyses performance. Initial porosity (ϵ_0) was calculated as $1 - BD/\rho$ being BD the bulk density of the pile and ρ the actual density of the waste. Fresh samples were used to measure electrical conductivity (EC) and pH in a 1:10 w/w water extract. Moisture content and volatile solids (VS) content were also measured. About 500 g of the sample was dried and milled to a particle size smaller than 1 mm in an IKA® A 11 basic mill. Carbon concentration was determined on dry matter (DM) by dry combustion followed by infrared detection of CO₂ (TOC Shimadzu 5050A equipment). Nitrogen and phosphorus were measured in a pre-treated dry solid sample according to the APHA Standard Methods (1998). The pre-treatment consisted on the digestion of 0.4 mg of milled dry sample with 10 mL H₂SO₄ at 150 °C for 3 h in an ECO16 thermoreactor (Velp Scientifica). Heavy metal and nutrient analyses were performed in 0.5 g of milled dry sample previously treated in a microwave digester (0.5 g dry sample with 10 mL HNO₃) and the resulting liquid was diluted with deionized water and, after filtration, used to measure heavy metals with ICP-Mass Spectrometry and Na, Ca, K, Fe and Mg by atomic absorption spectroscopy. The analyses for the initial mixtures are presented in Table 2.

2.3. Carbon degradation model

In order to determine the kinetic constant of the carbon biodegradation process, it was necessary to develop a mathematical model. Most models used by different authors are inductive models i.e., they relate directly the input to the output. For waste treatment processes, Monod kinetics and first order kinetics are commonly used (Bari et al., 2000; Hamelers, 2004). The subject of composting kinetics is a complex issue, because it can be limited by hydrolysis of particulate substrates, solubilisation and mass transfer stages among others (Komilis, 2006). Because of this, and with the aim to increase the potential for practical application, a lumped-parameter model defining all these stages at the same time was used. With this aim, the carbon biodegradation rate constant was defined as function of the characteristics of the wastes and the environmental conditions. This simplified model was based on the following assumptions:

The composting pile was supposed to be a batch reactor where the substrates contained in the wastes were degraded under aerobic conditions. Taking into account that during the composting

Table 1
Characteristics of raw wastes

	(EGM ^a)	(CMS ^b)	(MSW ^c)	(GS ^d)
Moisture (%)	68.3	69.0	48.1	44.4
C (g kg ⁻¹ DM ₀)	390	400	490	490
VS (g kg ⁻¹ DM ₀)	698	820	760	775
N (g kg ⁻¹ DM ₀)	41	33	40	17
pH	5.8	8.1	7.0	7.3

^a EGM: exhausted grape marc.

^b CMS: cow manure mixed with straw.

^c MSW: organic fraction of municipal solid waste.

^d GS: grape stalks.

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